

BOOK OF ABSTRACTS

07 – 11 September 2014
Congress Center Würzburg (CCW) · Germany

ISEC 2014

International Solvent Extraction Conference

www.ISEC2014.com



© Congress-Tourismus-Wirtschaft Würzburg

COMMITTEES

INTERNATIONAL SCIENTIFIC COMMITTEE

Hans-Jörg Bart	University of Kaiserslautern/D
Sarah Bélair	Emrat Research, Trappes/F
Peter Cole	TWP Project Plant (Pty) Ltd., Johannesburg/SA
Christian Ekberg	Nuclear Chemistry, Göteborg/S
Masahiro Goto	Kyushu University, Fukuoka/JP
Baruch Grinbaum	Bateman Advanced Technologies, Yokneam/IL
Gary A. Kordosky	Henkel Corporation, Tucson, AZ/USA
Huizhou Liu	Chinese Academy of Sciences, Beijing/RC
Guangsheng Luo	Tsinghua University, Beijing/RC
Kenneth L. Nash	Washington State University, Pullman, WA/USA
Susana Ortiz	Imperial College, London/UK
Hans Reinhardt	MEAB Metallextaktion AB, Askim Göteborg/S
Gordon M. Ritcey	Nepean/CDN
Geoff Stevens	The University of Melbourne/AUS
Lawrence L. Tavlarides	University of Syracuse, NY/USA
Evgeny V. Yurtov	Mendelev University of Chemical Technology, Moscow/RUS

TECHNICAL COMMITTEE

Sophie Charton	CEA Marcoule, Bagnols-sur-Cèze/F
Rudolf Eggers	Hamburg University of Technology/D
Sabine Enders	TU Berlin/D
Thomas Gamse	Graz University of Technology/A
Volkmar Jordan	Fachhochschule Münster, Steinfurt/D
Eugeny Kenig	University Paderborn/D
Matthias Kraume	TU Berlin/D
Guisepppe Modolo	Forschungszentrum Jülich GmbH/D
Pawel Plucinski	University of Bath/GB
Norbert Rübiger	University of Bremen/D
Stefan Schlosser	Slovak University of Technology, Bratislava/SL
Michael Schlüter	Hamburg University of Technology/D
Boelo Schuur	University of Twente, Enschede/NL
Matthäus Siebenhofer	Graz University of Technology/A
Irina Smirnova	Hamburg University of Technology/D
Jochen Strube	Clausthal University of Technology, Clausthal-Zellerfeld/D

LOCAL ORGANIZING COMMITTEE

Werner Bäcker	Bayer Technology Services GmbH, Leverkusen/D
Hans-Jörg Bart	University of Kaiserslautern/D
Uwe Delfs	VDI e.V., Düsseldorf/D
Andreas Förster	DECHEMA e.V., Frankfurt/D
Andreas Geist	Karlsruher Institut für Technologie – KIT/D
Karsten Gloe	TU Dresden/D
Wilfried Gutknecht	H.C. Starck GmbH, Goslar/D
Andre B. de Haan	TU Eindhoven/NL
Michael Häberl	Merck KGaA, Darmstadt/D
Leo Nick	DECHEMA e.V., Frankfurt/D
Daniel Pfeiffer	BASF SE, Ludwigshafen/D
Jörg Koch	Sulzer Chemtech AG, Allschwil/CH
Jörg Leistner	Evonik Industries AG, Marl/D
Andreas Pfennig	Graz University of Technology/A
Manfred Weber	INEOS Phenol GmbH, Gladbeck/D

TABLE OF CONTENTS

Sponsors / Exhibitors	4
Programme at a Glance	5 – 9
Lecture Programme	
Monday, 8 September 2014	10 – 15
Tuesday, 9 September 2014	16 – 17
Wednesday, 10 September 2014	18 – 21
Thursday, 11 September 2014	22 – 25
Poster Programme	26 – 36
Abstracts	37

SPONSORS / EXHIBITORS

SPONSORS

The organizers give their sincere thank for support to:

Platinum Sponsor



Ternova Bateman Technologies
Yokneam/IL

INEOS Phenol

Ineos Phenol GmbH
Gladbeck/D

RHODIUS 
Safety and Environmental Solutions

Rhodius GmbH
Weißenberg/D

SULZER

Sulzer Chemtech AG
Allschwil/CH

LIST OF EXHIBITORS



BASF SE
Ludwigshafen/D

 **COSMOlogic**
Predicting Solutions

Cosmologic GmbH & Co. KG
Leverkusen/D

MEAB

MEAB Metallextraktion AB
Askim/SE

Outotec

Outotec (Finland) Oyi
Espoo/FIN

RHODIUS 
Safety and Environmental Solutions

Rhodius GmbH
Weißenberg/D



Shell Global Solutions Int. BV
Amsterdam/NL

SOPAT 
Smart Online Particle Analysis Technology

Sopat GmbH
Berlin/D

SULZER

Sulzer Chemtech AG
Allschwil/CH



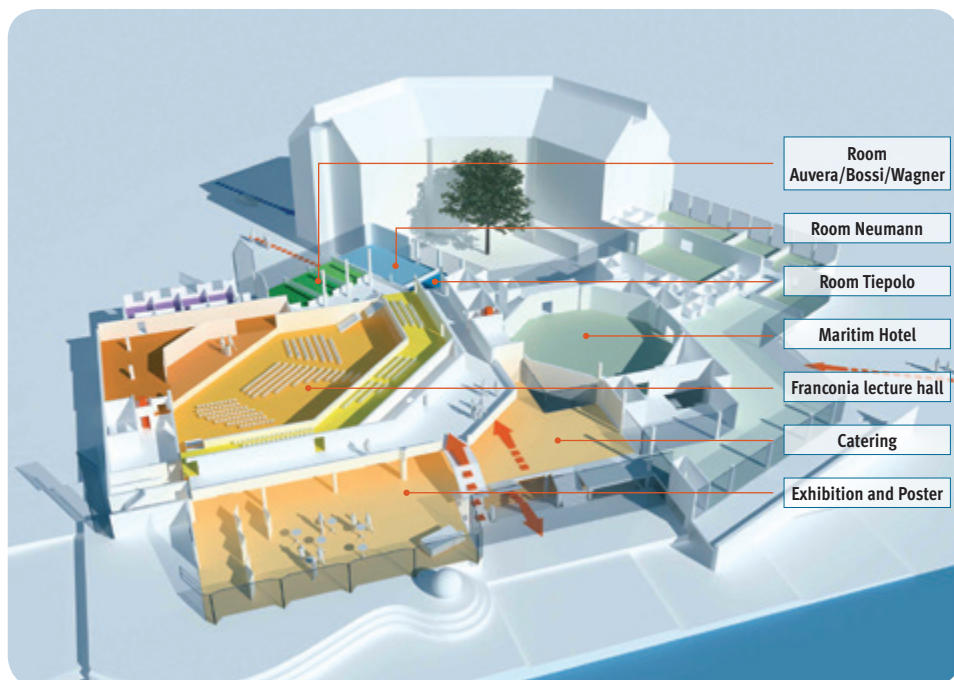
Ternova Bateman Technologies
Yokneam/IL

PROGRAMME AT A GLANCE

Sunday, 7 September 2014

9:00 – 16:00	Advanced Course	Room Neumann
12:00	ISCE Meeting	Room Tiepolo
16:00 – 18:00	Registration	
18:00 – 20:00	Welcome Reception	

OVERVIEW – CONGRESS CENTER WÜRZBURG



PROGRAMME AT A GLANCE

Monday, 8 September 2014

	Franconia lecture hall			
8:30	OPENING			
8:40	B. Moyer – Oak Ridge National Laboratory/USA			38
9:25	COFFEE BREAK AND SNACKS			
	Franconia lecture hall	Room Neumann	Room Auvera/Bossi/Wagner	Room Tiepolo
	Hydrometallurgy and metals extractions	Nuclear fuel reprocessing	Fundamentals/ Novel reagents, materials and techniques	Extraction on mini-scale
9:55	T. Vander Hoogerstraete 46 University of Leuven/B	T. Todd 111 Idaho National Laboratory/USA	D. Bourgeois 160 ICSM/F	A. Holbach 202 TU Dortmund/D
10:20	J. Quinn 47 Australian Nuclear Science and Technology Organisation/AUS	K. Nash 118 Washington State University/USA	J. Mendez-Quezada 164 Universidad de Guanajuato/MEX	J. Hereijgers 203 Vrije Universiteit Brussel/B
10:45	J. Yang 53 Chalmers University of Technology/S	C. Marie 124 CEA/F	M. Mohammadi 170 KTH Royal Institute of Technology/S	J. Tan 204 Tsinghua University/CHN
11:10	M.A. Halim 61 Process Research ORTECH Inc./CDN	A. Wilden 130 Forschungszentrum Jülich GmbH/D	P. Hewitson 171 Brunel University/UK	G. Liu 205 Tsinghua University/CHN
11:35	R. Egashira 69 Tokyo Institute of Technology/J	C. Wagner 136 Universität Heidelberg/D	C.A. Hawkins 172 University of California/USA	K. Smith 206 The University of Melbourne/AUS
12:00	LUNCH BREAK			
	Franconia lecture hall			
13:30	A. Geist – KIT – Karlsruhe Institute of Technology/D			39
14:00	B. Rüngeler – RWTH Aachen/D			45
14:30	COFFEE BREAK			
	Franconia lecture hall	Room Neumann	Room Auvera/Bossi/Wagner	Room Tiepolo
15:00	C. Tunsu 70 University of Technology, Gothenburg/S	H. Galán 137 Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Madrid/E	P. Chuttrakul 178 Graz University of Technology/A	Y. Miyazaki 212 Japan Atomic Energy Agency/J
15:25	K. Huang 77 Chinese Academy of Sciences/CHN	A. Wilden 144 Forschungszentrum Jülich GmbH/D	H. Watarai 179 Osaka University/J	M. Awual 213 Japan Atomic Energy Agency/J
15:50	M. Goto 78 Kyushu University, Fukuoka/J	J. Law 150 Idaho National Laboratory/USA	K. Wieszczka 183 Poznan University of Technology/PL	Y. Wang 214 Tsinghua University/CHN
16:15	K. Larmour-Ship 84 Tenova Bateman Technologies, Yokneam/IL	R. Berlemont 151 CEA Marcoule/F	Y. Baba 189 University of Miyazaki/J	G. Hellé 220 CEA Saclay/F
16:40	COFFEE BREAK AND SNACKS			
17:10	G.Q. Zhang 93 Central South University/CHN	M.C. Charbonnel 157 CEA/F	O. Riechert 195 TU Dortmund/D	P.R. Martins Bento 226 University of Utah, Salt Lake City/USA;
17:35	L. Zeng 99 Central South University/CHN	K. Takeshita 158 Tokyo Institute of Technology/J	S. Dourdain 196 University of Montpellier 2/F	C. Priest 227 University of South Australia/AUS
18:05	V. Vanel 105 CEA/F	R. Taylor 159 National Nuclear Laboratory/UK	D. Gorri 197 University of Cantabria/E	W. De Malsche 233 Vrije Universiteit/B
18:30	POSTER PARTY (18:30 – 21:00)			

PROGRAMME AT A GLANCE

Tuesday, 9 September 2014

	Franconia lecture hall			
8:30	E. Paatero – Outotec Oyj/FIN			234
9:15	COFFEE BREAK AND SNACKS			
	Franconia lecture hall	Room Neumann	Room Auvera/Bossi/Wagner	Room Tiepolo
	Novel reagents, materials and techniques	Fundamentals	Process chemistry and engineering	Biotechnology, pharmaceutical, life science and organic products
9:45	S. Schlosser Slovak University of Technology/SK 240	D. Dherbecourt CEA/F 255	E.W. Barega Eindhoven University of Technology/NL 270	C. Ladd Effio Karlsruhe Institute of Technology (KIT)/D 287
10:10	P. Lozano University of Murcia/E 241	R.F. Engberg University of Paderborn/D 256	W. Hengeveld Spinid B.V./NL 277	J. Mündges TU Dortmund/D 288
10:35	A. Urtiaga University of Cantabria/E 247	M. Kraume TU Berlin/D 262	R. Schulz TU Dortmund/D 278	C. Brandenbusch TU Dortmund/D 289
11:00	M. Dietz University of Wisconsin/USA 253	O. Diat ICSM/F 263	A. Salum Universidade Federal de Minas Gerais/BR 279	E. Alvarez-Guerra Universidad de Cantabria/E 291
11:25	M. Grambicka University of Twente/NL 254	T. Grunert TU Berlin/D 264	A. Bednarz RWTH Aachen 286	S. Ignatova Brunel University/UK 297
11:50	LUNCH BREAK			
13:50	Excursion "City tour through Würzburg"			



© Congress-Tourismus-Wirtschaft Würzburg

PROGRAMME AT A GLANCE

Wednesday, 10 September 2014

	Franconia lecture hall			
8:30	F. Chemat – Avignon University/F			298
9:15	COFFEE BREAK AND SNACKS			
	Franconia lecture hall	Room Tiepolo	Room Auvera/Bossi/Wagner	Room Neumann
	Hydrometallurgy and metals extractions	Fundamentals	Extraction of natural products from plants	Novel reagents, materials and techniques
9:45	K. Soldenhoff 299 ANSTO/AUS	E. Cvetkovic 350 Graz University of Technology/A	B. Bol 388 Graz University of Technology/A	S. Nusen 437 CSIRO/AUS
10:10	D. Singh 301 Bhabha Atomic Research Centre/IND	H. Chen 351 East China University of Science and Technology/CHN	R. Orozco Mena 389 Autonomous University of Chihuahua/MEX	V. Herdegen 443 TU Bergakademie Freiberg/D
10:35	A. Chagnes 302 ENSCP/F	F. Gebauer 357 University of Kaiserslautern/D	R. Racheva 395 Hamburg University of Technology/D	K. Ohto 449 Saga University/J
11:00	O. Pecheur 303 Commissariat à l'Energie Atomique de Marcoule/F	J. Villwock 358 TU Berlin/D	S.B. Pérez-Vega 401 Autonomous University of Chihuahua/MEX	G. Cote 455 ENSCP/F
11:25	M. Miguiditchian 304 CEA/F	J. Kamp 359 TU Berlin/D	Y. Saotome 402 University, Kameino/J	L. Li Tsinghua University/CHN
11:50	LUNCH BREAK			
	Franconia lecture hall			
13:20	M.W. Hlawitschka – University of Kaiserslautern/D			408
13:50	J. Herguijuela – Sulzer Chemtech AG/CH			415
14:20	COFFEE BREAK			
	Franconia lecture hall	Room Tiepolo	Room Auvera/Bossi/Wagner	Room Neumann
				CFD applications
14:50	S. Archer 310 DRA Mineral Projects (Pty) Ltd/ZA	J.P. Simonin 360 Université P.M. Curie, Paris/F	Y. Du 416 University of Twente/NL	E. Keshavarz Alamdari 457 Amirkabir University of Technology/IR
15:15	N. Davidson 318 Johnson Matthey/UK	R. Poirot 366 CEA/ICSM/LCPA/F	F. Deng 422 Chinese Academy of Sciences/CHN	E. Sanz 468 IFP Energies nouvelles/F
15:40	J. Yang 324 Chalmers University of Technology/S	K. Wieszczzycka 372 Poznan University of Technology/PL	S. Bassil 423 Laboratoire de Chimie Agro-Industrielle/F	E. Aksamija 469 Graz University of Technology/A
16:05	R. Luckay 331 University of Stellenbosch/ZA	A. Klamt 378 COSMOlogic GmbH & Co. KG/D	S. Mohammad 424 TU Dortmund/D	S. Charton 470 CEA/F
16:30	COFFEE BREAK AND SNACKS			
			Nuclear fuel reprocessing	
17:00	M. Siebenhofer 337 Graz University of Technology/A	N. Paul 379 TU Berlin/D	K. Nash 425 Washington State University/USA	H. Chen 471 East China University of Science and Technology/CHN
17:25	J. Lipp 338 Tenova Bateman Technologies, Yokneam/IL	D. Ibana 380 Curtin University/AUS	Y. Sasaki 431 Japan Atomic Energy Agency/J	S. Miskovic 477 University of Utah/USA
17:55	J.P.J. Matinheikki 344 Outotec (Finland) Oy/FIN	H. Cui 387 Chinese Academy of Sciences, Changchun/CHN	C. Sorel 436 CEA/F	E. Keshavarz Alamdari 478 Amirkabir University of Technology/IR
19:00	CONFERENCE DINNER (19:00 – 23:00)			

PROGRAMME AT A GLANCE

Thursday, 11 September 2014

	Franconia lecture hall			
8:30	R. Grant – Johnson Matthey Technology Centre/UK			480
9:15	COFFEE BREAK AND SNACKS			
	Room Auvera/Bossi/Wagner	Room Neumann	Room Tiepolo	Franconia lecture hall
	Hydrometallurgy and metals extractions	Nuclear fuel reprocessing	Process Chemistry and Engineering	Novel reagents, materials and techniques
9:45	C.Y. Cheng 486 CSIRO/AUS	B. Moyer 532 Oak Ridge National Laboratory/USA	M. Haneke 576 Evonik Industries AG/D	P. Zalupski 628 Idaho National Laboratory,/USA
10:10	E.M.R. Araújo 492 Universidade Federal de Minas Gerais/BR	S. Baker 533 EnergySolutions plc,/USA	M. Weber 577 Ineos Phenol GmbH/D	L. Berthon 634 CEA Marcoule, Bagnols- sur-Ceze/F
10:35	M.A. Halim 499 Process Research ORTECH Inc., Mississauga/CDN	K. Nee 539 University of California/USA	G.W. Stevens 583 The University of Melbourne/AUS	H. M. Krieg 640 North-West University/ZA
11:00	Y. Baba 500 Kyushu University, Fukuoka/J	S.P. Mezyk 545 California State University/USA	A. Boam 589 Evonik Membrane Extraction Technology Ltd./UK	A. Paiva 641 University of Lisbon/P
11:25	S.M.M. Noori 512 University of Tehran/IR	M. Nilsson 551 University of California/USA	A. Matsuoka 590 Kobe Steel, LTD./J	P. Tasker 647 University of Edinburgh/UK
11:50	LUNCH BREAK			
	Franconia lecture hall			
13:20	B. Grinbaum – Yokneam/IL			596
13:50	Award Session			
14:20	COFFEE BREAK			
	Room Tiepolo	Room Neumann	Franconia lecture hall	Room Auvera/Bossi/Wagner
				Biotechnology, pharmaceutical, life science and organic products
14:50	B. Onghena 518 Heverlee/B	G.J. Lumetta 557 Pacific Northwest National Laboratory, Richland/USA	E. Pecharroman 602 Técnicas Reunidas/E	N. Dobrin 653 Tenova Bateman Technologies/IL
15:15	A. Trofimenko 519 Belarusian State University/BY	M. Nilsson 563 University of California/USA	L. John 609 DRA Mineral Projects (Pty) Ltd., Johannesburg/ZA	S. Ignatova 659 Brunel University/UK
15:40	S. Dourdain 525 University of Montpellier/F	S. Mezyk 569 California State University/USA	K. Babic 616 DSM/NL	D. Glatz 660 Koch Modular Process Systems, LLC/USA
16:05	H. Hein 526 Onyxio Engenharia Limitada, Providencia/RCH	M. Ozawa 575 Tokyo Institute of Technology/J	M.F. Vancas 622 Tenova Bateman Technologies MESA/USA	P. Scherübel 664 Graz University of Technology/A
16:35	CLOSING CEREMONY			
16:45	End of Conference			

Monday, 8 September 2014

Franconia lecture hall

Chair: K. Gloe, TU Dresden/D

08:30	OPENING	
08:40	Strategies for selective liquid-liquid anion exchange	38
	B. Moyer, Oak Ridge National Laboratory, TN/USA	
09:25	COFFEE BREAK AND SNACKS	

Franconia lecture hall

Room Neumann

	Hydrometallurgy and metals extractions		Nuclear fuel reprocessing	
	Chair: K. Gloe/TU Dresden/D		Chair: A. Geist, Karlsruher Institut für Technologie - KIT/D	
09:55	Ionic liquid technology for metal separation and NdFeB magnet recycling T. Van der Hoogerstraete, K. Binnemans, University of Leuven, Heverlee/B	46	Separation of trivalent actinides from lanthanides: current progress and trends T. Todd, Idaho National Laboratory, Idaho Falls, ID/USA	111
10:20	Separation of rare earth elements using Cyanex 572 J. Quinn, K. Soldenhoff, Australian Nuclear Science and Technology Organisation, Sydney/AUS; G. Stevens, The University of Melbourne/AUS	47	Synthesis and characterization of a new nitrogen-containing ligand for actinide/lanthanide separations K. Nash, J. Muller, Washington State University, Pullman, WA/USA	118
10:45	Recovery of In, Y, Nd and Eu from WEEE by solvent extraction J. Yang, C. Ekberg, T. Retegan, Chalmers University of Technology, Gothenburg/S	53	Separation of americium from a concentrated raffinate by liquid-liquid extraction C. Marie, M.-T. Duchesne, CEA, Bagnols sur Cèze/F; S. Watanabe, JAEA, Tokai Mura/J; V. Pacary, V. Vanel, M. Montuir, D. Rudloff, M. Bertrand, M. Miguirditchian, CEA, Bagnols sur Cèze/F	124
11:10	Innovative process for the recovery of rare earth elements using mixed chloride leach process V.I. Lakshmanan, R. Sridhar, J. Chen, M.A. Halim, Process Research ORTECH Inc., Mississauga/CDN	61	Spiked laboratory-scale continuous counter-current centrifugal contactor demonstration of a novel innovative-SANEX process A. Wilden, G. Modolo, P. Kaufholz, F. Sadowski, S. Lange, M. Sypula, D. Bosbach, Forschungszentrum Jülich GmbH/D; D. Magnusson, U. Müllich, A. Geist, Karlsruhe Institute of Technology (KIT)/D	130
11:35	Effects of operating conditions in the solvent extraction process to separate rare earth metals R. Egashira, H. Habaki, Tokyo Institute of Technology, Meguro/J	69	A new system for separating americium from PUREX raffinate C. Wagner, Universität Heidelberg/D; U. Müllich, Karlsruhe Institute of Technology (KIT)/D; P.J. Panak, Universität Heidelberg/D; A. Geist, Karlsruhe Institute of Technology (KIT)/D	136
12:00	LUNCH BREAK			

Monday, 8 September 2014

Franconia lecture hall

Chair: K. Gloe, TU Dresden/D

08:30	OPENING	
08:40	Strategies for selective liquid-liquid anion exchange	38
	B. Moyer, Oak Ridge National Laboratory, TN/USA	
09:25	COFFEE BREAK AND SNACKS	
	Room Auvera/Bossi/Wagner	Room Tiepolo
	Fundamentals/Novel reagents, materials and techniques	Extraction on mini-scale
	<i>Chair: N. Dobrin, Tenova Bateman Technologies, Yokneam/IL</i>	<i>Chair: M. Kraume, TU Berlin</i>
09:55	Fluorinated malonamides for L/L extraction of f-elements 160	Process development of enantioselective extraction of aromatic acids in intensified lab columns 202
	M.C. DuI, D. Bourgeois, S. Dourdain, S. Pellet-Rostaing, D. Meyer, ICSM, Bagnols-sur-ceze/F	A. Holbach, J. Godde, N. Kockmann, TU Dortmund/D
10:20	Liquid-liquid extraction of Rh(III) from chloride medium using tetralkyl phosphonium salts as extractants 164	A flat channel membrane microcontactor for liquid-liquid extraction 203
	J. Mendez-Quezada, D. Cholic-Gonzalez, S. Gutiérrez-Granados, P. Gonzalez, R. Navarro, I. Saucedo, Universidad de Guanajuato/MEX; C. Ponce de León, University of Southampton/UK; M. Avila-Rodriguez, Universidad de Guanajuato/MEX	J. Hereijgers, Vrije Universiteit Brussel/B; T. Breugelmans, University of Antwerp/B; W. De Malsche, Vrije Universiteit Brussel/B
10:45	Investigation of carriers for supported liquid membrane extraction of rare earth elements 170	Process intensification of high-phase-ratio extraction with gas-liquid-liquid microdispersion system 204
	M. Mohammadi, J. Martínez, K. Forsberg, A. Rasmuson, KTH Royal Institute of Technology, Stockholm/S	J. Tan, J.H. Xu, G.S. Luo, Tsinghua University, Beijing/CHN
11:10	Intermittent counter-current extraction in continuous downstream processing 171	Intensification of mass transfer by coupling membrane dispersion and microbeads packed column for high two-phase ratio system 205
	P. Hewitson, I.A. Sutherland, S. Ignatova, Brunel University, Uxbridge/UK	G. Liu, J. Tang, G.S. Luo, Tsinghua University, Beijing/CHN
11:35	Investigations of water-soluble Schiff base ligands for the separation of actinyl and non-actinyl cations 172	Influence of plate wettability on the performance of a pulsed disc and doughnut column 206
	C.A. Hawkins, C. Bustillos, University of California/USA; R. Copping, I. May, Los Alamos National Laboratory, NM/USA; M. Nilsson, University of California/USA	T. Grabin, K. Smith, K. Mumford, Y. Wang, G. Stevens, The University of Melbourne/AUS
12:00	LUNCH BREAK	

Monday, 8 September 2014

Franconia lecture hall

Chair: A. Pfennig, Graz University of Technology/A

13:30	The hydrometallurgical co-separation of neptunium, plutonium, americium, and curium by the EURO-GANEX process 39 R. Malmbeck, European Commission, Joint Research Centre, ITU, Karlsruhe/D; M. Carrott, National Nuclear Laboratory, Sellafield/UK; A. Geist, Karlsruhe Institute of Technology (KIT)/D; X. Hérès, Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Marcoule/F; D. Magnusson, Karlsruhe Institute of Technology (KIT)/D; G. Modolo, Forschungszentrum Jülich GmbH/D; C. Sorel, Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Marcoule/F; R. Taylor, National Nuclear Laboratory, Sellafield/UK; A. Wilden, Forschungszentrum Jülich GmbH/D
14:00	Liquid-liquid extraction design under uncertainty 45 B. Rüngeler, RWTH Aachen/D; A. Pfennig, TU Graz/A
14:30	COFFEE BREAK

Franconia lecture hall

Room Neumann

Hydrometallurgy and metals extractions

Chair: C. Ekberg, Nuclear Chemistry, Göteborg/S

Nuclear fuel reprocessing

Chair: S. Charton, CEA Marcoule, Bagnols-sur-Cèze/F

15:00	Recovery of La, Ce, Eu, Gd, Tb and Y from fluorescent lamp waste using solvent extraction: solvent choice studies 70 C. Tunsu, C. Ekberg, M. Gregoric, T. Retegan, Chalmers University of Technology, Göteborg/S	Stability and recyclability of SO₃-Ph-BTP for i-SANEX process development 137 H. Galán, A. Núñez, J. Cobos, Centro de Investigaciones Energéticas, Medio-ambientales y Tecnológicas, Madrid/E; D. Munzel, U. Müllich, A. Geist, Karlsruhe Institute of Technology/D
15:25	Kinetic non-equilibrium extraction and separation of praseodymium and neodymium by a novel gas-assistant column extractor 77 K. Huang, H.Z. Liu, Chinese Academy of Sciences, Beijing/CHN	Process development studies towards an r-SANEX process using C₅-BPP – selective separation of trivalent actinides from lanthanides 144 A. Wilden, G. Modolo, F. Sadowski, S. Lange, Forschungszentrum Jülich GmbH/D; A. Bremer, P. Panak, A. Geist, Karlsruhe Institute of Technology (KIT)/D
15:50	New extractants applicable to industrial solvent extraction process for rare metal separation 78 M. Goto, Y. Baba, F. Kubota, Kyushu University, Fukuoka/J	Development and testing of an Am/Ln separation flowsheet based on Am oxidation with sodium bismuthate 150 J. Law, B. Mincher, T. Garn, M. Greenhalgh, V. Rutledge, Idaho National Laboratory, Idaho Falls, ID/USA
16:15	Continuous piloting to recover nickel from Çaldağ Nikel leach solution using the Nicksyn™ and versatic 10 acid synergistic solvent extraction system 84 K. Larmour-Ship, Tenova Bateman Technologies, Yokneam/IL; C. Er, Caldag Nikel, Manisa/TR; M. Koetze, Mintek, Johannesburg/ZA; A.C. du Preez, Mintek, Johannesburg/ZA	Kinetics extraction of uranium(VI) and plutonium(IV) by N,N-dialkylamides using the single drop method 151 R. Berlemont, A. Lelias, M. Miguiditchian, CEA Marcoule, Bagnols-sur-Cèze/F; J.-P. Simonin, Université P.-M. Curie, Paris/F
16:40	COFFEE BREAK AND SNACKS	

Monday, 8 September 2014

Franconia lecture hall

Chair: A. Pfennig, Graz University of Technology/A

13:30	The hydrometallurgical co-separation of neptunium, plutonium, americium, and curium by the EURO-GANEX process 39 R. Malmbeck, European Commission, Joint Research Centre, ITU, Karlsruhe/D; M. Carrott, National Nuclear Laboratory, Sellafield/UK; A. Geist, Karlsruhe Institute of Technology (KIT)/D; X. Hérès, Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Marcoule/F; D. Magnusson, Karlsruhe Institute of Technology (KIT)/D; G. Modolo, Forschungszentrum Jülich GmbH/D; C. Sorel, Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Marcoule/F; R. Taylor, National Nuclear Laboratory, Sellafield/UK; A. Wilden, Forschungszentrum Jülich GmbH/D
14:00	Liquid-liquid extraction design under uncertainty 45 B. Rüngeler, RWTH Aachen/D; A. Pfennig, TU Graz/A

14:30 COFFEE BREAK

	Room Auvera/Bossi/Wagner	Room Tiepolo
	Fundamentals/Novel reagents, materials and techniques	Extraction on mini-scale
	<i>Chair: A. Pfennig, Graz University of Technology/A</i>	<i>Chair: G. Luo, Tsinghua University, Beijing/RC</i>
15:00	Analyzing the sedimentation and coalescence behavior of polydisperse droplets in opaque systems using ultrasonic technique 178 P. Chuttrakul, A. Pfennig, Graz University of Technology/A	Cesium separations with crown ether derivatives containing aromatic groups 212 Y. Miyazaki, T. Kobayashi, S. Suzuki, H. Shiwaku, M. Awual, Y. Okamoto, R. Motokawa, T. Yaita, Japan Atomic Energy Agency, Hyogo/J
15:25	Novel magnetic and optical measurements of liquid-liquid interfacial reactions 179 H. Watarai, Osaka University/J	Lanthanide separations by functionalized mesoporous silica-transportations and coordination 213 M. Awual, T. Kobayashi, H. Shiwaku, Y. Miyazaki, R. Motokawa, S. Suzuki, Y. Okamoto, T. Yaita, Japan Atomic Energy Agency, Hyogo/J
15:50	Zinc(II) ions recovery from multimetal acidic chloride solutions using pyridinium ketoximes 183 K. Wieszczycka, A. Wojciechowska, M. Krupa, Poznan University of Technology/PL	Process intensification of light rare earth metals extraction via gas-liquid-liquid microdispersion system 214 Y. Wang, Tsinghua University, Beijing/CHN
16:15	Synthesis of a new extractant with phenylphosphinic acid and selective extraction of In(III) and Ga(III) over Zn(II) from acidic media 189 Y. Baba, A. Koshimoto, T. Oshima, University of Miyazaki/J	Liquid-liquid microflow patterns and mass transfer of two radionuclides: uranium (VI) and europium (III) 220 G. Hellé, C. Mariet, CEA Saclay, Gif-sur-Yvette/F; G. Cote, Chimie ParisTech, Paris/F
16:40	COFFEE BREAK AND SNACKS	

Monday, 8 September 2014

Franconia lecture hall		Room Neumann		
Hydrometallurgy and metals extractions		Nuclear fuel reprocessing		
Chair: G. A. Kordosky, Henkel Corporation, Tucson/USA		Chair:S. Ortiz, Imperial College London/UK		
17:10	A clean production process for tungsten hydrometallurgy based on the new technology of direct solvent extraction from alkaline medium <u>G.Q. Zhang</u> , W.J. Guan, L.S. Xiao, Q.X. Zhang, Central South University, Changsha/CHN	93	New thermodynamics data related to actinides separation <u>M.C. Charbonnel</u> , N. Boubals, F. Rodrigues, L. Berthon, P. Guilbaud, CEA, Bagnols-sur-ceze/F	157
17:35	Recovery of rare earths from acid leach solutions of spent nickelmetal hydride batteries using solvent extraction <u>L. Zeng</u> , Y. Xia, L. Xiao, J. Tian, Z. Li, Central South University, Changsha/CHN	99	Extraction chromatographic separation of Am(III) and Eu(III) by porous silica coating TPPEN-NIPA Gel (2) chromatographic column tests <u>K. Takeshita</u> , H. Oaki, Tokyo Institute of Technology//; T. Yaita, S. Suzuki, S. Koyama, Japan Atomic Energy Agency, Tokai//; A. Mori, Kobe University//	158
18:05	Modeling and simulation of molybdenum extraction by ion-exchanger and solvating extractant <u>V. Vanel</u> , C. Marie M.T. Duchesne, X. Hérès, V. Pacary, L. Berthon,D. Rudloff, M. Bertrand, CEA, Bagnols-sur-ceze/F; S. Watanabe, JAEA, Tokai-mura/J	105	“TRU-SANEX”: a variation on the EURO-GANEX process for heterogeneous recycling scenarios K. Bell, J. Brown, C. Campbell, M. Carrott, C. Gregson, J. Holt, C. Maher, C. Mason, M. Sarsfield, <u>R. Taylor</u> , National Nuclear Laboratory, Seascale/UK	159
18:30	COFFEE BREAK			
18:30	POSTER PARTY			
21:00				

Monday, 8 September 2014

Room Auvera/Bossi/Wagner			Room Tiepolo	
Fundamentals/Novel reagents, materials and techniques			Extraction on mini-scale	
Chair: W. Riedl, Fachhochschule Nordwestschweiz, MuttENZ/CH			Chair: E. Kenig, University Paderborn/D	
17:10	Phase equilibria of innovative solvent systems for homogenous catalysis <u>O. Riechert</u> , T. Zeiner, G. Sadowski, TU Dortmund/D	195	Comprehensive numerical and experimental analysis of copper solvent extraction in Y-Y microreactors <u>P.R. Martins Bento</u> , University of Utah, Salt Lake City, UT/USA; O. Kazemi, Amirkabir University of Technology, Tehran/IR; S. Miskovic, University of Utah, Salt Lake City, UT/USA	226
17:35	Recycling metals by controlled transfer of ionic species between complex fluids <u>S. Dourdain</u> , T. Zemb, University of Montpellier 2, Bagnols-sur-zeze/F	196	Extraction and throughput for micro-solvent extraction of platinum using a single chip and a multi-chip module <u>C. Priest</u> , F.H. Kriel, S.F. Hashmi, L. Parkinson, J. Ralston, University of South Australia, Mawson Lakes/AUS; S. Woollam, N. Plint, Anglo Research, Germiston/ZA; R.A. Grant, P. Ash, Johnson Matthey Technology Centre, Reading/UK	227
18:05	Polymer/ionic liquid composite membranes for olefin selective separation <u>D. Gorri</u> , R. Zarca, A. Ortiz, I. Ortiz, University of Cantabria, Santander/E	197	Membrane microcontactors for multi-stage countercurrent extraction J. Hereijgers, Vrije Universiteit Brussel/B; T. Breugelmans, University of Antwerp/B; <u>W. De Malsche</u> , Vrije Universiteit Brussel/B	233
18:30	COFFEE BREAK			
18:30	POSTER PARTY			
21:00				

Tuesday, 9 September 2014

Franconia lecture hall

Chair: H.-J. Bart, TU Kaiserslautern/D

08:30 **Recovery of minor metals from secondary sources using solvent extraction** 234
E. Paatero, Outotec Oyj, Espoo/FIN; S. Virolainen, Lappeenranta University of Technology/FIN

09:15 COFFEE BREAK AND SNACKS

Franconia lecture hall

Room Neumann

Novel reagents, materials and techniques

Fundamentals

Chair: H.-J. Bart, TU Kaiserslautern/D

Chair: S. Enders, TU Berlin/D

09:45 **Specific phenomena in extraction of organic acids with ionic liquids and formulation of solvents for extractive separations** 240
S. Schlosser, M. Blahusiak, J. Marták, Slovak University of Technology, Bratislava/SK

Flow modification induced by the presence of droplets in Taylor-Couette flows 255
D. Dherbecourt, M. Nemri, S. Charton, CEA, Bagnols-sur-ceze/F; E. Climent, IMFT, Toulouse/F

10:10 **Sponge-like ionic liquids. A new platform for synthesis and pure product separation** 241
P. Lozano, J.M. Bernal, University of Murcia/E; E. Garcia-Verdugo, University Jaume I, Castellon/E; G. Sanchez, University of Murcia/E; M.I. Burguete, S.V. Luis, University Jaume I, Castellon/E

A numerical investigation of the impact of Marangoni convection on oscillating rising droplets in liquid/liquid systems 256
R.F. Engberg, University of Paderborn/D; M. Wegener, TU Berlin/D; E.Y. Kenig, University of Paderborn/D

10:35 **Design of novel ionic liquids solvents for the selective recovery of carbon monoxide** 247
G. Zarca, I. Ortiz, A. Urutiaga, University of Cantabria, Santander/E

Analysis of drop breakage in turbulent flow 262
M. Kraume, S. Nachtigall, TU Berlin/D

11:00 **Factors influencing the modes of metal ion partitioning into room-temperature ionic liquids** 253
M. Dietz, University of Wisconsin – Milwaukee, WI/USA

Interfacial dynamic in liquid/liquid extraction processes probed by non-linear optics 263
O. Diat, P.M. Gassin, ICSM, Bagnols-sur-ceze/F; G. Martin-Gassin, ICGM, Montpellier 2/F; J.F. Dufreche, ICSM, Bagnols-sur-ceze/F; L. Couston, F. Canto, CEA Marcoule, Bagnols-sur-ceze/F; E. Benichou, P.F. Brevet, ILM, Villeurbanne/F

11:25 **Kinetics and mechanism of enantio-selective extraction of amino acid by organometallic complex** 254
M. Gramblicka, S.R.A. Kersten, University of Twente, Enschede/NL; H.J. Heeres, University of Groningen/NL; B. Schuur, University of Twente, Enschede/NL

Prediction of interfacial properties in demixed ternary system 264
T. Grunert, S. Enders, TU Berlin/D

11:50 LUNCH BREAK

13:50 Excursion

Tuesday, 9 September 2014

Franconia lecture hall

Chair: H.-J. Bart, TU Kaiserslautern/D

08:30 **Recovery of minor metals from secondary sources using solvent extraction** 234
E. Paatero, Outotec Oyj, Espoo/FIN; S. Virolainen, Lappeenranta University of Technology/FIN

09:15 **COFFEE BREAK AND SNACKS**

Room Auvera/Bossi/Wagner

Room Tiepolo

**Process chemistry
and engineering**

**Biotechnology, pharmaceutical, life science
and organic products**

Chair: D. Pfeiffer, BASF SE Ludwigshafen/D

Chair: A. de Haan, Delft University of Technology/NL

09:45 **Evaluation of a hydrocyclone technology for separation of industrial extraction systems** 270
E.W. Barega, E. Zondervan, A.B. de Haan, Eindhoven University of Technology/NL; W. Hoek, Lyondell Basell, Rotterdam/NL; K. Babic, DSM, Geleen/NL

Centrifugal partitioning chromatography – multistage aqueous two phase extraction of biopharmaceutical products 287
C. Ladd Effio, S.A. Oelmeier, J. Hubbuch, Karlsruhe Institute of Technology (KIT)/D

10:10 **Operating window of a multistage rotor-rotor spinning disc extractor** 277
W. Hengeveld, J. Vissers, R. van Kouwen, Spinid B.V., Eindhoven/NL; K. Babic, DSM, Geleen/NL; J.C. Schouten, J. van der Schaaf, Eindhoven University of Technology/NL

Multistage monoclonal antibody purification by aqueous two-phase extraction – experiment and modeling 288
J. Mündges, J. Zierow, T. Zeiner, TU Dortmund/D

10:35 **Investigation of the reactive extraction of terpenylamines with an acid-base reaction** 278
R. Schulz, R. Bongard, B. Szymplinski, T. Zeiner, A. Górak, TU Dortmund/D

Predicting phase behavior of aqueous-protein solutions 289
C. Brandenbusch, C. Kress, G. Sadowski, TU Dortmund/D

11:00 **Citric acid extraction by liquid surfactant membranes in a continuous pilot plant** 279
C. Konzen, J.S. Barbosa, Universidade Federal de Minas Gerais, Belo Horizonte/BR; L.C. Meira-Melo, Centro de Desenvolvimento de Tecnologia Nuclear, Belo Horizonte/BR; E.M.R. Araújo, J.C. Balarini, T.L.S. Miranda, A. Salum, Universidade Federal de Minas Gerais, Belo Horizonte/BR

Ionic liquid-based three phase partitioning for protein recovery 291
E. Alvarez-Guerra, A. Irabien, Universidad de Cantabria, Santander/E

11:25 **The use of option trees for the selection of solvents and reactive extractants for the design of biocompatible separation processes** 286
A. Bednarz, RWTH Aachen/D; P. Scherübel, TU Graz/A; A. Spieß, RWTH Aachen/D; A. Pfennig, TU Graz/A

Scalable technology for the extraction of pharmaceuticals 297
S. Ignatova, P. Hewitson, Brunel University, Uxbridge/UK; C. Thickett, N. Douillet, D. Johns, K. Freebairn, GlaxoSmithKline, Stevenage/UK; P. Wood, G. Harris, D. Rooke, Dynamic Extractions Ltd., Slough/UK; R. Brown, Pfizer Ltd., Sandwich/UK; I. A. Sutherland, Brunel University, Uxbridge/UK

11:50 **LUNCH BREAK**

13:50 **Excursion**

Wednesday, 10 September 2014

Franconia lecture hall

Chair: J. Stube, TU Clausthal/D

08:30	Green solvents for natural products extraction 298 F. Chemat, Avignon University/F
09:15	COFFEE BREAK AND SNACKS

Franconia lecture hall

Room Tiepolo

	Hydrometallurgy and metals extractions	Fundamentals
	<i>Chair: G. Modolo, Forschungszentrum Jülich GmbH/D</i>	<i>Chair: M.B. Mansur, Uni. Fed. de Minas Gerais, Belo Horizonte/BR</i>
09:45	Process for uranium recovery from mixed sulfate/chloride media 299 J. Quinn, K. Soldenhoff, ANSTO, Sydney/AUS	Combined sedimentation and mass-transfer experiments with a concentration gradient in the continuous phase 350 E. Cvetkovic, A. Pfennig, Graz University of Technology/A
10:10	Enhanced extraction of uranium from phosphoric acid with synergistic solvent mixture of DNPPA and bidentate octyl (phenyl) CMPO 301 D. Singh, S. Mondal, M. Anitha, J. Sharma, H. Singh, Bhabha Atomic Research Centre, Mumbai/IND	Prediction of holdup, droplet diameter and axial mixing in a rotating disc contactor 351 H. Chen, Z. Sun, G. Lu, X. Song, J. Yu, East China University of Science and Technology, Shanghai/CHN
10:35	Revisited physicochemistry of uranium (VI) extraction from wet phosphoric acid by D2EHPA-TOPO 302 D. Beltrami, G. Cote, ENSCP, Paris/F; H. Mokhtari, B. Courtaud, Areva, Bessines sur Gartempe/F; A. Chagnes, ENSCP, Paris/F	Ionic influence on coalescence and repulsion behavior in liquid-liquid dispersions 357 F. Gebauer, University of Kaiserslautern/D; J. Villwock, J. Kamp, TU Berlin/D; H.-J. Bart, University of Kaiserslautern/D; M. Kraume, TU Berlin/D
11:00	Comprehension of synergistic mechanisms for uranium extraction from phosphoric ores 303 O. Pecheur, D. Guillaumont, Commissariat à l'Energie Atomique de Marcoule, Bagnols-sur-ceze/F; S. Dourdain, Institut de Chimie Séparative de Marcoule, Bagnols-sur-ceze/F; F. Testard, Commissariat à l'Energie Atomique de Saclay, Gif-sur-Yvette/F	Influence of ion species and ionic strength on the dynamic coalescence of single drops 358 J. Villwock, J. Kamp, M. Kraume, TU Berlin/D; F. Gebauer, H.-J. Bart, University of Kaiserslautern/D
11:25	New process for the selective extraction of uranium from phosphoric ores 304 G. Bernier, M. Miguiditchian, C. Balaguer, X. Hérès, V. Pacary, M. Bertrand, B. Camès, CEA, Bagnols-sur-ceze/F; H. Mokhtari, AREVA NC, Bessines-sur-Gartempe/F	Impact of drop size and relative velocity on coalescence in liquid/liquid dispersions 359 J. Kamp, J. Villwock, M. Kraume, TU Berlin/D

11:50

LUNCH BREAK

Franconia lecture hall

Chair: J. Koch, Sulzer Chemtech AG, Allschwil/CH

13:20	1D to 3D CFD extraction column design – state-of-the-art and future challenges 408 M.W. Hlawitschka, H.-J. Bart, University of Kaiserslautern/D
13:50	Changing physical properties – a challenge for extraction equipment and processes 415 J. Herguijuela, J. Koch, Sulzer Chemtech AG, Allschwil/CH
14:20	COFFEE BREAK

Wednesday, 10 September 2014

Franconia lecture hall

Chair: J. Stube, TU Clausthal/D

08:30	Green solvents for natural products extraction 298 F. Chemat, Avignon University/F
09:15	COFFEE BREAK AND SNACKS

Room Auvera/Bossi/Wagner

Room Neumann

	Extraction of natural products from plants	Novel reagents, materials and techniques
	<i>Chair: J. Stube, TU Clausthal/D</i>	<i>Chair: M. Häberl, Merck KGaA, Darmstadt/D</i>
09:45	Optimizing plant-material extraction processes 388 J.B. Bol, A. Pfennig, Graz University of Technology/A	Recovery of germanium from synthetic leach solution of zinc refinery residue using novel synergistic solvent extraction 437 S. Nusen, CSIRO, Perth/AUS; T. Chairuangsi, Chiang Mai University/T; Z. Zhu, C.Y. Cheng, CSIRO, Perth/AUS
10:10	Solvent extraction optimization of added value components from oats: scale up perspective 389 R. Orozco Mena, E. Ortega Rivas, S. Pérez Vega, Autonomous University of Chihuahua/MEX	A new process design for lignite extraction by immersion 443 M. Wollmerstädt, F. Fehse, V. Herdegen, H.-W. Schröder, TU Bergakademie Freiberg/D; T. Naundorf, ROMONTA Unternehmensgruppe, Seegebiet Mansfelder Land/D; J.-U. Repke, TU Bergakademie Freiberg/D
10:35	Surfactant-based extraction of microalgae products 395 R. Racheva, Hamburg University of Technology/D; M. Kerner, SSC Ltd., Hamburg/D; I. Smirnova, Hamburg University of Technology/D	Lithium discriminating extraction with tripropyl-monoacetic acid derivative of calix[4]arene 449 K. Ohto, H. Sadamatsu, S. Morisada, H. Kawakita, Saga University/J
11:00	Enhanced early stage solvent selection and evaluation in the extraction of peanut skin polyphenols 401 S.A. Medina-González, H.F. Almeida-Trasviña, I. Salmerón-Ochoa, S.B. Pérez-Vega, Autonomous University of Chihuahua/MEX	New reagents for uranium(VI) extraction from concentrated phosphoric acid 455 D. Beltrami, A. Chagnes, ENSCP, Paris/F; H. Mokhtari, B. Courtaud, Areva, Bessines sur Gartempe/F; G. Cote, ENSCP, Paris/F
11:25	Extraction of apigenin from dried parsley (Petroselinum crispum L.) powder by water, organic solvent and supercritical carbon dioxide 402 Y. Saotome, M. Imai, Nihon University, Kameino/J	Synthesis of high purity didecylphosphinic acid for extraction of heavy rare earth L. Li, S. Xu, X. Wang, X. Liu, Tsinghua University, Beijing/CHN

LUNCH BREAK

Franconia lecture hall

Chair: J. Koch, Sulzer Chemtech AG, Allschwil/CH

13:20	1D to 3D CFD extraction column design – state-of-the-art and future challenges 408 M.W. Hlawitschka, H.-J. Bart, University of Kaiserslautern/D
13:50	Changing physical properties – a challenge for extraction equipment and processes 415 J. Herguívela, J. Koch, Sulzer Chemtech AG, Allschwil/CH
14:20	COFFEE BREAK

Wednesday, 10 September 2014

	Franconia lecture hall	Room Tiepolo
	Hydrometallurgy and metals extractions	Fundamentals
	<i>Chair: M. O. Garg, CSIR-Indian Institute of Petroleum/IN</i>	<i>Chair: M. Siebenhofer, Graz University of Technology/A</i>
14:50	Solvent extraction versus nano-filtration for upgrading uranium and recovery of acid from an ion exchange eluate 310 <u>S. Archer</u> , V. Coetzee, DRA Mineral Projects (Pty) Ltd, Johannesburg/ZA; A. Feather, BASF, Johannesburg/ZA; A. Manis, ANSTO, Sydney/AUS	Kinetics of liquid/liquid extraction of europium(III) cation by two malonic diamides 360 J.P. Simonin, Université P.M. Curie, Paris/F
15:15	Novel solvent extraction process for the recovery of gold from chloride media 318 <u>N. Davidson</u> , B. Eade, R.A. Grant, Johnson Matthey, Reading/UK	Palladium-malonamides: molecular aspects of L/L extraction 366 <u>R. Poirot</u> , CEA/ICSM/LCPA, Bagnols-sur-Ceze/F; D. Bourgeois, CNRS/ICSM/LCPA, Bagnols-sur-Ceze/F; D. Meyer, CEA/ICSM/LCPA, Bagnols-sur-Ceze/F
15:40	Metal separation from e-waste by solvent extraction with CYANEX 471X 324 <u>J. Yang</u> , S. Kosaraju, C. Ekberg, S. Allard, T. Retegan, Chalmers University of Technology, Gothenburg/S	Selective extraction of copper(II) from ammonia solution 372 <u>K. Wieszczycka</u> , M. Krupa, A. Wojciechowska, A. Olszanowski, Poznan University of Technology/PL
16:05	Outer-sphere coordination chemistry: use of amido-ammonium ligands as selective extractants for precious metals 331 <u>R. Luckay</u> , University of Stellenbosch/ZA; P. Tasker, G. Murray, M.A. Wilson, W. Roebuck, J.R. Turkington, J.B. Love, University of Edinburgh/UK	COSMO-RS as a powerful tool for solvent screening and liquid extraction simulation 378 <u>A. Klamt</u> , F. Eckert, J. Reinisch, COSMOlogic GmbH & Co. KG, Leverkusen/D
16:30	COFFEE BREAK AND SNACKS	
	<i>Chair: G. M. Ritcey, Nepean/CDN</i>	<i>Chair: M. Weber, Ineos Phenol GmbH, Gladbeck/D</i>
17:00	Recycling of Co_2^+, Cu_2^+ and Li^+ from Li-ion battery scrap 337 <u>M. Siebenhofer</u> , Graz University of Technology/A; H. Noll, AVL, Graz/A; M. Fritz, Epcos, Deutschlandsberg/A	Influences of interfacial phenomena on transport processes in micellar liquid/liquid systems 379 <u>N. Paul</u> , S.-J. Kim, M. Kraume, TU Berlin/D
17:25	LiSX™: A breakthrough in lithium production 338 J. Lipp, Tenova Bateman Technologies, Yokneam/IL	Electrostatically induced droplet agitation in solvent extraction 380 <u>S. Assmann</u> , <u>D. Ibana</u> , Curtin University, Kalgoorlie/AUS; C. McRae, Macquarie University, Sydney/AUS
17:55	Modular Mixer-Settler technology for medium scale satellite mining operations 344 <u>J.P.J. Matinheikki</u> , R.T. Saario, H.M. Fredriksson, Outotec (Finland) Oy, Espoo/FIN	Preparation of the novel ionic liquids functionalized resins with tunable structure for metal ions separation 387 <u>H. Cui</u> , J. Chen, Y. Liu, Chinese Academy of Sciences, Changchun/CHN
19:00 23:00	Conference Dinner	

Wednesday, 10 September 2014

	Room Auvera/Bossi/Wagner	Room Neumann
	Extraction of natural products from plants	CFD applications
	<i>H. Liu, Chinese Academy of Sciences, Beijing/RC</i>	<i>Chair: J. Koch, Sulzer Chemtech AG, Allschwil/CH</i>
14:50	2-Dibutylaminoethanol as a switchable solvent for lipid extraction from <i>Desmodemus</i> sp. 416 <i>Y. Du, K. Tran, B. Schuur, D.W.F. Brilman, University of Twente, Enschede/NL</i>	CFD simulation of mixer-settler systems; evaluation of the effect of fluid's velocity on the flow pattern and phase separation 457 <i>O. Kazemi, E. Keshavarz Alamdari, Amirkabir University of Technology, Tehran/IR</i>
15:15	Microwave-assited and cloud point extraction and separation of active ingredients from natural products 422 <i>F. Deng, X. Liang, C. Hua, H. Liu, Chinese Academy of Sciences, Beijing/CHN</i>	Experimental and CFD study of drop formation at high jet velocity 468 <i>E. Sanz, P. Béard, F. Augier, M. Le Möel, D. Leinekugel-Le-Cocq, A. Baudot, IFP Energies nouvelles, Solaize/F</i>
15:40	Valorization of hemp wood to obtain high value bioproducts 423 <i>S. Bassil, L. Candy, Laboratoire de Chimie Agro-Industrielle, Toulouse/F; A. Thuret, A. Masseron, Institut de Science des Matériaux de Mulhouse/F; V. Simon, C. Raynaud, Laboratoire de Chimie Agro-Industrielle, Toulouse/F</i>	Hybridisation of Taylor-Couette reactors and RDC columns 469 <i>E. Aksamija, M. Siebenhofer, TU Graz/A</i>
16:05	Salt influence on the partitioning of HMF in aqueous/organic systems 424 <i>S. Mohammad, C. Held, E. Altuntepe, G. Sadowski, TU Dortmund/D</i>	Modeling and study of the dispersed phase behaviour in a pulsed column 470 <i>A. Amokrane, S. Charton, CEA, Bagnols-sur-ceze/F; J.P. Klein, F. Puel, Université Lyon 1, Villeurbanne/F</i>
16:30	COFFEE BREAK AND SNACKS	
	Nuclear fuel reprocessing	
	<i>S. Schlosser, Slovak University of Technology, Bratislava/SL</i>	<i>M. Hlawitschka, TU Kaiserslautern/D</i>
17:00	New dipicolinic acid derivatives for actinide-lanthanide separations 425 <i>K. Nash, C. Heathman, Washington State University, Pullman, WA/USA</i>	A modified rotating disc contactor to eliminate flow dead zones 471 <i>Z. Sun, H. Chen, G. Lu, P. Li, J. Yu, East China University of Science and Technology, Shanghai/CHN</i>
17:25	Effect of the central frames and substituents attached to N atoms on extraction ability of podand-type extractants 431 <i>Y. Sasaki, Y. Kitatsuji, Y. Sugo, Y. Tsubata, T. Kimura, Y. Morita, Japan Atomic Energy Agency, Tokai/J</i>	Comprehensive numerical and experimental analysis of copper solvent extraction within Y-Y microreactors 477 <i>O. Kazemi, P. Ribeiro Martins Bento, S. Miskovic, University of Utah, Salt Lake City, UT/USA</i>
17:55	New developments with monoamide type extractants 436 <i>C. Sorel, M. Miguirditchian, CEA, Bagnols-sur-ceze/F</i>	Simulation of organic drop coalescence in a hypothetical settler: effect of geometry and fluid parameters 478 <i>O. Kazemi, S. Parvizi, E. Keshavarz Alamdari, Amirkabir University of Technology, Tehran/IR</i>
19:00 23:00	Conference Dinner	

Thursday, 11 September 2014

Franconia lecture hall

Chair: S. Bélair, Emrat Research, Trappes/F

08:30 **The role of solvent extraction in platinum group metal refining – past, present and future** 480
R. Grant, Johnson Matthey Technology Centre, Reading/UK; S.F. Woollam,
 Anglo American's Technical Solutions, Johannesburg/ZA

09:15 COFFEE BREAK AND SNACKS

Room Auvera/Bossi/Wagner

Room Neumann

Hydrometallurgy and metals extractions

Nuclear fuel reprocessing

Chair: W. Gutknecht, H.C. Stark GmbH, Goslar/D

Chair: H. Reinhardt, MEAB Metallextraktion AB, Askim Göteborg/S

09:45 **Separation of Fe(III) from a synthetic nickel laterite leach solution with high chloride concentration using DEDOA** 486
Z. Zhu, Y. Pranolo, C.Y. Cheng, CSIRO, Perth/AUS

Americium and curium separations 532
B. Moyer, Oak Ridge National Laboratory, TN/USA

10:10 **Extraction of cobalt from a liquor rich in nickel by liquid surfactant membrane and liquid-liquid extraction techniques** 492
E.M.R. Araújo, C. Konzen, J.C. Balarini, T.L.S. Miranda, A. Salum, Universidade Federal de Minas Gerais, Belo Horizonte/BR

A new appraisal of wastes from an aqueous solvent extraction based reprocessing facility 533
C. Phillips, W. Willis, R. Carter, EnergySolutions plc, Richland, WA/USA; S. Baker, UK National Nuclear Laboratory, Warrington/UK

10:35 **Separation and purification of zirconium with amines from sulphuric acid system: a review** 499
V.I. Lakshmanan, R. Sridhar, Z. Jankovic, M.A. Halim, Process Research ORTECH Inc., Mississauga/CDN

On-line monitoring of used nuclear fuel separation processes by spectroscopic analysis 539
K. Nee, University of California/USA; S. Bryan, T. Levitskaia, Pacific Northwest National Laboratory, Richland, WA/USA; M. Nilsson, University of California/USA

11:00 **Development of novel extractants with amino acid structure for highly effective recovery and separation of nickel and cobalt ions** 500
Y. Baba, F. Kubota, N. Kamiya, M. Goto, Kyushu University, Fukuoka/J

The redox chemistry of neptunium in gamma-irradiated aqueous nitric acid 545
B.J. Mincher, Idaho National Laboratory, Idaho Falls, ID/USA; M. Precek, Oregon State University, Corvallis, OR/USA; G. Elias, Idaho National Laboratory, Idaho Falls, ID/USA; S.P. Mezyk, California State University, Long Beach, CA/USA; L.R. Martin, Idaho National Laboratory, Idaho Falls, ID/USA; A. Paulenova, Oregon State University, Corvallis, OR/USA

11:25 **Recovery of Ni and Cd from spent Ni-Cd batteries by acid leaching and a synergistic solvent extraction system using D2EHPA and Cyanex 302** 512
A. Babakhani, N. Heidari, F. Rashchi, S.M.M. Noori, University of Tehran/IR

Microemulsions and aggregation formation in extraction processes for used nuclear fuel 551
M. Nilsson, A. Braatz, A. Jackson, University of California/USA; P. Zalupski, Idaho National Laboratory, Idaho Falls, ID/USA; R. Ellis, M. Antonio, Argonne National Laboratory, Chicago, IL/USA

11:50 LUNCH BREAK

Thursday, 11 September 2014

Franconia lecture hall

Chair: S. B  lair, Emrat Research, Trappes/F

08:30 **The role of solvent extraction in platinum group metal refining – past, present and future** 480
R. Grant, Johnson Matthey Technology Centre, Reading/UK; S.F. Woollam,
Anglo American's Technical Solutions, Johannesburg/ZA

09:15 COFFEE BREAK AND SNACKS

Room Tiepolo

Franconia lecture hall

**Process chemistry
and engineering**

**Novel reagents,
materials and techniques**

Chair: J. Leistner, Evonik Industries AG, Darmstadt/D

Chair: S. B  lair, Emrat Research, Trappes/F

09:45 **Application related design of liquid-liquid decanters of challenging technical systems** 576
M. Haneke, Evonik Industries AG, Marl/D;
J. Leistner, Evonik Industries AG, Darmstadt/D;
M. Mendorf, Evonik Industries AG, Marl/D

Gold, palladium, and platinum adsorption from leached electronic scrap using ordered mesoporous carbon nanoscaffolds 628
P. Zalupski, R. McDowell, Idaho National Laboratory, Idaho Falls, ID/USA

10:10 **An approach to predict the dispersing efficiency in static mixers, centrifugal pumps and turbulent pipe flow will be presented** 577
M. Weber, Ineos Phenol GmbH, Gladbeck/D

Molecular and supramolecular speciation in organic extractant solutions: influence of the metal concentration on extraction efficiency 634
L. Berthon, P. Guilbaud, Y. Meridiano, J. Muller, CEA Marcoule, Bagnols-sur-zeze/F; R. Ellis, M. Antonio, Argonne National Laboratory, IL/USA

10:35 **Comparison of the model prediction and industrial data in pulsed disc doughnut extraction column** 583
Y. Wang, K.A. Mumford, The University of Melbourne/AUS; S. Ballestrin, Uranium One Inc./AUS; K. Smith, T.F. Grabin, G.W. Stevens, The University of Melbourne/AUS

Process for the selective membrane-based solvent extraction recovery and enrichment of Pt, Pd and Rh from spent catalyst leaching solutions 640
D.J. van der Westhuizen, North-West University, Potchefstroom/ZA; E. Bringas, I. Ortiz, Universidad de Cantabria, Santander/E; H.M. Krieg, North-West University, Potchefstroom/ZA

11:00 **OSN (Organic Solvent Nanofiltration) – a new technology for hybrid processes with solvent extraction** 589
A. Boam, Evonik Membrane Extraction Technology Ltd., Wembley/UK; A. Kobus, Evonik Industries AG, Marl/D; C. Schnitzer, I. Rocha, V. Koleva, Y. Bouwhuis, Evonik Membrane Extraction Technology Ltd., Wembley/UK

Recovery of platinum(IV) and palladium(II) from complex hydrochloric acid matrices by a thiodiglycolamide derivative 641
A. Paiva, G. Carvalho, University of Lisbon/P; M. Costa, A. Costa, University of Algarve, Faro/P; C. Nogueira, Laborat  rio Nacional de Energia e Geologia, Lisbon/P

11:25 **Stacked multi channel reactor for solvent extraction process** 590
A. Matsuoka, K. Noishiki, Kobe Steel, LTD./J

Probing the outer coordination sphere to define the mode of action of unusually strong and selective metal extractants 647
P. Tasker, University of Edinburgh/UK; E. Carter, I. Fallis, Cardiff University/UK; R. Forgan, R. Gordon, J. Love, C. Morisson, University of Edinburgh/UK; D. Murphy, Cardiff University/UK

11:50 LUNCH BREAK

Thursday, 11 September 2014

Franconia lecture hall

Chair: B. Moyer, Oak Ridge National Laboratory/USA

13:20	Troubleshooting at Honeymoon – from trouble to success H. Aharon, <u>B. Grinbaum</u> , Bateman, Yokneam/IL	596
13:50	Award Session	
14:20	COFFEE BREAK	

Room Tiepolo

Room Neumann

	Hydrometallurgy and metals extractions		Nuclear fuel reprocessing	
	<i>Chair: G. Stevens, The University of Melbourne/AUS</i>		<i>Chair: B. Moyer, Oak Ridge National Laboratory/USA</i>	
14:50	Homogeneous liquid-liquid extraction of metals with ionic liquids <u>B. Onghena</u> , K. Binnemans, KU Leuven, Heverlee/B	518	Development of the actinide-lanthanide separation (ALSEP) process <u>G.J. Lumetta</u> , J.C. Carter, C.M. Niver, Pacific Northwest National Laboratory, Richland, WA/USA; A.V. Gelis, Argonne National Laboratory, IL/USA	557
15:15	Extraction of Zn(II), Cd(II), Hg(II) and Co(II) by a high quaternary ammonium salts <u>A. Trofimenko</u> , A. Gulevich, Belarusian State University, Minsk/BY	519	High LET radiolytic degradation of solvent extraction processes for used nuclear fuel J. Pearson, <u>M. Nilsson</u> , University of California/USA	563
15:40	About the origin of “synergism” in ion selectivity in metal salt extraction by microemulsions <u>S. Dourdain</u> , S. Pellet-Rostaing, D. Meyer, University of Montpellier 2, Bagnols-sur-ceze/F	525	The radiation chemistry of CMPO <u>S. Mezyk</u> , California State University, Long Beach, CA/USA; B.J. Mincher, Idaho National Laboratory, Idaho Falls, ID/USA; M. Nilsson, J. Pearson, California State University, Irvine, CA/USA; J. LaVerne, University of Notre Dame, IN/USA	569
16:05	Operational and design features related to copper solvent extraction wash stages <u>H. Hein</u> , R. Hein, Oryxeio Ingeniêria Limitada, Providencia/RCH	526	Adsorption characteristics of fission product elements constituting high level liquid wastes for macro-cyclic resins <u>M. Ozawa</u> , T. Kaneshiki, Tokyo Institute of Technology/J; T. Sychra, Slovak University of Technology, Bratislava/SK; M. Nomura, Tokyo Institute of Technology/J; Y. Ohishi, T. Sakurai, Atox, Tokyo/J	575
16:35	Closing Ceremony			
16:45	End of Conference			

Thursday, 11 September 2014

Franconia lecture hall

Chair: B. Moyer, Oak Ridge National Laboratory/USA

13:20	Troubleshooting at Honeymoon – from trouble to success H. Aharon, <u>B. Grinbaum</u> , Bateman, Yokneam/IL	596
13:50	Award Session	
14:20	COFFEE BREAK	

Franconia lecture hall

Room Auvera/Bossi/Wagner

Process chemistry and engineering	Biotechnology, pharmaceutical, life science and organic products
-----------------------------------	--

K. L. Nash, Washington State University, Pullman/USA

Chair: B. Schuur, University of Twente, Enschede/NL

14:50	Mooresboro zinc project: first solvent extraction plant in the world to produce zinc entirely from recycling G. Diaz, <u>E. Pecharroman</u> , S. Sanguilinda, Tecnicas Reunidas, Madrid/E; J. Pusateri, Horsehead Corporation, Pittsburgh, PA/USA	602	An innovative mixing technology to improve phase separation in recovery and purification of carboxylic acids by solvent extraction S. Roman, Turbulent Technologies Ltd., Jerusalem/IL; <u>N. Dobrin</u> , O. Lerner, Tenova Bateman Technologies, Yokneam/IL	653
15:15	State of the art of solvent extraction and electrowinning design <u>L. John</u> , DRA Mineral Projects (Pty) Ltd., Johannesburg/ZA; G.M. Miller, Miller Metallurgical Services Pty Ltd., Corinda/AUS	609	API recovery from pharmaceutical waste streams by continuous countercurrent extraction <u>S. Ignatova</u> , P. Hewitson, I.A. Sutherland, Brunel University, Uxbridge/UK; P. Wood, Dynamic Extractions Ltd., Uxbridge/UK; N. Douillet, C. Thickett, D. Johns, K. Freebairn, GlaxoSmithKline, Stevenage/UK	659
15:40	Recovery of phenol from catalytic pyrolysis bio-oil – an industrial perspective <u>K. Babic</u> , B. Engendahl, T. van Houtem, R. Parton, DSM, Geleen/NL	616	Recovery of valuable products from biomass using a KARR column T. Lightfoot, Koch Modular Process Systems, LLC, Houston, TX/USA; <u>D. Glatz</u> , Koch Modular Process Systems, LLC, Paramus, NJ/USA	660
16:05	Copper solvent extraction plant commissioning <u>M.F. Vancas</u> , Tenova Bateman Technologies MESA, Tucson, AZ/USA	622	A new approach to coil-planet centrifuges for extraction and phase separation in downstream processing <u>P. Scherübel</u> , A. Pfennig, Graz University of Technology/A	664
16:35	Closing Ceremony			
16:45	End of Conference			

ANALYTICAL AND PREPARATIVE APPLICATIONS

- P 1.1 **Determination of PCDD/Fs and dioxin-like PCBs in the ambient air of the cement industry using the CALUX bioassay and the sensitive H1L7.5c** 666
S. Khedidji, University Akli Mohand Oulhaj Bouira/DZ; K. Croes, Vrije Universiteit Brussel/B; N. Yassaa, Centre Développement Energies Renouvelable, Alger/DZ; R. Ladj, Centre Recherche Scientifique Technique Analyses Physico Chimiques, Alger/DZ; M. Elskens, W. Baeyens, Vrije Universiteit Brussel/B
- P 1.2 **Transport of Pd(II) and Au(III) through redox-active bulk liquid membranes and the simultaneous formation of gold micro- and nanoparticles** 667
M. Sánchez-Loredo, Universidad Autónoma de San Luis Potosí/MEX; M. Grote, Universität Paderborn/D
- P 1.3 **The extraction of Co(II) with Cyanex 272 in a neutral micellar system** 673
 F. Xiao, Y. Wang, The University of Melbourne/AUS; X. Shen, Henan University, Luo Yang/CHN; G.W. Stevens, J.M. Perera, The University of Melbourne/AUS
- P 1.4 **Optimizing crude oil separations – a study of turbulence and composition influence on the drop size distribution of crude oil in sea water** 679
 S. Maaß, SOPAT GmbH, Berlin/D

BIOTECHNOLOGY, PHARMACEUTICAL, LIFE SCIENCE AND ORGANIC PRODUCTS

- P 2.1 **Extraction of succinic acid by aqueous two phase system (ATPS) using ionic liquids and salts** 680
A.I. Pratiwi, M. Matsumoto, K. Kondo, Doshisha University, Kyotanabe/J
- P 2.3 **Reactive extraction of aminoacids – selective separation** 685
A.C. Blaga, D. Cascaval, L. Kloetzer, A. Carlescu, "Gheorghe Asachi" Technical University of Iasi/RO; A.I. Galaction, "Gr.T. Popa" University of Medicine and Pharmacy of Iasi/RO
- P 2.4 **Separation of zirconium and hafnium by solvent extraction from nitric liquor – part 1** 686
D. Carlos, C.B.S. Janúbia, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte/BR
- P 2.5 **Multistage extraction as a method of dicarboxylic acids removal from glycerol bioconversion fermentation broths** 692
M. Regel-Rosocka, A. Krzyzkowska, D. Bednarska, M. Wisniewski, Poznan University of Technology/PL

CFD APPLICATIONS

- P 3.1 **Drop formation at a nozzle hole in a plate for quiescent continuous phase** 693
N. Sen, K.K. Singh, S. Mukhopadhyay, K.T. Shenoy, S.K. Ghosh, Bhabha Atomic Research Center, Mumbai/IND
- P 3.4 **Modelling approach to estimate droplet interaction parameters** 699
H. Jildeh, University of Kaiserslautern/D; M. Attarakih, University of Jordan, Amman/JOR; H.-J. Bart, University of Kaiserslautern/D

POSTERPROGRAMME

EXTRACTION OF NATURAL PRODUCTS FROM PLANTS

P 4.2	Green extraction of aromas from herbs and spices using alternative solvents: theoretical and experimental solubility study <u>A. Filly</u> , Avignon University/F	705
P 4.3	Bioguided fractionation and isolation of natural anti-ulcerogenic compounds and <i>anti-Helicobacter pylori</i> from <i>Convolvulus austroaegyptiacus</i> <u>A. Al-Rifai</u> , A. Awaad, A. Aqel, King Saud University, Riyadh/SAR	706
P 4.4	Salt influence on the partitioning of HMF in aqueous/organic systems <u>S. Mohammad</u> , C. Held, E. Altuntepe, G. Sadowski, TU Dortmund/D	707
P 4.5	Three-liquid-phase extraction and gas-assisted three-liquid-phase extraction of anthraquinones from rhubarb <u>X. Yang</u> , X. Liang, L. Yang, Q. Liu, H. Liu, Chinese Academy of Sciences, Beijing/CHN	708

EXTRACTION ON MINI-SCALE

P 5.1	Pertraction of neodymium by N, N-dibutylacetamide <u>M. Toure</u> , CEA Marcoule and University of Montpellier 2, Bagnols-sur-ceze/F; G. Borda, J. Duhamet, CEA Marcoule, Bagnols-sur-ceze/F; S. Pellet-Rostaing, CNRS, Bagnols-sur-ceze/F	709
P 5.2	A new approach to achieve countercurrent multi-stage micro-extraction <u>S. Li</u> , S. Jing, Tsinghua University, Beijing/CHN	710
P 5.5	Application of microreactor system in solvent extraction of metal ion with calixarene derivatives <u>M. Maeki</u> , Kyushu University, Kasuga/J; J.Y. Kim, Saga University/J; M. Miyazaki, AIST, Tosu/J; K. Ohoto, Saga University/J	711
P 5.6	Concepts for efficient extraction in micro and milli structures – feasibility of countercurrent extraction with segmented flow <u>F. Kaske</u> , D.W. Agar, TU Dortmund/D	716
P 5.7	Simulation based design of extraction columns for aqueous two-phase systems <u>M. Schmidt</u> , M. Wessling, RWTH Aachen/D; A. Pfennig, TU Graz/A	717
P 5.8	Reactive mass transfer in a microstructured counter-current apparatus <u>S. Willersinn</u> , H.-J. Bart, University of Kaiserslautern/D	718

FUNDAMENTALS

P 6.2	How H-bonding networks in reverse micelles drive the extractive transport of Eu(III) nitrate <u>R. Ellis</u> , Argonne National Laboratory, Lemont, IL/USA	725
P 6.3	Experimental and model study on extraction of phenol by toluene <u>Z. Li</u> , K. Mumford, K. Smith, G. Stevens, The University of Melbourne/AUS	726
P 6.4	Mass transfer and hydrodynamic investigation of a hybrid pulsed extraction column <u>Y. Wang</u> , Tsinghua University, Beijing/CHN	732

POSTERPROGRAMME

P 6.5	A new electrochemical approach for solvent extraction processes N. Sadegi, <u>E. Keshavarz Alamdari</u> , Amirkabir University of Technology, Tehran/IR	738
P 6.6	Numerical modelling of centrifugal settlers based on experimental data R. Macher, A. Pfennig, Graz University of Technology/A	745
P 6.7	Influence of the nature of an extragent on the rate of extraction a REE at vibration on a dynamical interfacial layer N. Kizim, E.N. Golubina, Mendelev University of Chemical Technology, Novomoskovsk/RUS	749
P 6.8	Solvation free energies of lead nitrate in mixed DMF-water solvents G. Esam, Mansoura University/ET	750
P 6.9	Gibbs solvation free energies for lead nitrate in mixed dimethylformamide-water solvents E. Gomaa, Mansoura University/ET	751
P 6.10	Heteropolynuclear 3d/4f metal complexes in solvent extraction N. Kelly, K. Schnaars, A. Heine, T. Doert, F. Taube, M. Acker, K. Gloe, K. Gloe, J.J. Weigand, TU Dresden/D	752
P 6.12	Solvent extraction and separation of samarium(III) using hexaacetato calix[6]arene Y.S. Thakare, Amravati University/IND; <u>S.T. Gawhale</u> , D.D. Malkhede, University of Pune/IND	759
P 6.14	Numerical analysis and experimental validation of droplet collision F. Gebauer, M.W. Hlawitschka, University of Kaiserslautern/D; J. Villwock, J. Kamp, TU Berlin/D; H.-J. Bart, University of Kaiserslautern/D; M. Kraume, TU Berlin/D	766
P 6.15	Activity coefficients of di-(2-ethyl hexyl) phosphoric acid by vapor pressure osmometry and slope analysis M. Gray, University of California/USA; P. Zalupski, Idaho National Laboratory, Idaho Falls, ID/USA; G. Modolo, Forschungszentrum Jülich GmbH/D; M. Nilsson, University of California/USA	772
P 6.16	Study of the aggregation of Cyanex 272 and Ionquest 290 by vapor pressure osmometry M. Dehestre, Eramet Research, Trappes/F and Ecole Centrale Paris/F; M. Stambouli, Ecole Centrale Paris/F; M. Gohin, Eramet Research, Trappes/F; D. Pareau, Ecole Centrale Paris/F; Y. Le Quesne, Eramet Research, Trappes/F	778
P 6.17	Multi-scale modelling of droplet interactions in liquid-liquid systems <u>L. R. Mason</u> ; G. W. Stevens; D.J. E. Harvie, The University of Melbourne/AU	784

FUNDAMENTALS/NOVEL REAGENTS, MATERIALS AND TECHNIQUES

P 7.2	Tuning strength of phenolic pyrazole extractants using outer-sphere H-bond buttressing M. Healy, University of Edinburgh/UK; V. Cocalia, Cytec Industries Inc., Stamford, CT/USA; E. Doidge, University of Edinburgh/UK; A. Fischmann, Cytec Industries Inc., Stamford, CT/USA; J. Love, C. Morrison, J. Roebuck, University of Edinburgh/UK; T. Sassi, Cytec Industries Inc., Stamford, CT/USA; P. Tasker, University of Edinburgh/UK	785
P 7.3	Influence of the nature of an extragent on the rate of extraction a REE at vibration on a dynamical interfacial layer N. Kizim, E.N. Golubina, Mendelev University of Chemical Technology, Novomoskovsk/RUS	791

POSTERPROGRAMME

P 7.6	Nitrate based ionic liquid as a new solvent for extraction of aromatic from alkane B. Mokhtarani, CCERCI, Tehran/IR; J. Musavi, Semnan University/IR; A. Sharifi, CCERCI, Tehran/IR; M. Parvini, Semnan University/IR	796
P 7.7	Solvent extraction of precious metal ions with phenylurea type of trident molecule Y. Ueda, S. Morisada, H. Kawakita, K. Ohto, Saga University/J	802
P 7.8	Non-steroidal analgesics and beta-lactam antibiotics extraction with binary extracting agents A.L. Gulevich, V.I. Kuksa, Belarusian State University, Minsk/BY	808
P 7.9	Sorption behaviour of Cd(II) sorption from aqueous solutions using polymeric microcapsules containing an acidic organophosphonic extractant V. Ide, A. Valdés, C. Basualto, J. Sapag, C. Araneda, F. Valenzuela, Universidad de Chile, Santiago/RCH	813
P 7.10	Formation and extraction ability of reverse micelle by intermolecular interaction between di(2-ethylhexyl)phosphoricacid and ethanolamines K. Shiomori, K. Ejima, University of Miyazaki/J; S. Kiyoyama, Miyakonojyo NCT/J; T. Sana, Sansei Giken Co. Ltd., Yoshikawa/J	819
P 7.11	Solvent extraction of palladium from hydrochloric acid media by N,N-disubstituted thioamides A. Paiva, Lisbon University/P; O. Ortet, Lisbon University/P and Cape Verde University, Praia/CV	820
P 7.13	Synthesis of alkylpiperazine and its application to a polymer inclusion membrane for selective separation of Cd(II) over Zn(II) and Ni(II) Y. Baba, C. Aso, T. Oshima, University of Miyazaki/J	826
P 7.14	Synergistic effect of 8-quinolinol derivatives on the supercritical carbon dioxide extraction of gallium(III) with D2EHPA A. Ohashi, N. Kawashima, Haeng-Boo Kim, College of Science, Ibaraki University, Mito/J	832

HYDROMETALLURGY AND METALS EXTRACTIONS

P 8.1	Effect of aggregation on synergistic mechanism for liquid/liquid extraction J. Rey, S. Dourdain, S. Pellet-Rostaing, T. Zemb, CEA Marcoule, Bagnols-sur-Cèze/F	837
P 8.2	Separation of nickel from calcium and magnesium by using mixtures of Cyanex 272 and D2EHPA M.B. Mansur, A.S. Guimaraes, P.S. Silva, Universidade Federal de Minas Gerais, Belo Horizonte/BR	838
P 8.3	A study on solvent extraction reaction of uranium (VI) sulfate with Alamine 336 É. Avelar, G. P. de Souza Resende, M. B. Mansur, Universidade Federal de Minas Gerais, Belo Horizonte/BR	843
P 8.4	Separation of Fe(III) from chloride solution by solvent extraction method and tri-n-butyl phosphate (TBP) N. Sadeghi, E. Keshavarz Alamdari, Amirkabir University of Technology, Tehran/IR	849

P 8.5	Evidence of a predictable difference between nitrate and sulphate anions in the solvent extraction of base metals by acidic extractants <u>M. Hutton-Ashkenny</u> , Curtin University and Direct Nickel Pty. Ltd., Kalgoorlie/AUS; K. Barnard, CSIRO, Perth/AUS; D. Ibana, Curtin University, Kalgoorlie/AUS	855
P 8.6	Partial inhibition of cobalt(III)-LIX®860 formation by organic acids <u>M. Hutton-Ashkenny</u> , Curtin University and Direct Nickel Pty. Ltd., Kalgoorlie/AUS; K. Barnard, CSIRO, Perth/AUS; D. Ibana, Curtin University, Kalgoorlie/AUS	861
P 8.9	Separation of metals from HEV Li-ion batteries, Part1- from nitrate leach liquor <u>S. Kosaraju</u> , C. Ekberg, S. Allard, Chalmers University of Technology, Gothenburg/S	867
P 8.10	Separation of metals from HEV Li-ion batteries, Part2- from sulphate leach liquor <u>S. Kosaraju</u> , C. Ekberg, S. Allard, Chalmers University of Technology, Gothenburg/S	873
P 8.11	Separation of metals from HEV Li-ion batteries, Part3- from chloride leach liquor <u>S. Kosaraju</u> , C. Ekberg, S. Allard, Chalmers University of Technology, Gothenburg/S	879
P 8.12	Separation of copper(II), zinc(II) and nickel(II) from chloride solutions with pyridinecarboxamides P. Budziszewska, I. Madrzak-Litwa, <u>K. Wieszczycka</u> , A. Borowiak-Resterna, Poznan University of Technology/PL	885
P 8.13	Rare earth elements recovery from used NdFeB magnets by leaching and solvent extraction V. Haquin, <u>M. Miguirditchian</u> , CEA Marcoule, Bagnols-sur-CEze/F; R. Laucournet, E. Billy, CEA, Grenoble/F	886
P 8.14	Alkyl derivatives of 2,2'-bibenzimidazole as extractants of d-electron metal ions I. Madrzak-Litwa, <u>K. Wieszczycka</u> , A. Borowiak-Resterna, Poznan University of Technology/PL	887
P 8.15	Zinc extraction from sulfate-chloride solutions with mixtures of a trialkyl amine and carboxylic acids <u>I.Yu. Fleitlikh</u> , G.L. Pashkov, N.A. Grigorieva, Institute of Chemistry and Chemical Technology, Krasnoyarsk/RUS; O.A. Logutenko, Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk/RUS; A.M. Kopanyov, Khimpolitekh Ltd., Novosibirsk/RUS	888
P 8.16	Solvent extraction studies for the separation of rare earth elements using neutral and acidic organophosphorus extractants <u>S. Omanovic</u> , G. Modolo, F. Sadowski, D. Bosbach, Forschungszentrum Jülich GmbH/D	898
P 8.17	Direct extraction of molybdenum from high acid leach solution of Ni-Mo ore using an oxime extractant of HBL@101 <u>L. Zeng</u> , X.L. Liao, L.S. Xiao, Y.H. Sun, Central South University, Changsha/CHN	899
P 8.18	Solvent extraction of zinc and nickel by various methods from zinc plant filter cake <u>D. Moradkhani</u> , University of Zanjan, Zanjan/IR; H. Kamran Haghighi, Amirkabir University of Technology, Tehran/IR; B. Sedaghat, Research and Engineering Company for Nonferrous Metals, Zanjan/IR	96
P 8.19	High selectivity for cobalt / magnesium separation by solvent extraction in a pilot plant <u>M. Moraes Castanho de Almeida</u> , A. Cotrim, Produç�mica Ind�stria e Com�rcio S.A., Suzano/BR	907

POSTERPROGRAMME

P 8.21	Versatic 10 acid/NICKSYN™ synergistic system versus Cyanex 272 for the recovery of cobalt from typical DRC/Zambian copper-Co <u>S. Archer, V. Coetzee, J. Scheepers, DRA Mineral Projects (Pty) Ltd., Johannesburg/ZA; R. du Preez, M. Kotze, Mintek, Johannesburg/ZA</u>	908
P 8.22	Stripping of calcium-loaded DzEHPA with strong and weak sulphuric acid strip liquors <u>S. Archer, V. Coetzee, DRA Mineral Projects (Pty) Ltd., Johannesburg/ZA; M. Kotze, Mintek, Johannesburg/ZA; M. Craddock, MC Process, Johannesburg/ZA</u>	916
P 8.23	Experimental design for solvent extraction of rare earth light and medium elements in hydrochloric acid media using DzEHPA in isoparaffin <u>C. Sousa Junior, IFRJ, Rio de Janeiro/BR; M. Nascimento, C.B. Da Costa, Cetem, Rio de Janeiro/BR</u>	924
P 8.24	Recovery of zinc from HCl industrial effluents <u>M.L. F. Gameiro, Remígio M. Machado, J.M.A. Rodrigues, K. Staszak, M. Regel-Rosocka, K. Wieszczycka, M. Rosinda C. Ismael, M. Teresa A. Reis, J.M.R. Carvalho, Instituto Superior Técnico, Lisbon/P</u>	934
P 8.25	Mechanism and thermodynamics of synergistic separation of vanadium and nickel from sulfate media using DzEHPA and Cyanex 272 <u>S.M.M. Noori, F. Rashchi, University of Tehran/IR; E. Vahidi, University of South Florida, Tampa, FL/USA; A. Babakhani, University of Tehran/IR</u>	941
P 8.27	Application of the liquid surfactant membranes technique for the removal of Cr⁶⁺ from a galvanising industry <u>T.L.S. Miranda, V.O. Silva, A. Salum, C. Konzen, E.M.R. Araújo, F.E.B. Coelho, J.C. Balarini, Universidade Federal de Minas Gerais, Belo Horizonte/BR</u>	947
P 8.28	Study of the solvent extraction of the lighter lanthanide metal ions by means of organophosphorus extractants <u>L. Molina, C. Basualto, F. Valenzuela, J. Sapag, University of Chile, Santiago/RCH</u>	955
P 8.29	Vanadium recovery by extraction in spent catalyst used in the manufacture of sulphuric acid <u>M. Musadi, National Institute of Technology, Bandung/RI</u>	961
P 8.30	Extraction of chromium (VI) by liquid-liquid extraction using Cyphos IL 101 <u>Z. Gamiño-Arroyo, E.A. Franco-García, L.E. Sánchez-Cadena, I. Cano-Rodríguez, F.I. Gómez-Castro, J. Ramírez Flores, A.R. Uribe-Ramírez, Universidad de Guanajuato/MEX</u>	966
P 8.31	Extraction of rhodium(III) and ruthenium(III) ions from chloride solutions with phosphonium ionic liquids as extractants <u>M. Regel-Rosocka, M. Rzelewska, M. Wisniewski, Poznan University of Technology/PL</u>	972
P 8.32	Preparation of the novel ionic liquids functionalized resins with tunable structure for metal ions separation <u>H. Cui, J. Chen, Y. Liu, Chinese Academy of Sciences, Changchun/CHN</u>	977
P 8.34	Innovation of solvent extraction for metal separation in mixed chloride media: case studies for different value metals <u>V.I. Lakshmanan, R. Sridhar, M.A. Halim, Process Research ORTECH Inc., Mississauga/CDN</u>	988

POSTERPROGRAMME

P 8.35	Precious metals extraction with sulfur function supported on methylacrylate-styrene copolymer <u>M. Iwakuma</u> , S. Nakajima, M. Ishikawa, Miyakonojo National College of Technology//; Y. Baba, University of Miyazaki/J	996
P 8.36	A hydrometallurgy process for extracting cerium(IV) and thorium (IV) from bastnasite using primary amine N1923 and Cyanex923 <u>D. Li</u> , J. Lu, S. Liu, H. Li, Y. Bai, X. Sun, Y. Wang, Changchun Institute of Applied Chemistry/CHN	1002
P 8.37	Global experiences with a dearomatized diluent (Escaid™ 110) in SX processes <u>D. Bien</u> , ExxonMobil Chemical Asia Pacific, Singapore/SGP; P.Y. Guyomar, ExxonMobil Chemical Europe, Brussels/B; J. Hu, ExxonMobil Asia Pacific Research & Development Co., Ltd., Shanghai/CHN	1003
P 8.38	Extraction and separation of uranium and thorium by di-(2-ethylhexyl) 2-ethylhexyl phosphonate <u>Y. Wang</u> , C. Zhao, W. Liao, D. Li, Changchun Institute of Applied Chemistry/CHN	1004
P 8.39	Partition of copper and iron ions in aqueous two phase system <u>A. Jimenez</u> , Universidad Tecnica de Oruro/BOL; Y.P. Jimenez, H.R. Galleguillos, Universidad de Antofagasta/RCH	1005
P 8.40	Solvent extraction recovery of zinc and molybdenum from steelmaking dusts <u>S. Virolainen</u> , T. Sainio, Lappeenranta University of Technology/FIN	1006
P 8.41	Separation of rare earth metal ions by synergistic system with 2-thenoyltrifluoroacetone and TOPO <u>F. Kubota</u> , Z. Zhao, Y. Baba, N. Kamiya, M. Goto, Kyushu University, Fukuoka/J	1007
P 8.42	Synthesis of novel ditopic ligands for the extraction of transition metal salts <u>R. Luckay</u> , H.-M. Smuts, J.C. Hensberg, University of Stellenbosch/ZA	1013
P 8.43	Separation of indium and zinc by solvent extraction from sulfuric liquor generated from the leaching of the coating dust of the scrapped computer screens <u>D. Carlos</u> , A.C.V. Zuccheratte, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte/BR	1020
P 8.44	Laboratory plant problems on the example of nickel(II) solvent extraction from leaching solution <u>G. Pietek</u> , L. Gotfryd, Z. Szołomicki, K. Becker, J. Piwowońska, Instytut Metali Nieżelaznych, Gliwice/PL	1026

INDUSTRIAL PRACTICE

P 9.1	Montan wax extraction using a laboratory belt extractor: development, construction and commissioning <u>M. Wollmerstädt</u> , <u>V. Herdegen</u> , H.-W. Schröder, TU Bergakademie Freiberg/D; T. Naundorf, ROMONTA Unternehmensgruppe, Seefeld Mansfelder Land/D; J.-U. Repke, TU Bergakademie Freiberg/D	1027
P 9.2	Computer aided design of liquid-liquid extraction columns <u>M. Hlawitschka</u> , H. Jildeh, University of Kaiserslautern/D; M.W. Attarakih, University of Jordan/JOR; H.-J. Bart, University of Kaiserslautern/D	1033

- P 9.3 **Choose the right material of construction – wetting in extraction columns** 1039
J. Koch, J.R. Herguijuela, Sulzer Chemtech AG, Allschwil/CH

NOVEL REAGENTS, MATERIALS AND TECHNIQUES

- P 10.1 **Trivalent actinide and lanthanide separations using tetraalkyldiglycolamides (TCnDGA) in molecular and ionic liquid diluents** 1040
B. Mincher, R. Fox, Idaho National Laboratory, Idaho Falls, ID/USA; M. Mincher, C. Wai, University of Idaho, Moscow, ID/USA
- P 10.3 **Intramolecular cooperative effect of a macrocyclic receptor bearing β -diketone fragments on the extraction of strontium into an ionic liquid** 1046
H. Okamura, H. Naganawa, Japan Atomic Energy Agency, Tokai-mura/J; H. Imura, Kanazawa University/J; K. Shimojo, Japan Atomic Energy Agency, Tokai-mura/J
- P 10.4 **Comprehensive extraction separation study of metal ions using N,N-diocetyl diglycolamic acid DODGAA** 1052
K. Shimojo, H. Naganawa, Japan Atomic Energy Agency, Ibaraki/J
- P 10.5 **Separation of rhodium from palladium, platinum and base metals with amide-containing tertiary amine compounds** 1058
H. Narita, K. Morisaku, M. Tanaka, National Institute of Advanced Industrial Science and Technology, Tsukuba/J; K. Nagao, T. Fuchikami, T. Yoshida, K. Kuroda, Chemicrea Inc., Tokyo/J
- P 10.6 **Modelling the outer-sphere bonding and solvation in chloridometalate extraction** 1064
K.J. MacRuary, University of Edinburgh/UK; R.A. Grant, R.J. Gordon, Johnson Matthey, Reading/UK; J.B. Love, C.A. Morrison, P.A. Tasker, A.M. Wilson, University of Edinburgh/UK
- P 10.7 **Synergistic extraction of divalent metal ions with p-tert-octylphenoxycetic acid and N-donors** 1070
T. Oshima, K. Kaneizumi, Y. Baba, University of Miyazaki/J
- P 10.8 **In-situ droplets monitoring in a lab-scale pulsed column** 1076
A. Amokrane, CEA, Bagnols-sur-ceze/F; S. Maass, SOPAT GmbH, Berlin/D; H. Roussel, F. Lamadie, S. Charton, CEA, Bagnols-sur-ceze/F
- P 10.9 **Liquid-liquid extraction of scandium with O,O-bis(2-ethylhexyl) hydrogen thiophosphate** 1077
K. Fujinaga, Kanazawa Institute of Technology, Nonoichi/J; Y. Nakajima, Daiichi Kigenso Kagaku Kogyo Co., LTD., Osaka/J; S. Oshima, Y. Watanabe, S. Tsurubou, Kanazawa Institute of Technology, Nonoichi/J; J. Noro, Nissan Arc. Ltd., Yokosuka/J; Y. Komatsu, Kanazawa Institute of Technology, Nonoichi/J
- P 10.10 **Ammonium and phosphonium ionic liquids as extractants for metal ions from aqueous solutions** 1083
I. García-Díaz, F.J. Alguacil, F.A. López, Centro Nacional de Investigaciones Metalúrgicas, Madrid/E; M. Regel-Rosocka, M. Wisniewski, Poznan University of Technology/PL
- P 10.11 **Molybdenum(VI) extraction from sulphate media by quaternary pyridinium ketoxime salts** 1088
K. Ochrowicz, K. Wejman, Wrocław University of Technology/PL; A. Wojciechowska, K. Wieszczycka, Poznan University of Technology/PL

POSTERPROGRAMME

P 10.12	Transport of zinc(II) from chloride solutions with phosphonium ILs as metal ion carriers by L-L extraction and polymer inclusion membranes	1094
	<u>M. Regel-Rosocka</u> , R. Casas Jaraices, M. Baczynska, M. Wisniewski, Poznan University of Technology/PL	
P 10.13	Solvent impregnated resin: Cyanex272 immobilised Amberlite XAD-2 column for gadolinium(III) enrichment	1100
	<u>M. Karve</u> , K. Pandey, University of Mumbai/IND	
P 10.14	3-Pyridylketoxime as Zn(II) extractant from chloride solutions in pseudo-emulsion based hollow fibre strip dispersion (PEHFS)	1106
	<u>K. Wieszczycka</u> , M. Regel-Rosocka, K. Staszak, Poznan University of Technology/PL; T.A. Reis, R.M.C. Ismael, M.L.F. Gameiro, J.M.R. Carvalho, Technical University of Lisbon/P	
P 10.15	Encapsulation of PC-88A in microcapsules of cross-linked gel of poly(vinyl alcohol)/alginate acid and its extraction property of Co(II)	1110
	<u>K. Shiomori</u> , S. Komatsu, N.I. Inda, University of Miyazaki/J; S. Kiyoyama, Miyakonojo NCT/J; T. Takei, M. Yoshida, Kagoshima University/J	
P 10.16	Development of a highly selective solvent extraction system for the separation of Pd(II) from a solution of a leached automotive catalyst	1115
	<u>J. Traeger</u> , H.-J. Holdt, University of Potsdam/D	
P 10.17	Thermo responsive gel including thiocrown ether unit for extraction of class b metal ions	1121
	<u>K. Chayama</u> , T. Hirooka, S. Iwatsuki, Konan University, Kobe City/J	
P 10.19	Recovery of gallium and indium from synthetic leach solution of zinc refinery residues using novel synergistic solvent extraction	1122
	<u>S. Nusen</u> , CSIRO, Perth/AUS; T. Chairuangsi, Chiang Mai University/T; Z. Zhu, C.Y. Cheng, CSIRO, Perth/AUS	
P 10.20	Selective enrichment of palladium in HNO₃ solution by micro-sized silica particles grafted with macrocyclic ligands	1128
	<u>G. Ye</u> , Tsinghua University, Beijing/CHN; Y. Leng, China University of Petroleum, Beijing/CHN	

NUCLEAR FUEL REPROCESSING

P 11.1	Molecular simulations of solvent extraction of lanthanides and actinides with diglycolamide and pyridine amide	1129
	<u>K. Yoshizuka</u> , The University of Kitakyushu/J; M. Hirata, T. Kimura, Japan Atomic Energy Agency, Tokai-mura/J	
P 11.2	Stability studies of considered grouped actinide extraction (GANEX) solvent systems	1136
	<u>H. Galán</u> , A. Núñez, J. Cobos, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid/E	
P 11.3	Phenyl trifluoromethyl sulfone as diluent in a GANEX solvent	1142
	<u>J. Halleröd</u> , E. Aneheim, C. Ekberg, M. Foreman, E. Löfström-Engdahl, Chalmers University of Technology, Gothenburg/S	
P 11.4	PAREX, a powerful tool for La Hague reprocessing plant operators	1148
	<u>J. Bisson</u> , AREVA NC, Beaumont-Hague/F; B. Dinh, CEA, Bagnols-sur-zeze/F; C. Huel, AREVA NC, Beaumont-Hague/F	

POSTERPROGRAMME

P 11.5	Investigation of heat of formation of reverse micelles using isothermal titration calorimetry	1156
	<u>A. Jackson</u> , University of California/USA; P. Zalupski, Idaho National Laboratory, Idaho Falls, ID/USA; M. Nilsson, University of California/USA	
P 11.6	Extraction chromatographic separation of Am(III) and Eu(III) by porous silica coating TPPEN-NIPA gel (1) - gel synthesis and temperature effect	1162
	K. Takeshita, Y. Inaba, Tokyo Institute of Technology/J; T. Yaita, S. Suzuki, Japan Atomic Energy Agency, Tokai/J; A. Mori, Kobe University/J	
P 11.7	Development of a TODGA-based liquid-liquid extraction system for the separation of americium(III) from a simulated PUREX raffinate	1163
	<u>P. Kaufholz</u> , A. Wilden, G. Modolo, F. Sadowski, S. Lange, D. Bosbach, Forschungszentrum Jülich GmbH/D; L.M. Harwood, A.W. Smith, University of Reading/UK	
P 11.8	New actinide recovery process using N,N-dialkylamide and phenanthroline amide	1165
	<u>S. Shinichi</u> , K. Tohru, Y. Tsuyoshi, Japan Atomic Energy Agency, Tokai-mura/J	
P 11.9	Application of annular centrifugal contactors in a cold test of a new total partitioning process with simulated high level liquid waste	1166
	<u>W. Duan</u> , J. Wang, J. Chen, Tsinghua University, Beijing/CHN	
P 11.10	Transient extraction behavior analysis of plutonium in reprocessing	1167
	<u>G. Uchiyama</u> , H. Abe, Japan Atomic Energy Agency, Tokai-mura/J	
P 11.11	Application of annular centrifugal contactors in a cold test of a new total partitioning process with simulated high level liquid waste	1173
	<u>W. Duan</u> , J. Wang, J. Chen, Tsinghua University, Beijing/CHN	
P 11.13	Process uranium recovery from mixed Sulfate/chloride media	1179
	<u>K. Soldenhoff</u> , J. Quinn, ANSTO Minerals, Lucas Heights/AUS	
P 11.14	Probing ligand exchange kinetics in actinide/lanthanide solvent extraction systems using NMR spectrometry	1185
	<u>C. Marie</u> , CEA Marcoule, Bagnols-sur-ceze/F; K. Nash, E. Krahn, Washington State University, Pullman, WA/USA	

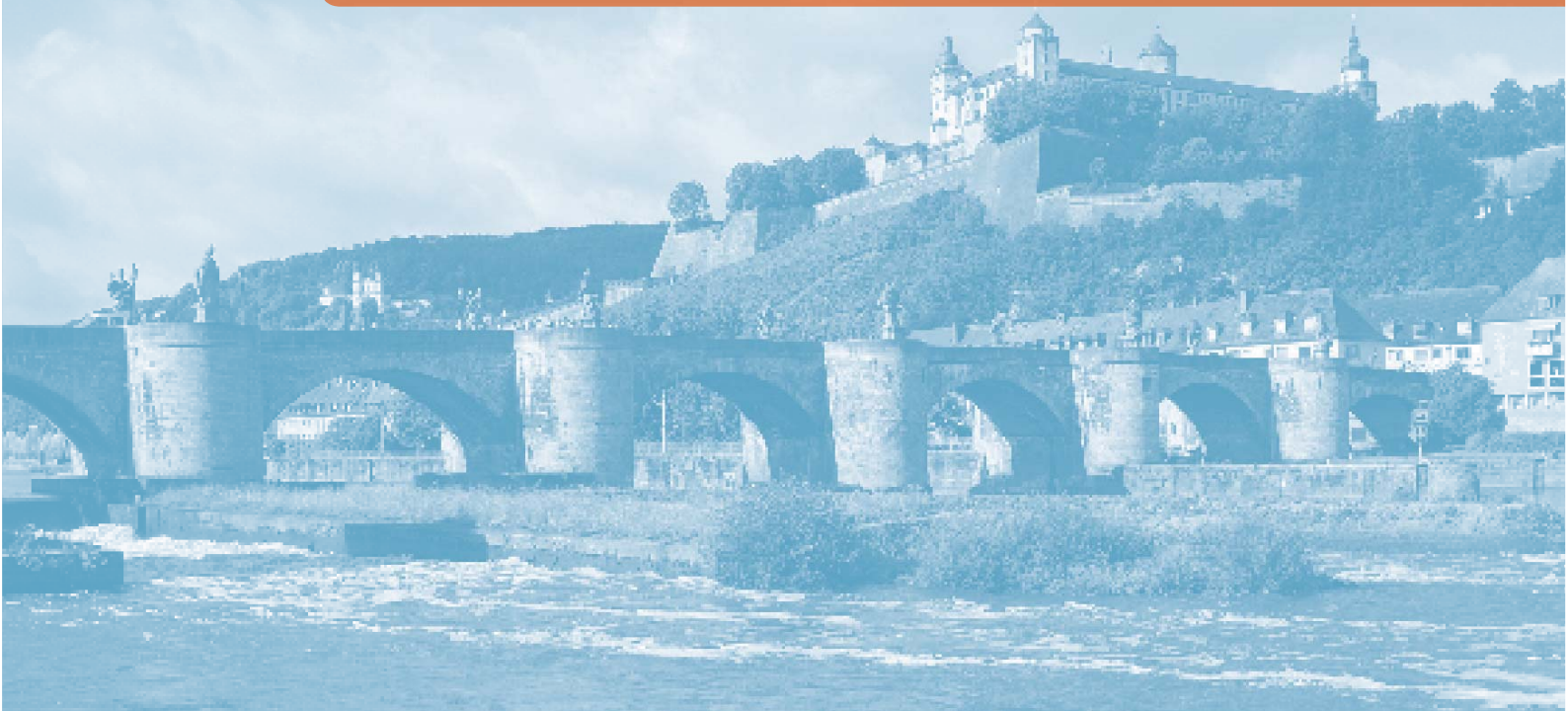
PROCESS CHEMISTRY AND ENGINEERING

P 12.1	Intensification of liquid-liquid mass transfer with gas agitation for the preparation of caprolactam	1191
	<u>J.S. Zhang</u> , K. Wang, X.Y. Lin, Y.C. Lu, G.S. Luo, Tsinghua University, Beijing/CHN	
P 12.3	Liquid membranes to improve resource efficiency in the surface treatment industry	1192
	E. Bringas, <u>A.M. Urtiaga</u> , I. Ortiz, Universidad de Cantabria, Santander/E	
P 12.4	Ant colony optimization for sequencing of solvent extraction stages and optimization of their performance	1198
	<u>F. Vasilyev</u> , S. Virolainen, T. Sainio, Lappeenranta University of Technology/FIN	
P 12.5	Preventing the introduction of air into emulsion in SX mixers	1199
	<u>R. Sheinman</u> , Y. Kokotov, L. Braginsky, Turbulent Technologies Ltd., Jerusalem/IL	

POSTERPROGRAMME

P 12.6	Study on preparation of KH_2PO_4 in microreactors by a reaction-extraction coupling process	1205
	<u>F. Zhao</u> , G.S. Luo, Y.C. Lu, K. Wang, Tsinghua University, Beijing/CHN	
P 12.7	Impact of particle size distribution in packed bed for solid-liquid extraction for Montan wax	1206
	<u>Y. Wang</u> , V. Herdegen, J.U. Repke, TU Freiberg/D	
P 12.8	Extractive desulfurization of hexadecane using ionic liquid as a solvent	1212
	<u>B. Mokhtarani</u> , H. Mansurzareh, H.R. Mortaheb, A. Sharifi, CCERC, Tehran/IR	

ABSTRACTS



Strategies for Selective Liquid-Liquid Anion Exchange

Bruce A. Moyer, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

Selective anion extraction remains a fundamental challenge because the selectivity tends to be strongly governed by anion solvation favoring the extraction of charge-diffuse anions. While this bias-type selectivity has served well when the target anions are large metallate complex anions, for example, it proves limiting in general. Our approach to addressing this limitation has entailed the use of anion receptors under the hypothesis that the specific binding affinity of the anion receptor is reflected in the resulting extraction selectivity. Two general approaches will be outlined in this paper, involving ion-pair extraction and anion exchange, with a focus on liquid-liquid anion exchange (LLAE). In many practical systems, LLAE relies on the use of simple anion exchangers such as alkyl ammonium salts that are sufficiently lipophilic to remain highly partitioned to a water-immiscible organic solvent even when the counter-anion is highly hydrophilic. This anion, often chloride or nitrate, is easily exchanged for less hydrophilic anions in the aqueous phase. An attractive approach to enhancing LLAE selectivity entails the synergistic combination of a lipophilic neutral anion receptor with an anion exchanger, which in our experiments has been a quaternary ammonium chloride or nitrate salt. A variety of macrocyclic anion receptors has been examined in the context of these studies, revealing a uniquely strong enhancement when employing calixpyrroles as the neutral synergist. In this case, the anion receptor and quaternary ammonium cation can act as a supramolecular unit in binding the anion. Recent results on LLAE will be summarized regarding synergistic anion exchange together with new directions employing positively charged anion receptors capable of anion exchange.

This submission has been authored by a contractor of the U. S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U. S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for the U. S. Government purposes.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

The Hydrometallurgical Co-separation of Neptunium, Plutonium, Americium and Curium by the EURO-GANEX Process

*R. Malmbeck,^{*1} M. J. Carrott,² A. Geist,³ X. Hérès,⁴ D. Magnusson,³
M. Miguirditchian,⁴ G. Modolo,⁵ C. Sorel,⁴ R. J. Taylor,⁴ A. Wilden⁵*

The EURO-GANEX process was developed to co-separate all transuranic (TRU) elements from used nuclear fuel without generating a pure plutonium product. A solvent consisting of TODGA + DMDOHEMA in kerosene co-extracts TRU together with the lanthanides(III). Co-extraction of Zr and Pd is suppressed by CDTA. A solution containing SO₃-Ph-BTP + AHA in HNO₃ is used to strip TRU from the organic phase. The remaining lanthanides(III) are stripped by dilute HNO₃. Based on the results of a spiked test and some further flow sheet calculations a hot demonstration test was performed in a 16 + 16 stage centrifugal contactor setup. A genuine feed solution was prepared by dissolving irradiated fast reactor fuel and removing uranium by a GANEX 1st cycle process. The raffinate from this process, containing TRU and fission products, was adjusted to 10 g/L Pu and was used as feed for the EURO-GANEX process. The product solution of this process contained > 99.8% of the TRU inventory and < 0.1% of the lanthanide(III) inventory.

Introduction

Recycling actinides from used nuclear fuel is an important aspect of a sustainable nuclear energy production. The required separations are achievable using solvent extraction processes. An example is the commercially applied PUREX process for separating U and Pu. Currently, further processes for separating the “other” actinides (the so-called minor actinides Np, Am and Cm) are under development in many national and international projects.

GANEX (grouped actinide extraction) processes have been developed and tested to simultaneously co-separate all transuranic (TRU) actinide elements (Np, Pu, Am, and Cm) from used nuclear fuel. They show potential benefit regarding process simplification and proliferation resistance because there is no pure Pu stream throughout the process. After the separation of U from irradiated fuel in the 1st GANEX cycle, TRU are co-separated in the 2nd cycle. Both cycles have successfully been hot tested using highly radioactive feed solutions obtained from dissolving used nuclear fuel [1,2].

Recently, alternative 2nd cycle processes have been developed and tested within the European 7th Framework ACSEPT [3] project, the CHALMEX [4,5,6,7] process and the EURO-GANEX process [8,9,10,11]. The CHALMEX process is based on the direct co-extraction of TRU, separating them from lanthanides(III) and the other fission products. EURO-GANEX is based on the co-extraction of TRU +

¹ European Commission, Joint Research Centre, ITU, Karlsruhe, Germany

² National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, UK

³ Karlsruhe Institute of Technology, INE, Karlsruhe, Germany

⁴ Commissariat à l'Énergie Atomique et aux Énergies Alternatives, DEN, Marcoule, France

⁵ Forschungszentrum Jülich, IEK-6, Jülich, Germany

lanthanides(III), separating them from the other fission products, followed by selective TRU back extraction using water soluble complexing agents.

EURO-GANEX: system and spiked test

TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide, Figure 1 left) extracts actinides in different oxidation states, An(III,IV,VI) together with lanthanides(III) [12]. Unfortunately, it does not extract Pu(IV) in concentrations relevant to a GANEX process (in the 10 g/L range) without 3rd phase or precipitate formation. Finally, a solvent able to extract > 10 g/L Pu together with the other TRU was developed [8,10], consisting of 0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxyethyl)malonamide (Figure 1 right) in a kerosene diluent (Exxsol D80). This solvent co-extracts actinides(III,IV,VI) and lanthanides(III). TRU are present in the feed solution as Np(V,VI), Pu(IV), Am(III) and Cm(III). Care must be taken that Np is present as Np(IV) or Np(VI) since Np(V) is not sufficiently extracted by this solvent. This is achieved by a sufficiently high HNO₃ concentration in the feed [13,14].

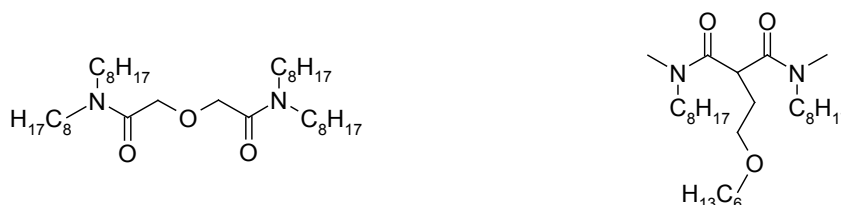


Figure 1. TODGA and DMDOHEMA, EURO-GANEX extracting agents.

Since the EURO-GANEX solvent co-extracts Zr and Pd, CDTA (1,2-cyclohexane-diaminetetraacetic acid, Figure 2) is added to mask them [15,9]. A solution of SO₃-Ph-BTP (2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine tetrasodium salt) [16] + AHA (acetohydroxamic acid [17], Figure 2) in HNO₃ is used to selectively strip TRU from the organic phase loaded with TRU + lanthanides(III) [9]. Lanthanides(III) are kept in the organic phase by a sufficiently high HNO₃ concentration (0.5 mol/L).

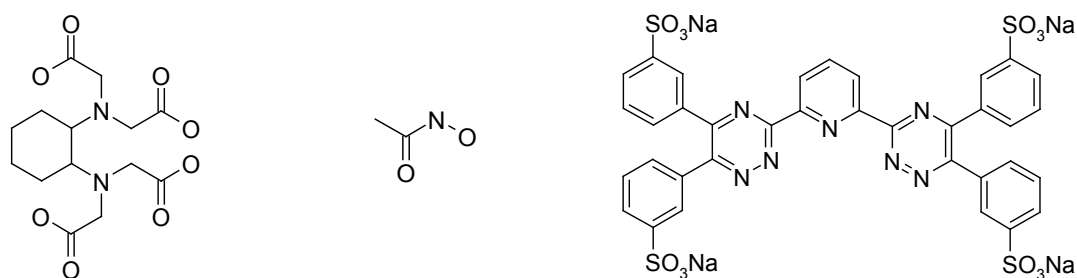


Figure 2. CDTA, AHA and SO₃-Ph-BTP.

Hot test

Based on the results of the hot GANEX 1st cycle test [1] and the spiked EURO-GANEX test [11], a full hot test was performed. Irradiated fast reactor fuel was oxidised and dissolved. U was selectively extracted from the dissolution solution by a GANEX 1st cycle process [1]. The raffinate from this process was used as feed solution for the EURO-GANEX process.

Fuel dissolution

116.8 g (with cladding) of fast reactor UC, UN or U(C,N) fuel pieces of less than 10 mm length were selected, thermally treated for oxidation and subsequently dissolved in 6 mol/L HNO₃ to yield about 560 mL fuel solution. After adjustment of the HNO₃ concentration this solution was used as feed for the 1st GANEX cycle. The solution was characterised by ICP-MS measurements and titration for the acidity, see Table 1.

Table 1. Concentration of actinides and HNO₃ in the fuel dissolution solution and in the GANEX feed solutions.

	Fuel sol'n	1 st cycle	2 nd cycle
U	118 g/L	103 g/L	0.034 g/L
Np	0.021 g/L	0.017 g/L	0.097 g/L*
Pu	24.8 g/L	22.7 g/L	10.1 g/L
Am	0.35 g/L	0.33 g/L	0.13 g/L
Acidity	4.0 mol/L	5 mol/L	5.9 mol/L

**additional Np added to feed*

GANEX 1st cycle

The GANEX 1st cycle is based on a selective uranium extraction by a monoamide (*N,N*-di(2-ethylhexyl)isobutyramide, DEHiBA) dissolved in kerosene at an acidity of roughly 5 mol/L HNO₃. Co-extracted Tc and Np are reduced and scrubbed by hydrazine in a scrubbing section at 1.5 mol/L HNO₃. Uranium is stripped into 0.01 mol/L HNO₃. The GANEX 1st cycle has previously been demonstrated on genuine fuel solution using mixer-settlers [1].

Based on the experience gained, a new flowsheet was designed, taking into account the higher Pu concentration in the feed (23 g/L vs. 2.5 g/L [1]) as well as the shorter hold up times of the centrifugal contactors used (Robatel BXP-012). Since only 16 centrifugal contactors are available, the test was run in two steps: extraction and scrubbing (collecting the loaded organic phase) followed by uranium back extraction.

The U product solution contained 99.9% of U, 3.1% of Np, 0.1% of Pu and 24.4% of Tc; Am and lanthanides were not detected. The raffinate (to be used as feed for the 2nd

Essentially all uranium was removed and all other actinides were routed to the raffinate. So whilst some optimisation of the GANEX 1st cycle can be made, the main goal of this experiment was demonstrated, i.e. removal of the large mass of uranium before the 2nd cycle GANEX. About 600 mL of feed solution to the 2nd GANEX process was produced, enough for a demonstration test.

GANEX 2nd cycle (EURO-GANEX) – hot demonstration test

The flow sheet used for the hot test is based on the flow sheet tested in spiked centrifugal contactor trials [11]. Following further modelling, some modifications were introduced in order to improve the control of key species across the flow sheet whilst adapting to the 16 stage set-up available for the hot test. As 16 stages are not enough to cover the complete flow sheet it was decided to divide the demonstration test into two consecutive days, 16 stages for extraction and scrubbing and 16 stages for back extraction.

To prepare the feed solution, the raffinate from the 1st GANEX cycle was adjusted to 10 g/L Pu and the acidity increased to 5.9 mol/L HNO₃ (Table 1). In addition, CDTA was added [15] to suppress extraction of problematic fission products (Pd, Zr) and a small amount of Np was added to increase concentration and the ease of analysis. 12 extraction stages in combination with the higher acidity was chosen to optimise Np(V) disproportionation [10] and efficiency of extraction.

Day 1 – Extraction and scrubbing: The day 1 flow sheet (extraction and scrubbing) is shown in Figure 3. The experiment was started up with 5.9 mol/L HNO₃ as feed solution, switching to the real feed only after stable conditions and good phase separation had been obtained. The experiment was run for 6 hours to build up steady state conditions and continued for another 10 hours for collection of loaded organic phase at steady state. After shutting down, around 300 mL of loaded organic phase had been produced, which was sufficient as feed for the second day back extraction flow sheet.

Recoveries are shown in Figure 3. Using 12 extraction stages near complete separation of actinides was achieved. In particular, Np loss to the raffinate was minimal (< 0.1%). This is a substantial improvement over the spiked test [11] (with approximately 25% lost to the raffinate) — probably due to the radiation induced oxidation and faster disproportionation of Np(V) due to higher temperatures in the hot test caused by self heating of the radioactive solutions..

Day 2 – Back extraction: In order to minimise degradation by radiolysis of the loaded organic phase, the back extraction experiment was started as soon as possible after ending the extraction experiment. In practice, about one day (24 hours) was needed as preparation time. The flow sheet used for the back extraction of actinides and lanthanides is shown in Figure 4. Selective back extraction of actinides is achieved by a solution of 0.055 mol/L SO₃-Ph-BTP + 1 mol/L AHA in 0.5 mol/L HNO₃

actinides, using fresh organic phase. Finally, 4 stages are used for back extraction of lanthanides(III) using 0.01 mol/L HNO₃.

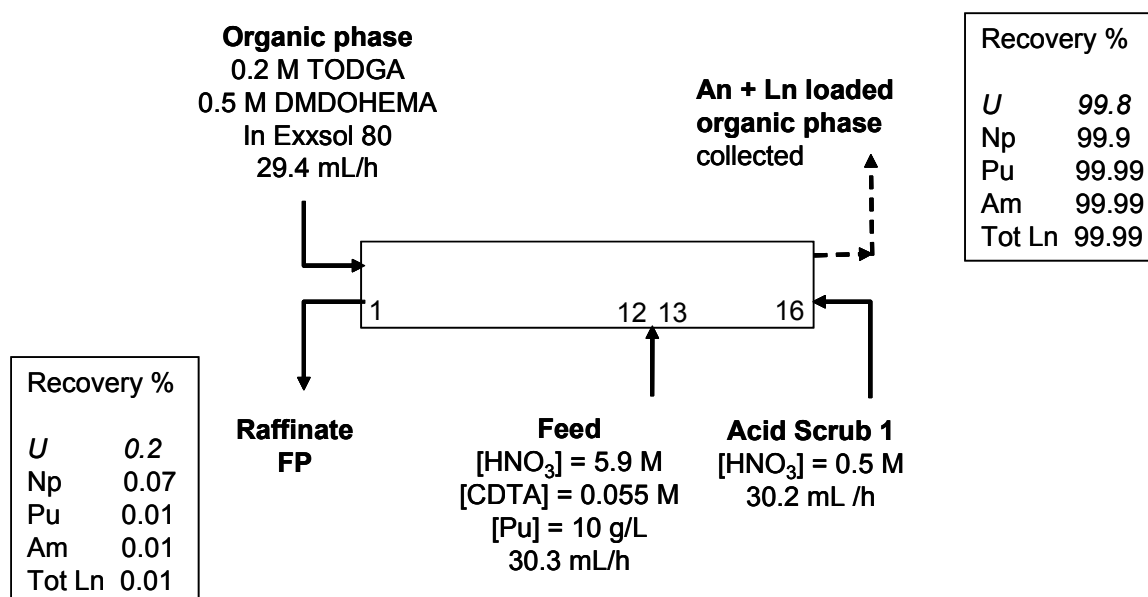


Figure 3. EURO-GANEX flow sheet – day 1, TRU extraction and scrubbing.

The experiment was started up using the loaded organic solvent from the steady state build up phase of the previous extraction experiment. This was run for about 3 hours before switching to the loaded organic solvent from the steady state collection. The experiment continued for approximately 4 hours, enough to attain steady state conditions of the actinides.

Recoveries of actinides and lanthanides are listed in Figure 4. It is evident that the process has been highly successful. An almost complete recovery of Pu, Np and Am has been achieved. The selectivity is also excellent with less than 0.1% of the lanthanides mass in the actinide product. The lanthanides have also been efficiently back extracted into the Ln product (> 99.9%), together with less than 0.1% of the actinides. The level of impurities in the used solvent is also less than 0.1%. Impurity levels can be managed to even lower levels if more stages are added. Note that the U results (in italics) relate to the very small fraction of U present in the 2nd cycle feed solution (34 mg/L).

Conclusions

With these experiments a new GANEX 2nd

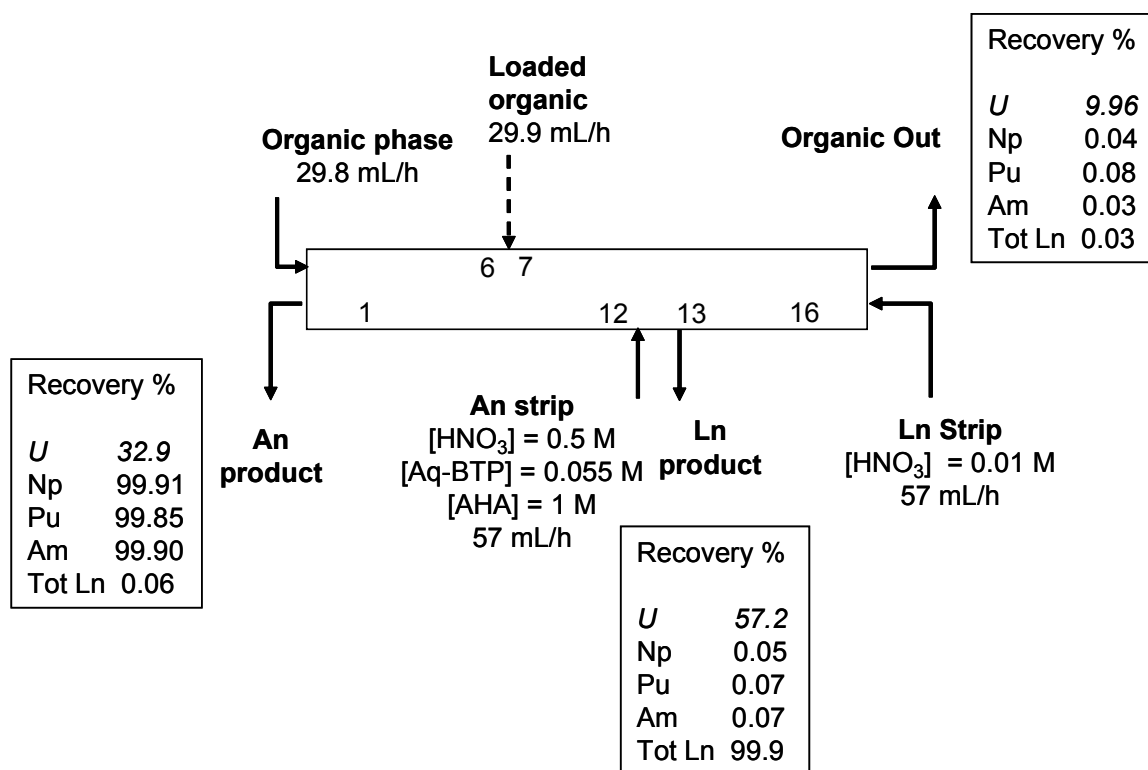


Figure 4. EURO-GANEX flow sheet – day 2, TRU back extraction.

Acknowledgement

The research leading to these results has been performed in the ACSEPT project (project № 211267) funded by the European Atomic Energy Community Seventh Framework Programme.

References

1. Miguiditchian, M. et al., Proc. Internat. Conf. GLOBAL 2009, Paris, France, 6–11 September 2009, paper 9377.
2. Miguiditchian, M. et al., Proc. Internat. Conf. GLOBAL 2009, Paris, France, 6–11 September 2009, paper 9378.
3. Bourg, S. et al., Nucl. Eng. Des. **2011**, 241, 3427–3435.
4. Aneheim, E. et al., Solvent Extr. Ion Exch. **2010**, 28, 437–458.
5. Aneheim, E. et al., Solvent Extr. Ion Exch. **2011**, 29, 157–175.
6. Aneheim, E. et al., Sep. Sci. Technol. **2012**, 47, 663–669.
7. Aneheim, E. et al., Solvent Extr. Ion Exch. **2013**, 31, 237–252.
8. Bell, K. et al., Procedia Chem. **2012**, 7, 392–397.
9. Bell, K. et al., Nuclear Fuel Cycle Conference, Manchester, UK, 23–25 April 2012.
10. Carrott, M. J. et al., Solvent Extr. Ion Exch. **2013**, 31, 463–482.
11. Carrott, M. J. et al., Solvent Extr. Ion Exch. **2014** (accepted).
12. Sasaki, Y.; Tachimori, S., Solvent Extr. Ion Exch. **2002**, 20, 21–34.
13. Dinh, B. et al., Proc. Internat. Solvent Extr. Conf. (ISEC 2008), Tucson, Arizona, USA, 15–19 September 2008, pp. 581–586.
14. Taylor, R. J. et al., Solvent Extr. Ion Exch. **2013**, 31, 442–462.
15. Sypula, M. et al., Solvent Extr. Ion Exch. **2012**, 30, 748–764.
16. Geist, A. et al., Solvent Extr. Ion Exch. **2012**, 30, 433–444.

Liquid-liquid extraction design under uncertainty

Bettina Rüngeler, RWTH Aachen University, AVT – Thermal Process Engineering, Aachen, Germany, Andreas Pfennig, TU Graz, Institute of Chemical Engineering and Environmental Technology, Graz, Austria

In the field of liquid-liquid extraction a variety of new processes like extraction from fermentation broths, aqueous two-phase systems or extraction with high viscous media is investigated in the recent years. Process engineers often do not have broad experience with these special applications of liquid-liquid extraction. Therefore it is necessary to find a metric to estimate the quality of a design solution and to compare different possible liquid-liquid extraction processes at an early stage of the design process. One possibility is to define an evaluation criterion like for example the overall process costs, which is determined for each option, and explicitly consider uncertainties in the design variables.

A framework for an easy comparison of different liquid-liquid extraction processes ranging from various solvents to diverse equipment during every stage of the process development is presented. Using uncertainty propagation the overall uncertainty of the chosen evaluation criterion is estimated. As each step of a design process is meant to reduce uncertainty about the final solution of the design challenge the following design steps are proposed in a way that the new information has the highest possible impact on deciding whether a process option is further investigated or not regarded in the next step. Within this framework it is possible to make sound decisions yet at an early stage of the process development and allocate resources for the process and equipment design in an efficient manner. To keep track on all investigated alternatives and decisions, results can be visualized and documented in option trees.

In this presentation an algorithm considering uncertainties in the design of liquid-liquid extraction is introduced and its general application on the design process is discussed.

Ionic liquid technology for metal separation and NdFeB magnet recycling

Tom Vander Hoogerstraete and Koen Binnemans

*KU Leuven, Department of Chemistry, University of Leuven, Celestijnenlaan 200f -
box 2404, 3001 Heverlee (Belgium)*

Ionic liquids (ILs) are defined as organic salts that melt below 100°C.¹ Solvent extraction systems using ILs as organic phase have some interesting properties which differ from conventional extraction systems using traditional molecular solvents such as kerosene, toluene or DCM. ILs have a negligible vapor pressure, they are non-flammable and they show a broad liquidus range. Although the applicability of ILs for metal separations on a larger scale has been proven,² the thresholds for applying these environmentally friendlier alternatives on a laboratory and industrial scale is often the price and their slower kinetics due to the high viscosity.

In 2010, the European Commission stressed the importance of starting up technospheric mining (recycling scrap or End-of-Life consumer goods) to cover rare earths.³ In their report, it was stated that these elements have the highest supply risk in the near future. As NdFeB magnets take almost half of the rare-market by value, it is of crucial importance to build valuable recycling routes.

In our extraction studies, simple, cheap and non-fluorinated ILs are used as an undiluted organic phase to separate transition metals from rare earths without the need of additional extractants.⁴ Special attention is given to the viscosity and the maximal metal loading of the IL, as these are important parameters towards the applicability of ILs in industrial hydrometallurgic separation systems. It will be shown that ILs can be used to separate very efficiently the elements present in NdFeB magnets.

1. R. D. Rogers and K. R. Seddon, *Science*, 2003, 302, 792-793.
2. S. Wellens, R. Goovaerts, C. Moeller, J. Luyten, B. Thijs, and K. Binnemans, *Green Chem.*, 2013, DOI: 10.1039/C3GC41519H.
3. European Commission, Report: Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials, 2010.
4. T. Vander Hoogerstraete, S. Wellens, K. Verachtert, and K. Binnemans, *Green Chem.*, 2013, 15, 919-927.

Separation of rare earth elements using Cyanex 572

*James Quinn^{*1}, Karin Soldenhoff², Geoff Stevens³*

The purification of rare earths from each other is one of the most challenging separations encountered in solvent extraction. The conventionally used extractant, lonquest 801, requires large acid concentrations to strip the heavy elements from the solvent. Recently Cytec developed Cyanex 572, a mixed phosphinic/phosphonic acid extractant designed to reduce the stripping acidity in rare earth separations. In this work we have examined the extraction of Ce, Pr, Nd and Sm by lonquest 801, Cyanex 272 and mixtures of the two, and compared the results with Cyanex 572. The effect of pH and solvent concentration on the extraction equilibrium was explored along with the role of antagonism in the process.

Introduction

Solvent extraction is the principle method used industrially to separate the rare earths (yttrium and the lanthanides) from each other. The most commonly used extractant is 2-ethylhexyl phosphonic acid 2-ethylhexyl ester (also known as lonquest 801, P-507, and PC88A). The separation factors for this extractant are relatively low, with the separation factors for adjacent elements ranging between 1.55 to 10.6¹. In addition, stripping of heavier elements (Tb-Lu and Y) requires a significant amount of acid. A reagent that offers better separation factors and/or requires lower stripping acidities would therefore be of great commercial significance.

Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid), a reagent used commercially in cobalt/nickel separations, has also been used industrially for rare earth separations². While the separation factors for the lanthanides are similar to lonquest 801, the phosphinic acid group is a weaker acid, which means that it can be stripped at lower acidities. The main drawback for this reagent is that the extracted complex is of lower lipophilicity, which limits the amount of rare earth that can be loaded into the organic phase³ and would therefore increase the required solvent inventory and size of the mixer settler circuit.

Cytec has recently released a new extractant called Cyanex 572, designed for rare earth separations. At the time of writing, little information on the extractant was available, other than that provided by the manufacturer. The extractant is a mixture of bis-2,4,4-trimethylpentyl-phosphinic acid and an undisclosed phosphonic acid ester. Cytec assert that the reagent offers lower stripping acidities and similar separation factors when compared with lonquest 801.

Mixtures of Cyanex 272 and lonquest 801 have been examined previously in the literature. Wang et al. found that the mixture was synergistic towards ytterbium extraction from chloride media⁴. Kim et al. found no improvement in the group

^{*1} James Quinn, Australian Nuclear Science & Technology Organisation, Sydney Australia, jamesq@ansto.gov.au

² Karin Soldenhoff, Australian Nuclear Science & Technology Organisation, Sydney Australia

³ Geoff Stevens, University of Melbourne, Australia.

separation factors for Dy and Y over Sm and Gd⁵, while Xiong et al. showed that the separation factors for Lu/Yb and Yb/Tm improved relative to both of the individual components⁶. The mixture has reportedly also been used industrially in China for heavy rare earth separations⁷.

This paper examines the solvent extraction of the Ce, Pr, Nd and Sm, by phosphonic and phosphinic acids and their mixtures. These elements were chosen as the Nd/Sm separation is often the first circuit in an industrial separation scheme. We have examined the synergism/antagonism in the extraction of these elements by mixtures of Ionquest 801 and Cyanex 272, and compared the results with Cyanex 572.

Method

Materials

Cyanex 272 was supplied by Cytec and twice purified by the emulsion method⁸ to remove the phosphine oxide impurity, which was not listed as a constituent of Cyanex 572. Cyanex 572 (Cytec) and Ionquest 801 (SNF FloMin) were not purified prior to use. The molarity of all solvents was determined by potentiometric titration in ethanol/water. Shellsol D60 (Shell), a commercial grade low aromatic kerosene, was used as the diluent in all experiments.

Rare earth stock solutions were prepared by dissolving either the oxides (Sm₂O₃, Pr₆O₁₁ or Nd₂O₃, 99% purity, Metall Rare Earth Ltd.) or carbonate (Ce₂(CO₃)₂, 99.9% purity, Metall Rare Earth Ltd.) in HCl. All other reagents were of analytical grade.

Procedure

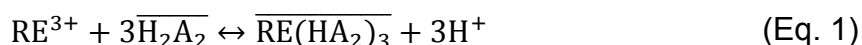
Experimental solutions were prepared by adding small amounts of the stock solutions to samples containing the required amounts of NaCl and HCl. The ionic strength in each solution was fixed at 1 mol·L⁻¹ (Na⁺, H⁺/Cl⁻) in all experiments. The total concentration of rare earths in feed solutions was 2.1×10⁻³ mol·L⁻¹ in most experiments to ensure that the solvent was in large excess. The exception was when examining solvent concentrations less than 0.1 mol·L⁻¹, for which the feed rare earth concentration was further reduced to 3.8×10⁻⁴ mol·L⁻¹.

Organic and aqueous samples were contacted in a stirred beaker for at least 20 minutes, with the pH of the aqueous phase measured using a Metrohm 6.0232.100 probe and 691 meter. The pH was controlled by addition of 1 mol·L⁻¹ NaOH. For the pH curves shown in Figure 1, 150 mL of each phase was contacted, with 10 mL sample of each phase withdrawn at each pH value. Otherwise, the volume of each phase was 15 mL and no thief samples were taken. After separating the phases, the organic samples were stripped using 5 mol·L⁻¹ HCl. The aqueous feed, equilibrium and organic strip samples were analyzed by ICP-MS for Ce, Pr, Nd and Sm. Mass balances were generally correct to +/- 5%.

Results/Discussion

Effect of pH on extraction by phosphonic and phosphinic acids and their mixtures

The effect of pH on the distribution ratios for extraction of Sm, Nd, Pr and Ce by 1.0 mol·L⁻¹ Lonquest 801, 1.0 mol·L⁻¹ Cyanex 272, 1.0 mol·L⁻¹ Cyanex 572 and a mixed solvent containing 0.5 mol·L⁻¹ Lonquest 801 and 0.5 mol·L⁻¹ Cyanex 272, are shown in **Figure 1**. The log D vs. pH plots all show straight lines with slopes close to 3, as predicted by the commonly quoted extraction mechanism for dimerised extractants (**Eq. 1-2**). The values for Lonquest 801 and Cyanex 272 are separated by about 0.95 pH units (pH_{0.5} of 0.71 and 1.64 respectively for Sm), which is consistent with previous results⁹. Lonquest 801, a phosphonic acid, has a lower pKa than Cyanex 272 (2.91 compared with 3.73¹⁰) and therefore extracts at a lower pH than the phosphinic acid does. The curves for the mixture of the two extractants fell between its two components (pH_{0.5} of 1.04 for Sm), and were close to the curves obtained for Cyanex 572 (pH_{0.5} 0.98 for Sm). This confirms that Cyanex 572 extracts at higher pH than lonquest 801, and therefore the stripping acidity required for this extractant would be lower.



$$\log K_{\text{ex}} = \log D - 3\text{pH} - 3\log[\overline{\text{H}_2\text{A}_2}] \quad (\text{Eq. 2})$$

The separation factors for all solvents calculated from the results of **Figure 1** were in the range of $\beta_{\text{Pr/Ce}}=1.9\text{-}2.1$, $\beta_{\text{Nd/Pr}}=1.5\text{-}1.7$ and $\beta_{\text{Sm/Nd}}=10.4\text{-}13.1$, similar to published data for Lonquest 801 and Cyanex 272^{1, 7}. The errors in the calculated separation factors are of the same order as the differences between the solvents, therefore further work would be required to determine whether there are any small differences in separation factors for the solvents examined.

Analysis of antagonism

The effect of solvent composition on the extraction of Sm by mixtures of lonquest 801 and Cyanex 272 is shown in **Figure 2**. The plots are the result of three separate experimental determinations of distribution values: one with lonquest 801 varied from 0.1 to 1.0 mol·L⁻¹ (D₁), one with Cyanex 272 varied from 1.0 – 0.1 mol·L⁻¹ (D₂), and a final experiment with fixed 1.0 mol·L⁻¹ total extractant, with the ratio of extractants varied (D₃). The pH was constant in all experiments (pH 0.95). The sum of the distribution coefficients for the separate extractants (D₁+D₂) was then compared with the distribution ratio for the reagent mixtures (D₃).

The results confirm that there is an antagonistic effect, as $D_3 < (D_1 + D_2)$, with the ratio of $D_3/(D_1 + D_2)$ reaching a minimum of 0.41. Similar results for Ce, Pr and Nd were also obtained (results not shown).

A plot of log D₁ vs. log [lonquest 801] (**Figure 3**) revealed a slope of 2.41 ± 0.08 , significantly lower than the value of 3 predicted by **Eq. 2**. In addition, a plot of residuals from the linear regression appeared to show an approximately quadratic

pattern. Polynomial regression of the data confirmed a statistically significant quadratic term ($p\text{-value}=0.0010$). This suggests a degree of non-ideal behavior, which is possibly due to the properties of the organic phase, and hence organic phase activity coefficients, changing significantly as the total extractant concentration was varied from 0.1 to $1.0 \text{ mol}\cdot\text{L}^{-1}$.

The literature value for the dimerization constant of lonquest 801 in kerosene ($\log K_2=4.09$)¹⁰ can be used to estimate the dimer concentration for a given concentration of lonquest 801. The extractant was predicted to be close to fully dimerized even at $0.1 \text{ mol}\cdot\text{L}^{-1}$, and calculating the slope using $\log[\text{H}_2\text{A}_2]$ rather than total extractant concentration results in a similar value of 2.39 ± 0.08 .

A repeat experiment at lower total extractant concentration ($0.01 - 0.1 \text{ mol}\cdot\text{L}^{-1}$ lonquest 801), also shown in Figure 3, resulted in a slope of 2.9 ± 0.1 . This supports our hypothesis that it is the change in the properties of the organic phase at high extractant concentrations, most probably a decrease in activity coefficient, that is responsible for the deviation away from linearity and a slope lower than 3. The same effect could also be responsible for the observed antagonism, if additional phosphinic acid affects the solvent in a similar way.

Estimation of reduction in strip acidity for Sm

In the stripping section of a circuit, the degree of stripping depends on the distribution ratio at the loaded strip end of the circuit and hence the loaded strip free acidity. A weaker solvent (i.e. smaller K_{ex} or lower extractant concentration in **Eq. 3**) will require a lower free acidity for a given distribution ratio.

For the four solvents examined, $1.0 \text{ mol}\cdot\text{L}^{-1}$ lonquest 801 (Solvent 1), $1.0 \text{ mol}\cdot\text{L}^{-1}$ Cyanex 572 (Solvent 2), $0.5 \text{ mol}\cdot\text{L}^{-1}$ lonquest 801 + $0.5 \text{ mol}\cdot\text{L}^{-1}$ Cyanex 272 (Solvent 3), and $1.0 \text{ mol}\cdot\text{L}^{-1}$ Cyanex 272 (Solvent 4), the $\text{pH}_{0.5}$ values for Sm are 0.71, 0.98, 1.04 and 1.64 respectively. Substitution into Eq.3 reveals that the left hand side of the equation is therefore 6.6 times lower for Solvent 2, 10.0 times lower for Solvent 3 and 617 times lower for Solvent 4 when compared with Solvent 1.

As a first approximation, the distribution ratios at the loaded strip end of a counter-current cascade are assumed to be approximately equal for each solvent option for a given degree of stripping. Given that the distribution ratio is inversely proportional to $[\text{H}^+]^3$, the loaded strip free acidities for Solvents 2, 3 and 4 would be 1.9, 2.2 and 8.5 times lower than for Solvent 1. The predicted free acid concentrations for Solvents 2, 3 and 4 are therefore 53%, 46% and 12% of the corresponding value for Solvent 1. Note the resulting savings in acid consumption would not include the amount of acid consumed in stripping the rare earths (3 moles of acid per mole of rare earth stripped), which is equal for each option.

$$K_{\text{ex}}[\overline{\text{H}_2\text{A}_2}]^3 = D[\text{H}^+]^3 \quad (\text{Eq. 3})$$

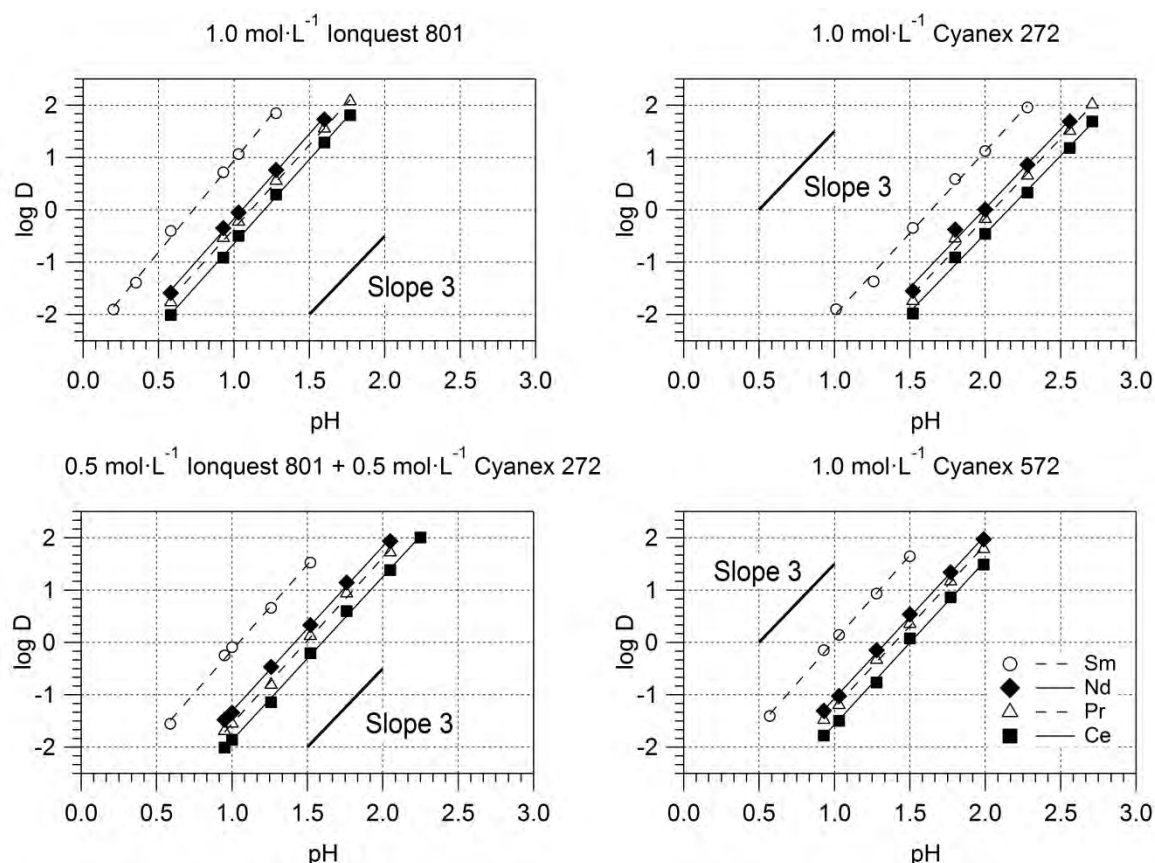


Figure 1: Effect of pH on extraction of Ce, Pr, Nd, and Sm by various solvents as indicated.

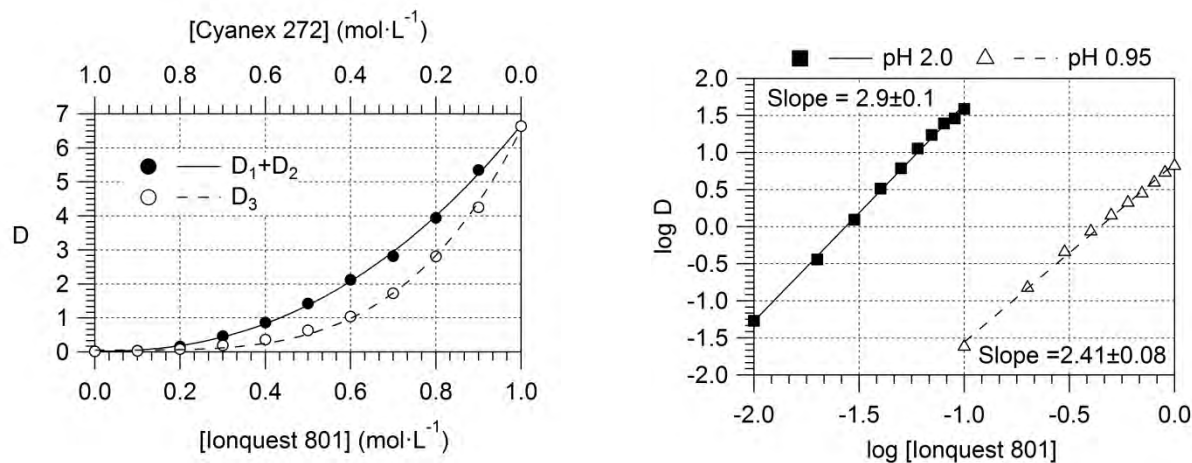


Figure 2 (left): Analysis of synergism by method of continuous variation (pH 0.95). Closed symbols sum of distribution ratios for separate samples of lonquest 801 (D_1) and Cyanex 272 (D_2), open symbols: distribution ratios for $1.0 \text{ mol}\cdot\text{L}^{-1}$ mixtures of lonquest 801 and Cyanex 272 (D_3).

Figure 3 (right): Effect of lonquest 801 concentration on Sm distribution ratios. Black squares: $0.01 - 0.1 \text{ mol}\cdot\text{L}^{-1}$ lonquest 801 (pH 2.0). White triangles: $0.1 - 1.0 \text{ mol}\cdot\text{L}^{-1}$ lonquest 801 (pH 1.0).

Conclusion

An equimolar mixture of lonquest 801 and Cyanex 272 was found to extract Ce, Pr, Nd and Sm at pH values between those of the separate components. The results for Cyanex 572, also a mixture of phosphonic and phosphinic acids, were similar to those of the lonquest 801/Cyanex 272 mixture. The mixture of lonquest 801 and

Cyanex 272 was antagonistic towards extraction of Ce, Pr, Nd and Sm under the conditions examined, while separation factors were similar to those of the individual components.

It has been suggested that the use of Cyanex 572 could result in savings in acid consumption in stripping sections of industrial plants. Our results suggest that the free acid required for Sm stripping would be 53% of the corresponding value for an equal concentration of Ionquest 801, while an equimolar mixture of Ionquest 801 and Cyanex 272 would produce a similar saving. Cyanex 272, the weakest solvent examined, was predicted to require only 12% of the free acidity of Ionquest 801. However, a final selection of solvent for industrial applications would include a consideration of the level of loading that can be achieved for each solvent option.

Acknowledgements

The authors wish to thank the Australian Nuclear Science and Technology Organisation for permission to publish this work, and Cytec Industries for supplying a sample of Cyanex 572.

References

1. Xu, G.; Huang, C.; Gao, S., *Rare Earths (in Chinese)*. Metallurgical Industry Press: Beijing, China, 1995; Vol. 2, p 534.
2. Xie, F.; Zhang, T. A.; Dreisinger, D.; Doyle, F., A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering* **2014**, 56 (0), 10-28.
3. Yuan, C.; Ma, H.; Pan, C.; Rickelton, W. C. Synergistic extraction of rare earths based on Cyanex 272. In *Proceedings of the International Solvent Extraction Conference*, Melbourne, Australia, Shallcross, D. C.; Paimin, R.; Prvcic, L. M., Eds. University of Melbourne: Melbourne, Australia, 1996; pp 733-738.
4. Wang, X. L.; Li, W.; Meng, S. L.; Li, D. Q., The extraction of rare earths using mixtures of acidic phosphorus-based reagents or their thio-analogues. *Journal of Chemical Technology and Biotechnology* **2006**, 81 (5), 761-766.
5. Kim, J. S.; Kumar, B. N.; Radhika, S.; Kantam, M. L.; Reddy, B. R., Studies on selection of solvent extractant system for the separation of trivalent Sm, Gd, Dy and Y from chloride solutions. *International Journal of Mineral Processing* **2012**, 112–113 (0), 37-42.
6. Xiong, Y.; Wang, X.; Li, D., Synergistic Extraction and Separation of Heavy Lanthanide by Mixtures of Bis(2,4,4-trimethylpentyl)phosphinic Acid and 2-Ethylhexyl Phosphinic Acid Mono-2-Ethylhexyl Ester. *Separation Science and Technology* **2005**, 40 (11), 2325-2336.
7. Li, D.; Bai, Y.; Sun, X.; Liu, S. Advances in solvent extraction and separation of rare earths. In *Proceedings of the 52nd Conference of Metallurgists*, Montreal, Canada, Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, Canada, 2013; pp 367-374.
8. Zhengshui, H.; Ying, P.; Wanwu, M.; Xun, F., Purification of organophosphorus acid extractants. *Solvent Extraction and Ion Exchange* **1995**, 13 (5), 965-976.
9. Fainerman-Melnikova, M.; Ho, E. M.; Solden hoff, K. Impact of sulphate media on the extraction of rare earths with organophosphorous reagents. In *Proceedings of the 19th International Solvent Extraction Conference*, Santiago, Chile, 3-7 October 2011; Gecamin Ltda.: Santiago, Chile, 2011; p 102.
10. Kolarik, Z., Review: Dissociation, Self-Association, and Partition of Monoacidic Organophosphorus Extractants. *Solvent Extraction and Ion Exchange* **2010**, 28 (6), 707-763.

Recovery of In, Y, Nd and Eu from WEEE by solvent extraction

Jiaxu Yang^{*1}, Christian Ekberg², Teodora Retegan²

Summary

Since flat panel displays (FPDs) first emerged, they have gradually become the most dominant type of displays on the market, replacing the cathode ray tube displays (CRTs). Similar trends have been observed in the waste flow as well. FPDs contain valuable metals such as Indium in the transparent electrode of glass panel, lanthanides in the phosphor powders of fluorescent backlights and neodymium in the magnets of speakers. All these metals could be of interest for recycling, due to large amount of discarded FPDs are to be expected in the near future. Many studies were conducted towards the recyclability, extraction and purification of these metals from waste electrical and electronic equipment (WEEE) by means of pyrometallurgical or hydrometallurgical methods.

Due to the fact that the aforementioned metals are trivalent in solution, it could be difficult to separate them. Therefore an investigation was carried out in order to assess the abilities of various organic extractants to separate the metals from each other. Many studies were and are carried-out for the separation of the actinides from lanthanides (trivalent oxidation state) from spent nuclear waste with solvents following the CHON principle (containing only carbon, hydrogen, oxygen and nitrogen) with very good results. However, in that context the systems were discarded due to their poor behavior towards radiolysis and hydrolysis. However these factors are not relevant for typical WEEE recycling, thus they have now been investigated in this context. Moreover, aside from distribution ratios, the behavior of the solvent (ligand and diluents) towards complexation and extraction of metals have been studied.

Key words: WEEE, recycling, solvent extraction, CHON, FPDs.

¹ Industrial Materials Recycling & Nuclear Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden. Jiaxu.yang@chalmers.se

² Industrial Materials Recycling & Nuclear Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden.

Introduction

The need for recycling has grown considerably in the recent years. This is especially true regarding Waste Electronic and Electrical Equipment (WEEE), which is one of the fastest growing waste streams in Europe[1]. Due to the extensive use of Flat Panel Displays (FPD) in products such as televisions, monitors and mobile devices, an increase of FPD waste is to be expected in the near future. A typical FPD device contains several types of chemical elements such as indium, yttrium, neodymium and other Rare Earth Elements (REEs) which are classified by European Commission as critical with respect to economical importance and supply risk[2]. Indium is present in FPD waste as Indium-Tin-Oxide (ITO), and is used as transparent electrode material in the panel glass. Neodymium is a component of permanent magnets found in hard disk drives and loud speakers. Y, Eu, Gd are used in the phosphor powders of lighting devices, like back lighting panels containing very thin fluorescent lamps. The content of these metals in a single device is low, therefore methods such as acid leaching followed by solvent extraction have been used to recover indium and REEs from FPD waste.

In many previous studies on the extraction and separation of indium and REEs from other elements, phosphate-based organic compounds have been common choices for metal extraction from acidic media. Examples include tri-butyl-phosphate (TBP) for extraction of indium and tin[3] and extraction of lanthanide(III) ions [4],. Additionally, studies on the separation of indium from other di- and trivalent metals[5], and metal recovery from spent Hybrid Electric Vehicle batteries were performed using Cyanex 923 (mixture of four different tri-octyl/hexyl-phosphates)[6].

Other than organophosphate extractants, there is another class of organic molecules, namely 6,6'-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)-[2,2']bipyridine (BTBP) and its derivatives. Extractants from BTBP-family has previously been used in the field of nuclear fuels reprocessing, e.g. DIAMide Extraction (DIAMEX), Selective ActiNide Extraction (SANEX) and Group ActiNide Extraction (GANEX) process [7]. The main environmental advantage of molecules such as BTBP over organophosphates is that the former contains only C,H,O and N.

The main focus of this work was to study the feasibility of different extractants and diluents for the purpose of developing a hydrometallurgical process to recover indium and REE from FPD waste. Aqueous phase used in the experiments was leachate of FPD waste material containing a large number of metal ions, which differs from previous work[3] where simulated stock solutions were often used. The ability of several extractants (TBP, Cyanex 923, CyMe₄-BTBP and C2-BTBP) to extract metal ions present in the acidic leachate solution was studied in a screening test. In addition, the effect of diluents on metal extraction was also investigated, since interactions between the diluent and extractants can have noticeable effects on the distribution of metal ions.

Methodology

The aqueous phase used in the extraction studies was obtained by leaching genuine solid FPD waste samples in H₂SO₄ (>95%, Sigma Aldrich), HCl (>37% Sigma Aldrich), and HNO₃ (65%, Sigma Aldrich) at 1 M and 6 M concentrations and 85±5°C for 16h. The solid-liquid (S/L) ratio was 0.1 g/ml and the acid solutions were mechanically stirred at 350 rpm. Solid samples were in the form of powders and were one of the fractions obtained from a FPD waste shredding line. Metal concentrations of the acid solutions after leaching are presented in Table 1, concentrations of the same metal differs somewhat between leachate solutions due to inhomogeneity in the solid sample. Results of some of the metals in Table 1 were not presented due to having low distribution ratio (Al, Ni) or having similar distribution ratio in all systems, e.g. Eu and Nd.

Table 1: metal concentrations in the aqueous phase (μM)

	1 M HCl	1 M HNO ₃	6 M HCl	6 M HNO ₃		1 M HCl	1 M HNO ₃	6 M HCl	6 M HNO ₃
Ag	120	5	230	20	In	500	340	400	230
Al	59000	44000	94000	25000	Mn	4600	1200	4900	1200
Co	110	56	120	1000	Mo	85	48	87	44
Cr	1200	220	1100	150	Nd	190	120	240	84
Cu	2800	1300	2400	1000	Ni	2600	750	2600	1200
Eu	270	180	180	90	Sn	1100	76	1100	420
Fe	55000	27000	20000	59000	Y	11000	7400	9300	5100
Gd	670	440	510	280	Zn	13000	8600	13000	5800

A screening test by batch extraction was performed in order to determine distribution ratios of metals between aqueous and organic phase. 1.5ml of each organic and aqueous phase was added to a 3.5ml glass vial. The extractions were performed at room temperature (21±1 °C). A simple kinetics study was performed and it was found that distribution ratios reached equilibrium after approximately 30 minutes of mechanical shaking (IKA VIBRAX VXR basic) at 1500 rpm. Therefore a contact time of 30 minutes was used. Distribution ratio was calculated as $D = [M_{org}]/[M_{aq}]$. Metal concentrations in the aqueous phase before and after extraction were measured and used to determine D.

The organic diluents studied were kerosene (Solvent 70, Statoil), MIBK (>99%, KEBO), n-octanol (96%, Acrös Organics) and cyclohexanone (99.8% Lab-Scan Analytical Science), and the extractants were TBP (97%, Sigma Aldrich), Cyanex 923 (93%, Cytec), C2-BTBP and CyMe₄-BTBP was synthesized in-house. 2% volume n-

decanol (99%, Sigma Aldrich) was added to organic phases containing TBP as third phase inhibitor.

Metal concentrations in the leach liquor were determined using Inductively Coupled Plasma with Optical Emission Spectrometer (ICP-OES, Thermo iCAP-6000). The metal content was quantified by calibrating with external standards. The detection limit of the instrument for the metals of interest is in the range of parts per billion ($<0.1 \mu\text{M}$), which is low enough for the quantification to be reliable. More precise values of distribution ratios below 0.01 were not presented due to measured values being near the detection limit of the instrument.

Results and Discussion

Due to limitations on solubility in e.g. 1-octanol and MIBK, the extractant concentrations for BTBP-class molecules were much lower than the others. There could be risk for loading if metals with concentration $> 5\text{mM}$ were extracted. This means that metal ions such as Fe(III) in the leachate solutions were extracted by C2-BTBP under loading. In addition, since miscibility between cyclohexanone and 6 M HCl/HNO₃ was too high, results for BTBP molecules diluted in cyclohexanone was not presented for the 6 M acid concentrations.

Chloride media:

Distribution ratios of metals between HCl and organic phases containing different solvating extractants are shown in Table 2 and 3. It can be seen that none of the extractants studied was able to extract REEs from chloride media. However, this means that it is possible to use HCl to selectively strip REEs from an organic solution containing Cyanex 923. The distribution ratio of iron for C2-BTBP is doubtful, due to high iron concentration in the aqueous phase relative to the extractant concentration.

Although it was observed that the solubility of C2-BTBP in octanol and MIBK was lower than that of CyMe₄-BTBP, results in Table 2 shows that distribution ratios of divalent ions such as Co(II) are higher for C2-BTBP than CyMe₄-BTBP. This selectivity of BTBP-class molecules for first row divalent transition metal ions has been noticed in an earlier work [8] and agrees well with the findings of the present study..

Table 2: metal distribution ratios between 6 M HCl and different organic phases, K=kerosene, O=1-octanol, M=MIBK.

1 M	1 M	0.005 M	0.005 M	0.01 M	0.01 M
Cyanex	TBP	C2-	C2-	CyMe4-	CyMe4-
923		BTBP	BTBP	BTBP	BTBP

	K	K	O	M	O	M
Ag	2.5	0.8	0.1	0.1	0.1	0.4
Co	4.7	0.7	54.2	1.6	0.3	<0.1
Cu	22	1.0	0.8	0.1	1.1	0.0
Fe	56	>100	>100	>100	4.0	3.0
In	54	19.0	3.4	2.7	<0.1	<0.1
Mn	0.8	0.8	1.1	0.1	<0.1	<0.1
Mo	41	>100	71	>100	6.7	5.4
Nd	<0.1	0.5	0.1	0.1	<0.1	0.2
Sn	>100	>100	8.5	7.4	4.9	4.0
Y	<0.1	0.7	<0.1	<0.1	<0.1	<0.1
Zn	51.7	1.3	<0.1	<0.1	0.3	0.2

For most metal ions, their distribution ratios are higher in 6 M HCl than 1 M HCl. This could be the result of increased chloride concentration, as all of the extractants studied were solvating extractants. On the other hand silver has shown the reversed trend. The decrease in distribution ratio can be attributed to the formation of anionic silver chloride complex at high chloride concentration. The ability of BTBP molecules to extract silver was studied in a previous work[9], where it was found that both C2- and CyMe₄-BTBP was able to extract silver from nitrate media, with CyMe₄-BTBP having higher distribution ratio.

Table 3: metal distribution ratios between 1 M HCl and different organic phases, K=kerosene, O=1-octanol, M=MIBK, C=cyclohexanone.

	1 M Cyanex 923 K	1 M TBP K	0.005 M C2- BTBP O	0.005 M C2- BTBP M	0.005 M C2- BTBP C	0.01 M CyMe ₄ - BTBP O	0.01 M CyMe ₄ - BTBP M	0.01 M CyMe ₄ - BTBP C
Ag	37	0.8	<0.1	0.2	1.6	0.3	0.2	1.7
Co	<0.1	0.9	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	24.5	1.0	0.2	<0.1	0.1	0.1	<0.1	0.3
Fe	0.4	0.7	0.1	<0.1	0.2	<0.1	0.1	0.1
In	39.4	0.8	0.1	0.1	0.9	<0.1	0.2	1.3
Mn	<0.1	0.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo	48	1.3	0.2	<0.1	0.2	0.1	<0.1	0.1
Nd	0.3	0.7	0.3	<0.1	<0.1	<0.1	<0.1	<0.1

Sn	>100	22.6	0.9	0.3	18	0.4	0.5	15.1
Y	0.1	0.9	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	37	0.7	0.1	<0.1	0.3	<0.1	<0.1	0.3

Nitrate media:

Distribution ratios of metals for 6 M and 1 M HNO₃ systems are shown in Table 4 and 5. It can be seen that in 6 M HNO₃, CyMe₄-BTBP selectively extracts certain divalent metal ions such as Cu(II) and Co(II). The same selectivity can also be observed at lower nitrate concentration. Furthermore, from Table 5 it can be observed that compared to 1-octanol and MIBK, Distribution ratios of e.g. Co(II) and Mn(II) are higher when cyclohexanone was used as diluent. This indicates that synergism exists between cyclohexanone and the extractant molecules.

Table 4: metal distribution ratios between 6 M HNO₃ and different organic phases, K=kerosene, O=1-octanol, M=MIBK.

	1 M Cyanex 923 K	1 M TBP K	0.005 M C2- BTBP O	0.005 M C2- BTBP M	0.01 M CyMe ₄ - BTBP O	0.01 M CyMe ₄ - BTBP M
Ag	4.7	1.2	<0.1	<0.1	<0.1	<0.1
Co	<0.1	0.7	<0.1	0.2	0.8	0.8
Cu	<0.1	0.9	0.5	0.2	12	12
Fe	1.3	0.7	<0.1	<0.1	<0.1	<0.1
In	<0.1	0.6	<0.1	<0.1	0.2	0.1
Mn	<0.1	1.0	<0.1	<0.1	0.3	0.5
Mo	22	0.9	0.6	<0.1	0.6	<0.1
Nd	0.2	0.7	<0.1	<0.1	<0.1	<0.1
Sn	48	0.8	<0.1	<0.1	<0.1	<0.1
Y	0.9	0.9	<0.1	<0.1	<0.1	<0.1
Zn	<0.1	0.5	<0.1	<0.1	0.3	0.2

With respect to recovery of indium and REE, 1 M Cyanex 923 diluted in kerosene was able to quantitatively extract the REEs and indium from 1 M HNO₃, while distribution ratios of divalent metal ions are low. Results in Table 2 and 3 shows that distribution ratios of REEs are low in both 1 M HCl and 6 M HCl, hence HCl can be used to selectively strip REEs from organic phase. However, due to Fe having low

distribution ratio in 1 M HCl, it will likely be stripped to the aqueous phase as well, whereas in 6 M Fe will remain in the organic phase.

Table 5: metal distribution ratios between 1 M HNO₃ and different organic phases, K=kerosene, O=1-octanol, M=MIBK, C=cyclohexanone.

	1 M	1 M	0.005 M	0.005 M	0.005 M	0.01 M	0.01 M	0.01 M
	Cyanex	TBP	C2-	C2-	C2-	CyMe4-	CyMe4-	CyMe4-
	923		BTBP	BTBP	BTBP	BTBP	BTBP	BTBP
	K	K	O	M	C	O	M	C
Ag	0.7	1.7	<0.1	<0.1	0.3	<0.1	<0.1	0.3
Co	<0.1	1.2	0.2	<0.1	5.3	0.1	0.2	2.4
Cu	<0.1	1.0	<0.1	<0.1	0.3	2.4	1.2	3.3
Fe	7.8	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
In	3.8	0.8	<0.1	0.1	0.3	<0.1	0.1	0.4
Mn	<0.1	<0.1	2.7	0.1	21	0.2	0.3	1.5
Mo	18	1.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nd	25	0.8	<0.1	<0.1	0.2	<0.1	<0.1	<0.1
Sn	15	1.3	<0.1	0.1	0.1	<0.1	0.1	<0.1
Y	53	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	<0.1	0.6	<0.1	<0.1	<0.1	0.1	0.2	0.1

Conclusion

In this work, the feasibility to extract and separate of indium and REEs was studied for different organic extractants and diluents. Compared to commercially available extractants, BTBP molecules showed selectivity for divalent metal ions, but were only able to extract indium from 6 M chloride media. REEs and indium could be extracted by either TBP or Cyanex 923, however separation between different metals were poor when TBP was used as extractant. For the purpose of developing a process to recover indium and REEs from FPD waste, it was concluded that extraction from 1 M HNO₃ to 1 M Cyanex 923 in kerosene, can be used as the first step. Further studies will be needed in order to find a way to separate extracted rare earth elements.

Acknowledgement

The authors would like to thank Recyval-Nano, a project in the EU Seventh Framework Program (no. 310312) for the financial support.

References

- [1] J. Huisman, F. Magalini, R. Kuehr, C. Maurer, S. Ogilvie, J. Poll, C. Delgado, E. Artim, J. Szlezak and A. Stevels, "2008 Review of Directive 2002/96/EC on waste electrical and electronic equipment (WEEE)," United Nations University, Bonn, Germany, 2007.
- [2] European Commission, "Critical raw materials for the EU," European Commission, 2010.
- [3] S. Virolainen, D. Ibane and E. Paatero, "Recovery of Indium from Indium-Tin-Oxide by Solvent Extraction," *Hydrometallurgy*, vol. 107, no. 1-2, pp. 56-61, 2011.
- [4] C. E. A. Ø.-J. K. Larsson, "Exotic reagents for separation of metals from nickel metal hydride batteries," Santiago, 2011.
- [5] B. Gupta, A. Deep and P. Malik, "Liquid-liquid extraction and recovery of Indium using Cyanex 923," *Analytica Chimica Acta*, vol. 513, no. 2, pp. 463-471, 2004.
- [6] C. E. A. Ø.-J. K. Larsson, "Using Cyanex 923 for selective extraction in a high concentration chloride medium on nickel metal hydride battery waste," *Hydrometallurgy*, Vols. 129-130, pp. 35-42, 2012.
- [7] P. Panak and A. Geist, "Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligand," *Chemical Reviews*, pp. 1199-1236, 2013.
- [8] M. Foreman, M. Hudson, A. Geist, C. Madic and M. Weigl, "An Investigation into the Extraction of Americium(III), Lanthanide and D-Block Metals by 6,6'-Bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP)," *Solvent Extraction and Ion Exchange*, vol. 23, no. 5, pp. 645-662, 2005.
- [9] E. Löfström-Engdahl, E. Aneheim, C. Ekberg, M. Foreman, G. Skarnemark, Z. Hájková and B. Grüner, "The Extraction of Silver and the Effect of Diluent, Ligand Side Group and Solvent Composition," *Procedia Chemistry*, vol. 7, pp. 239-244, 2012.

Innovation of Solvent Extraction for Metal Separation in Mixed Chloride Media: Case Studies for Different Value Metals

*V.I. Lakshmanan¹, R. Sridhar¹, M.A. Halim^{*1}*

Summary

Solvent extraction is one of the important unit processes in the commercial production of value metals in metallurgical industry. Process Research ORTECH Inc. (PRO) has developed the innovative mixed chloride-solvent extraction processes for the production of value metals from their different sources such as nickel, cobalt and iron from laterite; titanium, vanadium and iron from ilmenite and concentrates; and copper and iron from chalcopyrite. PRO process uses mixed chloride lixiviant ($\text{HCl}+\text{MgCl}_2$) to dissolve these metals in solution. The hydrochloric acid (HCl) leaching media provides the opportunity to regenerate the acid by pyrohydrolysis, while the presence of magnesium chloride (MgCl_2) in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude, making the lixiviant very aggressive and resulting in high recoveries of these metals. The developed process flowsheets are innovative, environmentally friendly and economically attractive.

Introduction

Demand of base metals including iron, titanium, vanadium, cobalt, nickel and copper is tremendously increasing for the development of science and technology in the world. Meanwhile the number of new ore bodies, and the easily exploited ore, are gradually decreasing. Moreover, a rising awareness of environmental protection has lead to more and more difficulty with the smelting process. On the contrary, chloride hydrometallurgy is emerging as an alternative process for the production of base metals [1-4]. Chloride chemistry is complex and quite different from corresponding other systems including sulfate. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. The solubility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is about one fifth that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions [5]. Also, the activity of water is $\ll 1$ in concentrated magnesium chloride solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration [6]. This enhances the leachability of minerals in mixed chloride solutions resulting in increased base metals recovery.

Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy and PRO's patented mixed chloride technology has been applied to the recovery of several value metals including base metals from laterite and sulfide ores, titanium dioxide from ilmenite ores, rare earth elements (REE) from alumino-silicate ores, platinum group metals (PGM) from sulfide ores and gold from refractory ores [7-15]. In this paper, application of PRO's mixed chloride technology for the recovery of iron, cobalt and nickel from laterite ore, iron, titanium and vanadium from ilmenite ore, and iron and copper from sulfide ore is described.

Recovery of Iron, Cobalt and Nickel from Laterite Ores

Lateritic ores are formed by prolonged weathering of ultramafic rocks and its use for production of nickel is gradually increasing [16]. Typical mineralogical profile of nickel laterite ore bodies is as described below [17, 18]:

¹Process Research ORTECH Inc., 2350 Sheridan Park Drive, Mississauga, ON, L5K 2T4, Canada

*Email: halim@processortech.com

- i. Overburden: This zone contains low nickel values ($< 0.8\%$ Ni) and is discarded.
- ii. Limonitic ore zone: This zone contains $\sim 1.2\text{--}1.7\%$ Ni, $\sim 40\%$ Fe and $\sim 1\text{--}4\%$ MgO. Hydrometallurgical processes are used to extract nickel from limonitic ore zone. High pressure acid leach (HPAL) process is used for high iron ($> 35\%$ Fe) limonitic ores.
- iii. Saprolitic ore zone: This zone contains ~ 1.7 to 2.3% Ni and low iron ($< 15\%$ Fe). Pyrometallurgical smelting processes are used to produce ferronickel or matte from saprolitic ores.
- iv. Base rocks: This zone contains $< 0.5\%$ Ni and it is not economic to extract nickel from base rocks.

In some ore bodies, the saprolitic ore profile is either absent or too trace. In ore bodies with rich saprolitic ore zone, the limonitic ores may be stockpiled and stored for later treatment till the higher grade saprolitic ore zone is exhausted.

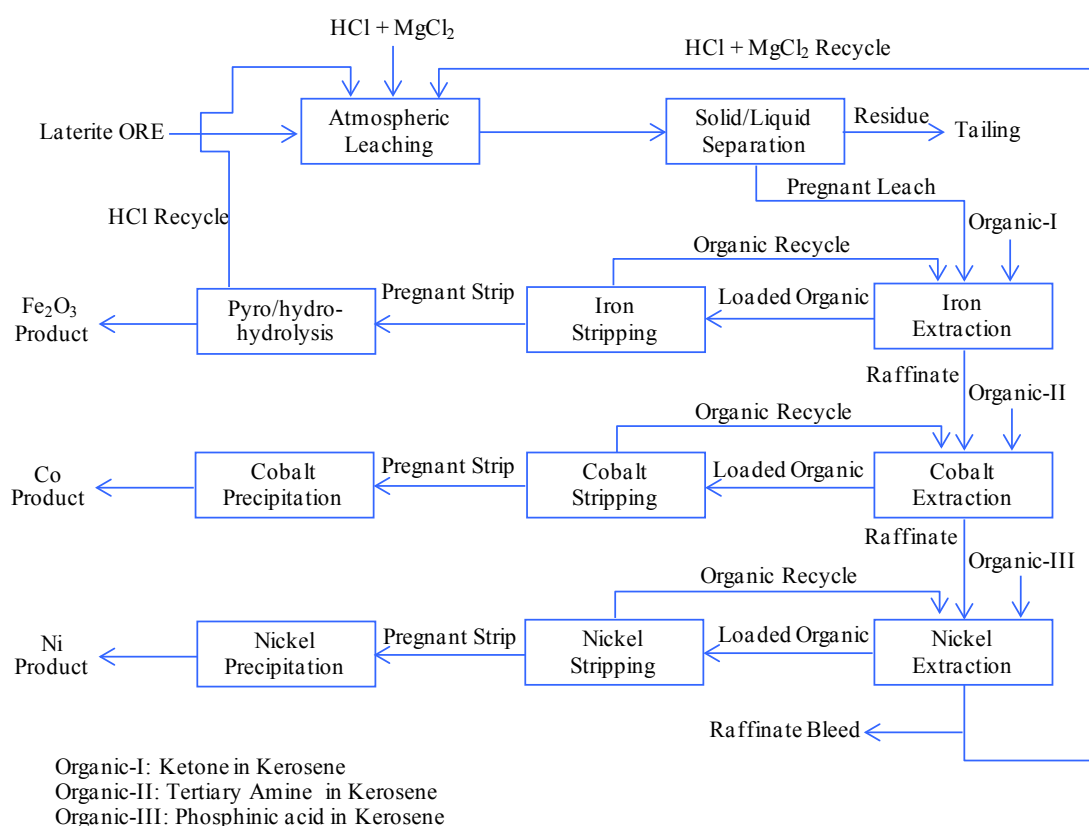


Fig. 1 PRO mixed chloride process flowsheet for the recovery of Fe, Co and Ni from lateritic ores [7].

PRO Laterite Process

Based on chloride hydrometallurgy, a innovative mixed chloride process has been developed by Process Research Ortech Inc. (PRO), which is applicable to both high and low iron laterite ores [7]. The process flowsheet is shown in Fig. 1 [7], which involves novel leaching and solvent extraction separation steps. This process is efficient and environmentally friendly. The salient features of the PRO Laterite Process are as follows:

- i. Leaching: Leaching is conducted in mixed chloride media to dissolve Fe, Ni, Co and Mg in solution.

- ii. Solvent Extraction: Solvent extraction steps are carried out for successive extraction and stripping of Fe, Co and Ni to obtain high purity concentrated pregnant strip solutions of Fe, Co and Ni, respectively.
- iii. Precipitation: Precipitation of Ni and Co from respective high purity concentrated pregnant strip solutions is conducted by the addition of MgO generated by pyrohydrolysis.
- iv. Pyrohydrolysis:
 - a. Fe_2O_3 is produced and HCl is regenerated by the pyrohydrolysis of the iron chloride rich pregnant strip solution.
 - b. MgO is produced and HCl is regenerated by the pyrohydrolysis of the bleed stream from the magnesium chloride containing raffinate of the nickel solvent extraction stage. MgO thus produced can be used for pH control as well as precipitation of Ni and Co from their respective pregnant strip solutions. Excess MgO produced can be sold.
- v. Recycling: HCl and MgCl_2 are recycled to leaching stage.

PRO Testwork

Tests were conducted with a laterite ore having a composition of 0.76% Ni, 0.11% Co and 42.61% Fe. Optimum leach recoveries of Ni, Co and Fe in PRO's proprietary mixed chloride lixiviant were 97.8%, 89.4% and 97.7%, respectively. After solid/liquid separation, the pregnant leach solution went through a series of solvent extraction separation steps to sequentially extract Fe, Co and Ni from the solution using different organic extractants. Loaded organics were stripped using dilute acidic solutions to generate high purity pregnant strip solutions of Fe, Co and Ni individually. The solvent extraction separation steps developed by PRO are highly selective for the target metals, which results in high purity pregnant strip solutions and consequentially high purity Fe, Co and Ni products. Iron oxide and magnesium oxide can be produced from respective solutions by pyrohydrolysis, which will also regenerate the hydrochloric acid. Pyrohydrolysis is a commercially proven process. PRO has developed a novel hydrothermal hydrolysis process that can be used to regenerate the hydrochloric acid and produce high purity iron oxide and magnesium oxide. PRO's hydrothermal hydrolysis process is more economical than pyrohydrolysis process as hydrothermal hydrolysis process runs at a much lower temperature.

Comparison of PRO Laterite Process with Commercial Processes

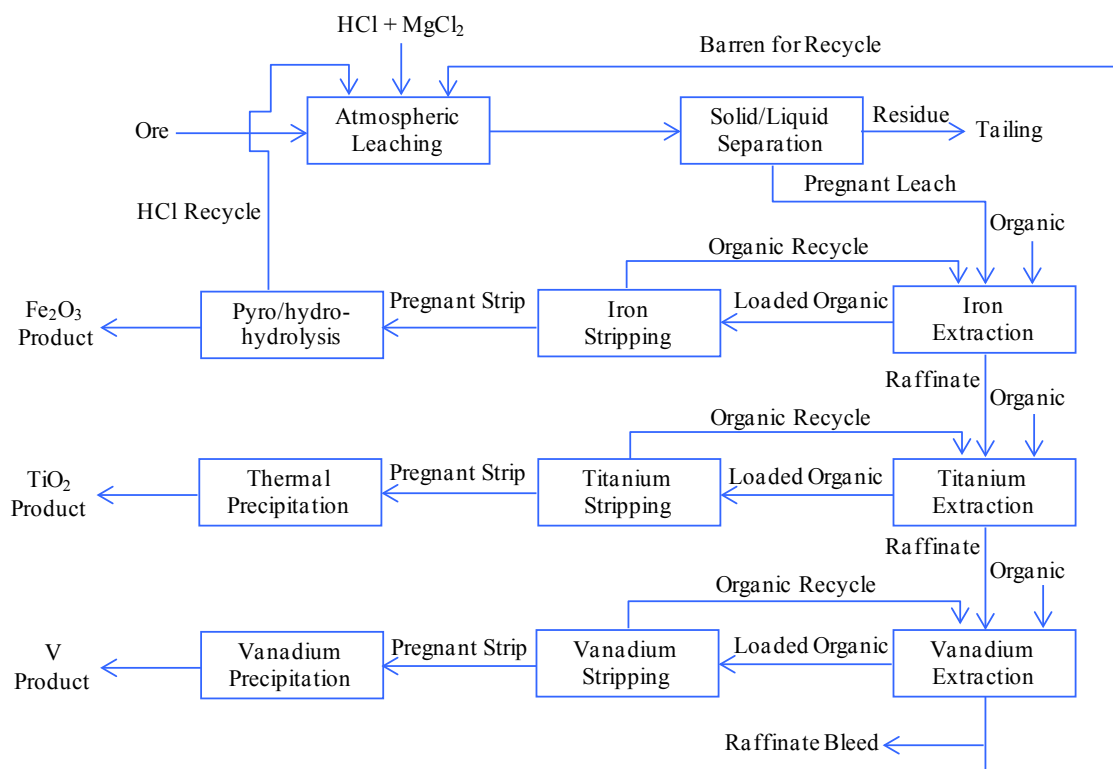
There are three commercial processes for the recovery of nickel from lateritic ores: Pyrometallurgical process, Caron process and High Pressure Acid Leach (HPAL) process [16]. The Pyrometallurgical process involves drying, calcining and smelting of entire ore body at successively higher temperatures and therefore is energy intensive. The Caron process involves ore drying followed by selective reduction of nickel, leaching with ammonia solution and nickel carbonate precipitation from pregnant leach solution. Nickel carbonate is decomposed to produce nickel oxide, which is then reduced to form nickel metal. In contrast, HPAL process involves high pressure leaching with H_2SO_4 followed by counter-current decantation and neutralization. Different options exist for purification of nickel containing solutions and separation of nickel and cobalt with solvent extraction, followed by electrowinning of nickel. A comparison of PRO laterite process with commercial processes is shown in Table 1.

Table 1 A comparison of PRO Laterite Process with commercial processes.

	Pyrometallurgical Process	Caron Process	HPAL Process	PRO Laterite Process
Ores that can be treated	Med-high Ni (1.8-2.5%), low-med Fe (10-20%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Both low Fe and high Fe ores
Ni recovery	~ 95%	~ 75%	~ 95%	> 90%
Co recovery	None	< 50%	~ 95%	> 90%
Fe recovery	No	No	No	Yes
Mg recovery	No	No	No	Yes
Capital cost	High	Medium	High	Low
Operating cost	High	Medium	High	Medium
Energy requirement	High (due to water removal from ore and high temperature processing)	High (due to water removal from ore and high temperature processing)	Low (no water removal from ore and low temperature process)	Medium (no water removal while pyrohydrolysis needed for acid regeneration adds energy cost)
Reagents	Not recycled	Not recycled	Not recycled	Recycled
Residue	High volume	High volume	High volume	Low volume
Environmental	Slag disposal	Residue disposal containing NH_3	Higher residue disposal	Inert residue
Sulphur price	No effect	No effect	Very dependent	No effect
Fuel price	High effect	Medium effect	Lower effect	Medium effect
Byproduct credit	None	None	None	Fe_2O_3 and MgO credit

Recovery of Iron, Titanium and Vanadium from Ilmenite

The main raw material for TiO_2 production is the mineral ilmenite ($\text{FeO} \cdot \text{TiO}_2$), which is commonly found in the mineral sand beaches. It also occurs as hard rock. In the processing of mineral sands, rutile ore is also recovered. Rutile ore is essentially TiO_2 and is used for the production of TiO_2 pigments by the chloride process.

**Fig. 2** The process flowsheet for the production of Fe, Ti and V oxides from ore [12, 15].

PRO Process

PRO has developed a proprietary mixed chloride Canadian Titanium Limited (CTL) process for the recovery of Fe, Ti and V from ilmenite concentrate [12,14, 15]. The process flowsheet is shown in Fig. 2 [12, 15]. This process consists of atmospheric mixed chloride leaching of ilmenite ore to bring Fe, Ti and V in solution. After solid-liquid separation, pregnant liquor is subjected to solvent extraction steps for subsequent extraction of Fe, Ti and V with different organic extractants followed by stripping and precipitation for product recovery.

PRO Testworks

An ilmenite ore containing 22.8 wt.% of Ti, 38 wt.% of Fe, 0.13 wt.% of Cr_2O_3 , 4.69 wt.% of SiO_2 and 2.82 wt.% of MgO with a mesh size of -100 was used as feed material for extraction of iron, titanium and vanadium with a solution of hydrochloric acid and magnesium chloride as a lixiviant under atmospheric pressure at $70-73^\circ\text{C}$ for 4 hours. The results show that extraction of Fe and Ti was achieved as high as 84.4% and 96.9%, respectively, for a solid loading of 8.8 %, 1.4 times of stoichiometric amount HCl and 300 g/L of MgCl_2 . Then, the slurry was filtered to separate the pregnant leach liquor from residue.

Solvent extraction was carried out for subsequent extraction of Fe, Ti and V with different organic extractants in kerosene from pregnant leach solution. Three different types of extractants namely acidic organophosphorus, neutral and amine extractants could be used to extract titanium followed by vanadium [12, 15]. Detailed explanation of these organics is given in the previous studies [12, 14, 15]. Loaded organics were stripped using acidic solutions to generate high purity pregnant strip solutions of Fe, Ti and V individually (Table 2). Iron oxide can be produced from pregnant strip solution by pyrohydrolysis, which will also regenerate the hydrochloric acid. The titanium pregnant strip was used for thermal precipitation of TiO_2 , while V was precipitated from its pregnant strip solution by increasing pH. The barren solution was used for reagent recovery and the regenerated liquor was recycled.

Table 2 Results of first stage stripping of Fe, Ti and V from their loaded organics with 0.05M HCl, 1M HCl and 1.5M H_2SO_4 , respectively, at the O/A ratio of 1 at room temperature.

Fe			Ti			V		
Concentration		Stripping	Concentration		Stripping	Concentration		Stripping
(g/L)		(%)	(g/L)		(%)	(g/L)		(%)
Organic phase	Pregnant strip		Organic phase	Pregnant strip		Organic phase	Pregnant strip	
37.8	35.6	94	9.8	7.6	78	5.2	4.6	88

Comparison of Titanium Dioxide Production Processes

TiO_2 is currently produced by either the sulphate process or the chloride process. PRO process is compared with the sulfate process and chloride process in Table 3.

Table 3 Comparison between TiO_2 production processes.

	The chloride process	The sulphate process	The CTL process
Raw material (\$/ton of feed)	Higher cost (\$2000 +)	Lower cost Ilmenite (\$300)	Lowest cost Ilmenite (\$250)
TiO_2 product (\$/ton of TiO_2)	High value (\$4500)	Low value (\$3500 +)	High value (\$4500)
Capex	Highest (including front-end)	Medium	Lowest
Opex	Highest (including front-end)	Medium	Lowest
Environmental	Medium challenges	Major challenges	Environmentally friendly
Flexibility in processing raw material	Limitation (Ca, Cr, Mn, Mg, V, size)	Limitation (Cr, V)	Flexible
Process Condition	High Temp. Chlorination (800-1000 °C)	High Temp Leaching (140-180 °C)	Low temp., atmospheric Leaching (70 °C), precipitation (90 °C)
Technology	Old	Old	Patented, New
End to end in one location	Not practiced	Possible	Possible
Pigment production	Rutile	Rutile/Anatase	Rutile/Anatase
Commercially Proven process	In practice	In practice	Innovatively applied, will soon be in practice
Environmental challenges	Disposal of iron and other byproduct chlorides	Disposal of large iron sulphate product and dilute acid	Minimum environmental impact, Iron oxide as byproduct
Safety Requirements	High (chlorine at high temperature)	High (High temperature acid digestion)	Low (no pressurized vessel and lower temperature)
chlorine and carbon/carbon containing chemicals at high temperature	Challenges to handle	N/A	N/A
Energy consumption	High	High	Efficient
Sulfur price	No effect	Substantial effect	No effect

Recovery of Iron and Copper from Sulfide Ores

Copper ore is mainly copper sulfide or copper oxide ore. The chalcopyrite concentrates, which account for about 70% of the world's known copper reserves. In the last 10 years, very few grass roots copper smelter-refinery complexes have been built, due to their very high capital cost. In contrast, there has been a gradual increase in the production of copper by leaching-solvent extraction-electrowinning operation, which is now account for about 30% of world copper production. There are a large number of reasons for looking at process alternatives for the smelter-refinery approach. They are: (i) capital cost; (ii) handling of impurities; (iii) precious metals in copper concentrates; (iv) recovery of valuable by-products; (v) use of existing SX-EW equipment; (vi) mine to market optimization; and (vii) overall economics [19, 20].

PRO Process

Process Research ORTECH (PRO) Inc. has been developed an innovation proprietary mixed chloride leaching technology for the recovery of Fe and Cu from sulfide ores/concentrates [11]. A tentative process flowsheet is shown in Fig. 3. The main features of this flowsheet include leaching of the ores/concentrates at 90-100 °C in recycled mixed chloride ($HCl+MgCl_2$) with an oxidant. In this leaching stage, Fe

and Cu are dissolved and sulphide sulphur is removed as H_2S , which is converted to elemental sulphur in a Claus reactor. Iron and Cu are recovered from leach solution by solvent extraction. Other steps include removal of impurities with lime and production of magnesia and regeneration of HCl by pyrohydrolysis.

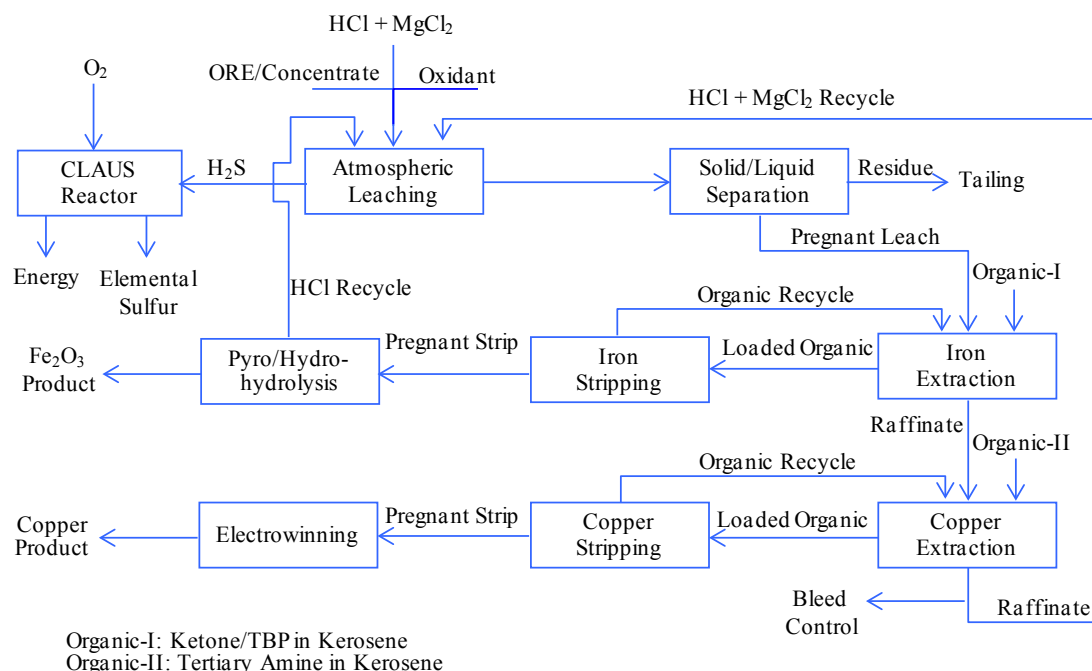


Fig. 3 A tentative process flowsheet for the production of Fe oxide and Cu from their sulfide ores.

PRO Testworks

A series of leaching tests were carried out using a copper ore containing 1.275% Cu, 2.61% Fe and 0.93% S and a leach solution of hydrochloric acid (4N) and magnesium chloride, at a total chloride ion concentration of 400 g/L. The leached solution was subjected to a solid/liquid separation followed by subsequent solvent extraction steps for separation and purification of Fe and Cu.

Iron followed by copper could be selectively separated from pregnant leach solution with an organic solvent containing a ketone/tri-butyl phosphate (TBP) and a tertiary amine in kerosene, respectively. Both of the Fe and Cu could be stripped from their loaded organics with a dilute acid. Barren organics could be recycled to the extraction circuits. The raffinate of the Cu extraction circuit can be treated for removal of impurities with lime followed by pyrohydrolysis to recover magnesia and HCl which can be recycled to the leaching stage. Iron oxide and HCl can be produced from Fe pregnant strip solution by pyrohydrolysis. Copper can be recovered from its pregnant strip solution by electrowinning.

References

1. Moyes, J., Houllis, F., Intec base-metal processes realizing the potential of chloride hydrometallurgy. Chloride Metallurgy 2002, Volume II, E. Peek, G. Van Weert, Eds., Montreal, Canada, October, 2002, 577-592.

2. Leimala, R., Hyvarinen, O., Hamalainen, M., Jyräla, M., The Outokumpu HydroCopper™ Process-design, implementation and operation of a demonstration plant, Copper 2003, 5th International Conference, Vol VI- Hydrometallurgy of Copper (Book 1), P.A. Riveros, D.G. Dixon, D.B. Dreisinger and J.M. Menacho, Eds., Santiago, Chile, 2003, 281-288.
3. Hyvarinen, O., Hamalainen, M., Leimala, R., Outokumpu HydroCopper™ Process-a novel concept in copper production. Chloride 2002, Volume II, E. Peek and G. Van Weert, Eds., Montreal, Canada, 2002, 609-613.
4. Harris, G. B., Lakshmanan, V.I., Magee, T.J., Sridhar, R., Atmospheric chloride leaching of base metal sulfides, Hydro-Sulfides 2004, International colloquium on hydrometallurgical processing of copper sulfides, Santiago, Chile, 2004, 384-398.
5. Lakshmanan, V.I., Sridhar, R., Harris, G.B., Magee, J., The Jaguar Nickel Inc. Sechol Laterite Project atmospheric chloride leach process, International laterite nickel symposium, W.P. Imrie, D.M. Lane, Eds., The Minerals, Metals and Materials Society, Charlotte, North Carolina, USA, March 14-18, 2004, 219-241.
6. Jansz, J.J.C., Estimation of ionic activities in chloride systems at ambient and elevated temperatures, Hydrometallurgy, 11(1), 1983, 13-31.
7. Lakshmanan, V.I., Sridhar, R., Chen, J. Halim, M.A., Separation of iron from value metals in leaching of laterite ores, 2013, U.S. patent application no. US 2013/0149219 A1.
8. Lakshmanan, V.I., Sridhar, R., Halim, M.A., Chloride process for the leaching of gold. 2013, U.S. patent application no. US 2013/0283976 A1.
9. Lakshmanan, V.I., Sridhar, R., Halim, M.A., Process for extraction of rare earth elements. U.S. patent application no US20130283977 A1.
10. Lakshmanan, V.I., Lawson, G.J., Nyholm, P.S., The extraction of copper(II) and iron(III) with Kelex 100 from aqueous media containing chloride ions. ISEC proceedings, 2, 1974, 1169-1183.
11. Harris, G.B., Lakshmanan, V.I., Sridhar, R., Puvvada, G., Process for the recovery of value metals from base metal sulfide ores. 2011, US patent no. US 7968065 B2.
12. Lakshmanan, V.I., Sridhar, R., Sheikhzeinoddin, T., Halim, M.A., Roy, R., Extraction of titanium and vanadium by chloride leach processes. Shijie Wang; John E. Dutrizac; Michael L. Free; James Y. Hwang; Daniel Kim, Eds., T. T. Chen, Honorary Symposium on Hydrometallurgy. Electrometallurgy and Materials Characterization TMS 2012, 295-301.
13. Lakshmanan, V.I., Sridhar, R., Roy, R., Ramachandran, V., Recovery of value metals from ores by mixed chloride extraction. Proceedings of Sixth International Symposium, Hydrometallurgy 2008, Phoenix, Arizona, August 17-20, 2008, 895-902.
14. Lakshmanan, V.I., Sridhar, R., Harris, G.B., Puvvada, G., Process for the recovery of titanium in mixed chloride media. U. S. patent, 2010, No. 7803336B2.
15. Lakshmanan, V.I., Ashok Bhowmick, Halim, M.A., Titanium dioxide: production, properties and application. Titanium Dioxide: Chemical Properties, Applications and Environmental Effects, Jerri Brown, Ed., Nova Science Publishers Inc., Chapter 5, 2014, 75-130.
16. Dalvi, A.D., Bacon, W.G., Osborne, R.C., The past and future of nickel laterites. PDAC 2004 International Convention, March 7-10, 2004, 1-27. Available online: <http://www.pdac.ca/pdac/publications/papers/2004/techprgm-dalvi-bacon.pdf>.
17. Golightly, J.P., Nickeliferous Laterites: a general description, International Laterite Symposium, D.J. Evans, R.S. Shoemaker, H. Veltman, Eds., New Orleans, Louisiana, The Society of Mining Engineers of AIME, New York, 1979, 3-23.
18. Alcock, R.A., The character and resources available to the nickel industry, extractive metallurgy of nickel and cobalt. Proceedings of a Symposium, The Metallurgical Society, C.P. Tyroler and C.A. Landolt Eds., 117th TMS Annual Meeting, Phoenix, Arizona, 1988, 67-89.
19. Dreisinger, D.B., New developments in hydrometallurgical treatment of copper concentrates. Hydro-Sulfides 2004, International Colloquium on Hydrometallurgical Processing of Copper Sulfides, Santiago, Chile, April 2004, 47-73.
20. Dreisinger, D.B., New developments in hydrometallurgical treatment of copper concentrates, Engineering and Mining Journal, 205(4), 2004, 32-35.

Effects of Operating Conditions in the Solvent Extraction Process to Separate Rare Earth Metals

Ryuichi Egashira, Tokyo Institute of Technology, Meguro, Japan;

Hiroaki Habaki, Tokyo Institute of Technology, Meguro, Japan

Objectives

The computational simulations of the solvent extraction process to separate rare earth metals were conducted with experimental values of equilibrium parameters, in order to examine the effects of operating conditions, which have not studied sufficiently yet and are quite important for the process synthesis and/or design as well as extraction mechanisms and equilibriums.

Process and Calculation

The process outline is shown in **Figure 1**. The extractor and scrubber are ideal multistage, where the aqueous phase and organic solvent phase containing extractant contact with each other countercurrently and the rare earth metal mixture in the feed is separated into heavier metal, readily extracted into organic phase, and lighter metal, remaining in aqueous phase. The separation of the mixture of lanthanum and cerium was simulated here using the previous equilibrium constants, $K_{ex,i}$ of these metals obtained with Solvesso150 solution of PC-88A as an organic solvent. The hydrogen ion concentrations in the feed and scrubbing phases, extractant, PC-88A, concentration, the flow rate ratio of solvent to feed, the stage numbers, etc. were varied.

Results and Discussion

The product purity and yield of cerium decreased and increased respectively with pHs in feed and scrubbing phases, PC-88A concentration, and flow rate of solvent. Especially, the effect of PC-88A concentration was remarkable, as presented in **Figure 2**. The stage numbers of extractor and scrubber did not affect obviously in the range of this work.

Consequently, the effects of operating conditions in this process were clarified. These results would be useful not only in rare earth metal extraction, but also in the extraction of various kinds of metals.

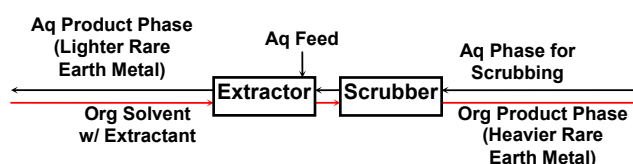


Fig. 1 Outline of the process

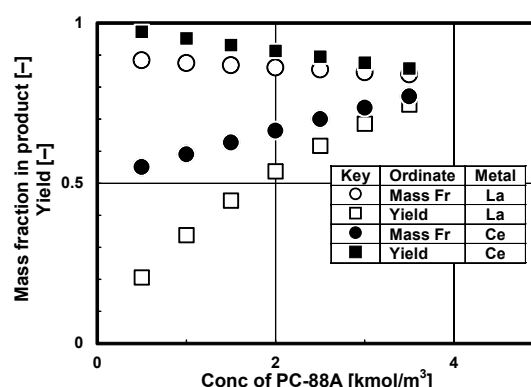


Fig. 2 Effects of extractant concentration on product purities and yields: feed flow rate = $0.001 \text{ m}^3 \text{ h}^{-1}$; concs of La and Ce in feed = 0.1 kmol m^{-3} ; pH in feed = 4; flow rate ratio of solvent to feed = 1.5; flow rate ratio of scrubbing phase to feed: 0.15; pH in scrubbing phase = 2; the number of stages in extractor = 10; the number of stages in scrubber = 10; $K_{ex,La} = 5.0 \times 10^{-5}$; $K_{ex,Ce} = 4.0 \times 10^{-4}$

Recovery of La, Ce, Eu, Gd, Tb and Y from fluorescent lamp waste using solvent extraction: solvent choice studies

*Cristian Tunsu^{*1}, Christian Ekberg, Marino Gergoric, Teodora Retegan*

Recovery of rare earth metals from various streams such as fluorescent lamp waste is receiving more and more attention. Hydrometallurgical treatment (leaching followed by solvent extraction) is suitable when taking into account the nature and chemical complexity of the material. A comparative study between two commercially available extractants (Cyanex 923 and tributyl phosphate) is presented, with regard to the choice of diluent (kerosene, TetraPropyleneHydrogenated, tertbutyl benzene and 1-octanol) and extraction kinetics. The highest distribution ratios of REMs were observed when using Cyanex 923. For both extractants, the distribution ratios were noticed to decrease in regard to the diluent used as follows: TetraPropyleneHydrogenated, kerosene, tertbutyl benzene, 1-octanol.

Introduction

The rare earth metals (REMs) are presently acknowledged to be of critical economical importance for many industrialized countries [1]. Their large variety of applications, together with their low market availability and short supply, led to questions regarding the recovery of REMs from various end-of-life products and industrial streams [2]. Fluorescent lamp waste is considered to be a feasible source of up to six REMs: La, Ce, Eu, Gd, Tb and Y. These metals are used in red, blue and green phosphors in tri-band fluorescent lamps [3]. Solvent extraction-based processes for the recovery of REMs from fluorescent lamp waste were investigated [4-8], however, large-scale applications are scarce [9, 10]. Additional research is needed for optimizing a sustainable process, especially for chemically complex and mercury contaminated phosphors-containing fractions.

When designing a solvent extraction process, the main research is often focused on the extractant and the extractable complexes. The choice of diluent plays, however, a very important role in the extraction process. It was, not surprisingly, shown that the distribution ratios (D) and separation factors (α) between metals extracted with different, or the same extraction mechanism, can change when changing the diluent [11, 12].

In this paper a hydrometallurgical treatment of real fluorescent lamp waste was investigated in the view of separating the REMs contained. The extraction capabilities of Cyanex 923, a commercial mix of trialkylphosphine oxides, and tributyl phosphate in four different diluents (kerosene, TetraPropyleneHydrogenated, tertbutyl benzene and 1-octanol) were investigated, with respect to phase contact time.

^{*1} Corresponding Author; tunsu@chamers.se. Industrial Materials Recycling, Chalmers University of Technology, Sweden

Experimental

Genuine fluorescent lamp waste originating from an end-of-life lamp processor was studied. The waste is a phosphors-containing fraction, and was obtained after crushing of mixed lamps, followed by separation of macro-fractions (glass, aluminium end caps etc.). The solvents were used as supplied by the manufacturer, with no additional purification. All solutions were analysed using Inductively Coupled Plasma-Optical Emission Spectroscopy (iCAP 6500, Thermo Fischer). A mass balance was used to calculate the distribution ratios for the solvent extraction studies (measurements of the aqueous phases before and after extraction). Due to the high acidity in the aqueous phases, sorption of metals is expected to be very low.

An estimation of the soluble metal content in the material was done by treating waste samples with aqua regia (120°C, 3 h, solid to liquid ratio of 10% v/w). To obtain the aqueous phase for the solvent extraction experiments, leaching of the material was carried out in two steps with 1 M HNO₃ solution (21°C, solid to liquid ratio of 10% v/w). In the first step, leaching was performed for 15 min to solubilize Ca and other contaminants. The remaining residue was subsequently leached for 48 hours for solubilisation of the REMs.

The organic phases consisted of 30% extractant dissolved in the selected diluent (v/v). The REMs-containing leachate was diluted 1:1 with 1 M HNO₃ solution in order to lower the concentration of metals, and prevent the premature loading of the organic phase. Because the solvating extraction with TBP requires a high concentration of weakly coordinating counter-ions in solution, the NO₃⁻ concentration in the aqueous phase used with TBP was increased to 6M using NaNO₃. Batch extraction experiments were performed using a phase ratio of 1 (1 ml aqueous and organic phase, respectively). Phase contact was facilitated by using a thermostatic shaking machine (20°C, 2000 vibrations per minute). The extraction behaviour of metals was investigated for each system at various points in time: 1, 5, 10, 20 and 30 min, respectively. Triplicate tests were performed and the uncertainties reported are based on the standard deviation calculated for these samples.

Results and discussions

Metal content in the waste and the associated aqueous phase

The estimated soluble content for several metals in the waste is presented in Table 1. Ce, Eu, Gd, La, Tb and Y were the REMs identified, with a total content of 211 ± 5.01 g REMs/kg dry waste. Y accounts for the vast majority (187.15 ± 4.42 g/kg), followed by Eu (11.39 ± 0.24 g/kg). These two elements account for approx. 94% of the total REMs content. The recycling potential of fluorescent lamp waste, together with a comprehensive leaching study, was recently published [13]. It was concluded that Eu and Y can be easily dissolved at room temperature, in the first 24 hours, using diluted

mineral acid solutions. The efficient leaching of the other REMs (Ce, Gd, La and Tb) requires more concentrated acids, a longer leaching time, and temperature.

Table 1 - Soluble content for several metals in the waste investigated

Metal	g metal/kg waste	Metal	g metal/kg waste	Metal	g metal/kg waste
Al	13.12 ± 0.19	K	0.43 ± 0.02	W	0.21 ± 0.01
B	2.91 ± 0.04	Mg	2.55 ± 0.04	Zn	0.42 ± 0.0004
Ba	15.67 ± 0.36	Mn	2.57 ± 0.03	Ce	3.06 ± 0.098
Ca	97.00 ± 2.49	Na	2.58 ± 0.09	Eu	11.39 ± 0.24
Cd	0.26 ± 0.004	Ni	0.10 ± 0.002	Gd	5.51 ± 0.08
Cr	0.03 ± 0.0003	Pb	0.21 ± 0.004	La	2.14 ± 0.13
Cu	0.13 ± 0.002	Sb	1.25 ± 0.02	Tb	1.76 ± 0.04
Fe	1.74 ± 0.02	Si	0.26 ± 0.002	Y	187.15 ± 4.42
Hg	0.30 ± 0.002	Sn	0.07 ± 0.001	<i>Total REMs</i>	<i>211 ± 5.01</i>

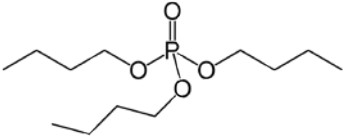
Approx. 80% of the Ca and Pb, 70% of the Ba, Fe, Ni, Sb and Zn, over 90% of the Cd and Cu, and over 60% of the Sn and W were solubilized in 15 min with 1 M HNO₃ solution. Due to slower kinetics, the solubilisation of each REM was between 1-4%. The REM concentrations in the solution obtained after the second leaching step (1 M HNO₃; 48 h) were: 0.03 g/l Ce, 1 g/l Eu, 0.07 g/l Gd, 0.02 g/l Tb, and 17.5 g/l Y. La was present in trace concentration (2.5 mg/l) and, due to subsequent extraction and dilutions, its concentration dropped below the detection limit of the ICP-OES (0.05 mg La/l). For this reason, La was omitted in the calculations of distribution ratios.

Extraction kinetics and diluent role

The types of diluents and the diluent effect in solvent extraction were summarized by Löfström-Engdahl et al. [14]. The authors emphasize that the extraction of a complex is a function of two main steps: i) the collapsing of the cavity containing the complex in the aqueous phase, followed by the transfer from the aqueous phase, and ii) breaking the bounds between the water molecules which solvate the complex, followed by creation of a cavity in the organic phase and dissolving of the complex. It was concluded that the nature of the diluent influences the attractive energies between the extracted species and the organic phase, and also the energy that is needed for cavity formation.

The extraction kinetics for REMs in the investigated systems was fast. Equilibrium was achieved in less than one minute, regardless of the type of extractant or diluent used. As expected, with both extractants, the distribution ratios of lanthanides tend to increase with a decrease in ionic radius, a consequence of the lanthanide contraction. Gd showed, however, distribution ratios smaller than Eu. This was previously observed in other solvent extraction systems [15] and it is explained by the half-filled electron shell of Gd (4f⁷).

Table 2 – Matrix summarizing the main results of the extraction of REMs from HNO_3 -based leachates of fluorescent lamp waste, when using 30% v/v extractant in diluent. The distribution ratios and separation factors are taken for a 1 min contact time between the phases.

DILUENT	EXTRACTANT			
	Kerosene	TetraPropyleneHydrogenated	Tertbutyl benzene	1-octanol
 Cyanex 923 (TRPO) 14% Trioctylphosphine oxide 42% Dioctylmonohexylphosphine oxide 31% Dihexylmonooctylphosphine oxide 8% Trihexylphosphine oxide	$D_{\text{Ce}} = 12.47 \pm 0.93$ $D_{\text{Eu}} = 21.15 \pm 1.06$ $D_{\text{Gd}} = 16.36 \pm 0.72$ $D_{\text{Tb}} = 28.74 \pm 1.49$ $D_{\text{Y}} = 10.22 \pm 0.7$ $\alpha_{\text{Eu/Y}} = 2.07 \pm 0.04$ Equilibrium: < 1 min Co-extracted: $D_{\text{Fe}} = 0.16 \pm 0.02$ $D_{\text{Hg}} = 4.76 \pm 0.17$ $D_{\text{Sb}} = 0.16 \pm 0.02$	$D_{\text{Ce}} = 13.57 \pm 1.02$ $D_{\text{Eu}} = 23.6 \pm 1.08$ $D_{\text{Gd}} = 17.8 \pm 0.96$ $D_{\text{Tb}} = 48.36 \pm 9.91$ $D_{\text{Y}} = 12.64 \pm 0.42$ $\alpha_{\text{Eu/Y}} = 1.87 \pm 0.03$ Equilibrium: < 1 min Co-extracted: $D_{\text{Fe}} = 0.11 \pm 0.02$ $D_{\text{Hg}} = 5.41 \pm 0.26$ $D_{\text{Sb}} = 0.28 \pm 0.02$	$D_{\text{Ce}} = 8.58 \pm 0.65$ $D_{\text{Eu}} = 16.51 \pm 0.34$ $D_{\text{Gd}} = 12.07 \pm 0.26$ $D_{\text{Tb}} = 14.97 \pm 1.38$ $D_{\text{Y}} = 6.38 \pm 0.14$ $\alpha_{\text{Eu/Y}} = 2.59 \pm 0.01$ Equilibrium: < 1 min Co-extracted: $D_{\text{Fe}} = 0.1 \pm 0.02$ $D_{\text{Hg}} = 4.8 \pm 0.05$ $D_{\text{Sb}} = 0.24 \pm 0.02$	$D_{\text{Ce}} = 0.5 \pm 0.02$ $D_{\text{Eu}} = 0.27 \pm 0.02$ $D_{\text{Gd}} = 0.24 \pm 0.03$ $D_{\text{Tb}} = 0.38 \pm 0.01$ $D_{\text{Y}} = 0.33 \pm 0.01$ $\alpha_{\text{Eu/Y}} = 1.2 \pm 0.06$ Equilibrium: < 1 min Co-extracted: $D_{\text{Fe}} = 0.07 \pm 0.02$ $D_{\text{Hg}} = 1.91 \pm 0.07$ $D_{\text{Sb}} = 0.1 \pm 0.02$ $D_{\text{B}} = 0.17 \pm 0.01$
 Tributyl phosphate (TBP)	$D_{\text{Ce}} = 0.49 \pm 0.01$ $D_{\text{Eu}} = 1.44 \pm 0.02$ $D_{\text{Gd}} = 1.33 \pm 0.01$ $D_{\text{Tb}} = 1.73 \pm 0.3$ $D_{\text{Y}} = 0.98 \pm 0.03$ $\alpha_{\text{Eu/Y}} = 1.46 \pm 0.02$ Equilibrium: < 1 min Co-extracted: $D_{\text{Hg}} = 1.61 \pm 0.03$	$D_{\text{Ce}} = 0.51 \pm 0.01$ $D_{\text{Eu}} = 1.45 \pm 0.05$ $D_{\text{Gd}} = 1.38 \pm 0.03$ $D_{\text{Tb}} = 1.82 \pm 0.02$ $D_{\text{Y}} = 1 \pm 0.01$ $\alpha_{\text{Eu/Y}} = 1.46 \pm 0.02$ Equilibrium: < 1 min Co-extracted: $D_{\text{Hg}} = 1.39 \pm 0.05$	$D_{\text{Ce}} = 0.2 \pm 0.02$ $D_{\text{Eu}} = 1.05 \pm 0.03$ $D_{\text{Gd}} = 0.94 \pm 0.02$ $D_{\text{Tb}} = 1.18 \pm 0.01$ $D_{\text{Y}} = 0.72 \pm 0.01$ $\alpha_{\text{Eu/Y}} = 1.46 \pm 0.02$ Equilibrium: < 1 min Co-extracted: $D_{\text{Hg}} = 1.47 \pm 0.02$	$D_{\text{Ce}} < 0.01$ $D_{\text{Eu}} = 0.01$ $D_{\text{Gd}} = 0.03 \pm 0.02$ $D_{\text{Tb}} = 0.04 \pm 0.01$ $D_{\text{Y}} = 0.01$ $\alpha_{\text{Eu/Y}} = 1$ Equilibrium: < 1 min Co-extracted: $D_{\text{Hg}} = 2 \pm 0.17$ $D_{\text{B}} = 0.2 \pm 0.02$

In most systems, Y showed distribution ratios lower than those of the middle lanthanides (Eu and Gd). This allows for a separation of Y, as this element accounts, together with Eu, for the vast majority of the REMs in the aqueous phase.

The choice of diluent affects both the distribution ratios and separation factors of elements. A matrix with the observations made when using the two extractants in all diluents was constructed (Table 2), and it is further discussed in the sub-sections below. Comparisons between the extractant in the same diluent will be addressed first, followed by the choice of diluent for each extraction system.

Cyanex 923 compared to TBP in the same diluents

Higher distribution ratios and separation factors between Eu and Y were noticed for Cyanex 923 compared to TBP in the same diluent. This is because REMs, which are strong Lewis acids, form stronger complexes with trialkylphosphine oxide molecules, which are stronger Lewis bases than TBP [16]. The extraction mechanism of REMs nitrates in both TBP and Cyanex 923 was previously investigated, and it was concluded that 3 extractant molecules are involved in the extraction of REMs [17].

Co-extraction of other metals besides the REMs was noticed with both extractants. Cyanex 923 extracted Fe, Sb and Hg. For the later one, the presence of Cl^- ions in the aqueous phase (originating from the dissolution of various Cl-containing phosphors [3]) is responsible for extraction, as mercury chloride complexes are extracted by Cyanex 923 [18]. The distribution ratios of Fe and Hg were found to increase with an increase in phase contact time. For example, D_{Fe} is small at the 1 min point (0.16 ± 0.02 for Cyanex 923 in kerosene) and becomes larger as the contact phase time increases (2.83 ± 0.12 for Cyanex 923 in kerosene, at 30 min). A selective stripping of REMs from Fe and Hg is possible using HCl solution [19]. No obvious extraction of Fe and Sb was noticed with TBP.

Cyanex 923 in various diluents

The choice of diluent influences the extraction efficiency with Cyanex 923. The highest distribution ratios were noticed when using TetraPropyleneHydrogenated, a diluent used in the PUREX process in La Hague (similar to dodecane). Slightly lower distribution ratios were obtained with kerosene (with low aromatic content). The dispersive interactions between aliphatic hydrocarbon molecules are weak, meaning that the energy cost for cavity formation in the organic phase is low; also, there is no permanent dipole moment which increases the attractive interactions between the complex and the diluent [14]. Tertbutyl benzene, an aromatic diluent, led to lower distribution ratios. With 1-octanol (an alcohol, thus a polar solvent) the distribution ratios were very low. Cyanex 923 is a solvating-type extractant, which form REM complexes with low solubility in this type of solvent.

The highest separation factors between Eu and Y were noticed when using tertbutyl benzene as diluent. Separation of Eu and Y becomes troublesome if 1-octanol is used. This, together with the low distribution ratios of REMs and the fact that B is also extracted, makes this diluent unsuitable for this purpose.

TBP in various diluents

The choice of diluent in the TBP systems shows a similar trend as that discussed for the Cyanex 923 systems. The distribution ratios decrease in the order: TPH, kerosene, tertbutyl benzene, 1-octanol, the last one showing very poor distribution ratios and an impossible separation of Eu and Y.

Conclusions

The extraction behaviour of metals from HNO₃-based leachates of fluorescent lamp waste was investigated using various solvents. The choice of diluent plays an important role in the extraction of REMs. These elements can be effectively recovered with either Cyanex 923 or TBP. The former gives better distribution ratios and separation factors between the two most abundant REMs in solution (Eu and Y). For both Cyanex 923 and TBP, the distribution ratios were noticed to decrease in regard to the diluent used as follows: TetraPropyleneHydrogenated, kerosene, tertbutyl benzene, 1-octanol.

Acknowledgements

Project 211-2010-2266 (Chalmers 21290013) funding granted by Formas and Energimyndigheten, Sweden, is acknowledged for financial support.

References

1. European Commission. Critical raw materials for EU. Report of the Ad-hoc Working Group on defining critical raw materials, 2010.
2. Binnemans K. et al. Recycling of rare earths: a critical review. Journal of Cleaner Production, 2013. 51: 1-22.
3. Ronda, C.R., T. Justel, and H. Nikol. Rare earth phosphors: fundamentals and applications. Journal of Alloys and Compounds, 1998. 275: 669-676.
4. Mei G.J. et al. Separation of red (Y₂O₃:Eu³⁺), blue (BaMgAl₁₀O₁₇:Eu²⁺) and green (CeMgAl₁₀O₁₇:Tb³⁺) rare earth phosphors by liquid/liquid extraction. Journal of Wuhan University of Technology - Materials Science Edition, 2009. 24(4): 603-607.
5. Nakamura T., S. Nishihama, and K. Yoshizuka. Separation and Recovery Process for Rare Earth Metals from Fluorescence Material Wastes Using Solvent Extraction. Solvent Extraction Research and Development Japan, 2007. 14: 105-113.

6. Rabah M.A. Recyclables recovery of europium and yttrium metals and some salts from spent fluorescent lamps. *Waste Management*, 2008. 28(2): 318-25.
7. Shimizu R. Supercritical fluid extraction of rare earth elements from luminescent material in waste fluorescent lamps. *J. of Supercritical Fluids*, 2005. 33(3): 235-241.
8. Yang F. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. *Journal of Hazardous Materials*, 2013. 254: 79-88.
9. Meyer L. and B. Bras. Rare earth metal recycling in International Symposium on Sustainable Systems and Technology, 2011.
10. UNEP. Recycling Rates of Metals: A Status Report, 2011.
11. Mason G.W. et al. Diluent effects in the extraction of selected metallic cations by bis(hexoxy-ethyl) phosphoric acid. *Journal of Inorganic Nuclear Chemistry*, 1967. 29: 1103-1112.
12. Retegan T., A. Fermvik, G. Skarnemark. A comparative study of some BTP and BTBP class ligands. *Proceedings of ISEC*, 2008.
13. Tunsu C., C. Ekberg C., T. Retegan. Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. *Hydrometallurgy*, 2014. 144-145: 91-98.
14. Löfström-Engdahl E. et al. Diluents effects in solvent extraction. *Proceedings of the First ACSEPT International Workshop, Lisbon*, 31 Mar – 2 Apr 2010.
15. Nilsson M. et al. Separation of Actinides(III) from Lanthanides(III) in Simulated Nuclear Waste Streams using 6,6'-Bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP) in Cyclohexanone. *Solvent Extraction and Ion Exchange*, 2006. 24(6): 823-843.
16. Cox, M. Solvent extraction equilibria in Rydberg, J., Cox, M., Musikas, C., Choppin, G.R. (Eds.), *Solvent extraction principles and practice*, second edition, revised and expanded. Marcel Dekker, Inc., New York, 2004.
17. Reddy M.L.P. et. al. Cyanex 923 as an extractant for trivalent lanthanides and yttrium. *Solvent Extraction and Ion Exchange*, 1998. 16: 795-812.
18. Meera R., T. Francis and M.L.P Reddy. Studies on the liquid–liquid extraction of mercury(II) from acidic chloride solutions using Cyanex 923. *Hydrometallurgy*, 2001. 61: 97-103.
19. Tunsu C. Leaching and solvent extraction of rare earth metals from fluorescent lamp waste. Licentiate thesis. Chalmers University of Technology, Sweden, 2014.

Controllable Interfacial Mass Transfer Intensification for Kinetic Non-equilibrium Extraction and Separation of Praseodymium and Neodymium by a Novel Gas-Assistant Column Extractor

Kun HUANG, Huizhou LIU*

*Key Laboratory of Green Process and Engineering, Institute of Process Engineering,
Chinese Academy of Sciences, Beijing 100190, P.R.China*

** E-mail: khuang@home.ipe.ac.cn , Tel: +86-10-82544910*

Solvent extraction (SX) is one of the most important techniques for separation of rare-earths. However, separation of adjacent lanthanide elements, such as Praseodymium (Pr) and Neodymium (Nd), is very difficult due to their extremely similar physical and chemical properties. Generally, thermodynamic separation factor between Pr and Nd by traditional oil-water two phase solvent extractions are below 2. The aim of present work is to develop a kinetic non-equilibrium extraction method for separation of Pr and Nd by a novel gas-assistant column extractor. Diethylenetriaminepentaacetic acid (DTPA) was previously added into aqueous solution containing Pr and Nd, then organic solution of 2-ethylhexylphosphonic acid mono-2-ethylhexyl Ester (P507) in kerosine was bubbled into the column extractor. Various influences from solution pH values, initial metal concentrations, air bubbling rate, solvent flow rate and aqueous-to-oil phase ratio on kinetic separation of Pr and Nd were investigated. Experimental results found that kinetic separation factor of Pr/Nd in air-bubbling extraction process can achieve above 10 under appropriate conditions. Interfacial reaction rate of Pr and Nd ions with air-bubbling dispersed P507 molecules can be controllable. Dissociation reactions of DTPA-Ln(Pr/Nd) complex play an important role in kinetic separation of Pr and Nd. A kinetic separation mechanism based on interfacial non-equilibrium mass transfer model was proposed. The present works highlight a promising strategy to achieve kinetic non-equilibrium extraction and separation of adjacent lanthanide elements, so that it is feasible for future industrial application in process Intensification for purification of rare-earths from various complicated low-content leaching solutions.

New extractants applicable to industrial solvent extraction process for rare metal separation

Masahiro Goto^{*1,2}, Yuzo Baba¹, Fukiko Kubota¹

Summary

A new extractant, *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) was developed applicable for an industrial solvent extraction process of critical metals. Extraction ability and selectivity were found to be based on the glycine and alkylamide moieties in the structure. The novel extractant, D2EHAG, was simply synthesized through a two-step reaction and not expensive for a kg-scale production. We conducted a durability test of the extractant for ensuring an industrial application under the guidance of Sumitomo Metal Mining (SMM) Co. Ltd. In the lecture, we focus on scandium (Sc^{3+}) separation from lanthanides (such as Nd^{2+} and Dy^{3+}) and alkaline earth metals (Ca^{2+} and Mg^{2+}). Extraction equilibrium of these metals was elucidated and this extractant was found to have superior extraction and separation abilities to Sc^{3+} over lanthanides. A quantitative back-extraction was successfully conducted using 1 mol/L sulfuric acid. In addition, we investigated extraction behavior of precious metal ions (platinum group metals (PGMs) and gold), which exist as anionic metal species such as $[\text{AuCl}_4]^-$. In a hydrochloric acid solution, D2EHAG showed a high selectivity to Au and Pt over Pd, and it worked as a protonated ion-pair extractant.

Introduction

Scandium is a very important metal in high-technology industries because scandium and its compounds have been found wider applications such as in optical, electronic, aeronautical, automotive and transportation industries [1], therefore their demand has been increasing in recent years. Scandium has been classified as a rare earth element together with yttrium and lanthanides. Among the rare earth elements, scandium is very expensive metal for its scarcity and the rather complicated metallurgical processes for its purification and recovery, and is commonly found in nature together with yttrium and lanthanides [2,3]. These rare earth metals have very similar fundamental chemical properties, which make it difficult to separate them into individual elements. That is a major reason why these metals are expensive.

Liquid–liquid extraction is one of the most effective methods for the separation and purification of various metal ions. The extractant plays a key role in the extraction efficiency and the separation operation. The selection of an appropriate extractant often determines the success of an extraction process. In an industrial extraction process, commercially available organophosphorus extractants [4], such as D2EHPA, PC-88A, and TOPO are widely used with high extraction efficiencies. However, some disadvantages have been still remained such as a high stripping acidity, which is required for acidic organophosphorus extractants, and a poor selectivity for neutral organophosphorus extractants. Carboxylic acids have also been used to extract

* M. Goto, Tel.: +81-92-802-2806, E-mail address: m-goto@mail.cstm.kyushu-u.ac.jp

¹ Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

² Center for Future Chemistry, Kyushu University, Fukuoka, Japan

metals from a high pH solution [4]. However, the high pH treatment is a disadvantage from a practical point of view, in addition the selectivity toward scandium over other rare earth metals is not enough to obtain highly purified scandium.

As is described above, an acidic organophosphorus extractant shows a high selectivity to scandium [1]. However, such extractants are not fully combustible, leaving phosphorous residues as a secondary waste. Thus, extractants composed of only C, H, O, and N atoms (CHON principle) have attracted much attention as a green extractant to establish a new residual waste-free extraction process based on their complete combustibility. So far, a variety of CHON-type extractants have been developed for the extraction of lanthanides, for example, carboxylic acid compounds [5], β -diketones [6], and calixarenes [7]. However, almost all the CHON-type extractants showed low extraction and separation properties for scandium.

Recently, some extractants have much attention for mutual separation among rare earth elements. One is *N,N*-dioctyldiglycol amic acid (DODGAA)[8-10], which is an anionic tridentate ligand with an amide group and a carboxy group. Another is *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN)[9], which is a neutral hexadentate ligand with four pyridyl groups. Diglycolamide and nitrogen-donor type extractants have been under intense study on extraction and group separation of actinides and lanthanides in the field of nuclear industries [11] and also offer considerable potential as extractants for mutual separation among lanthanides.

We have developed a *N*-[*N,N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine(D2EHAG) [12] which is a new tridentate ligand extractant with an amide group and a carboxy group connected by a secondary amino group (-NH-) instead of the ether chain of DODGAA. No industrial extractants of a tridentate ligand have been developed except DODGAA and diglycolamides for the group separation of actinides, lanthanides, and precious metals.

We report on the extraction of precious metals (platinum group metals (PGMs; Pt^{4+} , Pd^{2+} , Rh^{3+}) and gold (Au^{3+})), too. The new extractant has a secondary amine in the center of the structure. In many cases, extractants having an amine moiety behave as an ion-pair extractant under high acidic conditions [13]. Therefore, it is thought that D2EHAG acts as the ion-pair extractant in an acidic solution and chloride metal anions such as $[\text{AuCl}_4]^-$ are considered to be extracted by using the protonated D2EHAG. Here, we present extraction behavior of rare earth metals, platinum group metals and gold ions. In addition, we discuss the possibility of the new extractant D2EHAG applicable for industrial solvent extraction operation.

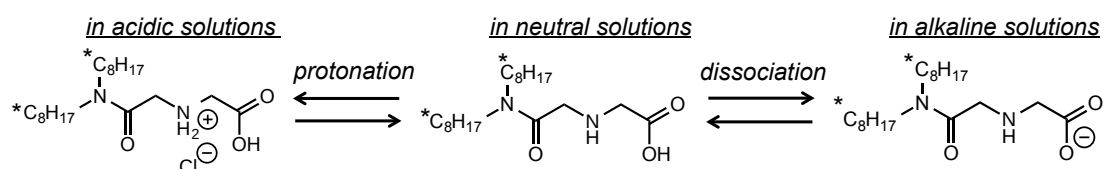


Fig. 1 Structure changes of D2EHAG in solutions (* branched chain).

Experimental

Extraction Procedure

D2EHAG was synthesized by a two-step reaction in my laboratory [12]. DODGAA was synthesized according to an article published by Shimojo *et al.* [8-10]. Tri-*n*-octyl amine (TOA) was purchased from Wako Pure Chemical Industries (Osaka, Japan). All other reagents and solvents were analytical grade, and were used as received.

Extraction Procedure (rare earth metal ions)

The extracting organic phase was prepared by dissolving D2EHAG in *n*-dodecane. An aqueous solution containing 0.1 mmol dm⁻³ metal ions was prepared by dissolving their nitrates in 0.1 mol dm⁻³ HNO₃ or NH₄NO₃. The pH in the aqueous solution was adjusted by mixing these aqueous solutions and/or adding 28 wt% ammonia solution.

Equal volumes (5 cm³) of the aqueous and organic solutions were mixed in a sealed tube by a vortex mixer and then shaken gently for more than 1 h to attain extraction equilibrium at 298K. After phase separation, the metal ions in the organic phase were stripped using an acid solution. (Fig. 2)

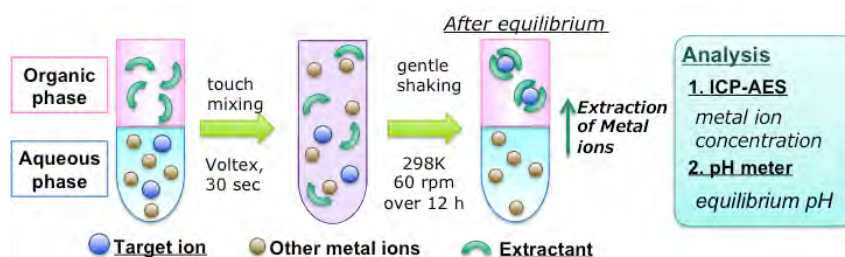


Fig. 2 Scheme of extraction experiments.

The metal concentrations in the aqueous phase for the extraction and stripping tests were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 5300, Perkin Elmer Co, Waltham, Ma, USA). The pH was measured using a pH meter (HM-30R, DKK-TOA Co, Tokyo, Japan). The extraction E [-] and Distribution D [-] ratios were calculated using Eqs (1) and (2):

$$E = \frac{[M]_{org,eq}}{[M]_{aq,init}} = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,init}} \quad (1) \quad D = \frac{[M]_{org,eq}}{[M]_{aq,eq}} = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,eq}} \quad (2)$$

([M] : metal ion concentration, *aq* : aqueous phase, *org* : organic phase, *init* : initial state, *eq* : after equilibration)

Extraction Procedure (PGMs)

The extracting organic phase was prepared by dissolving D2EHAG in *n*-dodecane. An aqueous solution containing 0.1 mmol dm⁻³ platinum group metal ions (Pt⁴⁺, Pd²⁺, Rh³⁺) and gold ions (Au³⁺) was prepared by dissolving their chlorides in 0.1~10 M HCl. Extraction experiments were performed as the same method as extraction experiments of rare earth metals, and E and D were calculated using Eqs (1) and (2).

Results and discussion

Extraction of rare earth metal ions and alkaline earth metals

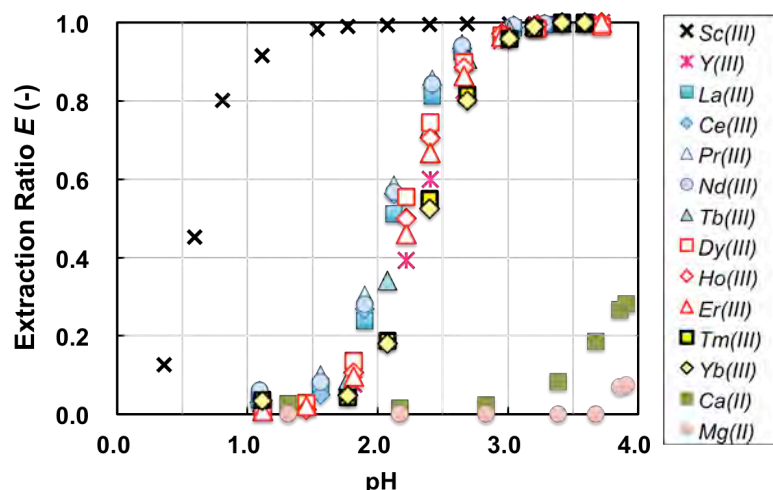


Fig. 3 Extraction behavior of rare earth metals (scandium, yttrium, lanthanides) and alkaline earth metals (calcium, magnesium).

Figure 3 shows the extraction behavior of rare earth metals (Sc^{3+} , and Y^{3+}), lanthanides (La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+}) and alkaline earth metals (Mg^{2+} , and Ca^{2+}) using D2EHAG as a function of the equilibrium pH. The extraction of rare earth metals is promoted with increasing pH. Quantitative extraction is achieved in a middle pH region ($1.5 \leq \text{pH} \leq 3.5$) except for Sc^{3+} . Scandium ion (Sc^{3+}) was extracted under higher acidic conditions ($0 < \text{pH} \leq 1.5$) and efficiently separated from the other rare earth metals (yttrium, lanthanides) and alkaline earth metals (Mg^{2+} , Ca^{2+}). In addition, light rare earth group metals (La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+}) were slightly more extracted in the lanthanides. This trend was similar to that of TPEN. On the other hand, DODGAA, which has either oxygen, has heavier rare earth metals selectivity. Using D2EHAG, the coordination ability is caused by the secondary amine, which exists at the center of the D2EHAG molecule.

This extractant D2EHAG was considered to exist as a dimer such as alkyl monocarboxylic acids (Versatic 10) in an aliphatic solvent [14]. A linear relationship between $\log D$ and pH with a slope of 3 and a linear relationship between $\log D$ and $\log [\text{D2EHAG}]_2$ (extractant dimer) with a slope of 2 were obtained for Sc^{3+} extraction. These results suggest that three protons are released from the D2EHAG molecule, and one scandium ion is extracted with two D2EHAG molecules into the organic phase to form a neutral complex. On the basis of the slope analysis, the extraction equilibrium equation of scandium ions with D2EHAG is expressed by Eq. (3). (HR: extractant)

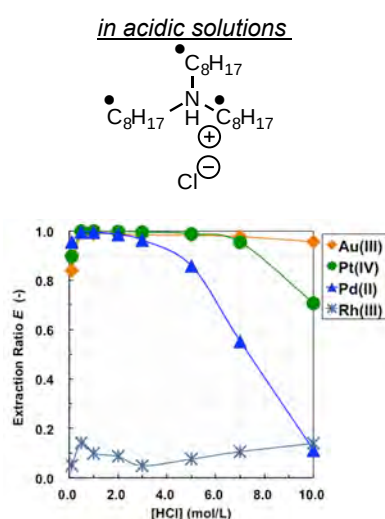


Extracted metal ions were stripped (over 90% of each metal ion) using 1 M H_2SO_4 . Therefore, we can perform mutual separation of scandium (Sc^{3+}), other rare earth metals, and alkaline earth metals (Mg^{2+} , Ca^{2+}) by solvent extraction with D2EHAG.

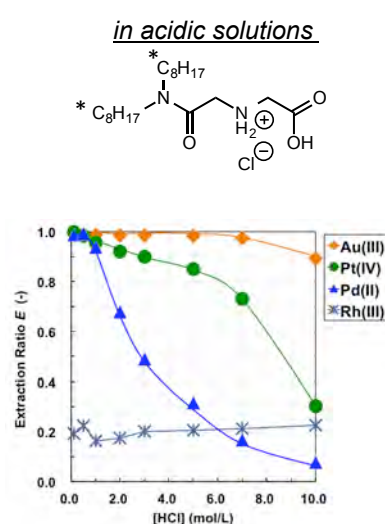
Extraction PGMs

The extraction of PGM and gold ions from the aqueous feed phase containing four different metal ions (Pt^{4+} , Pd^{2+} , Rh^{3+} , and Au^{3+}) with D2EHAG in *n*-dodecane is shown in Figure 4 as a function of hydrochloric acid concentration. Figure 4(a) shows extraction behavior of PGMs and gold ions from hydrochloric acid solutions with tri-*n*-octyl amine (TOA), which is a conventional industrial extractant for PGMs and gold [15]. Pt^{4+} , Pd^{2+} , Rh^{3+} and Au^{3+} exist as anions (such as $[\text{PtCl}_6]^{2-}$, $[\text{PdCl}_4]^{2-}$, and $[\text{AuCl}_4]^-$) in a high hydrochloric acid solution.

(a) TOA 10 mM



(b) D2EHAG 10mM



(c) DODGAA 10mM

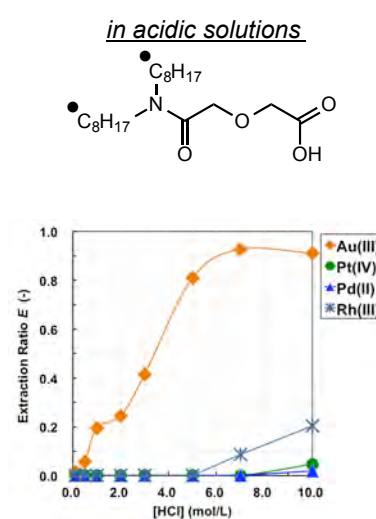


Fig. 4 Extraction behavior of gold (Au(III)), platinum (Pt(IV)), palladium (Pd(II)), and rhodium (Rh(III)). [HCl concentration dependency] (* branched chain(di-2(ethylhexyl)), • straight chain(*n*-octyl)).

As TOA is protonated under the present conditions, TOA forms an ion pair through electrostatic interaction. Figure 4 (a) shows high extraction abilities of Au^{3+} , Pt^{4+} , and Pd^{2+} . These metal ions were considered to be extracted by the ion pair mechanism.

Figure 4(b) shows extraction behavior of PGMs and gold with a new extractant D2EHAG. In 0.1M~0.5M HCl concentration range, D2EHAG has a similar extraction trend to TOA, because the amino group plays a similar role in the ion pair extraction. However in a high HCl concentration, a degree of extraction of palladium was significantly decreased. Therefore, D2EHAG showed higher separation ability of Au^{3+} and Pt^{4+} over Pd^{2+} above 5M HCl concentration.

In comparison, Fig. 4 (c) shows extraction behavior with DODGAA. The extractant does not have a structure to be protonated therefore ion pair extraction behavior was not seen. When using this extractant in a high HCl concentration range, highly selective separation of Au^{3+} was performed from Pd^{2+} and Pt^{4+} . This trend was thought to be caused by the ether structure. For example, di-butyl carbitol (DBC), which has three oxygen atoms is famous for Au^{3+} extraction from PGMs in an industrial process [16]. Above all, the ion-pair complex formation was seen using D2EHAG because it has a secondary amine in the center of the structure, and separation of Au^{3+} and Pt^{4+} from Pd^{2+} was achieved in a high HCl range (< 5M HCl).

Conclusion

A novel acidic extractant *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) was developed, which has glycine and alkylamide structures. We investigated extraction performance of the new extractant and found a superior separation ability to Sc³⁺ against the other rare earth metal ions and alkaline rare earth metals. In an acidic solution, the D2EHAG worked as an ion-pair extractant because the secondary amine in the structure was protonated. We could control the extraction ability of PGMs and gold ions by adjusting the hydrochloric acid concentration in the aqueous feed solution.

Reference

1. W. Wang, C. Y. Cheng (2011), *J. Chem. Technol. Biotechnol.*, **86**, 1237-1246.
2. M. Karve, B. Vaidya (2008), *Sep. Sci. Tech.*, **43**, 1111-1123.
3. D. Wu, C. Niu, D. Li, Y. Bai (2004), *J. Alloy. Compd.*, **374**, 442-446.
4. A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant, J. B. Love (2014), *Chem. Soc. Rev.*, **43**, 123-134
5. Y. G. Wang, S. T. Yue, D. Q. Li, M. J. Jin, C. Z. Li (2002), *Solvent Extr. Ion Exch.*, **20**, 701-716.
6. V. M. Jordanov, M. Atanassova, I. L. Dukov (2002), *Sep. Sci. Technol.*, **37**, 3349-3356.
7. K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, T. Nagasaki (1995), *Anal. Sci.*, **11**, 893-902.
8. H. Naganawa, K. Shimojo, H. Mitamura, Y. Sugo, J. Noro, M. Goto (2007), *Solvent Extr. Res. Dev., Jpn.*, **14**, 151-159.
9. K. Shimojo, H. Naganawa, J. Noro, F. Kubota, M. Goto (2007), *Anal. Sci.*, **23**, 1427-1430
10. K. Shimojo, N. Aoyagi, T. Saito, H. Okamura, F. Kubota, M. Goto, H. Naganawa (2014), *Anal. Sci.*, **30**, 263-269.
11. S. A. Ansari, P. Pathak, P. K. Mohapatra, V. K. Manchanda (2012), *Chem. Rev.*, **112**, 1751-1772.
12. Y. Baba, F. Kubota, N. Kamiya, M. Goto (2014). *Ind. Eng. Chem. Res.*, **53**, 812-818
13. H. Narita, K. Morisaku, M. Tanaka (2008), *Chem. Commun.*, **2008**, 5921-5923.
14. J. S. Preston (1985), *Hydrometallurgy*, **14**, 171-188.
15. J. Jiang, Y. He, H. Gao, J. Wu (2005), *Solvent Extr. Ion Exch.*, **23**, 113-129.
16. I. V. Minorov (2012), *Russ. J. Inorg. Chem.*, **57**, 1513-1519.

Continuous Piloting to Recover Nickel from Çaldağ Nickel Leach Solution using the Nicksyn™ and Versatic 10 Acid Synergistic Solvent Extraction System

*Keren Larmour-Ship^{*1}, Cevat Er², Marthie Kotze³, A C (René) du Preez⁴*

Summary

Lateritic nickel deposits are increasingly being explored and exploited, as they represent the majority of nickel reserves globally. Mining companies are considering direct recovery of nickel and cobalt without having to produce an intermediate mixed hydroxide precipitate (MHP), which requires re-leaching prior to recovery of the final products. Tenova Bateman Technologies developed and tested a solvent extraction process flow sheet for Çaldağ Nickel using Mintek's proprietary Nicksyn™ reagent in a synergistic mixture with Versatic 10 acid to effectively reject calcium, magnesium and manganese from the iron and aluminium-free lateritic leach liquor. Cyanex® 272 was used to separate the cobalt from the resultant Ni/Co strip liquor. Bench-scale work confirmed the technical viability of the solvent extraction process. Successful mini-pilot trials were conducted, resulting in cobalt and nickel recoveries in excess of 99%. The test work confirmed that the process is viable and highlighted the importance of optimisation of operating parameters in the extraction process. Test work results were used to complete the Ni/Co solvent extraction/electrowinning circuit for a Definitive Feasibility Study for Çaldağ Nickel. Should the project go ahead, the test work described in this paper provides confidence for Çaldağ Nickel to install the first lateritic Ni/Co SX/EW process to use a synergistic mixture with Mintek's Nicksyn™ reagent.

Background

Çaldağ Nickel is located in central western Turkey, approximately 75km by road from the nearest sea port of Izmir. The deposit is a lateritic nickel and cobalt deposit with reported average ore grades shown in Table 1.⁽¹⁾ Heap leaching tests were carried out during 2004 and 2005 with the aim of producing a saleable mixed hydroxide precipitate (MHP).

Table 1, Average Caldag Ore Chemical Analyses

Ni	Co	Fe	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	Moisture
%	%	%	%	%	%	%	%	%	%	%
1.13	0.07	21.66	30.97	30.84	1.91	5.02	3.2	0.41	1.62	15

In 2012 the present owners of Çaldağ Nickel decided to investigate solvent extraction (SX) and electrowinning (EW) to produce metal instead of MHP and approached Tenova Bateman Technologies (TBT) to conduct a conceptual engineering study followed by proof-of-concept test work and mini-pilot testing.

^{*1} Corresponding Author, Tenova Bateman Technologies, keren.larmour@tenova.com

² Author 2 Çaldağ Nickel, Manisa, Turkey

³ Author 3 Lanxess (Pty) Ltd, Modderfontein, South Africa

⁴ Author 4 Mintek, Randburg, South Africa

Flowsheet Development

TBT considered several SX regimes, including the LIX 63/ Versatic 10 process developed by Cheng at CSIRO^(2,3) and the Nicksyn™ Synergist/ Versatic 10 process developed by Mintek^(4,5) and tested in a demonstration plant at Tati Nickel⁽⁶⁾ in 2006. The Goro Nickel process⁽⁷⁾ was not considered because of its proprietary nature and because the extractant Cyanex® 301 requires an essentially oxygen-free environment.⁽⁸⁾

Versatic 10 acid has been used to extract nickel and cobalt; however it also extracts considerable manganese, magnesium and calcium. Figure 1, published by Mintek⁽⁵⁾, showed that the addition of Nicksyn™ increases the pH difference and hence selectivity between Ni/Co and Mn, Mg and Ca compared with Versatic 10 alone.

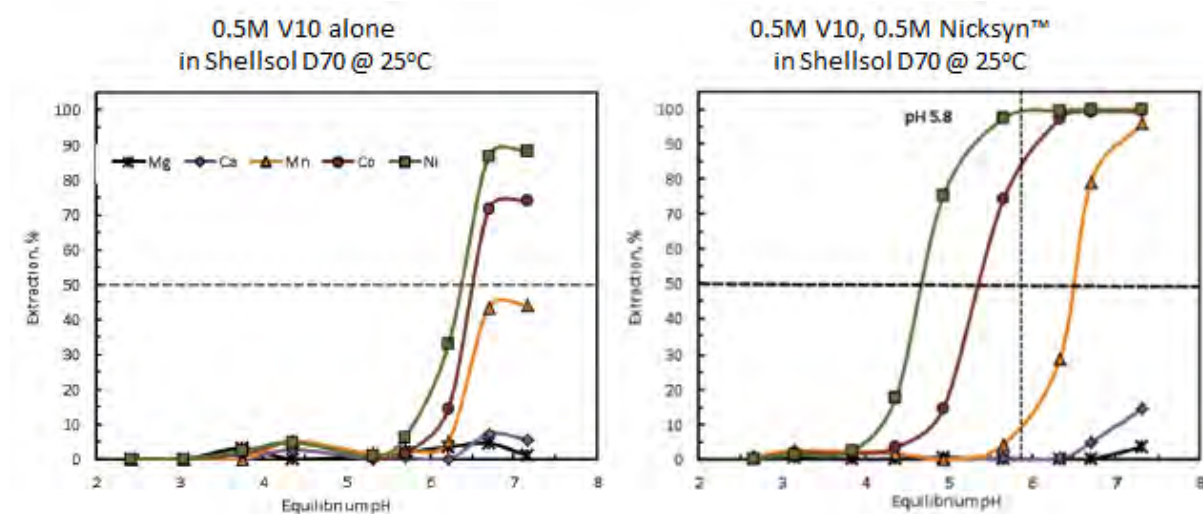


Figure 1, Comparison of metal extraction from synthetic laterite leach solution ⁽⁵⁾

That the separation of Co from Ni/Co solutions is achievable using Cytec's dialkyl phosphinic acid reagent, Cyanex 272 is well known ⁽⁹⁾. Figure 2 shows the Cyanex 272 metal extraction as a function of pH.

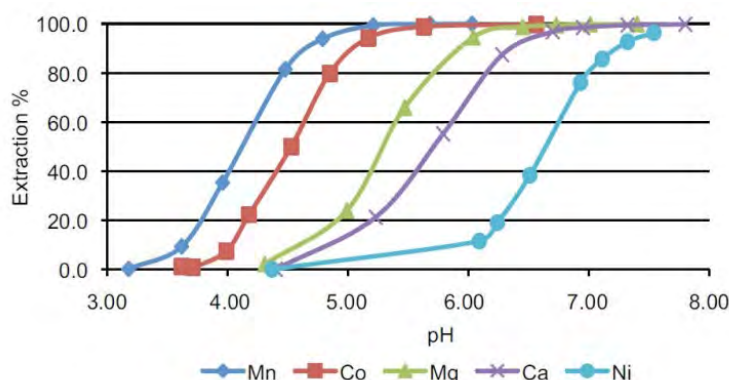


Figure 2, CYANEX 272 Metal Extraction as a Function of pH ⁽¹⁰⁾

Solution conditions: 0.001 M Metal (as sulfates), 0.1 M CYANEX 272, O/A = 1, Temperature = 50°C

The conceptual flow sheet for Çaldağ Nickel is shown in Figure 3. Nicksyn™ / V10 is used to extract Ni and Co, rejecting Mn, Ca and Mg to the raffinate. Ni spent

electrolyte is used to strip the Ni and Co. A second extraction circuit using Cyanex 272 removes the Co from the advance electrolyte, leaving a clean Ni advance electrolyte.

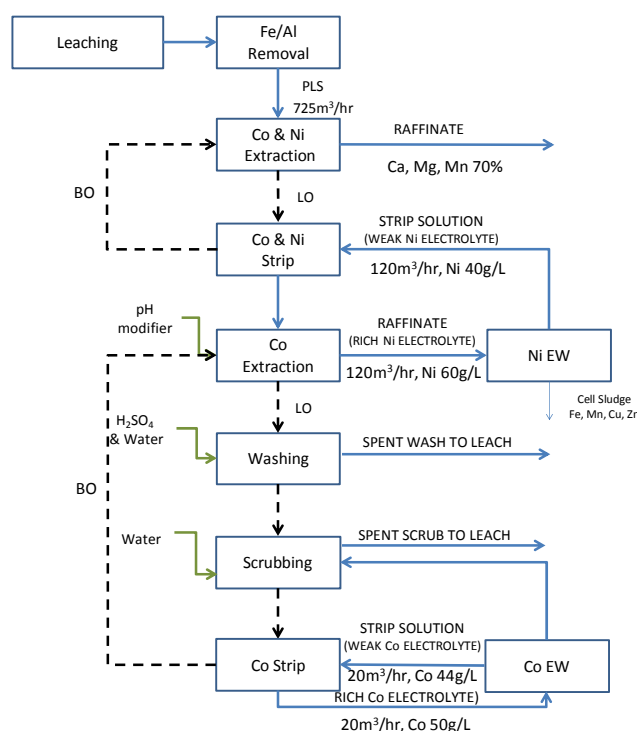


Figure 3, Proposed SXEW Flowsheet

Bench-Scale Testing

The PLS liquor received from Çaldağ Nikel was "spiked" with additional $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$ in order to raise the Ni tenor to approximate that expected in the plant. Table 2 below has the PLS analyses for all phases of the testwork.

The test work consisted of simple contact tests to prove the concept of the proposed flowsheet. Shake-flask contacting of solvent and aqueous phases led to a persistent emulsion, making stage-wise pH control almost impossible.

It was found necessary to neutralize the PLS to pH 4.5 and filter out a white (Al) precipitate before to prevent precipitation during testing.

Table 2, PLS Analyses for all Tests

	Ni g/L	Co g/L	Mn g/L	Ca g/L	Mg g/L	Fe mg/L	Cu mg/L	Al g/L	SG g/L	pH g/L
Bench – as rec'd	1.1	0.036	0.19	0.53	2.7	29	2.5	0.73	1.028	2.7
Bench - spiked	3.1	0.17	0.69	0.38	38	n.m	n.m	0.47	1.216	2.9
Pilot 1 – as rec'd	2.5	0.12	0.69	0.53	20	220	n.m	0.01	n.m	3.5
Pilot 1 - decanted	2.4	0.11	0.65	0.51	19.5	182	n.m	0.01	n.m	3.6
Pilot 2 – as rec'd	3.4	0.15	0.90	0.57	8.8	<1	1	0.02	n.m	4.4
Pilot 2 - doped	4.1	0.25	1.6	0.53	8.8	<1	<1	0.02	n.m	4.5
Pilot 3 – strip sol'n	86	1.4	0.42	0.007	0.02	12	54	0.04	n.m	0.8

Upon the advice of Mintek, the two phases were contacted via magnetic stirring using a water-jacketed glass vessel controlling the temperature at 35°C. The pH of the aqueous phase was adjusted to the targeted pH using 5M NaOH (prepared in distilled water) for coarse adjustment and 1M NaOH for finer adjustment. In some tests, 5M and 1M NH₃ in distilled water was used. The organic phase was added and stirred for 10 minutes, after which time the pH was measured. The pH was re-adjusted to the target using the same NaOH or NH₄OH solution. This was repeated until the pH remained essentially stable between one measurement and the subsequent one.

The organic reagents used were 0.4M Versatic Acid (V10); 0.4M Nicksyn™ in Cleansol 63 (equivalent kerosene diluent) for Ni/Co extraction and 10% v/v Cyanex 272 in Cleansol 63 for cobalt extraction. The Cyanex 272 barren solvent was pre-equilibrated with 23% NaOH to 50% stoichiometric replacement of H⁺ by Na⁺. It was pre-contacted with 60 g/L Ni solution to replace the Na⁺ ions with Ni⁺².

Stripping tests were performed using the same apparatus. The artificial nickel spent electrolyte contained 60 g/L Ni (from NiSO₄·6H₂O) and 35 g/L H₂SO₄ in distilled water.

The cobalt strip solution contained 40 g/L Co (from CoSO₄·7H₂O) and 8g/L H₂SO₄

Table 3 shows the results from these tests. It was noted that as Ni/Co extraction pH was raised, the cobalt recovery improved, but at the expense of increased Mn extraction. The results are from a single contact stage. A single test simulating a second contact increased the Co recovery beyond 97%.

Table 3, Metal Recovery % for Bench Scale Tests

Process	pH	O:A ratio	Ni	Co	Al	Mn	Mg	Ca
Ni/Co Extraction	5.5 - 6.2	1:1	86-97	29-90 ¹	n.d	2-13	0.1-2	<1
Ni/Co Stripping	1.7-1.8	6:1	97-99	80-90	87	68-93	45-55	63-71
Co Extraction	5.7	1:1	7	99	n.d	98	82	69
Co Stripping	3.0	1:1	99	99	n.d	6	0.70	27

A further set of tests, using the same apparatus was done to simulate 3 stages of extraction. Figure 4 shows the experimental design and result.

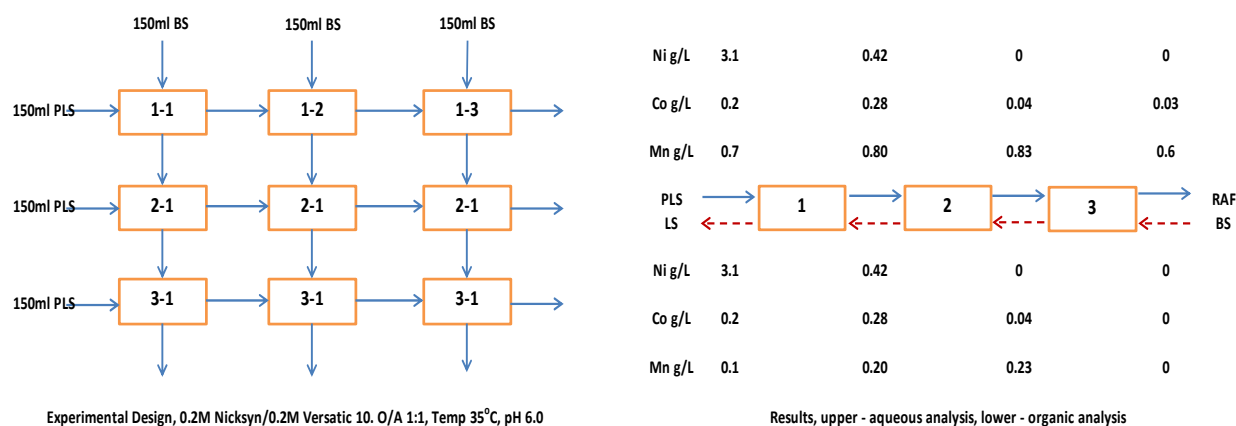


Figure 4, Simulation of 3 extraction stages

It appeared from Figure 4 that there was some "crowding off" of cobalt by the incoming nickel, as the Co concentration in the first stage raffinate was higher than that in the PLS. This phenomenon was further examined by constructing isotherms as shown in Figures 5a and 5b.

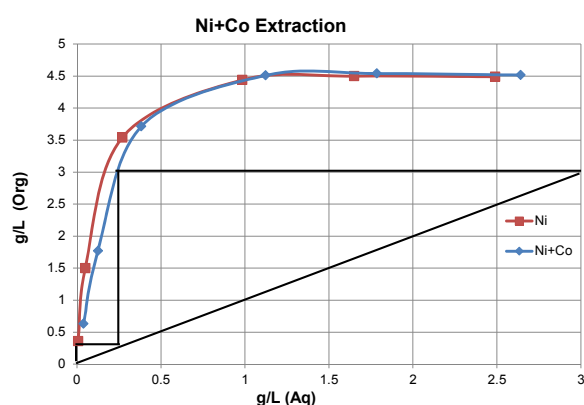


Figure 5a

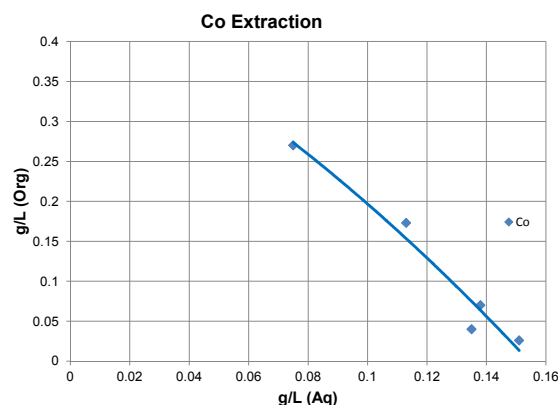


Figure 5b

Extraction Isotherms, 0.2M Nicksyn™/ 0.2M Versatic 10, pH=6.2, 35°C

Plotting the Co alone shows that the cobalt extraction is inhibited by the Ni loading. Therefore, even though the isotherm in Figure 5a suggests two stages, 3 stages were recommended to enable Co extraction.

A series of stripping tests were conducted using the artificial strip solutions at different equilibrium pH values ranging from 2 - 4. The results showed that the ideal pH for stripping was well below 3, and preferably at 2, to achieve full extraction of Ni, Co and Mn.

A single extraction and stripping test was done using Cyanex 272. Co extraction exceeded 99%, however, around 7% Ni was extracted as well. The strip test, using artificial solutions and artificial loaded solvent, was undertaken to demonstrate cobalt stripping. In a single stage, at an O:A ratio of 10:1, 96% of the cobalt was stripped, suggesting that two stages of stripping would be required. Around 77% of the nickel

(artificially added at 4.4g/L Ni in the organic) was also stripped, resulting in a strip solution nickel tenor of 0.17 g/L Ni. This suggests the necessity of a scrubbing circuit.

The conclusion drawn from the bench-scale work was that the recovery of Ni and Co using the proposed Nicksyn™ and Cyanex 272 flow sheet was technically feasible.

Mini-Pilot Testing

The pilot testing was conducted in 3 phases. The first two phases piloted the Nicksyn™ circuit using site-generated PLS. The third phase piloted the Cyanex 272 circuit using artificial spent Ni electrolyte.

Pilot 1

The pilot plant consisted of 1 litre mixer-settlers set up as 4E (extraction), 2W (wash) and 2S (strip) stages. The mixer-settlers were set up on a heating pad which maintained the circuit at 35-40°C.

The PLS flow-rate was 600 mL/hr with O/A ratios of 1:1, >20:1 and 6:1 for extraction, washing, and stripping, respectively. The extractant for the first pilot run was 0.2M Nicksyn™ / 0.2M Versatic 10 in Cleansol 63. The solvent loop was closed with barren solvent recycled to extraction after stripping. The pH in the extraction circuit was controlled by 3 – 6% (w/w) NH₄OH solution. The synthetic strip solution was made up using NiSO₄·6H₂O to contain 64.4 g/L Ni and sufficient concentrated (98%) H₂SO₄ was added to make the solution up to 45.5 g/L H₂SO₄. This acid concentration represented a delta of 27 g/L Ni across the electrowinning circuit. Strip solution was collected. Wash solution was distilled water.

The PLS (see Table 2) arrived with some turbidity. It was allowed to settle and was decanted ahead of the pilot run. When the PLS was depleted, artificial PLS was generated by adding Ni and Co salts to the pilot raffinate.

The pilot plant ran for 200 hours. pH control was manual during the first 100 hours and generally the target pH was not achieved. A dosing pump was installed which enabled much better pH control.

The results were quite scattered, however, it was possible to confirm that the process is robust within the correct pH range of 6.2 – 6.4, as can be seen in the graphs. Mn extraction became problematic above pH 6.2, while at that pH Co extraction was only 90%.

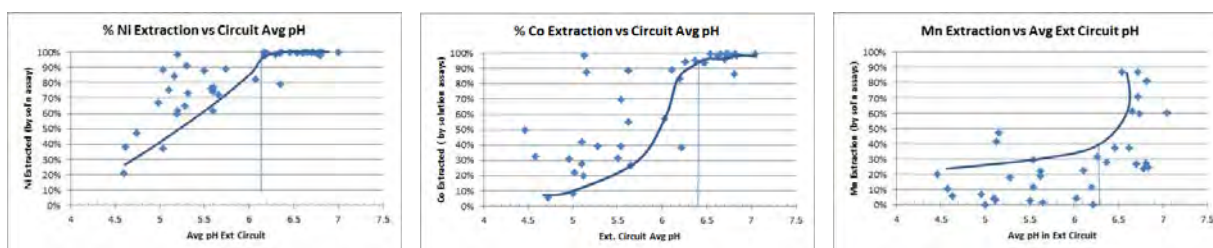


Figure 6, Pilot Run 1 Extraction vs pH data (0.2M Nicksyn™/0.2M V10, 35°C, O:A = 1:1)

A minor washing effect of all metals was evident. Stripping was satisfactory. Table 4 below shows the average barren organic analyses for the entire pilot plant run.

A minor but persistent yellow crud was noticed, likely related to iron because it almost disappeared when the PLS from the spiked raffinate was used.

Table 4, Average Barren Solvent Analyses

	Ni mg/L	Co mg/L	Mn mg/L	Ca g/L	Mg g/L	Fe mg/L	Cu mg/L	Al g/L
Pilot 1 BS	10	<0.5	3	<0.5	0.5	9	n.m	n.m

Pilot 2

The second pilot run, using site generated PLS at a higher Ni tenor of 4.1 g/L (see Table 2) ran for 100 hours. The results showed that a 0.2M Nicksyn™/ 0.2M Versatic 10 solvent mixture was inadequate to complete Co extraction. At Mintek's suggestion, the extractant strength was increased to 0.5M Nicksyn™/ 0.5M Versatic 10 and excellent (>99.5%) recoveries of Ni and Co were achieved. At that reagent concentration, around 35% of the Mn was co-extracted, however, less than 1% of the Ca and Mg was extracted. The Mn co-extraction could be minimized by a somewhat lower pH in the first extraction stage or a lower O:A phase ratio.



Figure 7, Pilot Equipment

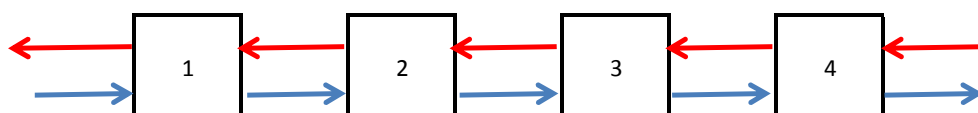
The pH in the extraction circuit was measured continuously. The measurement was performed by inserting a pH meter into the aqueous phase (bottom) of the settler. The pH was controlled by injecting 180 g/L Na₂CO₃ solution by syringe pumps into each extraction mixer. The pH was

very stable and was kept in the range of 5.8-6.3. The consumption of 180 g/L Na₂CO₃

solution was found to be ~1 mL solution / 20 mL PLS, which is an important consideration in the industrial plant process mass and water balances.

Figure 8 shows a typical "good" extraction circuit profile.

	LS		Org E2		Org E3		Org E4		BS
Ni [mg/L]	4320		777		69		1.2		0
Co [mg/L]	384		197		22		5.3		0



	PLS		Aq E1		Aq E2		Aq E3		Raff
Ni [mg/L]	3920		395		20		1.4		<1
Co [mg/L]	248		110		24		2		<1
pH	4.22		6.15		6.1		6.23		

Figure 8 Extraction Circuit Profile Hour No. 101 (0.5M Nicksyn™/ 0.5M Versatic 10, pH 6.0 - 6.3, ~ 35°C, O:A ratio 1:1)

Pilot 3

The third pilot plant run was conducted to prove the already well-known process of extracting Co away from Ni using Cyanex 272. Ni/Co strip solution from the previous pilot plant runs was spiked with expected contaminants based upon the plant design PLS and contacted with 5% v/v Cyanex 272 in Cleansol 63. The process involved partial pre-equilibration of the solvent with 180 g/L Na₂CO₃ solution, followed by displacement of the sodium ions with Ni ions from an electrolyte bleed. Around 50-60% of the Cyanex 272 was pre-equilibrated.

When left cold overnight, a gel formed in the pre-equilibrated mixture. It dissolved upon heating to 50°C. A white cloudiness was noticed at the O/A interface. According to Cytec, this is a phenomenon due to the Cyanex 272 being fresh and indeed the cloudiness disappeared with time.

Only the extraction circuit was tested during the pilot campaign. Scrubbing and stripping were demonstrated using bench-scale tests. The strip solution for the cobalt circuit was 44 g/L Co and 13 g/L H₂SO₄ in distilled water. The scrub solution was 15 g/L Co and 4.2 g/L H₂SO₄.

Table 5, Typical Metals Deportment with 5% v/v Cyanex 272 at pH 5.5, O:A 1:1

Element	Co	Ni	Mn	Zn	Cu	Fe	Al	Ca	Mg
Units	g/L	g/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Feed 17:00	1090	85444	363	315	50	18	26	98	243
Raff 17:00	5.8	78425	<1	<1	<1	<1	<1	72	89
LS	1182	1344	393	312	60	14.1	?	12	177

Results were as expected, with complete extraction of Co and less than 0.1% of the Ni reporting to the strip solution. Nevertheless it appears that scrubbing is required. Depending upon the required cobalt product quality, an ion exchange (IX) column may be required to clean up the rich strip liquor stream of Cu and Fe.

Conclusions

The main conclusion drawn from the continuous mini-pilot tests was that the process is robust.

The key to the process is choosing the correct Nicksyn™ / Versatic10 concentration for the targeted extraction and controlling the extraction pH within a very tight target range of 5.8 – 6.3. Overall recoveries of >99% Ni and Co were achieved, with the rejection of 99% of the Ca, 99% of the Mg and 65% of Mn to the raffinate.

Acknowledgments

The authors would like to acknowledge Limor Halay and Nadav Dobrin, both Senior Process Engineers at TBT in Israel and all the management and staff at the TBT Research Centre in Katzrin, for their excellent work in running the pilot tests and to

Malcolm Dilley, metallurgical consultant to Caldag for his presence and support during Pilot 1. The results are a tribute to the late Sezai Timur, Process Engineer from Caldag who championed TBT and the process to his management prior to his tragic road accident.

References

1. Oxley, Anne, Nurcun Sirvanci and Simon Purkiss " Çaldağ Nikel Laterite Atmospheric Leach Project" Metallurgija-Journal of Metallurgy, Association of Metallurgical Engineers of Serbia (AMES), Review Paper, ALTA 2006
2. Cheng, Chu Yong, "Solvent Extraction Process for Separating Cobalt and/or Manganese from Impurities in Leach Solutions" PCT International Publication No WO 2005/073315 A1, 11 Aug, 2005
3. Cheng, Chu Yong, "Solvent Extraction Process for Separating Cobalt and/or Nickel from Impurities in Leach Solutions" PCT International Publication No WO 2005/073316 A1, Aug 11, 2005
4. Du Preez, AC and MH Kotze, "Laboratory and Pilot Plant Investigations of the Performance of a Synergistic Versatic 10 Acid Solvent Extraction System for the Recovery of Nickel from Calcium Saturated Streams", South African Institute of Mining and Metallurgy, Base Metals Conference 2009, pp 83-100
5. Du Preez, AC and MH Kotze, "Evaluation of a Versatic 10 Acid/Nicksyn™ Synergistic System for the Recovery of Nickel and Cobalt from a Typical Laterite Leach Liquor", South African Institute of Mining and Metallurgy, Base Metals Conference 2013
6. Du Preez, René, Marthie Kotze, Gerhard Nel, Simon Donegan and Huziel Masiima, "Solvent Extraction Test Work to Evaluate a Verstaic10/Nicksyn™ System for Nickel Calcium Separation", South African Institute of Mining & Metallurgy, The Fourth Southern African Conference on Base Metals pp 193 – 210
7. Mihaylov Indje O, Eberhard Prause, Steve Laundry and Cuong V Luong, "Process for the Extraction and Separation of Nickel and/or Cobalt", US Patent No 5,378,262, Jan 03, 1995
8. Bacon G, Mihaylov I, "Solvent Extraction as an Enabling Technology in the Nickel Industry", The Journal of the South African Institute of Mining and Metallurgy, Nov-Dec 2002, pp 435 – 443
9. Flett, Douglas S, "Cobalt Nickel Separation in Hydrometallurgy: A Review", Chemistry for Sustainable Development, 12 (2004) pp 81-91
10. Soderstrom, Matthew, Cyril Bourget, Boba Jakovljevic and Troy Bednarski, "The Development of Process Modelling for Cyanex® 272 Extractant", Presented at ALTA, 2010

A clean production process for tungsten hydrometallurgy based on direct solvent extraction from alkaline medium

Guiqing Zhang^{*1), 2)}, Wenjuan Guan^{1), 2)}, Liansheng Xiao^{1), 2)}, Qixiu Zhang^{1), 2)}

Abstract: The principle, flow sheet and characteristics of a new clean production process for tungsten hydrometallurgy based on direct solvent extraction with quaternary ammonium salt from alkaline medium were introduced. The pilot tests and industrial tests of this new technology for different tungsten ores were conducted. The result indicated that the novel process exhibited extensive adaptability for the treatment of leach solutions from not only autoclave-soda leaching but also caustic soda leaching with different tungsten ores. The process of tungsten extraction from alkaline medium was run stably. The impurities of P, As, Si, Sn were almost removed while sodium tungstate solution transformed to ammonium tungstate solution. The behavior of molybdenum in the process was similar as tungsten. The concentration of WO_3 in strip liquor reached 170 g/L and it would be beneficial to preparation of ammonium paratungstate by evaporative crystallization. The raffinate could be returned to leaching step directly or with properly treatment. The water and alkali could be reused, and the consumption of alkali and discharge of wastewater were decreased greatly in this process. The new technology exhibited obviously advantages including short flowsheet, low consumption of chemical reagent, low wastewater discharge and high recovery of tungsten. The application of this clean process in industry was expected to make important impact on the hydrometallurgical extraction of tungsten and to deliver good economical benefits.

Key words: Tungsten; Solvent extraction; Quaternary ammonium salt; Clean production

1. Introduction

Ammonium paratungstate (APT) is the main intermediate in the manufacture of tungsten metal and tungsten carbide. The traditional technology for APT production from alkaline leach liquor of tungsten ores is that solvent extraction with weakly alkaline organic ammonium in acid media ($pH = 2\sim 3$). The content of free alkali in the leach liquor is always relatively high, especially when low grade ore is concerned^[1]. Thus, lots of acid was needed to neutralize and acidify the leach liquor, and the valuable chemical – alkali (Na_2CO_3 or $NaOH$) and acid (H_2SO_4 or HCl) becomes the useless inorganic salt in raffinate, which is harmful to environment. In addition, the anion impurities of P, As, Si, Sn can not be removed in this process because of the formation of heteropolyacid, and special operations of removing P, As, Si, Sn by precipitation are needed, which brings on loss of tungsten.

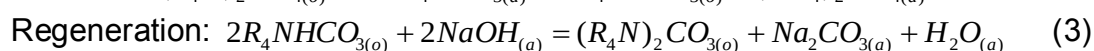
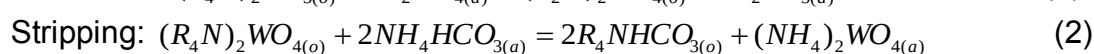
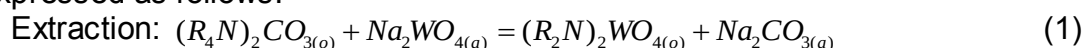
To solve the problems mentioned above, the direct solvent extraction of tungsten from alkaline medium was proposed and studied since 1960s^[2]. In 1990s, the research was acquired breakthrough in the selection of solvent extraction system used in direct solvent extraction of tungsten from soda leach liquor, in which quaternary ammonium carbonate salt was chosen as the extractant, ammonium hydrocarbonate the stripping reagent and sodium hydroxide the regeneration reagent. However, two problems have limited the application of this proposed process in industry, which are poor phase separation and relatively low concentration of WO_3 in the strip liquor ($\sim 100g/L$) resulting high energy consumption in following crystallization by evaporation^[3].

^{*1),2)}Corresponding author, 1).School of Metallurgy and Environment, Central South University, Changsha 410083, China; 2). National Engineering Laboratory for Efficient Utilization of Refractory Non-ferrous Metals Resources, Central South University, Changsha 410083, China.
Email:gq_zhang@163.com.

Long and deep study on the key obstacles in industrialization of this technology was conducted by our group since 1990s^[4~7]. The problem of low concentration of WO_3 in the strip liquor and the slow speed of phase separation in the extraction system have been successfully solved by choosing the proper composition of the organic phase and the stripping agent, and valuable results in the industrial application was acquired. The results of the consecutive pilot test for the autoclave-soda leaching solution of the scheelite and the caustic soda leaching solution of the wolframite, and the results of the industrial test for the autoclave-soda leaching solution of the low-grade scheelite were reported in this paper.

2. Principles

The main reaction equations during extraction, stripping and regeneration are expressed as follows:



3. Experiments

The flowsheet of experiments are shown in Fig.1. Multi-stage mixer-settler (with individual effective volumes of 1.2L for mixer and length ratio of the mixer and the settler is 2.8:1) system was used for the pilot tests, while the multi-stage annular centrifugal extractor(the diameter of the drum is 120mm) system for industrial tests.

Three sorts of feed used in the experiment were Feed A, the autoclave-soda leaching solution of the scheelite, Feed B, caustic soda leaching solution of the wolframite, Feed C, autoclave-soda leaching solution of the low-grade scheelite. The main components of the three sorts of feed are shown in Table 1.

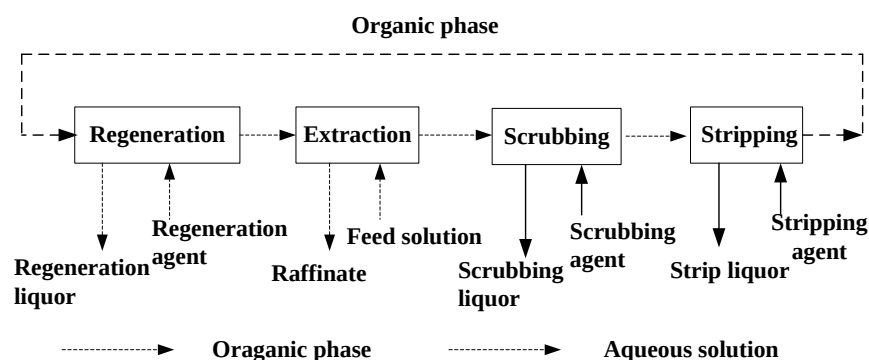


Fig.1 Flowsheet of the direct extraction of tungsten from alkaline medium

Table 1 Main components of the experimental feed solution

No.	Concentration of the main components (g/L)										pH
	WO_3	Mo	P	As	SiO_2	Sn	Cl^-	F^-	Na_2CO_3	NaOH	
A	110.4	0.70	1.02	0.30	0.800	0.0027	1.62	1.42	133.1	2.89	12.45
B	146.2	0.63	1.44	0.70	0.750	0.0018	3.90	2.62	/	27.6	/
C	58.3	6.45	0.072	/	0.430	/	/	/	100.7	6.00	/

The organic system was composed of TOMAC(tri-n-octylmethylammonium chloride) and 2-octanol diluted in sulfonated kerosene, in which TOMAC was 450g/L. The TOMAC was transformed into quaternary ammonium carbonate before extraction. Pure water was used as scrubbing agent and mixed solution of NH_4HCO_3 and NH_4OH as the stripping agent.

4. Result and discussion

4.1 Pilot test for caustic soda leach liquor of wolframite

The pilot test was conducted in the multi-stage mixed settler system with 9-stage extraction, 4-stage scrubbing, 14-stage stripping and 1-stage regeneration, and it had been consecutively ran for 76 hours. The results showed that the process was stable and easy to control, and it was with clear phase separation in every stage. The typical experimental results are shown in Table 2 and Table 3.

Table 2 Concentration of WO_3 in different solution at different time in pilot test with caustic soda leaching liquor of wolframite

Running time (h)	Concentration of WO_3 (g/L)			
	Feed	Raffinate	Strip liquor	Loaded organic phase
12	146.5	3.03	170.4	71.0
24	146.5	2.78	162.7	71.8
48	146.5	4.45	160.0	71.1
60	146.5	4.28	160.9	70.8
72	146.5	2.14	152.5	71.3

As is shown in Table 2, the concentration of WO_3 in raffinate was lower than 5.0g/L, while the concentration of WO_3 in the loaded organic phase was rather stable for about 71 g/L and that in the stripping liquor around 160g/L.

As is shown in Table 3, the 98.00% of WO_3 and 89.48% of Mo were extracted respectively in the process. The result exhibits similar behavior of tungsten and molybdenum in the process of solvent extraction, which shows that the process can not remove molybdenum from tungsten effectively. The removal of the impurity of P, As, Si, Sn were 99.67%, 98.77%, 93.60% and 94.66% respectively, which shows excellent removal of P, As, Si, Sn of this process. It has also been shown in Table 3 that the removal rate of Cl^- and F^- were 43.40% and 92.83% respectively, indicating most of the Cl^- enter strip liquor, while most of the F^- remains in the raffinate liquor in the process. The anions like Cl^- will not accumulate infinitely in the organic phase and will not result in the decreasing capacity of the organic phase.

The new technology possessed excellent impurity removal except Mo. The content of impurities except Mo in strip liquor were very low, which can meet the requirement of 0-grade APT (China national standard) production.

Table 3 Typical result of the pilot test for caustic soda leaching liquor of wolframite

Item	WO_3	Mo	P	As	SiO_2	Sn	Cl^-	F^-
Feed solution (g/L)	146.5	0.63	1.44	0.701	0.321	0.0018	3.09	2.62
Strip liquor (g/L)	152.5	0.92	< 0.005	0.009	0.034	0.0001	1.82	0.25
Raffinate (g/L)	2.14	0.041	1.20	0.623	0.480	0.0006	0.42	1.69
Scrubbing liquor (g/L)	10.9	0.027	/	/	/	/	0.69	0.51
Extraction (%)	98.00	89.48	/	/	/	/	/	/
Removal (%)	/	/	99.67	98.77	93.60	94.66	43.40	90.83

4.2 Pilot test for autoclave-soda leach liquor of scheelite

The multi-stage mixed settler system was same as that for *caustic soda leach liquor of wolframite*, and the pilot test had been consecutively ran for 64 hours. The results also showed that the process were stable and easy to control, and it was with clear phase separation in every stage. The typical experimental results are shown in Table 4 and Table 5.

As is shown in Table 4, the concentration of WO_3 in the loaded organic phase was comparatively stable to be around 71.0g/L and that in the strip liquor around 170g/L, and that in the raffinate liquor was around 5g/ L.

Table 4 Concentration of WO₃ in different solution at different time in pilot test results

Time (h)	Concentration of WO ₃ (g/L)			
	Feed solution	Raffinate	Strip liquor	Loaded organic
16	112.5	5.71	162.3	71.3
24	109.3	2.83	173.5	70.9
36	111.6	6.06	176.0	71.1
48	110.4	4.19	175.1	71.9
63	110.4	4.99	162.7	71.4

It is shown in Table 5 that the extraction ratio of WO₃ and Mo were 94.87% and 89.20% respectively in the process, which also exhibits similar behavior of tungsten and molybdenum. The removal of the impurity of P, As, Si and Sn were 99.67%, 98.64%, 95.34% and 97.49% respectively, and similar as in the processing of caustic soda leaching solution of the wolframite. Similarly, the content of impurities except Mo in strip liquor also can meet the requirement of 0-grade APT production.

Table 5 Typical result of the pilot test for soda leach liquor of scheelite

Item	WO ₃	Mo	P	As	Si	Sn
Feed solution (g/L)	110.4	0.70	1.02	0.300	0.343	0.0027
Strip liquor (g/L)	162.7	1.28	0.005	0.006	0.024	0.0001
Raffinate (g/L)	4.99	0.056	0.69	0.178	0.364	0.0021
Scrubbing liquor (g/L)	11.05	/	/	/	/	/
Extraction (%)	93.89	89.20	/	/	/	/
Removal (%)	/	/	99.67	98.64	95.34	97.49

4.3 Industrial test for autoclave-soda leach liquor of low grade scheelite

The industrial test was conducted in a multi-stage annular centrifugal extractor (the diameter of the drum is 120mm) system with 8-stage extraction, 3-stage scrapping, 13-stage stripping and 1-stage regeneration, and the experiment had been ran for 18 months. The results of long time running of industrial test showed that the centrifugal extractor system can realize fast mixing and phase separation, the process ran stably and was easy to control. The typical industrial test results are shown in Table 6.

Table 6 Typical results of the industrial test with the autoclave-soda leaching liquor of the low-grade scheelite

No.	Concentrations of raffinate		Concentrations of strip liquor				
	WO ₃ (g/L)	Mo (g/L)	WO ₃ (g/L)	Mo (g/L)	P/WO ₃ ($\times 10^{-4}$)	Si/WO ₃ ($\times 10^{-4}$)	Na/WO ₃ ($\times 10^{-4}$)
1	4.39	0.38	127.9	14.04	0.32	/	/
2	4.20	0.46	132.8	15.80	0.14	/	2.26
3	0.46	0.13	125.9	15.52	0.35	0.30	/
4	4.43	0.41	129.5	16.34	0.21	0.32	1.93
5	0.48	0.13	127.9	14.85	0.43	0.34	2.74

As is shown in Table 6, WO₃ in the raffinate was lower than 4.43g/L, and WO₃ and Mo in the strip liquor were higher than 125.9 g/L and 14.04 g/L respectively. The content of impurities except Mo in strip liquor was low. The concentration ratios of P/WO₃, Si/WO₃ were both less than 1×10^{-4} , while the concentration of Na was less than 0.03g/L, which shows that the impurity contents of P, Si, Na except Mo in the raffinate liquor can fully meet the requirement of 0-grade APT production. In addition, the long-term industrial test also shown that the organic system featured stable

reusability. Therefore the process can fully adapt to treat the practical industrial autoclave-soda leaching liquor of low-grade scheelite.

5. Flowsheet of the clean production process for tungsten hydrometallurgy

An novel clean production process for tungsten hydrometallurgy based on direct solvent extraction from alkaline medium was proposed according to pilot tests and industrial test (Fig.2).

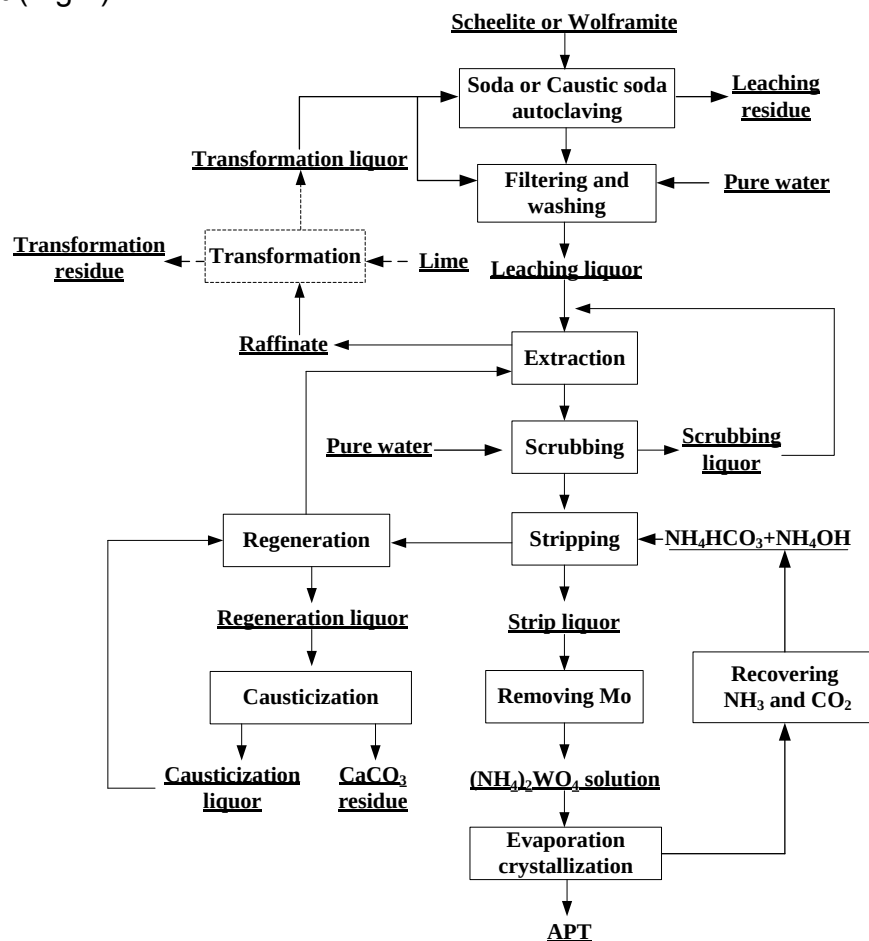


Fig.2 Flowsheet of the new clean production process for tungsten hydrometallurgy based on direct solvent extraction from alkaline medium

As is shown in Fig.2, The impurities of P, As, Si, Sn were almostly removed while sodium tungstate solution transformed to ammonium tungstate solution through the direct solvent extraction from alkaline medium to obtain the pure ammonium tungstate solution for APT production, whether it was the leaching solution from scheelite by soda or from wolframite by caustic soda. The WO_4^{2-} and MoO_4^{2-} were extracted into organic phase selectively, and the removal of impurity like P, As, Si and Sn was realized. The loaded organic phase was scrubbed with pure water, and the scrapping liquor was merged with leach solution for the feed of extraction. Then the organic phase was stripped with the mixed solution of NH_4HCO_3 and NH_4OH , and the strip liquor, i.e. ammonium tungstate solution with Mo was purified by Mo removal, and was sent to APT crystallization by evaporation. The stripped organic was regenerated by NaOH solution and returned for extraction. The regeneration liquor was causticized by lime and reused for regeneration again. The NH_3 and CO_2 produced in the process of crystallization could be recovered for stripping. The raffinate from autoclave-soda leach liquor of scheelite could be reused for leach and

the raffinate from caustic soda leach liquor of wolframite could be causticized by lime and reused for leach.

Both the organic phase and aqueous solution could form close-cycle in the leaching-solvent extraction process, organic phase and $\text{Na}_2\text{CO}_3/\text{NaOH}$ could recycle in the process. There was no consumption of acid in the process and the procedure of removing P, As, Si and Sn by precipitation was canceled.

Compared with the traditional technology, the new technology shows the advantages of short flowsheet, high recovery of WO_3 , low consumption of chemicals, and small discharge of waste water, and dramatically cost cut, with obvious economic and environmental benefits, making it a typical low-cost clean production technology.

6. Conclusion

1) The pilot tests for the direct extraction of tungsten from the autoclave-soda leaching solution of the scheelite and the caustic soda leaching solution of the wolframite with mixer-settler, and the industrial test of direct tungsten extraction from autoclave-soda leaching solution of the low-grade scheelite with centrifugal extractor had been conducted. The results indicated that, the new technology had excellent adaptability to different alkaline leaching solution of tungsten ores, when proper operational conditions were controlled, the impurities of P, As, Si, Sn could almost be removed while sodium tungstate solution transformed to ammonium tungstate solution in the process.

2) A novel clean production process for tungsten hydrometallurgy based on direct solvent extraction from alkaline medium had been proposed. Compared with the traditional APT production technology of "caustic soda or soda leaching-impurity removal-solvent extraction in acid medium-crystallization by evaporation", the new technology shows the advantage of short process flow, high recovery of WO_3 , low consumption of chemicals, and small discharge of waste water, and low operation cost, with obvious economic and environmental benefits.

References:

- [1] Zhang, Q.X., Zhao, Q.S. 2005. Tungsten and Molybdenum Metallurgy, first ed. Metallurgical Industry, Beijing.
- [2] DROBNICK, J. L., LEWIS, C. J. Recovery and Purification of tungsten by liquid ion exchange process[C]//Unit Processes in Hydrometallurgy. London: Gordon and Breach Science Publishers, 1964: 504-514.
- [3] Pzaitsev, V., Ivanov, I.M., Kalesh, N.K., et al. Scientific foundations of a new extraction technology for the processing of tungsten containing solutions, In: Proceedings of the Second International Conference on Hydrometallurgy(ICHM), 1992, Changsha:International Academic Publishers: 768-772.
- [4] Zhang, G.Q., Zhang, Q.X. The study of tungsten extraction from caustic soda leach liquor to produce ammonium tungsten solution, Journal of Central-South Institute of Mining and Metallurgy, 1994, 24(W Special): 97-105.
- [5] Zhang, G.Q., Zhang, Q.X. A new production technology for tungsten hydrometallurgy, Chinese Journal of Rare Metals, 2003, 27(2): 254-257.
- [6] GUAN, W. J., Zhang, G.Q., Extraction of tungsten from simulated autoclave-soda leaching liquor of scheelite with quaternary ammonium salt, The Chinese Journal of Nonferrous Metals, 2011, 21(7): 1756-1762.
- [7] Zhang, G.Q., GUAN, W. J., Zhang, Q.X., XIAO, L. S. Continuous-running experiment for direct solvent extraction of tungsten from autoclave-soda leaching liquor of scheelite[J]. China Tungsten Industry, 2009, 24(5): 49-52.

Recovery of rare earths from acid leach solutions of spent nickel-metal hydride batteries using solvent extraction

Li Zeng, Yun Xia, Liansheng Xiao, Jiying TIAN, Zhaoyang Li*

Abstract: The extraction of rare earths from acid leach solutions of spent nickel-metal hydride batteries using primary amine extractant of N1923 was studied. The effects of feed pH, temperature, shaking frequency and time on the extraction of rare earth, as well as stripping reagent composition and concentration, stripping phase ratio on the stripping of rare earths was investigated. In addition, the extraction isotherm was determined. The pilot plant test results showed that the extraction of rare earth reached 99.99% after five counter current extraction. The rare earth precipitate with 98.5% purity and impurity content less than 0.05% was obtained by the addition of oxalic acid in loaded strip liquors. The extractant exhibited good selectivity of rare earths over other elements and stable performance.

Key Words: Rare earth; Spent nickel-metal hydride battery; Recovery; Solvent extraction

1. Introduction

The nickel-metal hydride (Ni-MH) batteries have been widely applied in many fields, such as electronic products and electric vehicles. China has the largest output of Ni-MH battery in the world and meanwhile the largest amount of spent Ni-MH battery. As a secondary resource, spent Ni-MH batteries are undoubtedly very important because of not only their enormous economic values, but also because of the environmental concerns associated with their disposal. Spent Ni-MH batteries usually consist of nickel, cobalt, iron and especially rare earths(RE).

A number of metallurgical processes are reviewed to recover rare earths from these batteries^[1]. The method of double salt precipitation could be easily industrialized since its simple operation, however, the recovery of RE are usually between 80% to 95% with a relatively low purity^[2,3]. Pyrometallurgical processes for the treatment of spent Ni-MH batteries exist disadvantages of large energy consumption and serious environmental pollution. In addition, the purity of mixed RE oxides is normally about 70%^[4]. The method of solvent extraction has also been reported to recover metal values from acid leach solutions of spent Ni-MH batteries. Fernandes et al. used a phosphonic acid extractant of PC88A to extract nickel and lanthanides followed by selective precipitation of lanthanides, but impurities such as Fe, Co and Zn have to be removed by other two SX systems in advance, resulting in complicated operation and unsatisfied comprehensive utilization^[5]. Zhang et al. has proposed a process in which RE and Zn, Al, Fe, Mn were co-extracted by D2EHPA at pH 2.6 followed by selective precipitation of RE with oxalic acid^[6]. The nickel and cobalt in raffinates were then separated by Cyanex 272. Due to the poor selectivity of D2EHPA, the purity of mixed RE oxides was relatively low. Recently, a new process of separation and recovery of RE using synthetic adsorbent was studied^[7]. In this process, RE were separated over impurities from acid leach solutions by precipitation with NaOH solution. The obtained precipitate was then leached by 2 mol/L HCl, and

*Corresponding author, School of Metallurgy and Environment, Central South University, Changsha 410083, China; National Engineering Laboratory for Efficient Utilization of Refractory Non-ferrous Metals Resources, Central South University. Email: yuanzhenxia_1104@aliyun.com

the adsorbent was used to extract RE from the HCl leach solution. The drawback of this process was large loss of RE and nickel.

The aim of this paper was to develop a new solvent extraction process for the recovery of RE from acid leach solutions of spent Ni-MH batteries.

2. Experimental

2.1 Materials

Cylinder-shaped batteries provided by a company in Hunan Chenzhou were used. After removal of the cases, the batteries were leached by sulfuric acid, and the leach solution were used as feed for batch tests. The compositions of feed are shown in Table 1.

Table 1 Main components of feed solutions

Elements	RE	Ni	Fe	Co	H ₂ SO ₄
Concentration(g/L)	5.15	19.0	2.0	1.2	48.02

Primary amine of N1923 with industrial grade(SG: 0.8154 g/L) was employed as extractant. The structure of extractant is shown in Fig. 1. The diluent of kerosene and the modifier of isooctanol was used. Before extraction, the organic system was contacted with 1 mol/L H₂SO₄ for the conversion of primary amine to primary ammonium salt.

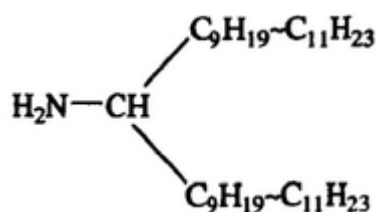


Fig. 1 Structure of primary amine N1923

2.2 Methods

The shakeout tests were carried out in a 125 mL separating funnel immersed in a temperature controlled water bath. To determine the metal extraction distribution isotherms, the organic system containing 10%N1923 in sulfonated kerosene was mixed with the acid leach solution at A/O ratio of 1:1 and 20°C using saturated solvent extraction method.

Samples were collected and analyzed to determine the concentrations of metals. The concentration of RE were determined with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The aqueous samples were assayed for other metals using Atomic Absorption Spectrum(AA).

2.3 Experimental fundamental

Primary amine extractant of N1923 has been widely used in the separation of Th and RE(III). In the sulfuric acid leach solution of spent Ni-MH batteries, ions of RE could react with SO₄²⁻ to form complexing anion RE(SO₄)_x^{3-2x} which can be selectively extracted by the primary amine^[8], other metals such as Fe, Ni, Co mainly exist as cations which remain in raffinates during extraction. The separation of RE(III) and Fe, Ni, Co is thus achieved.

3. Results and discussion

3.1 Extraction

3.1.1 Effect of feed pH

The organic system consisting of 10%N1923 and 4% isooctanol in sulfonated kerosene determined by preliminary tests was selected for the characterisation and optimisation of extraction of RE. The addition of isooctanol is to improve phase separation during extraction.

Fig. 1 shows the effect of feed pH on extractions of RE and other metals with an A/O ratio of 2/1 and 180 rpm at 20°C for 5 min.

It can be seen from Fig. 1 that RE was selectively extracted over other metals such as Cu, Mn, Ni, Fe and Zn during the pH range tested. It was also noted that the extraction of RE increased with the increase of pH. But the phase separation became poor when the feed pH reached 2.5. The separation coefficient $\beta_{RE/Ni}$ reached maximum value of 229 at pH 1.5. The feed pH of 1.5 was thus chose for subsequent experiment.

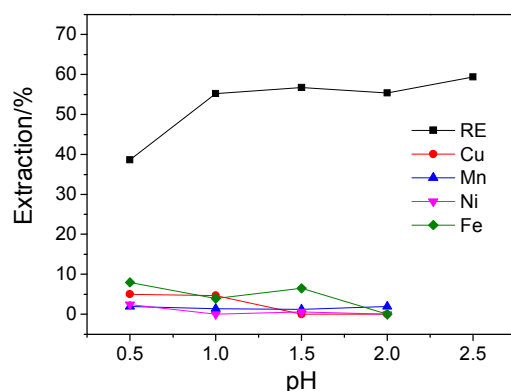


Fig. 1 Effect of feed pH on the extraction of metals (A/O=2/1, 180rpm, 20 °C, 5 min)

3.1.2 Extraction kinetics

The extraction kinetics of RE with 10%(v/v) N1923 and 4% isooctanol in sulfonated kerosene with the acid leach solution at an A/O ratio of 2/1 and 20°C is shown in Fig. 2. It was found that the extraction equilibrium was obtained within 3 min and about 70% RE extracted, indicating fast extraction kinetics.

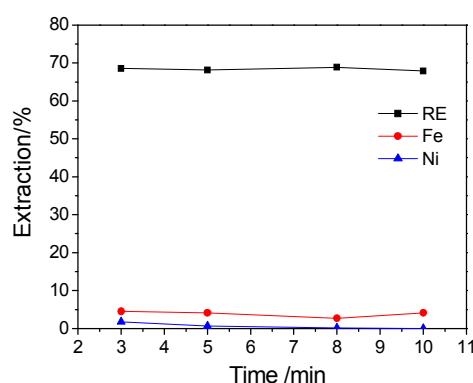


Fig. 2 Effects of mixing time on the extraction of metals(A/O=2/1, pH=1.5, 180 rpm, 20 °C)

3.2 Stripping

3.2.1 Effect of stripping reagent concentration

Two stripping reagents of 3 mol/L HCl and 3 mol/L H₂SO₄ solutions were used to strip loaded organic solutions containing 6.24 g/L RE with an A/O ratio of 3/1. The results demonstrated that HCl solution as the stripping reagent exhibited better

performance since the stripping of RE using HCl solution reached 99.5% in a single stage compared with that of 77.7% using H_2SO_4 solution.

The effect of HCl concentration on the stripping of RE(III) and Fe(III) with an A/O ratio of 3/1 and 180 rpm at 30°C for 5 min was shown in Fig. 3. As seen, both strippings of RE(III) and Fe(III) increased with the increase of HCl concentration and reached peak values with 2 mol/L HCl. Further increase of HCl concentration resulted in the decrease of strippings of both. The reason for this phenomenon could be explained that when HCl concentration reached 2 mol/L, free Cl^- in strip liquors would form complexing ions with RE(III) and Fe(III), which were re-extracted by the extractant, resulting in the decrease of both stripping. Therefore, the solution of 2 mol/L HCl was chose as optimum.

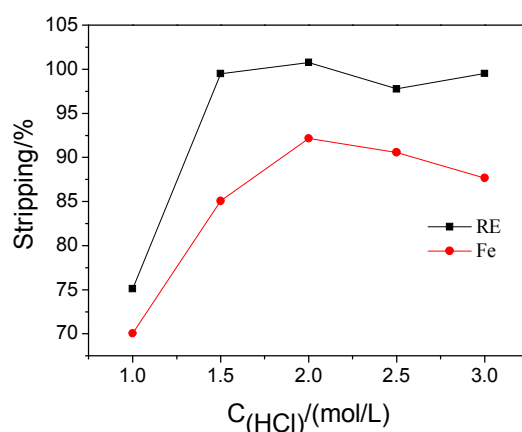


Fig. 3 Effects of HCl concentration on stripping of RE and Fe (30 °C, O/A=3/1, 180 rpm, 5 min)

3.3 RE distribution isotherms and extraction mechanism

The RE(III) extraction distribution isotherm was determined using 10%(v/v) N1923 and 4% isooctanol in sulfonated kerosene and the acid leach solution containing 1.2g/L RE with an A/O ratio of 1/1 at pH1.5 and 20 °C by saturated extraction method(Fig. 4). It can be seen from Fig. 4 that the saturated extraction capacity of RE(III) with the N1923 system was 7.41 g/L.

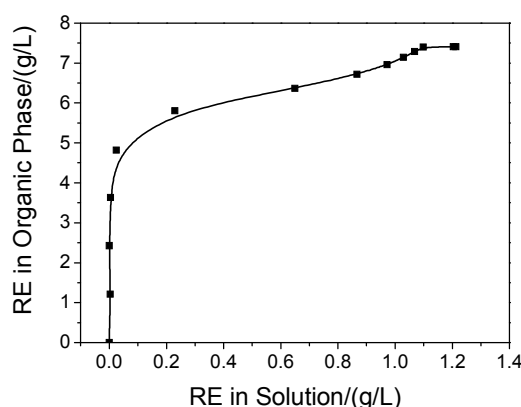


Fig. 4 The extraction isotherm of RE(20 °C, pH=1.5, O/A=1/1, 180 rpm, 5 min)

Based on specific gravity and molecular weight of N1923, the molar concentration of 10%(v/v) N1923 was calculated to be 0.241~0.288mol/L. The average molecular weight of mixed RE could be approximately estimated to be 140 since more than 90% of RE were lanthanum and cerium. The saturated extraction capacity of RE was

thus calculated to be 0.0529 mol/L. The molar ratio of primary amine N1923 to RE was 4.56~5.44:1, which is close to 5/1. The extraction reaction can be inferred as follows:



3.3 Fully-continuous pilot plant tests

The flowsheet of RE extraction from acid leach solutions of spent Ni-MH batteries for the pilot plant test is shown in Fig.5. The SX system of multi-stage mixer settlers (with individual effective volumes of 1L for mixer) was used in pilot plant tests. The system included 5 stages of extraction, 1 stage of scrubbing and 3 stages of stripping. The pilot plant test was operated for over 30 days.

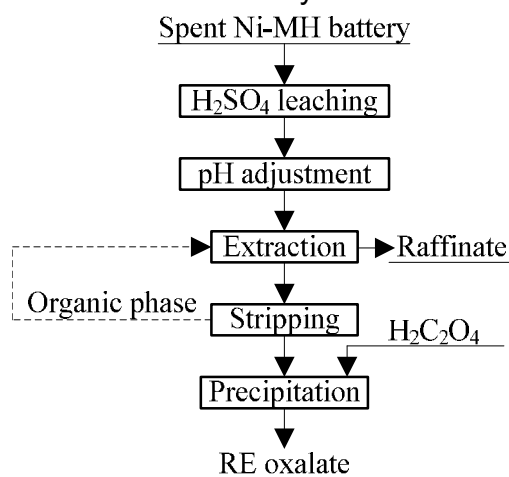


Fig. 5 Principle flowsheet of RE extraction from acid leach solutions of spent Ni-MH battery

The fully-continuous pilot plant test showed that the process was very stable and easy to control. The typical results in steady state are shown in Table 2.

It can be seen from Table 2 that the extraction of RE reached 99.99%, leaving 0.001 g/L RE in the raffinate. Some iron and very small amount of nickel/cobalt were co-extracted which can be separate from RE in the step of precipitation with oxalic acid. The removals of impurity such as Ni and Co were up to 99% except 95% for Fe, indicating most of impurities can be almost completely removed. The concentration of RE in strip liquor nearly reached 17 g/L, which was 3 times of that in feed.

Table 2 Fully-continuous pilot plant test results of RE extraction with N1923 system

Element(g/L)	RE	Ni	Co	Fe
Feed	5.15	25.99	1.37	13.66
Strip liquor	16.99	0.077	0.003	1.99
Raffinate	0.001	21.3	0.81	9.78
Extraction(%)	99.98	---	---	---
Impurity removal(%)	---	99.91	99.93	95.58

The obtained strip liquor was used to precipitate RE by the addition of oxalic acid at 70°C and pH 1.5~2. The quality of RE oxalate precipitate was shown in Table 3.

It was calculated from Table 3 that the purity of mixed RE oxalates reached 98.49%, while content of other impurities was less than 0.001%, except 0.01% Fe, 0.02% Na, 0.03% Al and 0.04% Ca.

Table 3 Chemical components of the sample of RE oxalates

La	Ce	Pr	Nd	Y	Cr	Cu	Ca	Fe	Pb	B	Co	K
31.39	14.12	2.039	1.185	0.334	0.0001	0.0001	0.04	0.01	0.0001	0.0001	0.0007	0.0001
V	Zn	Se	Al	Mg	Ba	Ni	Na	Cd	Mn	Li	As	Sr
0.0001	0.001	0.009	0.03	0.001	0.0003	0.0001	0.02	0.0001	0.0001	0.0001	0.0001	0.0001

4. Conclusion

Based on the results obtained from the current work, the following conclusions were made:

(1) The primary amine can be used to highly separate rare earths over Fe, Ni, Cu, Mn and Zn from acid leach solutions.

(2) HCl solution exhibited an excellent performance as the stripping reagent compared with H₂SO₄ solution. The stripping of rare earths reached 99.5% in a single stage when using 3 mol/L HCl solution.

(3) The saturated capacity of rare earths reached 7.41 g/L with organic system consisting of 10% primary amine and 4% isooctanol in sulfonated kerosene. The metal complexes can be inferred to be (RNH₃)₅RE(SO₄)₄

(4) The extraction of rare earths reached 99.99% with A/O ratio of 1.5/1 and 480 rpm at pH 1.5 and 20°C by five-stage counter current extraction of continuous running test. Rare earth oxides with purity of 98.5% can be obtained by the addition of oxalic acid into strip liquors. Application of the process in industry is expected to deliver a promising economical outcome.

References:

- [1] Pietrelli L, Bellomo B, Fontana D, Montereali M R. Rare earths recovery from Ni-MH spent batteries [J]. Hydrometallurgy, 2002, 66: 135-139.
- [2] LIAO Chun-fa, HU Li-gang, XIA Li-bin. Research on rare earth recovery from leaching solution of spent Nickel-Metal hydride batteries anode [J]. Hydrometallurgy of China, 2011, 30 (2): 152-154. (in Chinese)
- [3] XU Yan-hui, CHEN Chang-pin, WANG Xiao-lin. Recycling of metal materials from used Ni-MH cells [J]. Chinese Journal of Power Sources, 2002, 26 (3): 154-157. (in Chinese)
- [4] WANG Chang-chun, GUO Jing-hong, JIANG Bo, SHEN Xin. A method for recovering metals from spent nickel-metal hydride batteries: China, 102251118 A [P]. 2011-11-23. (in Chinese)
- [5] Fernandes A, Afonso J C, Dutra J B. Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation[J]. Hydrometallurgy, 2013, 220: 37-43.
- [6] ZHANG P, Yokoyama T, Itabashi O, Wakui Y, Suzuki T M, Inoue K. Recovery of metal values from spent nickel-metal hydride rechargeable batteries [J]. Journal of Power Sources, 1999, 77 (2): 116-122.
- [6] ZHANG P, Yokoyama T, Itabashi O, Wakui Y, Suzuki T M, Inoue K. Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries [J]. Hydrometallurgy, 1998, 50: 61-75.
- [7] Gasser M S, Aly M I. Separation and recovery of rare earth elements from spent nickel-metal-hydride batteries using synthetic adsorbent [J]. International Journal of Mineral Processing, 2013, 121: 31-38.
- [8] LI De-qian, JI En-rui, XU Wen, YU Ding-yu, NI Jia-zuan. Extraction mechanism of rare earth elements (III), iron (III) and thorium (IV) from sulfuric acid solutions by primary amine N1923 [J]. Chinese Journal of Applied Chemistry, 1987, 4 (2): 36-41. (in Chinese)

Separation of Americium from a Concentrated Raffinate by Liquid-Liquid Extraction

C. Marie, M.-T. Duchesne, V. Pacary, V. Vanel, M. Montuir, D. Rudloff, M. Bertrand, M. Miguirditchian

CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS, Bagnols-sur-Cèze, F-30207, France

Summary

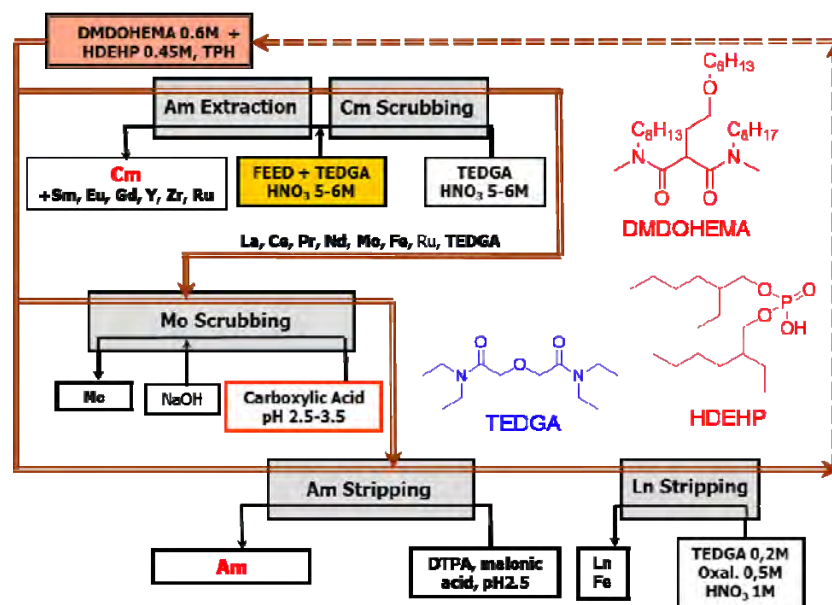
Recycling americium (Am) alone from the spent fuel is an important option studied for the future nuclear cycle (Generation IV systems) since Am is one of the main contributor to the long-term radiotoxicity and heat power of ultimate waste. The liquid-liquid extraction process called EXAm has been developed by the CEA to allow the recovery of Am alone from a PUREX raffinate (already cleared from U, Np and Pu). A mixture of DMDOHEMA (N,N' dimethyl-N,N' dioctyl-2 (2 (hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) in TPH is used as the solvent and the Am/Cm selectivity is improved using TEDGA (tetraethyldiglycolamide) as a selective complexing agent to maintain Cm and heavier lanthanides in the acidic aqueous phase (HNO₃ 5-6M). Americium is then stripped selectively from light lanthanides at low acidity (pH2.5-3) with a polyaminocarboxylic acid. In order to make the process and future plant associated more compact, the objective is now to adapt the EXAm process to a concentrated raffinate. The aqueous complexing agent is partially extracted into the organic phase and generates several complications in the process for higher concentrations of cations: risk of third phase formation, Am leaking at the Mo scrubbing step, decrease of lanthanide/americium separation factor during Am stripping. A "TEDGA scrubbing" battery was thus designed to keep its concentration in the organic phase lower than 10mM. Many experimental data were acquired in batch conditions at the different steps of the process. Solvent formulation, TEDGA and HNO₃ concentrations, pH buffer nature were optimized to manage high concentrations of americium and lanthanides in the loaded solvent and avoid 3rd phase formation but keeping a sufficient Am/Cm and Am/FP separation.

1. INTRODUCTION

In the future nuclear fuel cycle, one promising strategy for the treatment of long-lived radionuclides is partitioning and transmutation. The French Act of June 28th 2006 has defined several strategies to totally or partially recycle minor actinides (MA) from spent nuclear fuels in Generation IV systems. After recycling U, Pu, and Np, the remaining long term radiotoxicity is mainly due to MA, essentially americium and curium. After 100 years, americium is the main contributor to heat emissions in final spent fuel wastes, so removing Am will help to reduce the size of a deep geological storage.[1,2] Moreover, Cm reprocessing would be difficult to implement due to very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. Hence, one of the strategies considered is to recycle Am alone and leave Cm with vitrified fission products (FP). A hydrometallurgical process, called EXAm, was thus developed at the CEA to separate Am from a PUREX raffinate (Scheme 1).[3] Am is separated from curium in the extraction section using a mixture of HDEHP (di-2-ethylhexylphosphoric acid) and DMDOHEMA (N,N'-dimethyl-N,N'-dioctyl-hexyloxyethyl-malonamide) diluted in TPH. This separation is very challenging

since Am and Cm have very close physico-chemical properties. The DMDOHEMA extractant has a low selectivity for Am versus Cm ($SF_{Am/Cm} = 1.6$). Hence, the water soluble complexing agent TetraEthylDiglycolAmide (TEDGA) was added into the feed solution and at the scrubbing step to improve the Am/Cm selectivity ($SF_{Am/Cm} = 2.5$) and hence, to reduce the number of theoretical separation stages. Americium is finally selectively stripped from light lanthanides using a hydrophilic polyamino-carboxylate complexing agent at low acidity. Additional steps are necessary to strip Molybdenum and finally lanthanides and iron from the solvent.

The feasibility of this process was already demonstrated during pilote scale tests on a genuine PUREX raffinate in hot cells in ATALANTE facility.[4] In order to improve the compactness of the process and future plan associated, further studies were necessary to adapt the flowsheet and reduce the volume of effluent waste.



Scheme 1: Simplified flowsheet of the EXAm process

2. CHEMISTRY OF TEDGA AT HIGH ACIDITY (Am EXTRACTION)

The chemistry of the {lanthanides-TEDGA-DMDOHEMA-HDEHP} extraction system at high acidity was already studied and modelled.[5] TEDGA has a higher affinity for heavy lanthanides and curium maintaining them preferentially in the aqueous phase, whereas light lanthanides and americium are extracted by the EXAm solvent in the organic phase. The combination of DMDOHEMA and TEDGA allows to reach a Am/Cm separation factor close to 2.5.

Although TEDGA is a water-soluble complexing agent, its partial transfer to the solvent during the extraction process has to be taken into account. It is most probable that mixed species are formed in the organic phase with TEDGA and extractants DMDOHEMA and HDEHP. According to a recent complexation study[6] which indicates the preferential formation of 1:1 and 1:2 Ln:TEDGA complexes for the lighter lanthanides in the aqueous phase, it was concluded that such complexes are extracted into the organic phase, whereas heavier lanthanides and Cm should mainly form non-extractable 1:3 species.

To summarize, all extraction mechanisms that should be taken into account to describe the extraction of HNO_3 , TEDGA and Ln or An(III) cations in the EXAm process (at high acidity) are depicted in Figure 1. Distribution of TEDGA is a key

point of the process as it impacts the extraction properties, the Am/Cm selectivity and the solvent loading capacity. A thermodynamical model was developed to simulate all cations distribution in this step of the process and it takes into account more than 50 equilibria. [5]

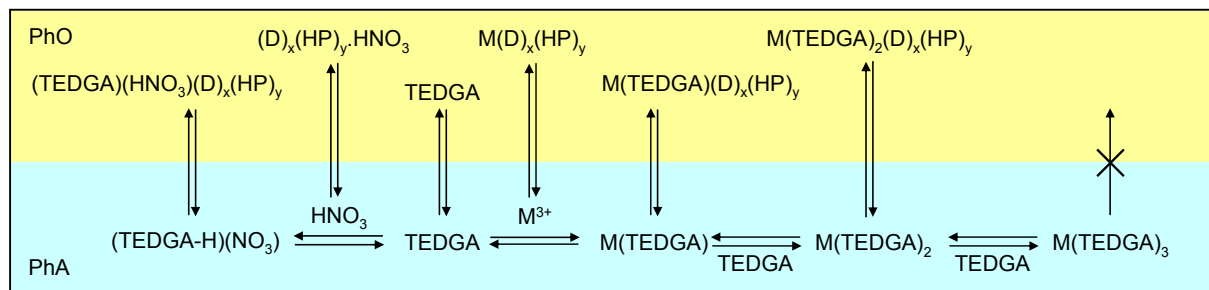


Figure 1: Schematic view of complexation equilibria and extraction mechanisms involving TEDGA in the biphasic system DMDOHEMA (D), HDEHP (HP) / HNO_3 , TEDGA, Ln/An (M)

3. INFLUENCE OF HIGH METAL LOADING ON Am/Cm SEPARATION

A classical PUREX UOx3 raffinate (corresponding to a 60 GWj/t fuel) contains around 20 mM of lanthanide cations (40 mM of fission products in total). In order to reach a concentration factor as high as possible, batch experimental data were acquired with an increasing concentration of lanthanides ($[TEDGA]_{tot} = 150\text{mM}$ and $[HNO_3] = 5.5\text{M}$) up to a concentration of the raffinate by a factor 15. As observed in Figure 2, an important decrease of the Am/Cm separation is observed when the total concentration of lanthanides gets higher. In fact, the Am/Cm selectivity in the system is ruled by the Cation/TEDGA ratio. To maintain the selectivity, it is thus necessary to increase the concentration of TEDGA as we increase the cation concentration.

Unfortunately, with a higher concentration of TEDGA (220mM and 340mM), a 3rd phase is formed (Table 1) with the solvent HDEHP 0.3M + DMDOHEMA 0.6M in TPH. This phenomenon could be due to the formation of ternary species Ln-TEDGA-DMDOHEMA when TEDGA is extracted in the organic phase, with a lower lipophilicity compared to Ln-DMDOHEMA complexes. To overcome this problem, the concentration of HDEHP was increased to 0.45M. As observed in Table 1, this is a good way to prevent demixion. But nevertheless, HDEHP concentration cannot be further increased or it will then be difficult to strip Am with DTPA. Finally, the PUREX raffinate could not be concentrated more than 3.5 times to maintain good process performances,.

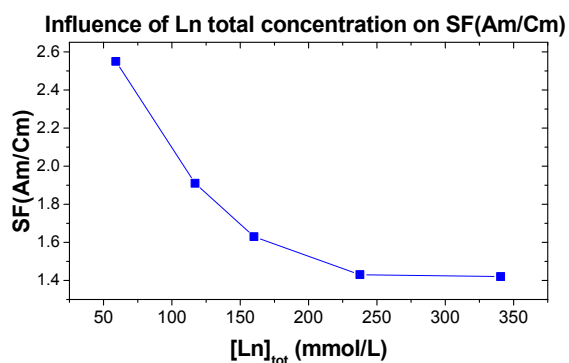


Figure 2: Influence of the total concentration of lanthanides on the Am/Cm separation factor. Solvent: HDEHP 0.3M + DMDOHEMA 0.6M in TPH, pre-equilibrated with HNO_3 5.5M with ^{241}Am and ^{244}Cm radiotracers and $[TEDGA]_{tot} = 150\text{ mM}$

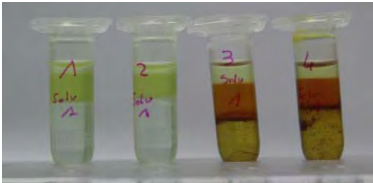
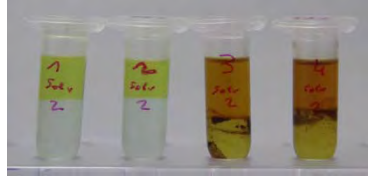
Conditions* [TEDGA] mM	Am Extraction		Cm Scrubbing	
	1	2	3	4
	220	220	340	340
Phases at equilibrium after contact with HDEHP 0.3M + DMDOHEMA 0.6M				
Phases at equilibrium after contact with HDEHP 0.45M + DMDOHEMA 0.6M				

Table 1: Impact of HDEHP concentration on 3rd phase formation. [HNO₃]=5M.

* Conditions 1 :
[Ln] (from La to Gd) = 10 mM, [Zr]=1.5 g/L, [TEDGA]=220mM
Conditions 2 :
[Ln] (from La to Gd) = 15 mM, [Zr]=1.5 g/L, [TEDGA]=220mM
Conditions 3 :
[Ln] (from La to Nd) = 20 mM, [Mo]=2.6 g/L, [Fe]=1.2g/L, [Pd]=2.9g/L, [TEDGA]=340mM
Conditions 4 :
[Ln] (from La to Nd) = 25 mM, [Mo]=2.6 g/L, [Fe]=1.2g/L, [Pd]=2.9 g/L, [TEDGA]=340mM

4. INFLUENCE OF TEDGA ON STRIPPING STEPS AT LOW ACIDITY

Since the concentration of TEDGA has to be increased to maintain a good Am/Cm separation in the first step of the process, the amount of TEDGA following americium and light lanthanides in the organic solvent is higher. As a consequence, the influence of TEDGA on “Molybdenum scrubbing” and “Am stripping” steps at low acidity was studied (Figure 3). An increase of TEDGA has no impact on Mo(VI) back extraction, but induces an important leak of americium (*left* Figure). Moreover, during selective stripping of Am with DTPA (diethylene-triamine-pentaacetic acid), TEDGA would compete with DTPA and decrease Am stripping performances with a lower Ln/Am selectivity (as seen in the *right* Figure with Eu).

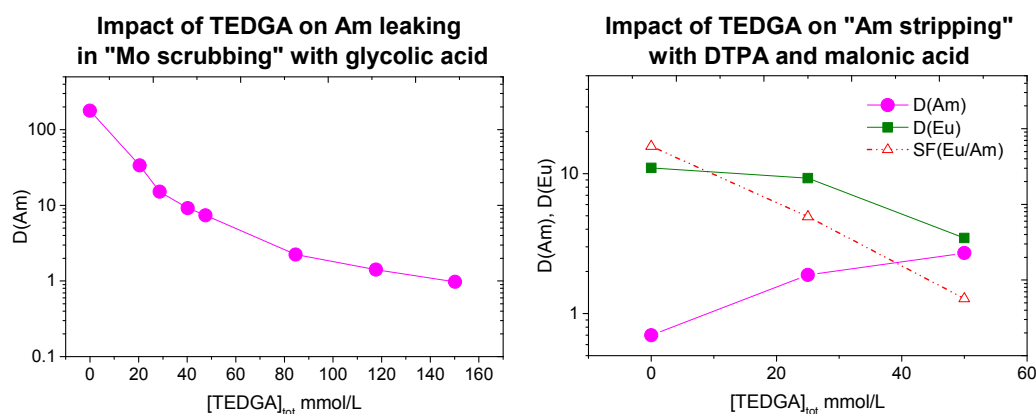


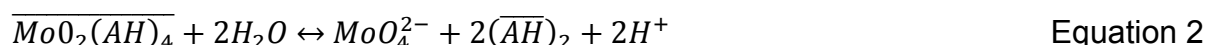
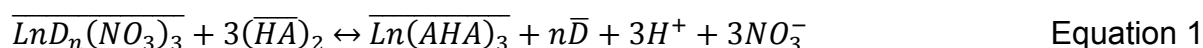
Figure 3 : (left) ²⁴¹Am distribution ratios during “Mo scrubbing” with the scrubbing solution glycolic acid 0.5M at pH 3 and 40m of Nd (to simulate other lanthanides); (right) distribution ratios of ²⁴¹Am and ¹⁵²Eu during back extraction of Am with DTPA 30mM and malonic acid 0.3M adjusted to pH 2.5 with hydroxylamine. Solvent HDEHP 0,45M + DMDOHEMA 0,6M in TPH.

Regarding those data, removing TEDGA from the organic phase prior to Mo and Am stripping steps appears to be a critical step to ensure selective and total recovery of Am from the solvent. As a consequence, few stages of mixer-settlers were added between “Cm scrubbing” and “Mo scrubbing” batteries where TEDGA was scrubbed with HNO₃ 4 M. This nitric acid concentration was chosen to avoid perturbations in

the “Cm scrubbing” section and obtain less than 10 mM of TEDGA in the organic phase.

5. INFLUENCE OF HIGH METAL LOADING ON “M₀ SCRUBBING”

Molybdenum has to be selectively stripped from the organic solvent right before the “Am stripping” step or it will be back-extracted together with Am due to its affinity for DTPA complexing agent. Mo is stripped selectively from americium and other cations using a α -hydroxy-carboxylic acid complexing agent at low acidity. This transition between “Am extraction” at high acidity and “Mo scrubbing” at low acidity is challenging because it is necessary to neutralize protons arriving with the loaded solvent with a flow of concentrated NaOH (Figure 4). The pH range to achieve is narrow: between 2.5 (to ensure Mo stripping) and 4 (to prevent from lanthanide hydroxides precipitation). During one of the first cold lab-scale tests performed in mixer-settlers with a simulated concentrated feed solution of fission products, important problems of pH stabilization were observed. As reported in Figure 4, the pH fluctuations in the Mo scrubbing battery (LX-LS) were important with glycolic acid 0.5M used as stripping/buffering solution. As a consequence, it was impossible to efficiently strip Mo. To overcome this phenomenon, which was not observed with lower concentrations of cations, it was important to better identify sources of protons to be neutralized directly at the introduction of the loaded solvent. Three sources of protons were identified: nitric acid extracted by DMDOHEMA during the previous “Am extraction” at high acidity, protons of HDEHP released according to Equation 1, protons released during Mo back extraction due the formation of Mo anionic species according to Equation 2.



D=DMDOHEMA, AH=HDEHP, n=2 or 3

With high concentrations of cations, a slight fluctuation in loaded solvent flow rate or cation composition will induce an important change in pH due to protons release according to those chemical equilibria. As a consequence, the buffering effect is very important and glycolic acid was not a good candidate anymore in those conditions. Despite its non-negligible affinity for Am, citric acid was then chosen because it has a pKa (2.8) closer to the optimal pH range (2.5-3.5) than glycolic acid (3.8). A thermodynamical model was developed to simulate Mo, Am and light lanthanides distribution and implemented in the PAREX simulation code.[7] Moreover, conditions of NaOH introduction and mixer-settlers parameters were optimized leading to a significant improvement of pH control. Indeed, during the last pilot test (EXAmCo6, February 2013), pH was close to 3 in all stages at equilibrium (Figure 5), and Mo was quantitatively stripped from the solvent. At the end of this test, samples of organic and aqueous phases in all stages were sampled, spiked with ²⁴¹Am and re-contacted to obtain the Am distribution profile Figure 5. According to distribution ratios, Am

should be correctly re-extracted in the first stages of the LX battery providing from any leak in the Mo raffinate.

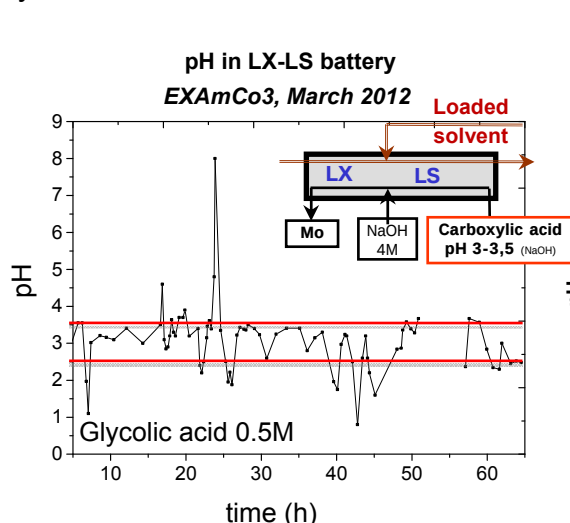


Figure 4: Problems of pH stabilization in “Mo scrubbing” battery during pilot scale test in mixer-settlers (March 2012, EXAmCo3) with glycolic acid (0.5M).

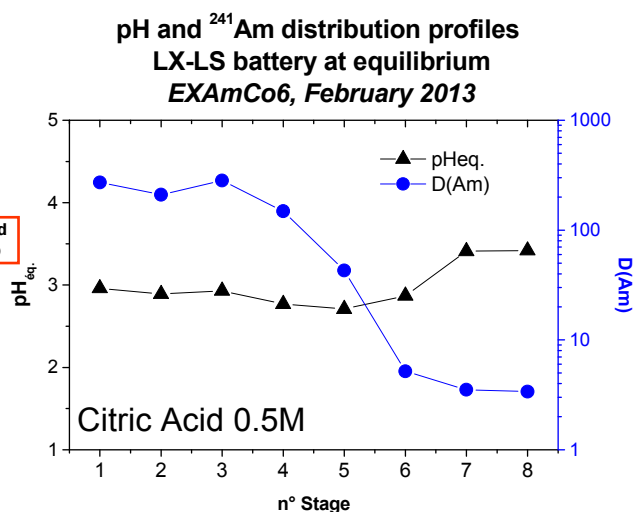


Figure 5: pH and ^{241}Am distribution profiles at equilibrium in the “Mo scrubbing” battery during pilot scale tests in mixer-settlers (February 2013, EXAmCo6) with citric acid (0.5M).

6. CONCLUSION

In order to adapt the EXAm process to higher concentrations of cations, it was first necessary to increase the concentration of HDEHP (from 0.3 to 0.45 M) to improve solvent loading capacity and avoid third phase formation. Nevertheless, the highest concentration factor of the feed solution achievable appeared to be 3.5 (compared to a UOx3 PUREX raffinate). To keep a high Am/Cm selectivity, the concentration of TEDGA complexing agent had to be increased, impacting the following stripping steps. As a consequence, additional stages were dedicated to TEDGA scrubbing with nitric acid 4 M to limit to 10 mM the concentration of TEDGA co-extracted with Am and light lanthanides in the organic phase. Nevertheless, important optimizations were still necessary on the “Mo scrubbing” step where important pH fluctuations were observed due to cation/proton exchanges. The buffering capacity is thus very important and citric acid was chosen as a selective complexing/buffering agent. Thermodynamical models were implemented in the PAREX code to predict Am, Cm, Ln but also Mo and other fission products behavior in all stages of the process at high and low acidity. With these improvements, the complete EXAm flowsheet will now be tested in ATALANTE facility hot laboratories on a surrogate raffinate containing small amounts (milligram scale) of ^{241}Am and ^{244}Cm .

[1] Poinssot, C.; Rostaing, C.; Greandjean, S.; Boullis, B. *Procedia Chem.* 2012, 7, 349–357.

[2] Rostaing, C.; Poinssot, C.; Warin, D.; Baron, P.; Lorraina, B. *Procedia Chem.* 2012, 7, 367–373.

[3] X. Heres, P. Baron, Patent WO2012069573 (2010).

[4] Bollesteros M.-J., Calor J.-N., Costenoble S., Montuir M., Pacary, C. Sorel V., Burdet F., Espinoux D., Heres X., Eysseric C. *Procedia Chem.* 2012, 7, 178-183.

[5] Pacary V., Burdet F., Duchesne M.-T. *Procedia Chem.* 2012, 7, 328-333

[6] Charbonnel M.-C., Miguiditchian M., Berthon C., Boubals N., Burdet F., Guilbaud P., Marie C. *Procedia Chem.*, 7, 20-26

[7] Vanel et al. ISEC 2014 Proceeding

Separation of trivalent actinides from lanthanides: Current progress and trends

*Terry A. Todd**¹

Summary

The separation of the trivalent actinides (americium and curium, or americium alone) from trivalent lanthanides is one of the most difficult challenges facing future advanced nuclear fuel cycles that involve partitioning and transmutation schemes. The chemical behavior of both actinides (III) and lanthanides (III) are very similar, making separation options complex and at best, difficult, particularly in a remotely operated nuclear operation. This problem has been the subject of broad research programs around the globe for the past decade and a half, involving the investigation of a number of concepts, yet a robust solution is still not evident. Within the last few years, many of the research programs appear to be converging on similar approaches and new concepts have emerged that appear to be promising. Most of these themes involve solvent extraction technology and include approaches that focus on simplification of processes, combination of processes into a single process, and separation of americium from curium and lanthanides.

Introduction

A number of advanced fuel cycle concepts are based on the partitioning of minor actinides, as well as uranium and plutonium, from the used fuel. The minor actinides would then be fabricated into new fuel or targets and burned in advanced thermal or fast reactors, or an accelerator driven system. The partitioning and transmutation concept, has been studied for several decades, and has two primary objectives: 1) significantly increase the utilization of the uranium resources used to fuel reactors and 2) by transmuting the minor actinides to stable or short-lived radionuclides, reduce the heat burden to a repository. The first objective could increase the overall utilization of uranium from the current once-through light water reactor fuel cycle of about 0.7 to greater than 90% for a multi-recycle fast reactor approach.^[1] This could mean that current uranium resources, estimated to be sufficient for approximately 100 years of light water reactor use, could be extended almost indefinitely with the use of fast reactors. It also significantly reduces the amount of uranium enrichment needed to support the multi-recycle approach, which helps lower potential proliferation risk. The large reduction in enrichment capability is offset, however, by the need for reprocessing/recycle capability. The second objective could enhance repository capacity and performance by removing the long-lived heat generating isotopes from the waste packages destined for a geologic repository. Short-term heat generating isotopes would likely require the high-level waste packages to be cooled for 60-90 years before placement in a repository, to benefit from the reduction in the long-term heat load. The processing of the fuel also provides the benefit of being able to place the radionuclides remaining in the fuel in a robust waste form, which will have a much better long-term performance than the used fuel itself. It

^{*1} Terry A. Todd, Idaho National Laboratory, Idaho Falls, Idaho, USA; terry.todd@inl.gov

should be noted that there has been much discussion about the reduction in radiotoxicity of the used nuclear fuel (or waste products from processing) due to recycle and transmutation of the actinides, particularly the minor actinides. While the reduction in radiotoxicity is valid, it does not reduce the need for a geologic repository or the time necessary for the waste to be isolated. It also does not affect most of the long-lived elements that dominate the dose in repository models (e.g. I-129, Tc-99, Cl-36, Se-79, etc).

Separation of the uranium and plutonium from used nuclear fuel is well known and has been practiced at industrial scale for over 60 years. Utilizing a well characterized extractant, tri-butyl phosphate (TBP), high degrees of recovery and purity of uranium and plutonium can be achieved using the PUREX process. A number of process variations have been developed, to extract only uranium (e.g. UREX, GANEX-1), and others that co-extract uranium and plutonium and strip a mixture of uranium and plutonium, rather than pure plutonium (e.g. COEX[®], NUEX). By careful adjustment of valence state, neptunium can be extracted and recovered with the uranium and plutonium. The greatest separations challenge for multi-recycle approaches is the separation of the trivalent minor actinides (Am, Cm) from the lanthanides, or (even more difficult) the separation of americium alone from curium and the lanthanide elements. This challenge has been the subject of extensive research programs around the world for the past two decades. Numerous technologies have been tested at laboratory scale; however, no technologies have progressed to a stage of engineering-scale development. European and U.S. programs appear to have a number of common themes, such as emphasis on process simplification and development of more robust processes that do not rely on precise pH control of highly-radioactive feed solutions.

Separation of Trivalent Actinides from Lanthanides

Two similar approaches to the separation of the trivalent actinides from lanthanides were developed independently in the U.S. and France in the last 20 years. The U.S. approach involved two processes, the first to separate trivalent actinides and lanthanides from the transition metals, then a follow-on step to separate the trivalent actinides from the lanthanides. The first process was the TRUEX process, which utilizes a bifunctional neutral extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).^[2] The second process was the TALSPEAK process, which utilizes an acidic extractant bis-(2-ethylhexyl)phosphoric acid (HDEHP).^[3] The TRUEX-TALSPEAK combination was tested successfully at laboratory-scale in 2-cm centrifugal contactors at Argonne National Laboratory in 2005 and 2006, where Pu and Np were removed with the trivalent actinides following a UREX process to removal uranium. In 2007 a similar test was completed where U, Np, and Pu were removed before the TRUEX-TALSPEAK processes.^[4] Finally, another laboratory-scale demonstration was performed in lab-scale mixer-settlers at the Oak Ridge National Laboratory, where the TRUEX-TALSPEAK process was performed on a feed after separation of U, Np, and Pu.^[5] Although the TRUEX-

TALSPEAK process was successfully demonstrated several times at laboratory scale, the strong dependence of distribution coefficients of the actinides and lanthanides on pH, and the lack of understanding of the fundamental process chemistry would make this process difficult to run in a large-scale nuclear plant operation.

The French approach also involved two sequential processes to separate trivalent actinides and lanthanides from the transition metals, then a follow-on step to separate the trivalent actinides from the lanthanides. The first process was the DIAMEX process which uses a malonamide extractant, dimethyl-dioctyl-hexaethoxymalonamide (DMDOHEMA).^[6] The second process was the SANEX (Selective Actinide Separation) process, which represents a class of similar processes used to selectively separate the trivalent actinides from lanthanides. An early version of the SANEX process utilized *Bis*-triazinyl-pyridine (BTP), as the extractant. This process was successfully tested at the laboratory scale at the Commissariat à l'énergie atomique et aux énergies alternative (CEA) Marcoule facility in 1999, however, development work was focused on other extractants, as the BTPs were not very radiation resistant.^[7] A follow on version of the SANEX process included one using the DMDOHEMA extractant, along with the HDEHP extractant to separate Am and Cm. This process was demonstrated at the laboratory scale, at the CEA Marcoule facility in 2005.^[8]

Until the mid-2000s the focus in both the U.S. and France was on a two-step process for minor actinide recovery. Engineering studies in the U.S. showed that the cost of additional extraction processes, along with the additional waste streams generated, significantly added to the cost of a closed fuel cycle. This helped shift the emphasis in the U.S. to developing simpler, more robust approaches for the recovery of the actinides. A similar emphasis was made in the European Union Framework R&D programs such as ACSEPT and now SACSESS.

The U.S. is studying a number of approaches that employ selective complexation of trivalent actinides over lanthanides, including mixed donor extractants, and a single-step approach to replace the TRUEX-TALSPEAK approach, called ALSEP (Actinide-Lanthanide Separations). In the European Union, similar approaches are being employed as a single-step approach with the development of innovative SANEX, 1-cycle SANEX and also some GANEX (Group Actinide Extraction) approaches. Many of these recent developments in minor actinide separation take advantage of diglycolamide derivatives, which were originally developed in Japan.^[9]

The ALSEP approach combines both neutral and acidic extractants into a single solvent. The ALSEP solvent consists of *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester HEH[EHP] in *n*-dodecane. Separation factors between Am and lanthanides range from about 15-20 and are relatively insensitive to pH in the range of 2.5-4.^[10]

The innovative SANEX approach utilizes *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA) to co-extract trivalent actinides and lanthanides, then employs a water soluble BTP or *Bis*-triazinyl-bipyridine (BTBP) compound to selectively strip the trivalent actinides from the lanthanides.^[11] This process has the advantage of extracting the actinides and lanthanides at molar concentrations of nitric acid, avoiding the need to control pH of highly radioactive streams. It also has relatively fast extraction kinetics. Actinide stripping is achieved with dilute (0.3-0.4 M) nitric acid, containing the BTP compound.^[12]

The 1-cycle SANEX approach utilizes TODGA and 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]-triazin-3-yl) [2,2']-bipyridine (CyMe₄-BTBP) to selectively extract trivalent actinides from lanthanides.^[13] A flowsheet was developed and tested on simulated feed solutions in laboratory-scale centrifugal contactors. Results of the test were successful in demonstrating the 1-cycle SANEX concept, but some process optimization is needed to improve extraction kinetics and remove irreversibly extracted elements (e.g. Ni, Cu, Cd).^[14]

There has also been a recent trend to investigate the separation of americium from curium and the lanthanides. This approach may make fuel fabrication of the transmutation fuel easier, and the curium isotopes have relatively short half lives, but there certainly isn't an international consensus on whether it is advantageous to separate americium alone. From the U.S. perspective, it is thought that adding an additional process to separate americium from curium after the two elements have already been separated from the lanthanides, would likely not be cost effective. The approaches that are being pursued by the U.S. and European programs all involve a single process in place of those previously mentioned for actinide (III) separation.

The U.S. approach is primarily focused on exploiting the higher valence states of americium, primarily Am (VI). Studies have shown that americium can be oxidized to Am (VI) from Am (III) effectively by sodium bismuthate, and extracted using TBP or Diamylamyl phosphonate (DAAP).^[15] Unfortunately, sodium bismuthate is a solid and has a low solubility in acidic solutions, so to be effective, it requires an excess of solid sodium bismuthate. Once oxidized to Am (VI) the americium will begin to be reduced in a matter of minutes (~5-10 minutes). The key to developing a successful Am (VI) extraction process will be to find a more effective oxidant, if one exists (to both oxidize and hold Am in hexavalent state). If an acceptable oxidant is found, this opens up the possibility of a single process to extract U, Np, Pu and Am, which could be a significant development.

A novel americium extraction (EXAm) process has been developed by the CEA. The process uses a solvent containing DMDOHEMA and HDEHP extractants and Am/Cm selectivity is increased by the use of an aqueous soluble complexant *N,N,N',N'*-tetraethyldiglycolamide (TEDGA). Americium stripping is performed with *N*-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) in a buffered solution containing citric acid to facilitate separation of the americium from the light

lanthanides. The process was tested with radioactive feed (after removal of U and Pu) in laboratory-scale equipment at the Marcoule facility in 2010. Americium recovery of 98.5% was achieved with a decontamination factor from Cm of about 500.^[16] Development and demonstration of this process represent a significant achievement, however, the process is complex and will require much more development and optimization to be useful in a large-scale facility.

Summary

Significant progress has been made in the separation of trivalent actinides from lanthanides in the past decade in research programs around the world. There is a very strong common theme of simplifying separation processes and making them more robust (e.g. operating extraction sections at molar nitric acid concentrations rather than in narrow pH ranges). In the context of simplification, both US and European programs have made progress in moving from two-step processes to a single-step process to separate trivalent actinides from lanthanides. However, while the number of process steps may be reduced, the chemistry of a single-step process may be far more complex than multiple-step processes. There are certainly trade offs that need to be evaluated to determine if the reduction in process steps is an improvement or not. The recent development of diglycolamides as extractant molecules and hydrophilic complexants, as well as bipyridine hydrophilic complexants, is evident in many of the new processes under investigation.

References

1. Bayes, S.E., Piet, S.J., Soelberg, N.R., Lineberry, M.J. and Dixon, B.W. Technology Insights and Perspectives in Nuclear Fuel Cycle Concepts, Idaho National Laboratory, INL/EXT-10-19977, September 2010.
2. Horwitz, E. P.; Kalina, D. G.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. The TRUEX Process – A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent. *Solvent Extr. Ion Exch.* **1985**, 3, 75-109.
3. Weaver, B., Kappelmann, F.A. Preferential Extraction of Lanthanides over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and by Mixtures of Carboxylic and Aminopolyacetic Acids, *J. Inorg. Nucl. Chem.* **1968**, 30, 263-272.
4. Pereira, C., et al. Lab-scale Demonstration of the UREX+1a Process using Spent Fuel, Proceedings of Waste Management Symposium 07, Tucson, AZ, February 2007.
5. Jubin, R.T., Collins, E.D., Felker, L.K., Spencer, B.B., Walker, E.A., Vedder, R.J., Taylor, R.D., Binder, J.L. CETE R&D at Oak Ridge National Laboratory Supporting Management of Nuclear Waste, Proceedings of Waste Management Symposium 09, Phoenix, AZ, March 2009.

6. Bisel, I., Nicol, C., Charbonnel, M. C., Blanc, P., Baron, P., Inactive DIAMEX Test with the Optimized Extraction Agent DMDOHEMA, proceedings of Fifth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mol, Belgium, November 1998.
7. Hill, C., Guillaneux, D., Berthon, L. SANEX-BTP Process Development Studies. Proceedings of the International Solvent Extraction Conference, ISEC 2002, K.C. Sole, P.M. Cole, J. S. Preston, and D. J. Robinson, ed., Capetown, South Africa, 2002.
8. Warin, D. Future Nuclear Fuel Cycles: Prospect and Challenges for Actinide Recycling. Actinides 2009, IOP Conference Series: Materials Science and Engineering 9, 2010. doi:10.1088/1757-899X/9/1/012063.
9. Sasaki, Y., Sugo, Y., Suzuki, S. Tachimori, S. The Novel Extractants, Diglycolamides, for the extraction of Lanthanides and Actinides in HNO₃-n-dodecane System, Solvent Extr. Ion Exch. 2001, 19,(1), 91-103.
10. Lumetta, G.J., Levitskaia, T.G., Rapko, B.M., Carter, J.C., Gelis, A.V. Development of the Actinide-Lanthanide Separation (ALSEP) Process. Proceedings of the International Solvent Extraction Conference, ISEC 2014, Würzburg, Germany, 2014.
11. Geist, A., Müllich, U., Magnusson, D., Kaden, P., Modolo, G., Wilden, A. Actinide(III)/lanthanide(III) Separation via Selective Aqueous Complexation of Actinides (III) using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-Yl)-Pyridine in Nitric Acid, Solvent Extr. Ion Exch. **2012**, 30,(5), 433-444.
12. Magnusson, D., Geist, A., Malmbeck, R., Modolo, G., Wilden, A. Flow-sheet Design for an Innovative SANEX Process using TODGA and SO₃-Ph-BTP. Procedia Chemistry, 7 (2012), 245-250.
13. Geist, A., Hill, C., Modolo, G., Foreman, M.R.S.J., Weigl, M., Gompper, K., Hudson, M.J., Madic, C. 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]-triazin-3-yl)[2,2']-bipyridine, an Effective Extracting Agent for the Americium (III) and Curium (III) from the Lanthanides. Solvent Extr. Ion Exch. **2006**, 24,(4), 463-483.
14. Wilden, A., Modolo, G., Schreinemachers, C., Sadowski, F., Lange, S., Sypula, M., Magnusson, D., Geist, A., Lewis, F., Harwood, L., Hudson, M. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe₄BTBP and TODGA as 1-Cycle SANEX Solvent Part III: Demonstration of a Laboratory-Scale Counter-Current Centrifugal Contactor Process. Solvent Extr. Ion Exch. **2013**, 31,(5), 519-537.
15. Martin, L.R., Mincher, B.J., Schmitt, N.C. Extraction of Am(VI) with a neutral organophosphorous ligand. *J. Radioanal. Nucl. Chem.* **2009**, 282, 523-526.
16. Warin, D. Recent Progress in Advanced Actinide Recycling Processes, OECD 11th Information Exchange Meeting on Partitioning and Transmutation, San

Francisco, CA, November 2010. https://www.oecd-neo.org/pt/iempt11/documents/IV-3_IEMPT11_Warin_031110.pdf

Synthesis and characterization of a new N-donor ligand for An(III)/Ln(III) separation

Julie M. Muller¹, Kenneth L. Nash¹*

A novel N-donor extractant for An(III)/Ln(III) separation, 6,6'-bis(1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine (EH-BTzBP) has been synthesized and its extraction performance tested. The ligand does not extract metal nitrates from acidic solutions, but was found to extract Am(III) with high separation factor over Ln(III) in the presence of the lipophilic co-extractant 2-bromohexanoic acid (HA). The synergistic system was found to efficiently extract Am(III) at < 0.1 M HNO₃; back-extraction can then be completed at higher nitric acid concentration. The ligand/extractant combination shows good solubility in toluene, fast phase transfer kinetics, resistance to acid hydrolysis and possibly to oxidizing agents created by radiolysis. The results of this analysis can be used to improve understanding and to direct the synthesis of additional novel N-donor extractant systems.

Introduction

To make used nuclear fuel safe and suitable for geological storage, its waste must be reprocessed. The sixty-year-old PUREX process offers a highly efficient approach to recycling reusable U and Pu. However, the raffinate from PUREX still contains significant quantities of the minor actinides (Am and Cm) and fission product lanthanides. The highly radiotoxic and long lived actinides could be transmuted into shorter-lived isotopes in fast neutron spectrum reactors. However the presence of the lanthanides limits the efficiency of this process due to the high neutron capture cross-sections of several members of the Ln series. To efficiently transmute minor actinides, it is essential to reduce the lanthanide content of any transmutation targets.

Separation of An(III) from Ln(III) is a complex task due to the prevalence of the trivalent oxidation state and similar ionic radii. One approach to accomplish An(III)/Ln(III) separation is through the use of soft N-donor ligands. Such polydentate ligands have been shown to exhibit a greater selectivity for the slightly softer actinides over the lanthanides.^{1,2} Several well-studied extractants such as bistriazinylpyridine (BTPs) and bistriazinylbipyridine (BTBPs) ligands have shown high selectivity for An(III) over Ln(III). Unfortunately, this class of ligands also suffer from important limitations such as low solubility, slow kinetics, difficult back-extraction or instability in contact with concentrated nitric acid or in a radiation field.³

In an attempt to overcome some of these drawbacks, new N-donor tetradentate ligands containing a bipyridine core substituted with 1,2,3-triazole rings have been synthesized and tested. The hypothesis of this work is that 1,2,3-triazole rings should be more resistant to acid hydrolysis and radiolytic degradation due to their strong basicity and the high stability of the π -conjugation of the 5-membered ring than the

*¹ Washington State University, Department of Chemistry P.O. Box 644630, Pullman, WA 99164-4630, email: julie.muller@wsu.edu

analogous 1,2,4-triazines. The synthesis, characterization and synergistic extraction performance of 6,6'-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-2,2'-bipyridine (EH-BTzBP) is presented in this paper.

Experimental

All reagents were purchased from Sigma-Aldrich, Acros or TCI America with purity better than 98% and used as received. All solvents were ACS or HPLC grade, supplied by Fischer or Acros.

Synthesis

The ligand was synthesized in two steps starting from 6,6'-dibromo-2,2'-bipyridine which was coupled with (trimethylsilyl)acetylene through the Sonogashira reaction.⁴ The 6,6'-bis(trimethylsilyl-ethynyl)-2,2'-bipyridine was then deprotected and coupled with 2-ethylhexylazide in a single step using Cu(I)-catalyzed Huisgen 1,3-cycloaddition⁵ to form the desired product with an overall yield of 64%. EH-BTzBP was shown by proton NMR to be free of impurities (> 99% pure).

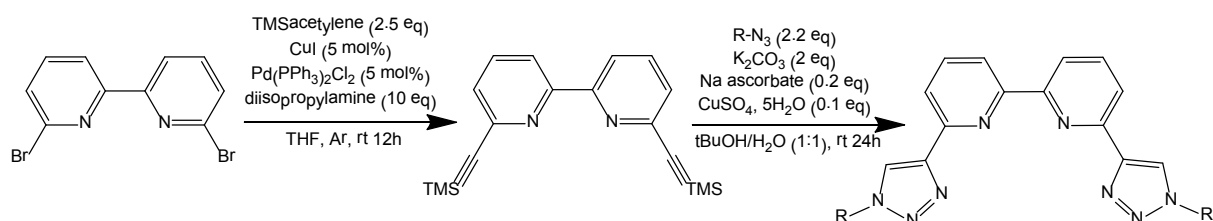


Figure 1: Synthesis of 6,6'-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-2,2'-bipyridine, with $R = 2\text{-ethylhexyl}$

Solvent Extraction

Solvent extraction experiments were conducted using organic phases containing the extractant EH-BTzBP and 2-bromohexanoic acid (HA) dissolved in toluene. All samples were prepared by mass. Aqueous phases were comprised of variable nitric acid concentration at appropriate p*H* with an ionic strength of 1.0 M H/NaNO₃. Radiotracers ¹⁵²⁻¹⁵⁴Eu and ²⁴¹Am were used to monitor metal distribution. Extractant phases were pre-equilibrated before contacting with metal-containing aqueous phases (0.5 mL each). Samples were mixed for 15 minutes by vortex (unless noted otherwise) followed by 10 minutes of centrifugation for phase separation. 200 μ L aliquots of each phase were collected for γ -counting on a Packard Cobra-II Auto-Gamma counter. For the extraction of non-radioactive lanthanides (La to Lu except Pm), aqueous solutions were spiked with 10 μ L of a stock solution of 1 mM of each Ln in HNO₃ 0.001 M. Portions of 100 μ L of the initial aqueous phase and 200 μ L of the aqueous phase after equilibrium were diluted in 5 mL HNO₃ 2% for ICP-MS analysis.

Results and Discussion

Solvent Extraction

The extraction of Am(III) and Eu(III) by EH-BTzBP is presented in Figure 2. Though it exhibited good solubility in toluene (up to 0.1 M), EH-BTzBP was found not to efficiently extract Am(III) and Eu(III) nitrates by solvation from nitric acid aqueous phases ($D_M < 0.5$). Addition of a lipophilic anion as phase transfer agent, 2-bromohexanoic acid (HA), made the extraction possible at $\text{HNO}_3 < 0.1 \text{ M}$ with a separation factor of approximately 70 for Am(III) over Eu(III). Extraction decreases with increasing HNO_3 which is consistent with a cation-exchange mechanism driven by HA in this synergistic system ($D_M < 0.1$ for 1.0 M HA at pcH 3). Assuming that the predominant form of HA in toluene is the dimer $((\text{HA})_2)$, the following equilibrium is considered:

(1)

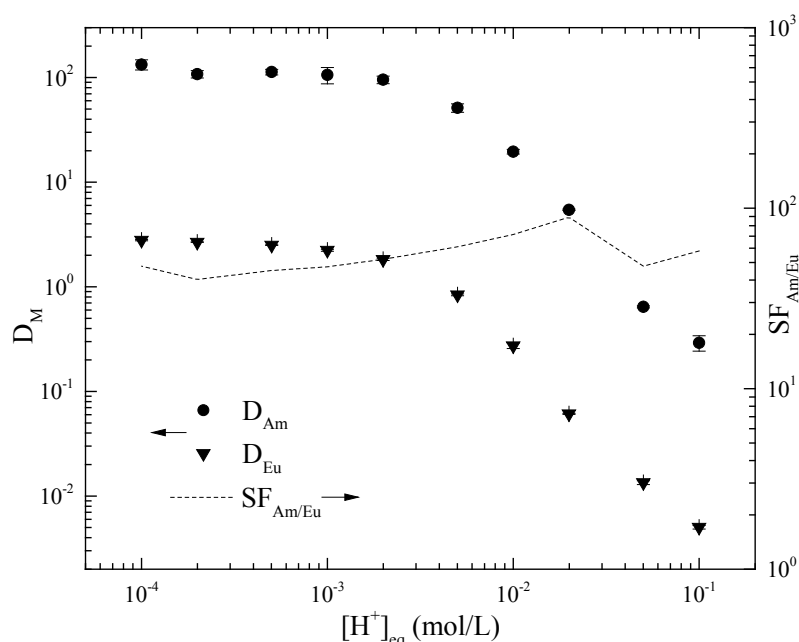


Figure 2: Extraction of Am(III) and Eu(III) as a function of acidity. Organic phase: 0.01 M EH-BTzBP + 1 M 2-bromodecanoic acid in toluene. Aqueous phase: Traces of $^{241}\text{Am(III)}$ and $^{152}\text{Eu}/^{154}\text{Eu(III)}$ in 1.0 M (H, Na, NO_3).

Some BTBP extractants have encountered difficulties in stripping post-extraction due to strong extraction. This is a problem because eventual recovery of the separated actinides in an aqueous solution is necessary in an industrial process. In the synergistic system 0.01 M EH-BTzBP / 1.0 M HA, stripping of the extracted metallic cations can be readily performed at 1.0 M HNO_3 .

Slope Analysis

Slope analysis was done as a function of [EH-BTzBP] and [HA] to establish the stoichiometry in the above equilibrium (Equation 1). The results of this slope analysis experiment are presented in Figure 3. A slope of 1.5 was obtained for the EH-BTzBP

dependency plot (Figure 3a), which suggests that either multiple extracted species are formed or association of organic ligands is occurring. The HA dependence plot (Figure 3b) gave slopes of approximately 3 which verify electro-neutrality of the complexes formed with trivalent metals and is consistent with Equation 1.

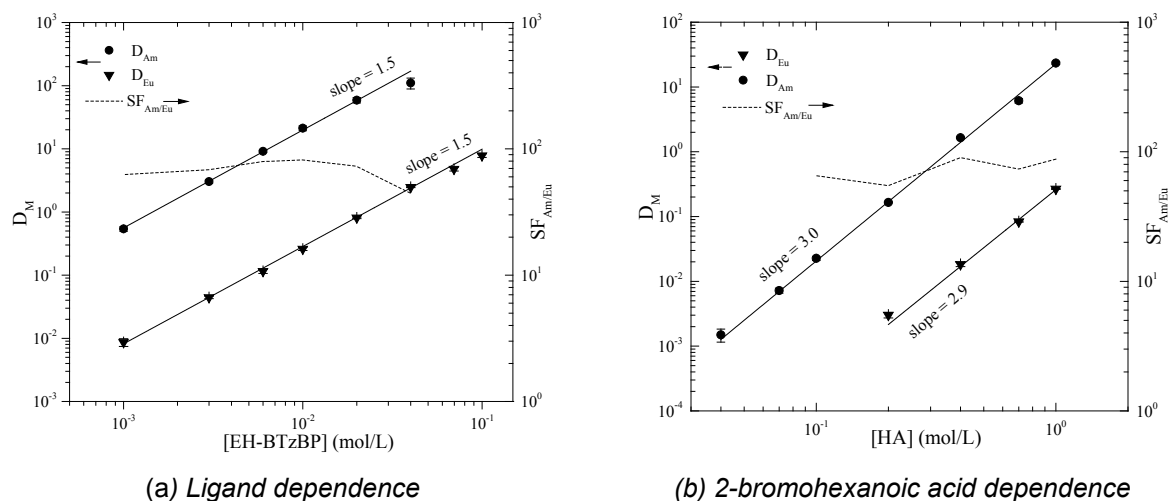


Figure 3: Extraction of Am(III) and Eu(III) as a function of EH-BTzBP or HA concentration. Organic phase: (a) EH-BTzBP + 1 M 2-bromohexanoic acid in toluene, (b). 0.01 M EH-BTzBP + 1 M 2-bromohexanoic acid in toluene Aqueous phase: Radiotracer $^{241}\text{Am(III)}$ and $^{152}\text{Eu}/^{154}\text{Eu(III)}$ in 1.0 M (H, Na, NO_3) at pCh 2.

Extraction of the Ln(III) series

Extraction experiments were performed with the lanthanide series (Ln = La-Lu, except Pm) to fully consider An(III)/Ln(III) separation (Figure 5). Extraction increases along the Ln series with increasing atomic number up to Ho(III), then declines slightly from Tm(III) through Lu(III). A group separation factor of 9 between Am(III) and Ho(III) was calculated. As the most important fission product lanthanides are La-Gd, lower separation factors for the heavy lanthanides is less troubling.

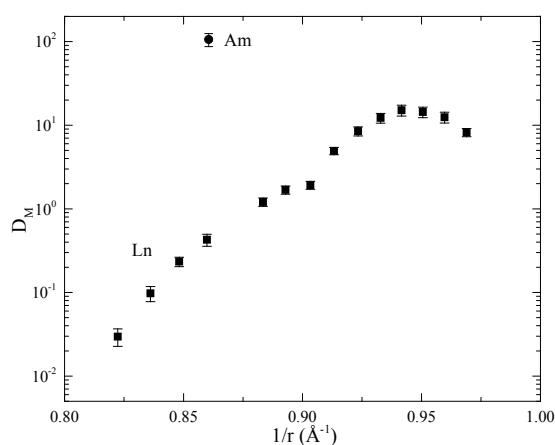


Figure 5: Extraction of the Ln(III) series and Am(III) as a function of their inverse ionic radii (CN = 9). Organic phase: 0.01 M EH-BTzBP + 1 M 2-bromohexanoic acid in toluene. Aqueous phase: 10^{-5} M of La-Sm and Eu-Lu in 1.0 M (H, Na, NO_3) at pCh 3, compared to Am(III) in the same conditions.

Kinetics

A major disadvantage of several N-donor ligands for process application is their slow phase transfer kinetics. EH-BTzBP/HA extraction kinetics were tested and results are shown Figure 6. The synergistic extraction system exhibits fast phase transfer kinetics with equilibrium reached in less than 5 min of mixing for both Am^{3+} and Eu^{3+} .

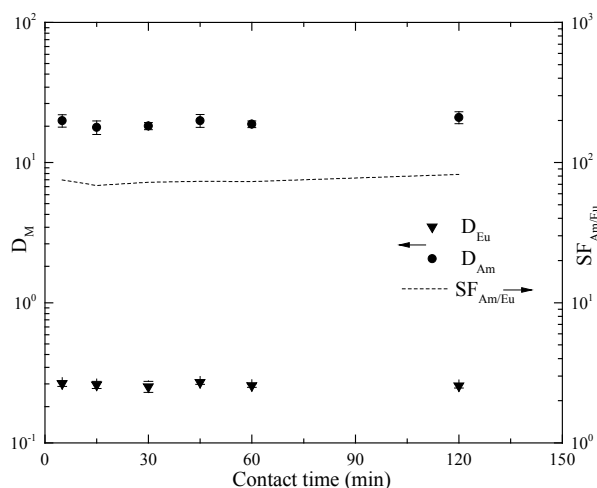


Figure 6: Extraction of Am(III) and Eu(III) as a function of contact time. Organic phase: 0.01 M EH-BTzBP + 1 M 2-bromodecanoic acid in toluene. Aqueous phase: Traces of $^{241}\text{Am}(\text{III})$ and $^{152}\text{Eu}/^{154}\text{Eu}(\text{III})$ in 1.0 M (H, Na, NO_3) at pH 2.

Stability of EH-BTzBP

Most N-donor ligands have a tendency to decompose in contact with HNO_3 and in a radiation field. Resistance of EH-BTzBP alone or in solution with HA was tested by contacting with 1 M HNO_3 or 0.1 M H_2O_2 for a period of 2 months. However, these conditions were found to have no effect on Am(III) and Eu(III) distribution ratios (Figure 7), or on the ligand ^1H NMR and FT-IR spectra. Contact of the ligand to 0.1 M H_2O_2 at 50°C for two weeks also was found not to affect the extraction. These results give an indication of good resistance of triazole-based ligands to degradation under high acidic and radiolytic conditions.

Conclusion

Extraction experiments performed on EH-BTzBP demonstrate that this new type of N-donor ligand may overcome several limits of the BTPs and BTBPs. The extractant demonstrates high selectivity for An(III) over Ln(III), fast extraction kinetics, high solubility in non-polar solvents and resistance to acid hydrolysis and simulated radiolytic conditions. While this ligand has some drawbacks such as the need for the co-extractant 2-bromohexanoic acid, the findings of this study can be utilized for further targeted synthesis of more suitable N-donor ligands for an An(III)/Ln(III) separation process.

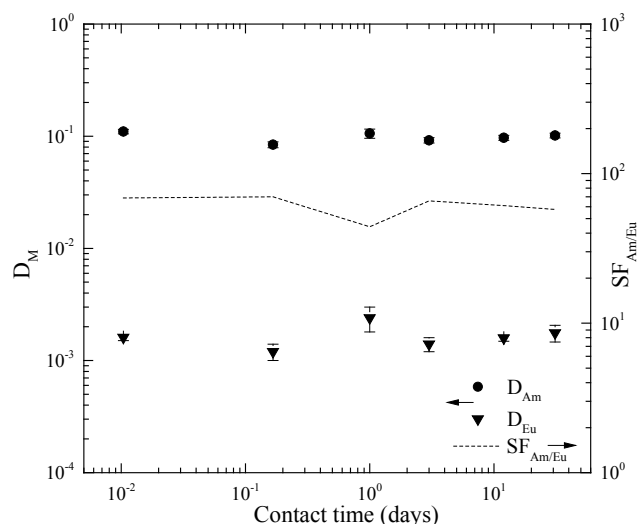


Figure 7: Extraction of Am(III) and Eu(III) as a function of contact time with 0.1 M H_2O_2 before extraction. Organic phase: 0.02 M EH-BTzBP + 1 M 2-bromodecanoic acid in toluene. Aqueous phase (for extraction): Traces of $^{241}Am(III)$ and $^{152}Eu/^{154}Eu(III)$ in 1.0 M HNO_3 .

Acknowledgement

Work performed with support from the U.S. Department of Energy, Office of Nuclear Energy, Nuclear Energy University Programs (NEUP) project number 10-881.

References

1. Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W., Use of Soft Heterocyclic N-Donor Ligands To Separate Actinides and Lanthanides. *Inorg. Chem.* **2013**, 52 (7), 3414-3428.
2. Kolarik, Z., Complexation and Separation of Lanthanides(III) and Actinides(III) by Heterocyclic N-Donors in Solutions. *Chem. Rev.* **2008**, 108 (10), 4208-4252.
3. Panak, P. J.; Geist, A., Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands. *Chem. Rev.* **2013**, 113 (2), 1199-1236.
4. Sonogashira, K., Development of Pd-Cu catalyzed cross-coupling of terminal acetylenes with sp(2)-carbon halides. *Journal of Organometallic Chemistry* **2002**, 653 (1-2), 46-49.
5. Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B., A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. *Angewandte Chemie-International Edition* **2002**, 41 (14), 2596-2599.

Separation of Americium from a Concentrated Raffinate by Liquid-Liquid Extraction

C. Marie, M.-T. Duchesne, V. Pacary, V. Vanel, M. Montuir, D. Rudloff, M. Bertrand, M. Miguirditchian

CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS, Bagnols-sur-Cèze, F-30207, France

Summary

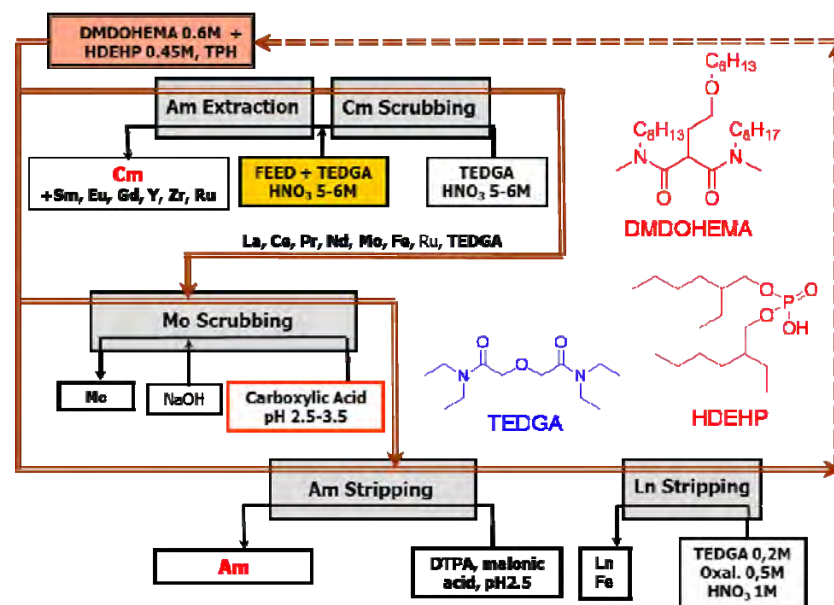
Recycling americium (Am) alone from the spent fuel is an important option studied for the future nuclear cycle (Generation IV systems) since Am is one of the main contributor to the long-term radiotoxicity and heat power of ultimate waste. The liquid-liquid extraction process called EXAm has been developed by the CEA to allow the recovery of Am alone from a PUREX raffinate (already cleared from U, Np and Pu). A mixture of DMDOHEMA (N,N' dimethyl-N,N' dioctyl-2 (2 (hexyloxy)ethyl)-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) in TPH is used as the solvent and the Am/Cm selectivity is improved using TEDGA (tetraethyldiglycolamide) as a selective complexing agent to maintain Cm and heavier lanthanides in the acidic aqueous phase (HNO₃ 5-6M). Americium is then stripped selectively from light lanthanides at low acidity (pH2.5-3) with a polyaminocarboxylic acid. In order to make the process and future plant associated more compact, the objective is now to adapt the EXAm process to a concentrated raffinate. The aqueous complexing agent is partially extracted into the organic phase and generates several complications in the process for higher concentrations of cations: risk of third phase formation, Am leaking at the Mo scrubbing step, decrease of lanthanide/americium separation factor during Am stripping. A "TEDGA scrubbing" battery was thus designed to keep its concentration in the organic phase lower than 10mM. Many experimental data were acquired in batch conditions at the different steps of the process. Solvent formulation, TEDGA and HNO₃ concentrations, pH buffer nature were optimized to manage high concentrations of americium and lanthanides in the loaded solvent and avoid 3rd phase formation but keeping a sufficient Am/Cm and Am/FP separation.

1. INTRODUCTION

In the future nuclear fuel cycle, one promising strategy for the treatment of long-lived radionuclides is partitioning and transmutation. The French Act of June 28th 2006 has defined several strategies to totally or partially recycle minor actinides (MA) from spent nuclear fuels in Generation IV systems. After recycling U, Pu, and Np, the remaining long term radiotoxicity is mainly due to MA, essentially americium and curium. After 100 years, americium is the main contributor to heat emissions in final spent fuel wastes, so removing Am will help to reduce the size of a deep geological storage.[1,2] Moreover, Cm reprocessing would be difficult to implement due to very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. Hence, one of the strategies considered is to recycle Am alone and leave Cm with vitrified fission products (FP). A hydrometallurgical process, called EXAm, was thus developed at the CEA to separate Am from a PUREX raffinate (Scheme 1).[3] Am is separated from curium in the extraction section using a mixture of HDEHP (di-2-ethylhexylphosphoric acid) and DMDOHEMA (N,N'-dimethyl-N,N'-dioctyl-hexyloxyethyl-malonamide) diluted in TPH. This separation is very challenging

since Am and Cm have very close physico-chemical properties. The DMDOHEMA extractant has a low selectivity for Am versus Cm ($SF_{Am/Cm} = 1.6$). Hence, the water soluble complexing agent TetraEthylDiglycolAmide (TEDGA) was added into the feed solution and at the scrubbing step to improve the Am/Cm selectivity ($SF_{Am/Cm} = 2.5$) and hence, to reduce the number of theoretical separation stages. Americium is finally selectively stripped from light lanthanides using a hydrophilic polyamino-carboxylate complexing agent at low acidity. Additional steps are necessary to strip Molybdenum and finally lanthanides and iron from the solvent.

The feasibility of this process was already demonstrated during pilote scale tests on a genuine PUREX raffinate in hot cells in ATALANTE facility.[4] In order to improve the compactness of the process and future plan associated, further studies were necessary to adapt the flowsheet and reduce the volume of effluent waste.



Scheme 1: Simplified flowsheet of the EXAm process

2. CHEMISTRY OF TEDGA AT HIGH ACIDITY (Am EXTRACTION)

The chemistry of the {lanthanides-TEDGA-DMDOHEMA-HDEHP} extraction system at high acidity was already studied and modelled.[5] TEDGA has a higher affinity for heavy lanthanides and curium maintaining them preferentially in the aqueous phase, whereas light lanthanides and americium are extracted by the EXAm solvent in the organic phase. The combination of DMDOHEMA and TEDGA allows to reach a Am/Cm separation factor close to 2.5.

Although TEDGA is a water-soluble complexing agent, its partial transfer to the solvent during the extraction process has to be taken into account. It is most probable that mixed species are formed in the organic phase with TEDGA and extractants DMDOHEMA and HDEHP. According to a recent complexation study[6] which indicates the preferential formation of 1:1 and 1:2 Ln:TEDGA complexes for the lighter lanthanides in the aqueous phase, it was concluded that such complexes are extracted into the organic phase, whereas heavier lanthanides and Cm should mainly form non-extractable 1:3 species.

To summarize, all extraction mechanisms that should be taken into account to describe the extraction of HNO₃, TEDGA and Ln or An(III) cations in the EXAm process (at high acidity) are depicted in Figure 1. Distribution of TEDGA is a key

point of the process as it impacts the extraction properties, the Am/Cm selectivity and the solvent loading capacity. A thermodynamical model was developed to simulate all cations distribution in this step of the process and it takes into account more than 50 equilibria. [5]

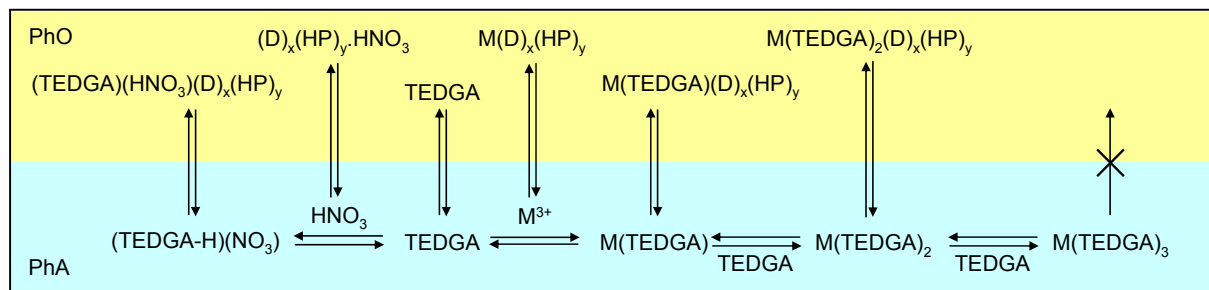


Figure 1: Schematic view of complexation equilibria and extraction mechanisms involving TEDGA in the biphasic system DMDOHEMA (D), HDEHP (HP) / HNO_3 , TEDGA, Ln/An (M)

3. INFLUENCE OF HIGH METAL LOADING ON Am/Cm SEPARATION

A classical PUREX UOx3 raffinate (corresponding to a 60 GWj/t fuel) contains around 20 mM of lanthanide cations (40 mM of fission products in total). In order to reach a concentration factor as high as possible, batch experimental data were acquired with an increasing concentration of lanthanides ($[TEDGA]_{tot} = 150\text{mM}$ and $[HNO_3] = 5.5\text{M}$) up to a concentration of the raffinate by a factor 15. As observed in Figure 2, an important decrease of the Am/Cm separation is observed when the total concentration of lanthanides gets higher. In fact, the Am/Cm selectivity in the system is ruled by the Cation/TEDGA ratio. To maintain the selectivity, it is thus necessary to increase the concentration of TEDGA as we increase the cation concentration.

Unfortunately, with a higher concentration of TEDGA (220mM and 340mM), a 3rd phase is formed (Table 1) with the solvent HDEHP 0.3M + DMDOHEMA 0.6M in TPH. This phenomenon could be due to the formation of ternary species Ln-TEDGA-DMDOHEMA when TEDGA is extracted in the organic phase, with a lower lipophilicity compared to Ln-DMDOHEMA complexes. To overcome this problem, the concentration of HDEHP was increased to 0.45M. As observed in Table 1, this is a good way to prevent demixion. But nevertheless, HDEHP concentration cannot be further increased or it will then be difficult to strip Am with DTPA. Finally, the PUREX raffinate could not be concentrated more than 3.5 times to maintain good process performances,.

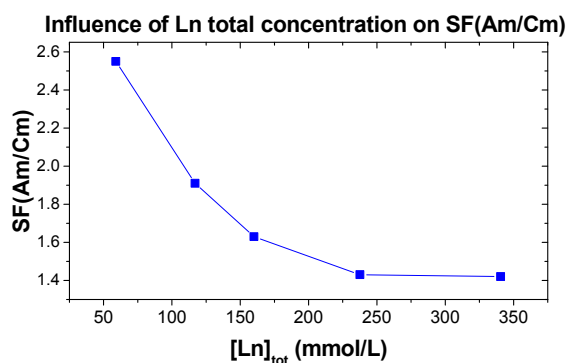


Figure 2: Influence of the total concentration of lanthanides on the Am/Cm separation factor. Solvent: HDEHP 0.3M + DMDOHEMA 0.6M in TPH, pre-equilibrated with HNO_3 5.5M with ^{241}Am and ^{244}Cm radiotracers and $[TEDGA]_{tot} = 150\text{ mM}$

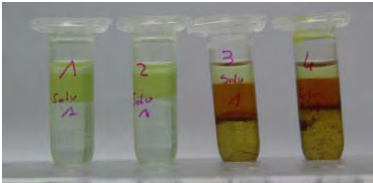
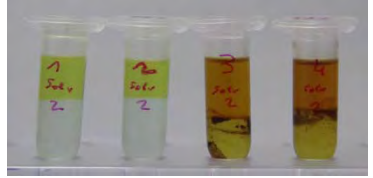
Conditions* [TEDGA] mM	Am Extraction		Cm Scrubbing	
	1	2	3	4
	220	220	340	340
Phases at equilibrium after contact with HDEHP 0.3M + DMDOHEMA 0.6M				
Phases at equilibrium after contact with HDEHP 0.45M + DMDOHEMA 0.6M				

Table 1: Impact of HDEHP concentration on 3rd phase formation. [HNO₃]=5M.

* Conditions 1 :
[Ln] (from La to Gd) = 10 mM, [Zr]=1.5 g/L, [TEDGA]=220mM
Conditions 2 :
[Ln] (from La to Gd) = 15 mM, [Zr]=1.5 g/L, [TEDGA]=220mM
Conditions 3 :
[Ln] (from La to Nd) = 20 mM, [Mo]=2.6 g/L, [Fe]=1.2g/L, [Pd]=2.9g/L, [TEDGA]=340mM
Conditions 4 :
[Ln] (from La to Nd) = 25 mM, [Mo]=2.6 g/L, [Fe]=1.2g/L, [Pd]=2.9 g/L, [TEDGA]=340mM

4. INFLUENCE OF TEDGA ON STRIPPING STEPS AT LOW ACIDITY

Since the concentration of TEDGA has to be increased to maintain a good Am/Cm separation in the first step of the process, the amount of TEDGA following americium and light lanthanides in the organic solvent is higher. As a consequence, the influence of TEDGA on “Molybdenum scrubbing” and “Am stripping” steps at low acidity was studied (Figure 3). An increase of TEDGA has no impact on Mo(VI) back extraction, but induces an important leak of americium (*left* Figure). Moreover, during selective stripping of Am with DTPA (diethylene-triamine-pentaacetic acid), TEDGA would compete with DTPA and decrease Am stripping performances with a lower Ln/Am selectivity (as seen in the *right* Figure with Eu).

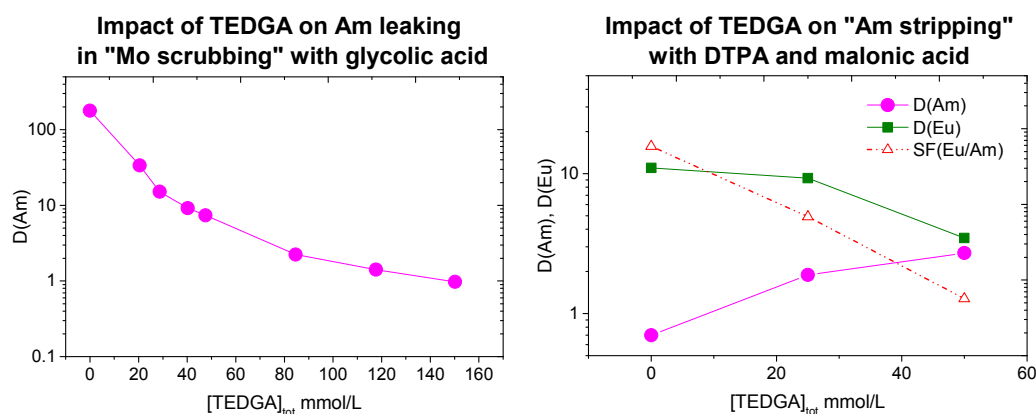


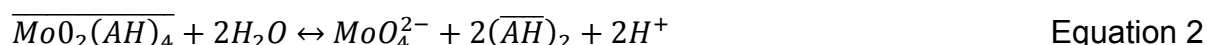
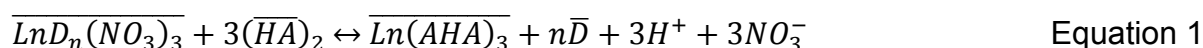
Figure 3 : (left) ²⁴¹Am distribution ratios during “Mo scrubbing” with the scrubbing solution glycolic acid 0.5M at pH 3 and 40m of Nd (to simulate other lanthanides); (right) distribution ratios of ²⁴¹Am and ¹⁵²Eu during back extraction of Am with DTPA 30mM and malonic acid 0.3M adjusted to pH 2.5 with hydroxylamine. Solvent HDEHP 0,45M + DMDOHEMA 0,6M in TPH.

Regarding those data, removing TEDGA from the organic phase prior to Mo and Am stripping steps appears to be a critical step to ensure selective and total recovery of Am from the solvent. As a consequence, few stages of mixer-settlers were added between “Cm scrubbing” and “Mo scrubbing” batteries where TEDGA was scrubbed with HNO₃ 4 M. This nitric acid concentration was chosen to avoid perturbations in

the “Cm scrubbing” section and obtain less than 10 mM of TEDGA in the organic phase.

5. INFLUENCE OF HIGH METAL LOADING ON “M₀ SCRUBBING”

Molybdenum has to be selectively stripped from the organic solvent right before the “Am stripping” step or it will be back-extracted together with Am due to its affinity for DTPA complexing agent. Mo is stripped selectively from americium and other cations using a α -hydroxy-carboxylic acid complexing agent at low acidity. This transition between “Am extraction” at high acidity and “Mo scrubbing” at low acidity is challenging because it is necessary to neutralize protons arriving with the loaded solvent with a flow of concentrated NaOH (Figure 4). The pH range to achieve is narrow: between 2.5 (to ensure Mo stripping) and 4 (to prevent from lanthanide hydroxides precipitation). During one of the first cold lab-scale tests performed in mixer-settlers with a simulated concentrated feed solution of fission products, important problems of pH stabilization were observed. As reported in Figure 4, the pH fluctuations in the Mo scrubbing battery (LX-LS) were important with glycolic acid 0.5M used as stripping/buffering solution. As a consequence, it was impossible to efficiently strip Mo. To overcome this phenomenon, which was not observed with lower concentrations of cations, it was important to better identify sources of protons to be neutralized directly at the introduction of the loaded solvent. Three sources of protons were identified: nitric acid extracted by DMDOHEMA during the previous “Am extraction” at high acidity, protons of HDEHP released according to Equation 1, protons released during Mo back extraction due the formation of Mo anionic species according to Equation 2.



D=DMDOHEMA, AH=HDEHP, n=2 or 3

With high concentrations of cations, a slight fluctuation in loaded solvent flow rate or cation composition will induce an important change in pH due to protons release according to those chemical equilibria. As a consequence, the buffering effect is very important and glycolic acid was not a good candidate anymore in those conditions. Despite its non-negligible affinity for Am, citric acid was then chosen because it has a pKa (2.8) closer to the optimal pH range (2.5-3.5) than glycolic acid (3.8). A thermodynamical model was developed to simulate Mo, Am and light lanthanides distribution and implemented in the PAREX simulation code.[7] Moreover, conditions of NaOH introduction and mixer-settlers parameters were optimized leading to a significant improvement of pH control. Indeed, during the last pilot test (EXAmCo6, February 2013), pH was close to 3 in all stages at equilibrium (Figure 5), and Mo was quantitatively stripped from the solvent. At the end of this test, samples of organic and aqueous phases in all stages were sampled, spiked with ²⁴¹Am and re-contacted to obtain the Am distribution profile Figure 5. According to distribution ratios, Am

should be correctly re-extracted in the first stages of the LX battery providing from any leak in the Mo raffinate.

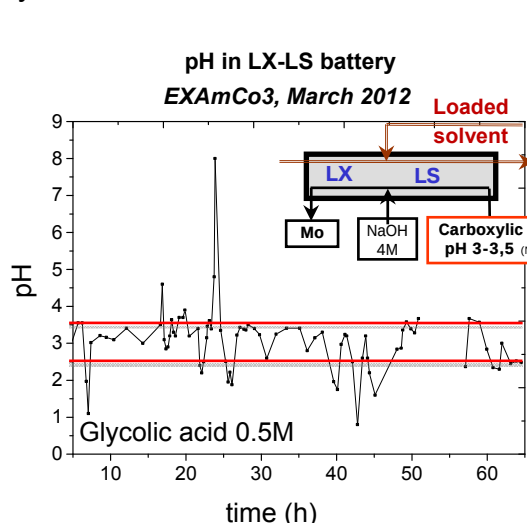


Figure 4: Problems of pH stabilization in “Mo scrubbing” battery during pilot scale test in mixer-settlers (March 2012, EXAmCo3) with glycolic acid (0.5M).

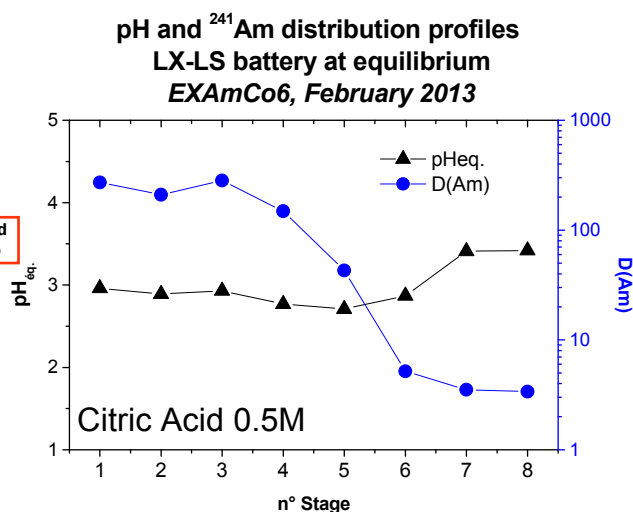


Figure 5: pH and ^{241}Am distribution profiles at equilibrium in the “Mo scrubbing” battery during pilot scale tests in mixer-settlers (February 2013, EXAmCo6) with citric acid (0.5M).

6. CONCLUSION

In order to adapt the EXAm process to higher concentrations of cations, it was first necessary to increase the concentration of HDEHP (from 0.3 to 0.45 M) to improve solvent loading capacity and avoid third phase formation. Nevertheless, the highest concentration factor of the feed solution achievable appeared to be 3.5 (compared to a UOx3 PUREX raffinate). To keep a high Am/Cm selectivity, the concentration of TEDGA complexing agent had to be increased, impacting the following stripping steps. As a consequence, additional stages were dedicated to TEDGA scrubbing with nitric acid 4 M to limit to 10 mM the concentration of TEDGA co-extracted with Am and light lanthanides in the organic phase. Nevertheless, important optimizations were still necessary on the “Mo scrubbing” step where important pH fluctuations were observed due to cation/proton exchanges. The buffering capacity is thus very important and citric acid was chosen as a selective complexing/buffering agent. Thermodynamical models were implemented in the PAREX code to predict Am, Cm, Ln but also Mo and other fission products behavior in all stages of the process at high and low acidity. With these improvements, the complete EXAm flowsheet will now be tested in ATALANTE facility hot laboratories on a surrogate raffinate containing small amounts (milligram scale) of ^{241}Am and ^{244}Cm .

[1] Poinssot, C.; Rostaing, C.; Greandjean, S.; Boullis, B. *Procedia Chem.* 2012, 7, 349–357.

[2] Rostaing, C.; Poinssot, C.; Warin, D.; Baron, P.; Lorraina, B. *Procedia Chem.* 2012, 7, 367–373.

[3] X. Heres, P. Baron, Patent WO2012069573 (2010).

[4] Bollesteros M.-J., Calor J.-N., Costenoble S., Montuir M., Pacary, C. Sorel V., Burdet F., Espinoux D., Heres X., Eysseric C. *Procedia Chem.* 2012, 7, 178-183.

[5] Pacary V., Burdet F., Duchesne M.-T. *Procedia Chem.* 2012, 7, 328-333

[6] Charbonnel M.-C., Miguiditchian M., Berthon C., Boubals N., Burdet F., Guilbaud P., Marie C. *Procedia Chem.*, 7, 20-26

[7] Vanel et al. *ISEC 2014 Proceeding*

Spiked Laboratory-scale Continuous Counter-Current Centrifugal Contactor Demonstration of a Novel innovative-SANEX Process

*Andreas Wilden^{*1}, Giuseppe Modolo¹, Peter Kaufholz¹, Fabian Sadowski¹, Steve Lange¹, Michal Sypula¹, Dirk Bosbach¹, Daniel Magnusson², Udo Müllich², Andreas Geist²,*

In this paper the development and laboratory-scale demonstration of a novel “innovative-SANEX” process using annular centrifugal contactors is presented. In this strategy, the An(III) and Ln(III) are co-extracted from simulated PUREX raffinate, and the loaded solvent is subjected to several stripping steps. A solvent comprising the TODGA extractant with addition of 5 vol.-% 1-octanol showed very good extraction efficiency of Am(III) and Cm(III) together with the trivalent lanthanides (Ln(III)) from simulated PUREX raffinate solution without 3rd phase formation. The problem of co-extraction of Zr and Pd was overcome using CDTA (cyclohexanediaminetetraacetic acid) as masking agent. The An(III) were selectively stripped using the hydrophilic complexing agent SO₃-Ph-BTP. For the subsequent stripping of the Ln(III), a citric acid based solution was used. A 32-stage process flow-sheet was designed using computer-code calculations and tested in annular miniature centrifugal contactors in counter-current mode. The innovative SANEX process showed excellent performance for the recovery of An(III) from simulated HAR solution and separation from the fission and activation products. More than 99.8% of An(III) was recovered with only low levels of impurities (0.4% Ru, 0.3% Sr, 0.1% Ln(III)). The separation from the Ln(III) was excellent and the Ln(III) were efficiently stripped by the citrate-based stripping solution. The only major contaminant in the spent solvent was Ru, with 14.7% of the initial amount being found in the spent solvent. Solvent cleaning and recycling therefore has to be further investigated. This successful spiked test demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle which is a great improvement over the former multi-cycle strategy. The results of this test are presented and discussed.

Introduction

For the advanced minor actinide (MA) partitioning following the PUREX process, several multi-cycle processes have been developed.¹ In the USA e.g. the TALSPEAK process² has been intensely investigated as part of the CTH and UREX processes.³ Recent research in Europe has focused on the development of single-cycle processes, e.g. 1-cycle SANEX⁴⁻⁶, EXAm⁷. The French CEA successfully demonstrated an An(III)/Ln(III) separation process based on a TODGA/TBP solvent with a selective An(III) stripping step using hydrophilic polyaminocarboxylic acid in a buffered solution.⁸

Single cycle processes are advantageous as they could make the advanced MA partitioning more economical and easier. However, the used extraction systems have to cope with a number of challenges, e.g. high nitric acid concentration, loading, selectivity for the desired trivalent actinides over fission and activation products, stability towards hydrolysis and radiolysis. Currently, no single molecule fulfils all the requirements and therefore, a sophisticated stepwise approach was chosen in this study.

1 Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Nuclear Waste Management (IEK-6), 52428 Jülich, Germany, * Corresponding Author: a.wilden@fz-juelich.de

2 Karlsruhe Institute of Technology, INE, Karlsruhe, Germany

The TODGA (*N,N,N',N'*-tetraoctyldiglycolamide, Figure 1) extractant is known to co-extract An(III) and Ln(III) efficiently from highly concentrated nitric acid solutions.⁹ The co-extraction of Zr and Pd was overcome using the polyaminocarboxylic acid CDTA (trans-1,2-diaminocyclo-hexane-*N,N,N',N'*-tetraacetic acid, Figure 1) as masking agent.¹⁰ Third phase formation was suppressed by addition of 5 vol-% 1-octanol.¹¹ For the selective recovery of the An(III) the hydrophilic complexing agent SO₃-Ph-BTP (Figure 1) was used.¹² Based on the selected extractants (TODGA), masking (CDTA) and selective stripping agents (SO₃-Ph-BTP), a novel innovative-SANEX process was developed and tested in a spiked counter-current demonstration test using annular centrifugal contactors. The results of this test are presented and discussed.

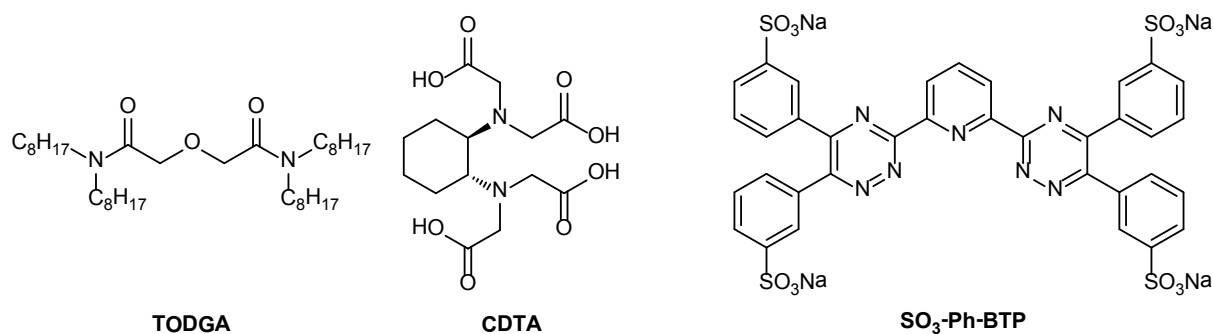


Figure 1. Chemical structures of TODGA, CDTA and SO₃-Ph-BTP.

Composition of the Feed Solution

The composition of the synthetic PUREX raffinate used as the feed solution for the innovative-SANEX process was prepared by a specific strategy for the dissolution of the reagents, which is mainly based on the use of metal nitrate salts.¹³ The initial HNO₃ concentration was 4.45 mol/L HNO₃. CDTA (0.05 mol/L) was added as a masking agent for Zr and Pd to the innovative SANEX feed.

Flow-sheet design

The main goals of the flow-sheet design were to achieve a high recovery yield of actinides (>99.9%) and to obtain decontamination factors for fission products (FP) that were as high as possible. The flow-sheets were optimized using batch data, single-stage centrifugal contactor experiments and data from previous TODGA processes.¹³⁻¹⁵ Calculations were carried out using the SX Process code, described in ref.¹⁶⁻¹⁸, which is designed for centrifugal contactors with an emphasis on a simple model for the system's kinetics. Details of the flow-sheet design for this process are described in ref.¹⁹ The final flow-sheet is shown in Figure 2.

Due to the availability of only 16 contactors in the laboratory, the test had to be split into two parts and performed on consecutive days. The loaded solvent leaving the Scrub 2 section of the contactor battery was collected, stored overnight in a closed bottle, and fed into the cleaned and newly prepared contactor battery as shown in Figure 2.

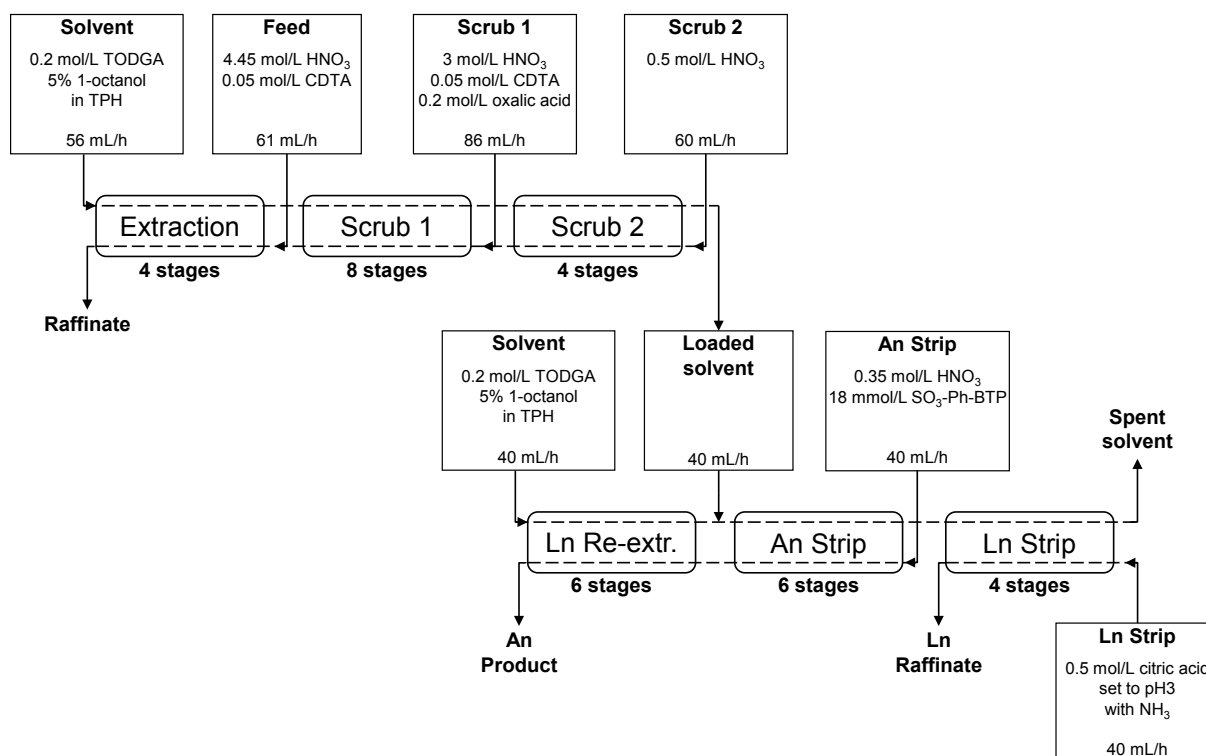


Figure 2. Flow-sheet of the $\text{SO}_3\text{-Ph-BTP}$ innovative SANEX demonstration process.

Results and Discussion

As described above, the demonstration test had to be performed in two parts on consecutive days. The ^{241}Am and ^{152}Eu profile of the first part, the extraction and scrubbing sections, is shown in Figure 3. An(III), Y(III) and Ln(III) were well extracted (>99.9%) and very high feed/raffinate decontamination factors were achieved (>750 for An(III)). Four stages were sufficient to reach the high feed/raffinate decontamination. The trivalent actinides and lanthanides stayed in the organic phase during the two scrubbing sections with high distribution ratios. The distribution ratios decreased slightly in the last 4 stages, due to the lower nitric acid concentration in those stages, which are needed for Sr scrubbing. The addition of 0.05 mol/L CDTA to the feed efficiently limited the co-extraction of Zr and Pd. The lower acidity Scrub 2 solution proved to be very efficient for scrubbing Sr, as distribution ratios of 0.21 were observed and only 0.3% of the initial amount of Sr was found in the collected organic solvent (stage 16). Sr was extracted very well and passed the Scrub 1 section. Only in the Scrub 2 section back-extraction was observed. This in turn led to an accumulation of Sr in the Extraction and Scrub 1 sections of the test. However, steady state was reached for Sr and the maximum concentration of Sr in the solvent accounted for only ~10% loading of TODGA (assuming a 1:2 Sr:TODGA complex²⁰). 16% of the initial Ru amount was co-extracted; the behavior of Ru was very similar to that observed in earlier tests using TODGA-based solvents.

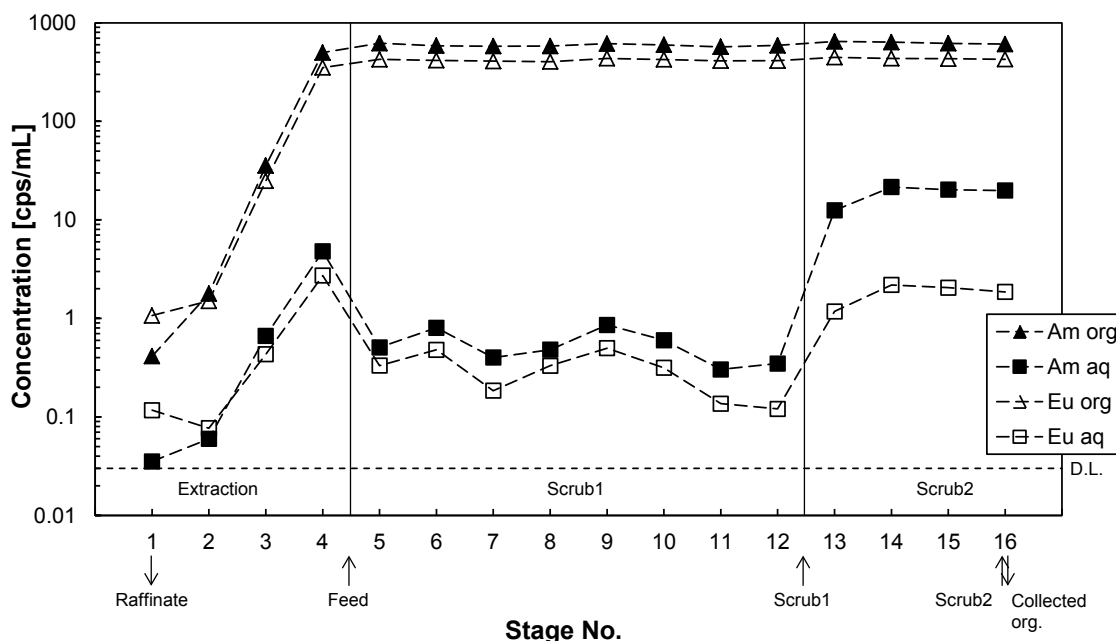


Figure 3. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the 1st part of the innovative SANEX test.

On the second day of the demonstration test, the selective back-extraction of An(III) with $\text{SO}_3\text{-Ph-BTP}$ was conducted. Figure 4 shows the ^{241}Am and ^{152}Eu profiles. Selective back-extraction of An(III) with $\text{SO}_3\text{-Ph-BTP}$ was very efficient with distribution ratios ≤ 0.06 . The An(III) were efficiently stripped within six stages and $>99.8\%$ Am(III) and Cm(III) were recovered in the An product fraction. Good separation from the Ln(III) was achieved in the Ln re-extraction section, the Am(III) + Cm(III) product was fairly clean and only contaminated with 0.3% Sr, 0.4% Ru and $<0.1\%$ Ln(III). The Ln(III) were very efficiently stripped in the last four stages using a citric acid based stripping solution. Only four stages were needed for nearly quantitative Ln(III) stripping. The spent solvent after stripping contained $<0.1\%$ of Am(III), Cm(III), and Eu(III). The only major contamination of the spent solvent was Ru. Ru was not stripped by $\text{SO}_3\text{-Ph-BTP}$ or the citric-acid based stripping solution and 14.7% Ru were found in the spent solvent. A similar behavior was already described for other demonstration tests using the TODGA extractant.¹³⁻¹⁴

The hydrodynamic behavior of the solvent was excellent during the whole spiked test and no phase entrainment or 3rd phase formation was observed.

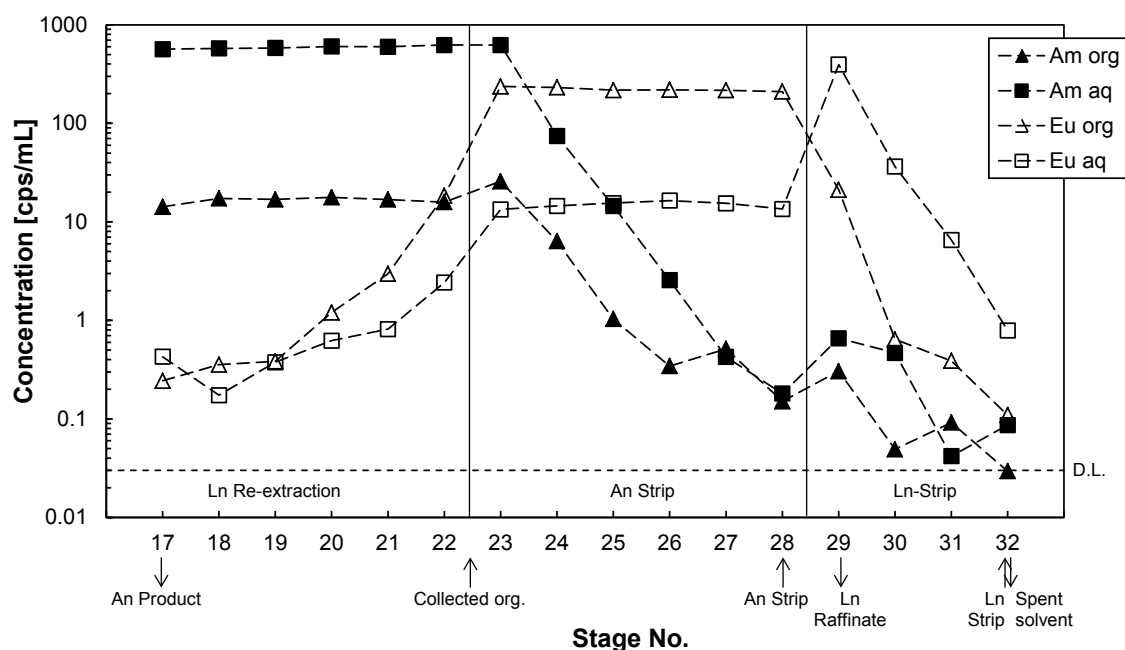


Figure 4. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the 2nd part of the innovative SANEX test.

Conclusions

The presented innovative-SANEX process showed excellent performance for the recovery of An(III) from simulated HAR solution using a TODGA-based solvent and An(III) selective stripping using $\text{SO}_3\text{-Ph-BTP}$. It demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle. The use of $\text{SO}_3\text{-Ph-BTP}$ is an improvement over the formerly use of buffered polyaminocarboxylic acid solutions, as precise pH control and salting out agents are no longer needed.

However, some drawbacks of the process have to be addressed. The process uses a sulphur-containing complexing agent, thus being incompatible with the CHON principle. Recycling of the An(III)-selective stripping agent $\text{SO}_3\text{-Ph-BTP}$ would be desirable for reduction of cost and waste minimization, a topic currently being studied.²¹ Recycling of the TODGA-based solvent must also be addressed, especially cleaning from co-extracted Ru and other minor metal impurities, but also cleaning from radiolysis degradation products.

It is important to improve the mechanistic understanding of the chemical and physical reactions involved in the solvent extraction processes (thermodynamics and kinetics) and the diverse safety issues involved in the chemical processes under operational and mal-operational conditions, which is currently being studied in the European collaborative research project SACSESS.

Acknowledgements

Financial support for this research was provided by the European Commission (projects ACSEPT – Contract No. FP7-CP-2007-211 267 and SACSESS – Contract

No. FP7-Fission-2012-323-282) and the German Federal Ministry of Education and Research (Contract No. 02NUK020E).

References

1. C. Hill, in *Ion Exchange and Solvent Extraction, A Series of Advances, Vol. 19* (Ed.: B. A. Moyer), CRC Taylor and Francis, **2009**, pp. 119-193.
2. B. Weaver, F. A. Kappelmann, **1964**.
3. M. Nilsson, K. L. Nash, *Solvent Extr. Ion Exch.* **2007**, *25*, 665-701.
4. A. Wilden, G. Modolo, C. Schreinemachers, F. Sadowski, S. Lange, M. Sypula, D. Magnusson, A. Geist, F. W. Lewis, L. M. Harwood, M. J. Hudson, *Solvent Extr. Ion Exch.* **2013**, *31*, 519-537.
5. D. Magnusson, A. Geist, A. Wilden, G. Modolo, *Solvent Extr. Ion Exch.* **2013**, *31*, 1-11.
6. A. Wilden, C. Schreinemachers, M. Sypula, G. Modolo, *Solvent Extr. Ion Exch.* **2011**, *29*, 190-212.
7. M.-J. Bollesteros, J.-N. Calor, S. Costenoble, M. Montuir, V. Pacary, C. Sorel, F. Burdet, D. Espinoux, X. Hérès, C. Eysseric, *Proc. Chem.* **2012**, *7*, 178-183.
8. D. Warin, C. Poinssot, S. Bourg, *GLOBAL*, Makuhari, Japan **2011**, 478580 (Paper No.).
9. S. A. Ansari, P. Pathak, P. K. Mohapatra, V. K. Manchanda, *Chemical Reviews* **2012**, *112*, 1751-1772.
10. M. Sypula, A. Wilden, C. Schreinemachers, R. Malmbeck, A. Geist, R. Taylor, G. Modolo, *Solvent Extr. Ion Exch.* **2012**, *30*, 748-764.
11. A. Geist, G. Modolo, *GLOBAL (The Nuclear Fuel Cycle: Sustainable Options & Industrial Perspectives)*, Paris **2009**, 1022-1026, paper 9193.
12. A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden, T. Zevaco, *Solvent Extr. Ion Exch.* **2012**, *30*, 433-444.
13. G. Modolo, H. Asp, H. Vijgen, R. Malmbeck, D. Magnusson, C. Sorel, *Solvent Extr. Ion Exch.* **2008**, *26*, 62-76.
14. D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, C. Sorel, *Solvent Extr. Ion Exch.* **2009**, *27*, 26-35.
15. D. Magnusson, A. Geist, A. Wilden, G. Modolo, R. Malmbeck, *GLOBAL*, Makuhari, Japan **2011**, 355757 (Paper No.).
16. D. Magnusson, R. Malmbeck, *Solvent Extr. Ion Exch.* **2012**, *30*, 115-126.
17. D. Magnusson, A. Geist, R. Malmbeck, *Chem. Eng. Sci.* **2013**, *99*, 292-297.
18. D. Magnusson, A. Geist, R. Malmbeck, U. Müllich, *Solvent Extr. Ion Exch.* **2013**, *31*, 578-589.
19. D. Magnusson, A. Geist, R. Malmbeck, G. Modolo, A. Wilden, *Proc. Chem.* **2012**, *7*, 245-250.
20. Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, T. Kimura, *Solvent Extr. Ion Exch.* **2013**, *31*, 401-415.
21. D. Munzel, H. Galán, A. Núñez, U. Müllich, J. Cobos, A. Geist, *Sustainable Nuclear Energy Conference*, Manchester, UK **2014**.

A New System For Separating Americium from PUREX Raffinate

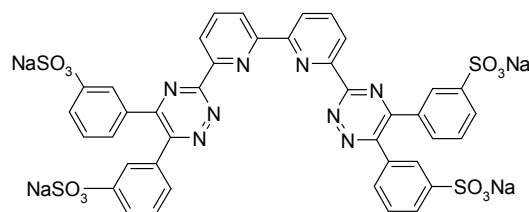
Christoph Wagner,^{a,b} Udo Müllich,^a Petra J. Panak,^{a,b} Andreas Geist^a

^aKarlsruhe Institute of Technology (KIT), Germany

^bRuprecht-Karls-Universität Heidelberg, Germany

The recycling of minor actinides as nuclear fuel is complicated by the presence of curium due to its short term thermal power and neutron dose rate. Thus processes for separating americium from curium have been developed. Ideally, this separation would be located early on in the process sequence. Hence, the French EXAm process was developed and successfully tested,¹ separating only americium from the PUREX or COEX raffinate.

A new system was developed to separate only americium, addressing some of the challenges with the EXAm process such as a narrow pH window. This development is based on our experience with SO₃-Ph-BTP (a water soluble BTP useful for selectively stripping Am(III) + Cm(III) from a TODGA organic phase loaded with Am(III) + Cm(III) + Ln(III)²⁻⁵). Using the analogous water soluble SO₃-Ph-BTBP,⁶ TODGA's slight preference for Cm(III) over Am(III) multiplies with SO₃-Ph-BTBP's inverse selectivity, yielding a separation factor $SF_{\text{Cm(III)/Am(III)}} \approx 2.5$ (a value similar to the EXAm system's) over a wide range of experimental conditions. This enables the system to keep Cm(III) + Ln(III) in the organic phase while selectively stripping Am(III) at a HNO₃ concentration of approx. 0-5-1 mol/L. Buffers or salting out agents are not required.



SO₃-Ph-BTBP.

Am(III) + Cm(III) + Ln(III) distribution ratios were determined in extraction experiments as a function of HNO₃ and SO₃-Ph-BTBP concentrations. Stripping Am(III) from a loaded TODGA solvent is not impeded by slow kinetics. Furthermore, the complexation of Cm(III) and Eu(III) with SO₃-Ph-BTBP was followed using time resolved laser fluorescence emission spectrometry (TRLFS). Both metal ions from 1:2 complexes, as is the case with hydrophobic BTBP extracting agents. Conditional complex formation constants were determined at pH 3 and in 0.5 mol/L HNO₃. The values determined for Cm(III) are two orders of magnitude higher than those for Eu(III), well reflecting the selectivity that was determined in the extraction experiments.

This system is currently being developed towards a lab scale process test.

1. Bollesteros, M.-J. et al., *Procedia Chem.* **2012**, 7, 178–183.
2. Geist, A. et al., *Solvent Extr. Ion Exch.* **2012**, 30 (5), 433–444.
3. Geist, A. et al., Minor actinide separation: simplification of the DIAMEX-SANEX strategy by means of novel SANEX processes. *Internat. Conf. GLOBAL 2013*, Salt Lake City, U.S.A., September 29 – October 3, 2013.
4. Wilden, A. et al., Spiked laboratory-scale continuous counter-current centrifugal contactor demonstration of a novel innovative-SANEX process. *Abstract submitted to SNEC 2014*.
5. Ruff, C. M. et al., *Dalton Trans.* **2012**, 41, 14594–14602.
6. Müllich, U. et al., EP2377861, 2011-10-19.

Stability and Recyclability of SO₃-Ph-BTP for *i*-SANEX Process Development

*Hitos Galán,^{*1} Denise Munzel,² Ana Núñez,¹
Udo Müllich,² Joaquín Cobos,¹ Andreas Geist²*

SO₃-Ph-BTP (2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine) is a water soluble complexing agent useful for selectively stripping trivalent actinides from a solvent loaded with trivalent actinides and lanthanides. SO₃-Ph-BTP was used earlier in a so-called *i*-SANEX process, generating a product solution containing trivalent actinides and SO₃-Ph-BTP in approx. 0.5 mol/L HNO₃.

The chemical and radiolytic stability of SO₃-Ph-BTP was studied by storing it in HNO₃ or irradiating it in a gamma source. The effect of acid contact and irradiation dose was checked by measuring distribution ratios of Am(III) and Eu(III) between an organic phase (0.2 mol/L TODGA + 5% 1-octanol in kerosene) and the aqueous phase (SO₃-Ph-BTP in 0.5 mol/L HNO₃). Furthermore, qualitative analysis of the irradiated samples was performed.

SO₃-Ph-BTP did not show any signs of degradation in contact with up to 3 mol/L HNO₃ over 120 days. However, gamma irradiation of ≥ 50 kGy had a negative impact on its performance. Following irradiation with 250 kGy, it was estimated that approx. 90% of the initial SO₃-Ph-BTP concentration was degraded.

Introduction

The separation of chemically similar trivalent actinides, An(III), from trivalent lanthanides, Ln(III), plays an important role in solvent extraction processes developed for the separation and recycling of actinides from used nuclear fuels [1]. This separation is possible using bis-triazinyl-pyridine (BTP) or bis-triazinyl-bipyridine (BTBP) *N*-donor extracting agents [2]. Alternatively, the required selectivity is achieved using selective hydrophilic complexing agents: An(III) and Ln(III) are co-extracted and An(III) are selectively stripped from the loaded solvent.

^{*1} hitos.galan@ciemat.es. Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Spain

² Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany

SO₃-Ph-BTP (2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine tetrasodium salt, Figure 1 left), a water soluble BTP, is useful for selectively stripping An(III) from an organic phase containing e.g. TODGA (*N,N,N',N'*-tetraoctyl diglycolamide, Figure 1 right) as extracting agent, loaded with An(III) and Ln(III) [3]. It has been used in several successful spiked and hot GANEX process tests [4,5] and in a spiked *i*-SANEX process test [6,7].

These processes generate a product solution containing actinide ions and SO₃-Ph-BTP in approx. 0.5 mol/L HNO₃. Further processing of actinides may require their separation from SO₃-Ph-BTP, which in turn offers the possibility of recycling SO₃-Ph-BTP. The separation of actinide ions from the SO₃-Ph-BTP solution is possible by re-extracting them into a new TODGA solvent. Then, the SO₃-Ph-BTP solution can be re-used for a new stripping cycle. This in turn requires a sufficient stability of SO₃-Ph-BTP versus HNO₃ and radiation, the latter because real concentrations of actinides (i.e. in the range of several 100 mg/L to several g/L) would cause a significant radiation dose to the SO₃-Ph-BTP solution [8].

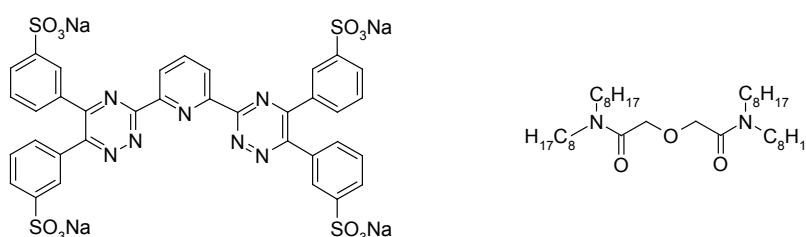


Figure 1. SO₃-Ph-BTP and TODGA.

Addressing the safety of actinide separation processes and the recyclability of SO₃-Ph-BTP, its stability versus HNO₃ and irradiation was studied. The effect of HNO₃ and irradiation was checked by measuring distribution ratios of Am(III) and Eu(III) between an organic phase (0.2 mol/L TODGA + 5% 1-octanol in kerosene) and the aqueous phase (10 mmol/L SO₃-Ph-BTP in HNO₃). Furthermore, a qualitative HPLC-DAD/MS analysis of the irradiated samples was performed. First results are presented.

Experimental

Chemicals, solutions and isotopes

TODGA was synthesised at CIEMAT in multi-gram scale, modifying an existing literature procedure under air and without drying solvent and glassware [9]. SO₃-Ph-BTP was synthesised as described in [3]. The diluents were odourless kerosene (OK), purity 98%, from Alfa Aesar and 1-octanol, purity > 99%, from Merck. All reagents were used from commercially available sources without further purification. Nitric acid solutions were prepared by diluting concentrated nitric acid (65%) with ultrapure water (18 MΩ/cm). The radiotracers ²⁴¹Am and ¹⁵²Eu were either supplied by Isotope Products Laboratories, California (USA) or taken from laboratory stocks.

Sample preparation for chemical stability test

Solutions of 10 mmol/L $\text{SO}_3\text{-Ph-BTP}$ in 0.5–3 mol/L HNO_3 and spiked with $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ were stored. After different time intervals, Am(III) and Eu(III) distribution ratios were determined by extraction experiments (see below).

Irradiation procedure

The irradiation was performed at CIEMAT Náyade facility, which is a pool 1.2 m² by 4.5 m deep. It consists of 60 sources of ^{60}Co distributed in six lots with total activity of $1.1 \cdot 10^{14}$ Bq. The irradiation container used provides homogeneous irradiation flux.

Samples of $\text{SO}_3\text{-Ph-BTP}$ (10 mmol/L in 0.5 mol/L HNO_3) were irradiated to doses of 0.05–1 MGy at dose rates of 1.78 kGy/h or 6.32 kGy/h. Extraction experiments (see below) using the irradiated samples were performed after the last step of irradiation. Reference samples for aging control were kept in the laboratory during the irradiation process.

Extraction experiments

Extraction experiments were performed contacting each 0.5 mL of organic (0.2 mol/L TODGA + 5% 1-octanol in kerosene) and aqueous (10 mmol/L $\text{SO}_3\text{-Ph-BTP}$ + $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ (2 kBq/mL each) in HNO_3) phases for 30 min. After centrifugation, samples of organic and aqueous phases (0.3 mL each) were analysed for ^{241}Am and ^{152}Eu activities by gamma spectrometry, and distribution ratios $D_{\text{Am(III)}}$ and $D_{\text{Eu(III)}}$ were determined.

UV-Vis and HPLC measurements

The chemical composition of the irradiated samples was characterised by UV-Vis and HPLC-DAD/MS. UV-Vis measurements were carried out by diluting irradiated samples tenfold in 0.5 mol/L HNO_3 . HPLC measurements were performed by using an HPLC-MS Agilent 1100 (Quadrupole detector 6120A) with a C-8 Prontosil column (50 mm, 5 μm), at 40 °C, using a gradient of mobile phase [(A: 0.1% HCOOH in CH_3CN), (B: 0.1% HCOOH in H_2O)], $\text{ESI}^{+/-}$ ionisation mode (SCAN), and at 280 and 320 nm. Samples for HPLC studies were analysed without pre-evaporation and diluted tenfold in (50/50)% $\text{MeOH}/\text{H}_2\text{O} + 0.1\%$ HCO_2H . All measurements were repeated twice.

Results and discussion

Stability of $\text{SO}_3\text{-Ph-BTP}$ versus nitric acid

Preliminary results indicate stability of $\text{SO}_3\text{-Ph-BTP}$ in 0.5 mol/L HNO_3 for more than two years but its degradation in 4.1 mol/L HNO_3 .

To study this behaviour in more detail, solutions of $\text{SO}_3\text{-Ph-BTP}$ in HNO_3 of varied concentration were stored. After different time intervals, Am(III) and Eu(III)

distribution ratios were determined after extraction into a TODGA solvent. Am(III) and Eu(III) distribution ratios as a function of storage time are shown in Figure 2.

Am(III) distribution ratios remain virtually constant over 120 days for all HNO₃ concentrations studied, i.e. 0.5–3 mol/L. The same is observed for Eu(III) distribution ratios. Note that Eu(III) distribution ratios for 1–3 mol/L HNO₃ could not be measured accurately because the activity in the aqueous samples was below the detection limit (Eu(III) distribution ratios > 1000 are expected [3] at these HNO₃ concentrations).

These results do not contradict the initial results, i.e. stability of SO₃-Ph-BTP in 0.5 mol/L HNO₃ for more than two years but its degradation in 4.1 mol/L HNO₃. Obviously, SO₃-Ph-BTP shows sufficient stability in contact with HNO₃.

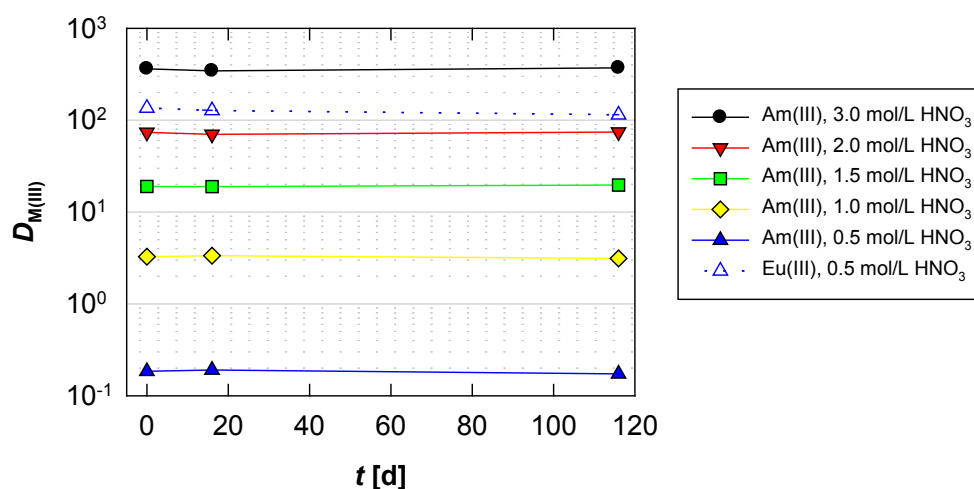


Figure 2. Am(III) and Eu(III) distribution ratios as a function of aqueous phase storage time. Organic phase, 0.2 mol/L TODGA + 5% 1-octanol in kerosene. Aqueous phase, 10 mmol/L SO₃-Ph-BTP + ²⁴¹Am(III) + ¹⁵²Eu(III) in HNO₃.

Radiolytic stability of SO₃-Ph-BTP versus gamma radiation

Solutions of 10 mmol/L SO₃-Ph-BTP in 0.5 mol/L HNO₃ were irradiated with varied doses (≤1 MGy) using homogeneous radiation gamma flux of external ⁶⁰Co sources at dose rates of 1.78 or 6.32 kGy/h.

First visual inspection of the irradiated solutions showed colour changes. No precipitate was observed but samples turned slightly red at an integrated dose of 300 kGy. Beyond 300 kGy the samples lost their colour. No volume decrease was observed during irradiation, hence evaporation is assumed to be negligible. The glass bottles then were stored in a freezer while awaiting further analysis.

The complexation properties of the irradiated SO₃-Ph-BTP samples were evaluated by determining Am(III) and Eu(III) distribution ratios. The distribution ratios obtained with fresh, aged and irradiated samples are compared in Figure 3.

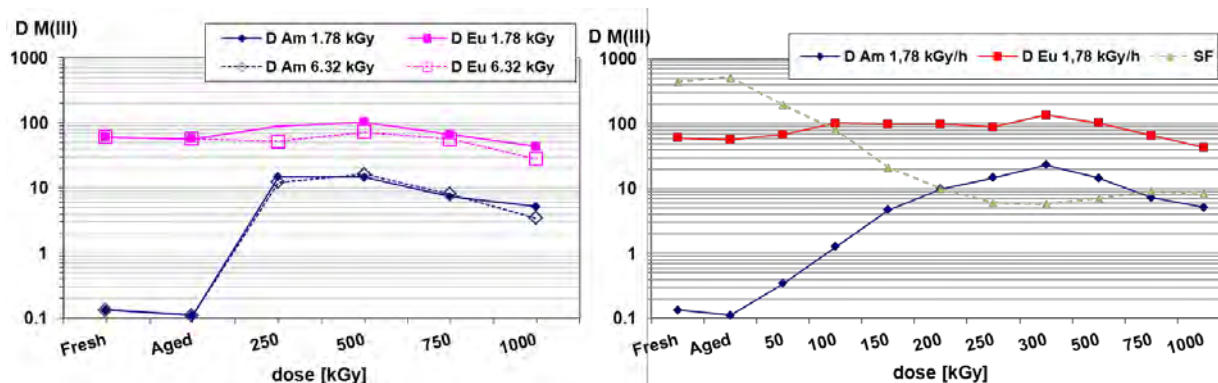


Figure 3. Am(III) and Eu(III) extraction with fresh, aged and irradiated SO_3 -Ph-BTP samples at different doses and dose rates. Organic phase, 0.2 mol/L TODGA + 5% 1-octanol in kerosene. Aqueous phase, 10 mmol/L SO_3 -Ph-BTP + $^{241}Am(III)$ + $^{152}Eu(III)$ in 0.5 mol/L HNO_3 .

Comparison of distribution ratios from fresh and aged control samples show that hydrolytic degradation is not significant after 30 days, in agreement with Figure 2. However, an effect of radiolytic degradation is observed from the first irradiation step (50 kGy). Am(III) extraction increases progressively, reducing the separation factor between Am(III) and Eu(III), $SF_{Eu(III)/Am(III)}$, along the irradiation procedure. Up to 200 kGy of integrated dose the separation factor remains higher than 10. Beyond, TODGA's selectivity is approached ($SF_{Eu(III)/Am(III)} \approx 7$ [3]). As shown in Figure 3 (left), different dose rates have the same effect. Moreover, the formation of small bubbles and a sulphur smell were detected for samples which had received between 250–500 kGy, right after they were removed from the irradiation pond.

The increase in Am(III) distribution ratios upon irradiation is explained by radiolytic degradation of SO_3 -Ph-BTP. Assuming that the degradation products do not interfere and taking into account the dependency of Am(III) distribution ratios on the concentration of SO_3 -Ph-BTP as reported in [3], the decrease in SO_3 -Ph-BTP concentration with increasing dose was estimated (Figure 4). Approx. 50% would be lost at a dose of 60 kGy; less than 10% would remain at 250 kGy.

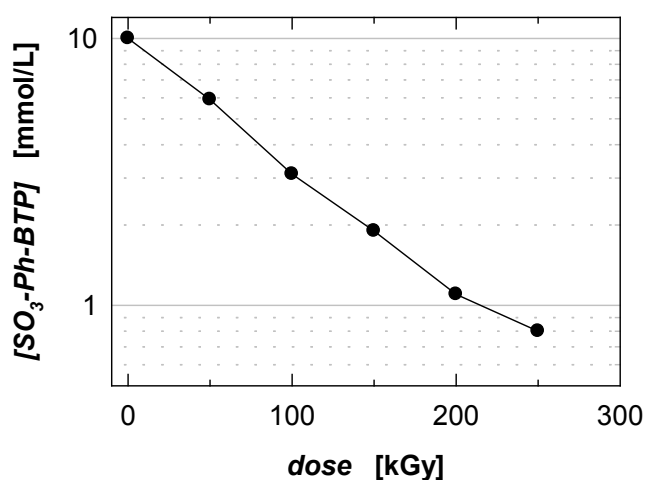


Figure 4. SO_3 -Ph-BTP concentration remaining after irradiation, estimated from the increase in Am(III) distribution ratios as a function of integrated dose (cf. Figure 3).

As observed in previous studies on the stability of diglycolamides [10], degradation fragments may interfere with the extraction process. Therefore, qualitative analysis was performed to evaluate degradation along the irradiation procedure.

Absorption spectra of irradiated aqueous samples showed drastic changes only for doses ≥ 500 kGy. However, already at a dose of 250 kGy no $\text{SO}_3\text{-Ph-BTP}$ could be detected by HPLC-DAD/MS analysis even though no degradation products were found (Figure 5). It seems some of them could be transferred to the organic phase, since colour changes in the organic phases were observed after extraction.

The analysis of the samples irradiated with lower doses showed decreasing intensity of the signal corresponding to $\text{SO}_3\text{-Ph-BTP}$ and appearance of new signals. The chromatogram after irradiation with 50 kGy shows the presence of at least three new peaks which may be attributed to degradation products. A preliminary evaluation of ESI^- spectra indicates loss of sulphonyl or sulfophenyl groups, oxidations and rupture of the pyridine-triazine bonds. The Identification of degradation products is under way.

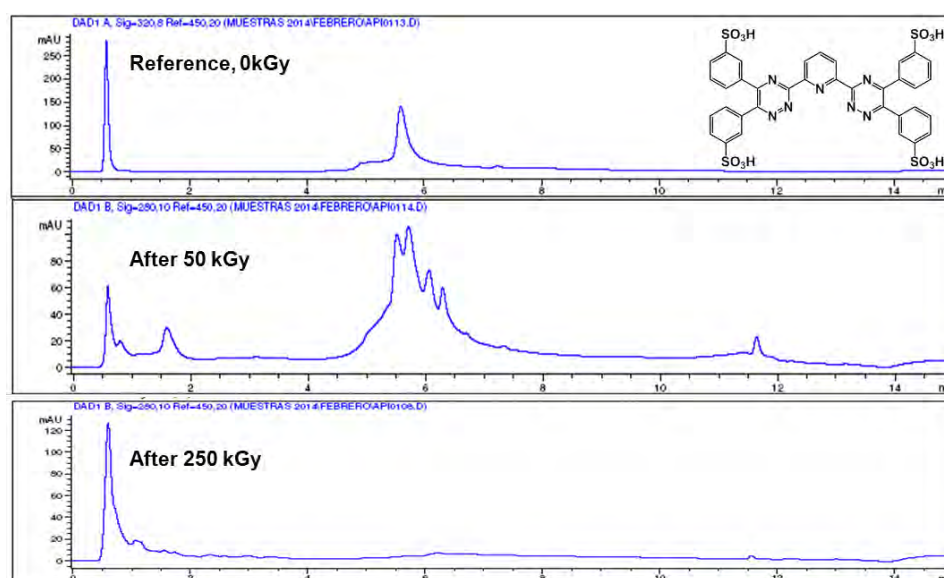


Figure 5. HPLC-DAD chromatograms (280 nm) of $\text{SO}_3\text{-Ph-BTP}$ samples in 0.5 mol/L HNO_3 : reference and after irradiation to doses of 50 and 250 kGy (at a dose rate of 1.78 kGy/h).

Conclusions

Studies on the chemical and irradiation stability of $\text{SO}_3\text{-Ph-BTP}$ were performed. These showed rather good stability versus HNO_3 . When storing solutions of $\text{SO}_3\text{-Ph-BTP}$ in 0.5–3 mol/L HNO_3 up to 120 days, constant Am(III) and Eu(III) distribution ratios were measured when extracting from these solutions into a TODGA solvent.

However, gamma irradiation with doses of ≥ 50 kGy had a negative impact on its performance. With increasing dose the Am(III) distribution ratios increased, reducing the separation factor along the irradiation. After 250 kGy, a loss of approx. 90% of the initial $\text{SO}_3\text{-Ph-BTP}$ concentration was estimated. For SANEX process have been

estimated dose rates from 0.03 to 0.2 kGy/h, and from 0.4 to 0.8 kGy/h, for UO₂ and MOX fuel, respectively [8].

Further experiments are being carried out to gain a better understanding of the radiolytic degradation of SO₃-Ph-BTP.

Acknowledgement

The research leading to these results is being performed in the SACSESS project funded by the European Atomic Energy Community Seventh Framework Programme under grant agreement № 323282.

- 1 Modolo, G. et al. *Radiochim. Acta* **2012**, 100 (8–9), 715–725.
- 2 Panak, P. J.; Geist, A. *Chem. Rev.* **2013**, 113 (2), 1199–1236.
- 3 Geist, A. et al. *Solvent Extr. Ion Exch.* **2012**, 30 (5), 433–444.
- 4 Carrot, M. J. et al. *Solvent Extr. Ion Exch.* **2014**, 32 (5), 447–467.
- 5 Malmbeck, R. et al. *Internat. Conf. ISEC 2014*, Würzburg, Germany, 7–11/9/2014.
- 6 Geist, A. et al. *Internat. Conf. GLOBAL 2013*, Salt Lake City, U.S.A., 29/9 – 3/10/2013.
- 7 Wilden, A. et al. *Internat. Conf. ISEC 2014*, Würzburg, Germany, 7–11 September 2014.
- 8 Magnusson, D. et al. *Radiochim. Acta* **2009**, 97, 497–502.
- 9 Horwitz, E. P. et al. *Solvent Extr. Ion Exch.* **2005**, 23, 319–344.
- 10 Galán, H. et al. *Eur. J. Org. Chem.* **2011**, (20&21), 3959–3969.

Process development studies and demonstration of an r-SANEX process using C5-BPP – selective separation of trivalent actinides from lanthanides

*Andreas Wilden^{*1}, Giuseppe Modolo¹, Fabian Sadowski¹, Steve Lange¹, Antje Bremer^{2,3}, Denise Munzel², Petra J. Panak^{2,3}, Andreas Geist²,*

In this study, an optimised solvent comprising 0.01 mol/L C5-BPP + 0.5 mol/L 2-bromo-hexanoic acid in a diluent mixture of TPH and 10% 1-octanol was developed and tested for the selective extraction of trivalent actinides from lanthanides. In batch experiments and single centrifugal contactor tests the equilibrium extraction data and kinetics of the system in extraction, scrubbing and stripping modes were evaluated and a 16-stage flow-sheet was developed. The flow-sheet was successfully tested in a spiked continuous counter-current centrifugal contactor demonstration test using a DIAMEX product simulate solution. However, it turned out that the number of contactor stages was insufficient for a complete recovery of An(III), although a fairly clean An(III) product fraction was obtained with only low contaminations of Ln(III). The high selectivity of the C5-BPP extractant for An(III) over Ln(III) was shown. The results of the spiked test are presented and discussed.

Introduction

The separation of Am(III) and Cm(III) from lanthanides (Ln(III)) plays a crucial role in the partitioning & transmutation strategy investigated in Europe and worldwide.¹⁻² Much effort has been conducted to develop liquid-liquid counter-current separation processes based on soft-donor extractants, leading to the successful demonstration of several processes.³⁻⁴ However, for a better understanding of the underlying fundamental principles of selectivity of these extractants, we stepped back and investigated similar extractants with structural modifications.

Besides the well-known BTP⁴ and BTBP⁵ class of An(III) selective extractants, alkylated bis-pyrazolypyridines⁶ (BPPs) also show a high selectivity for An(III) over Ln(III). A particular member of this class, C5-BPP (2,6-Bis(5-(2,2-dimethylpropyl)-1H-pyrazol-3-yl)pyridine, Figure 1), was studied in more detail. It was found that it may be suitable for use in an r-SANEX process for separating An(III) from Ln(III).⁷ However, the addition of a lipophilic anion (e.g. 2-bromohexanoic acid, Figure 1) is required, as the ligand does not extract the metal nitrates directly (in contrast to BTP and BTBP extractants). The extraction mechanism was found to follow an ion exchange mechanism. As shown by TRLFS,⁸⁻⁹ the extracted complexes consist of An(III) coordinated by three BPP molecules; the lipophilic anions required for charge compensation are not directly coordinated to the metal ion. Due to the ion exchange mechanism, An(III) extraction by C5-BPP is only possible from dilute nitric acid (~0.1 mol/L), while back-extraction can be performed at higher nitric acid concentrations. However, the extractant is protonated at nitric acid concentrations

1 Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Nuclear Waste Management (IEK-6), 52428 Jülich, Germany, * Corresponding Author: a.wilden@fz-juelich.de

2 Karlsruhe Institute of Technology, INE, Karlsruhe, Germany

3 University of Heidelberg, Institute of Physical Chemistry, 69120 Heidelberg

>1 mol/L and precipitates, which limits the use of highly concentrated HNO_3 . As the distribution ratios of An(III) at 1 mol/L HNO_3 were still too high for an efficient back-extraction, the addition of 10 vol.-% 1-octanol into the solvent was used to reduce the An(III) distribution ratios.⁷

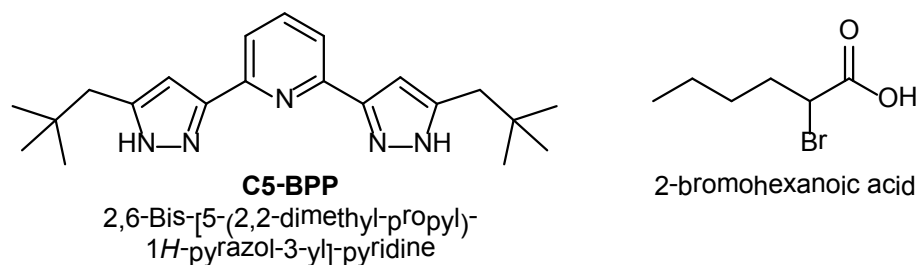


Figure 1. Chemical structures of C5-BPP and 2-bromohexanoic acid.

Flow-sheet design

The flow-sheet was designed based on equilibrium data obtained from batch shaking experiments as well as single centrifugal contactor tests using different flow-rates. Computer-code calculations were performed to optimise the number and distribution of the different process stages (extraction, scrubbing, and stripping), as described in ref.¹⁰. The total number of stages was limited to 16, due to the experimental setup of the centrifugal contactor battery, and the test was planned to be finished within one day. Therefore, 10 stages for extraction, 2 stages for scrubbing, and only 4 stages for An(III) stripping were planned, although the calculations already showed that this may not be enough to achieve sufficiently good separation and recovery of An(III). A schematic representation of the flow-sheet is given in Figure 2.

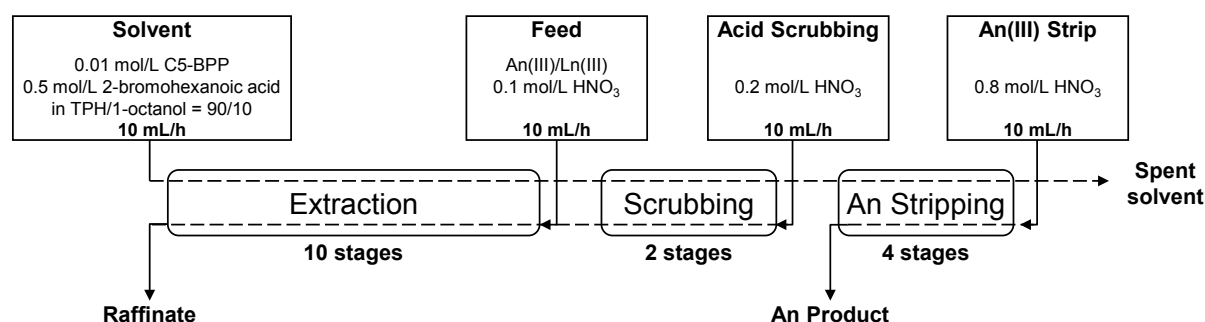


Figure 2. Flow-sheet of the C5-BPP demonstration process.

Results and Discussion

The r-SANEX process is foreseen to follow a preceding DIAMEX process, as known in the literature as the DIAMEX + SANEX strategy.¹¹ Therefore, the DIAMEX product will be the feed for the consecutive r-SANEX process, consisting of the trivalent lanthanides and actinides. In light water reactor fuel only the light lanthanides are present. However, we added also low amounts of the heavier lanthanides to our feed, for scientific curiosity reasons, while the concentrations of the light lanthanides

resemble those found in DIAMEX product solutions. The composition of the feed solution used for our process demonstration test is given in Table 1.

Table 1. Composition of the synthetic DIAMEX product solution.

Element	Concentration [mg/L or as shown]	Element	Concentration [mg/L]	Element	Concentration [mg/L]
²⁴¹ Am	5 MBq/L	Pr	265	Dy	22
²⁴⁴ Cm	5 MBq/L	Nd	980	Ho	19
¹⁵² Eu	9 MBq/L	Sm	193	Er	19
Y	93	Eu	59	Tm	19
La	297	Gd	74	Yb	16
Ce	564	Tb	18	Lu	13
HNO ₃	0.1 mol/L				

The process demonstration test was run in a 16-stage annular centrifugal contactor setup¹² installed in a fume-hood, following the flow-sheet shown in Figure 2. The test was run for 7 h, 15 min with regular sampling of the outlets of the contactor battery. After 7 h, 15 min the steady-state was reached and the test was stopped. The content of the contactors' mixing chambers was sampled and analysed. Figures 3 and 4 show the ²⁴¹Am and ¹⁵²Eu (gamma) as well as the ²⁴¹Am and ²⁴⁴Cm (alpha) profiles, respectively. Table 2 shows the mass balances, recoveries and process decontamination factors obtained during the C5-BPP test.

Am(III) was well extracted with a distribution ratio of 2.7 in the feed-stage. In the whole extraction section Am distribution ratios were quite low with values from 1.7 to 2.7, explaining the relatively flat profile. Surprisingly, the Am distribution ratios increased in the scrubbing section, with a maximum distribution ratio of 9.7. In this section, lower distribution ratios would have been expected, as the nitric acid concentration should have been slightly higher than in the extraction section. However, the aqueous/organic ratio and the total flow-rate in the scrubbing section changed and probably lead to higher extraction efficiency. In the stripping section, the Am profile was steeper and the distribution ratios decreased to 0.5. Obviously, the total number of stages was insufficient for sufficient decontamination and recovery of Am, so more stages in the extraction and stripping sections would be required.

Curium distribution ratios were even lower compared to Am with distribution ratios in the extraction section between 1.0 and 2.5. The lower extraction of Cm was expected from earlier experiments. This leads to a loss of Cm to the raffinate up to 24%. Of course, this value is far too high. However, with slight adjustments of the process, in particular a higher number of stages, the loss could be reduced. With further adjustments, in particular a precise nitric acid concentration control, also an Am/Cm separation might be possible. In the scrubbing and stripping sections the Cm distribution ratios were also lower compared to Am.

The Eu profile very well resembles the profile of all lanthanides (including the heavier lanthanides). For Eu, maximum distribution ratios of 0.05 were observed. The best extracted lanthanides Pr and Nd showed maximum distribution ratios of 0.16. The lanthanide profiles were flat in the extraction section and the lanthanides were routed to the raffinate. In the scrubbing section the profiles show a steep decrease in the concentrations, leading to a good separation from An(III).

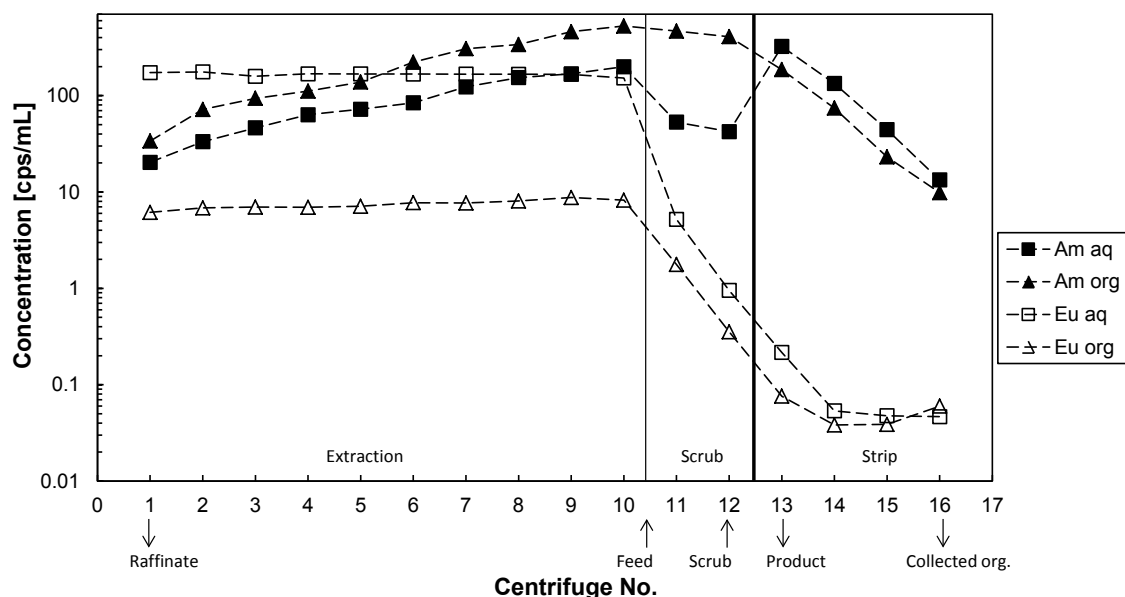


Figure 3. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu .

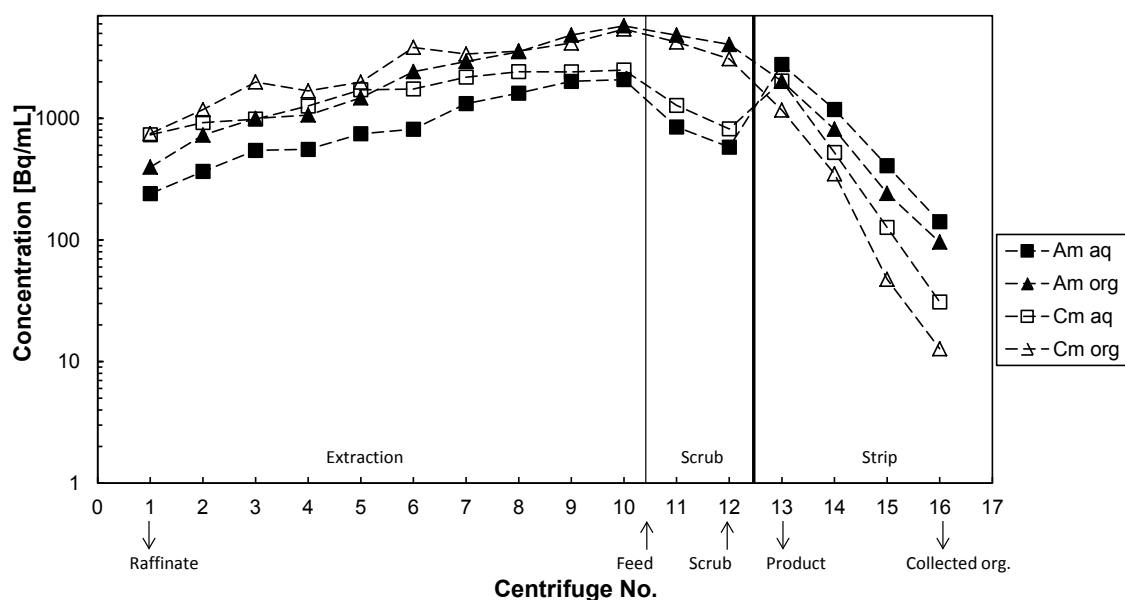


Figure 4. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{244}Cm .

The feed/raffinate process decontamination factors in Table 2 underline the observations made from the profiles. The lanthanides were mostly routed to the raffinate with only low amounts of the best extracted lanthanides found in the An product. The highest contamination was caused by Nd(III) with 1.2% found in the

product. The distribution of the lanthanides followed the trend described in ref.⁷ The feed/raffinate decontamination factors of Am (12.0) and Cm (4.2) were quite low and have to be increased. This could either be done by increasing the total number of stages or by decreasing the nitric acid concentration in the extraction section. Decreasing the nitric acid concentration would increase the An(III) distribution ratios.

The spent solvent was only contaminated with 1.7% Am(III). Here, also two options are available to decrease the spent solvent contamination: increasing the number of stripping stages or increasing the nitric acid concentration of the stripping solution. The use of a higher nitric acid concentration however is limited, as the extractant C5-BPP may be protonated and precipitated.

Table 2. Mass balance, recovery, and process decontamination factors obtained during the C5-BPP test.

Element	% in raffinate	% in spent solvent	% in An(III) product	DF _{feed/raffinate}
²⁴¹ Am	8.6	1.7	89.7	12.0
²⁴⁴ Cm	24.0	0.0	76.0	4.2
Ce	99.6	D.L.	0.4	1.0
Pr	99.1	D.L.	0.9	1.0
Nd	98.8	D.L.	1.2	1.0
Sm, and Gd	99.7	D.L.	0.3	1.0
Eu	99.9	0.0	0.1	1.0
Y, La, Tb, Dy, Ho, Er, Tm, Yb, and Lu	100.0	D.L.	0.0	1.0

D.L. = below detection limit

Conclusions

The presented r-SANEX process based on C5-BPP showed a good selectivity for An(III) over Ln(III). A 16-stage spiked demonstration test showed the principal feasibility of the desired An/Ln separation with this solvent. A high purity of the An(III) product was obtained with only low contaminations of Ln(III). However, the total number of stages would have to be increased to increase the An(III) recovery and to minimise losses to the raffinate and spent solvent.

Acknowledgements

Financial support for this research was provided by the German Federal Ministry of Education and Research (Contract No. 02NUK020E, 02NUK020D, and 02NUK020A).

References

1. OECD-NEA, **2011**, NEA No. 6894.

2. E. M. González-Romero, *Nucl. Eng. Des.* **2011**, *241*, 3436-3444.
3. G. Modolo, A. Wilden, A. Geist, D. Magnusson, R. Malmbeck, *Radiochimica Acta* **2012**, *100*, 715-725.
4. P. J. Panak, A. Geist, *Chemical Reviews* **2013**, *113*, 1199-1236.
5. M. J. Hudson, L. M. Harwood, D. M. Laventine, F. W. Lewis, *Inorg. Chem.* **2013**, *52*, 3414-3428.
6. M. A. Halcrow, *Coordination Chemistry Reviews* **2005**, *249*, 2880-2908.
7. A. Geist, U. Müllich, A. Wilden, S. Gülland, G. Modolo, *19th International Solvent Extraction Conference*, Santiago de Chile, Chile **2011**, P104.
8. A. Bremer, C. M. Ruff, D. Girnt, U. Müllich, J. Rothe, P. W. Roesky, P. J. Panak, A. Karpov, T. J. J. Müller, M. A. Denecke, A. Geist, *Inorg. Chem.* **2012**, *51*, 5199-5207.
9. A. Bremer, A. Geist, P. J. Panak, *Radiochimica Acta* **2013**, *101*, 285–292.
10. G. Modolo, P. Kluxen, A. Geist, *Radiochimica Acta* **2010**, *98*, 193-201.
11. C. Hill, in *Ion Exchange and Solvent Extraction, A Series of Advances, Vol. 19* (Ed.: B. A. Moyer), CRC Taylor and Francis, **2009**, pp. 119-193.
12. R. A. Leonard, in *Ion Exchange and Solvent Extraction, A Series of Advances, Vol. 19* (Ed.: B. A. Moyer), CRC Taylor and Francis, **2009**, pp. 563-616.

Development and testing of an Am/Ln separation flowsheet based on Am oxidation with sodium bismuthate

Jack Law, Bruce Mincher, Troy Garn, Mitchell Greenhalgh, Veronica Rutledge, Idaho National Laboratory, Idaho Falls, ID, USA

The separation of Am from the lanthanides and curium is a key step in proposed advanced fuel cycle scenarios. The partitioning and transmutation of Am desirable to minimize the long-term radiotoxicity of material interred in a future high-level waste repository. A separation amenable to process scale-up remains elusive. Given only subtle chemistry differences within and between the ions of the trivalent actinide and lanthanide series this separation is challenging; however, higher oxidation states of americium can be prepared using sodium bismuthate and separated via solvent extraction using diamylamylphosphonate (DAAP) extraction. Among the other trivalent metals only Ce is also oxidized and extracted. Due to the long-term instability of Am^{VI}, the loaded organic phase was readily selectively stripped to partition the actinide to a new acidic aqueous phase. Batch extraction distribution ratio measurements were used to design a flowsheet to accomplish this separation. Additionally, crossflow filtration was investigated as a method to filter the bismuthate solids from the feed solution prior to extraction. Results of engineering-scale testing with non-radioactive surrogate using the crossflow filtration unit coupled with centrifugal contactors to evaluate the extraction and stripping behavior of oxidized Ce will be detailed. In addition, the design and testing of the flowsheet in a glovebox with Am tracer will be discussed.

New Process for the Selective Extraction of Uranium from Phosphoric Ores

*Bernier G.*¹, Miguiditchian M.¹, Pacary V.¹, Bertrand M.¹, Camès B.¹,
Hérès X.¹, Mokhtari H.².*

Summary

In the fertilizer and food industries, commercially available phosphoric acid, obtained by action of sulphuric acid on calcium phosphate rocks (wet process phosphoric acid – WPA), contains low concentration of uranium (30 to 300 ppm of U_3O_8) with high concentrations of iron (several g/L). Liquid-liquid extraction processes have been developed during the seventies in order to recover uranium as a by-product of industrial phosphoric acid. The production stopped in the late 90s due to the decline in the price of uranium. Moreover the worldwide uranium resources associated with phosphorite deposits constitutes an important secondary source of uranium for nuclear applications. Further studies are in progress at CEA with AREVA since 2009 to propose a new extracting molecule improving extraction performances of uranium and greater selectivity versus other cationic impurities including iron, the main impurity. Parametric experiments in batch conditions led to select and optimize a new design of bitopic extracting molecule which shows a high extraction of uranium(VI) with a very high selectivity towards Fe(III): extraction and stripping isotherms to determine the stoichiometry of the complexes. A model was developed and implemented in the CEA PAREX simulation code to simulate the operations of solvent extraction in continuous laboratory contactors. A process flowsheet was proposed for the selective extraction of uranium from phosphoric acid solution and implemented successfully, on the laboratory platform PROUST at CEA Marcoule with a genuine solution of an industrial phosphoric acid. This process was further implemented on industrial solutions in the AREVA Mines facilities.

1 - Introduction

In the fertilizer and food industries, commercially available phosphoric acid, obtained by action of sulphuric acid on calcium phosphate (wet process phosphoric acid – WPA, 30% wt. P_2O_5), contains low concentration of uranium (30 to 300 ppm of U_3O_8) with high concentrations of iron and aluminium (ranging from 2 to 6 g/L) as well as other impurities such as molybdenum, vanadium or titanium. The recovery of uranium will allow to decontaminate the phosphoric acid and in the same time valorize uranium for the nuclear industry¹. Indeed, the worldwide uranium resources associated with natural phosphate rocks are estimated at approximately 4 Mt which constitutes an important secondary source for uranium production².

Separation of uranium from phosphoric acid has been a worldwide area of intense research. Several processes have been investigated to recover uranium from WPA. Solvent extraction is the most used method and various organic extractants have been developed ($D_2EHPA/TOPO$ ³, $URPHOS$ ^{4 5}, $OPAP$ ⁶, $OPPA$ ⁷, $URPHOS$ bis^{8 9}) to selectively extract uranium and purify it from other elements present in phosphoric acid to respect ASTM C 967 08 specifications. Separation of uranium from iron is the most difficult as iron is from ten to thirty times more concentrated than uranium in industrial phosphoric acids and can lead to the formation of cruds during the stripping

1

* G. Bernier, CEA, Nuclear Energy Division, RadioChemistry & Processes Department, F-30207 Bagnols sur Cèze, France; Tel. : +33 4 66 79 16 05; fax: + 33 4 66 79 65 67 E-mail address : gilles.bernier@cea.fr

2

AREVA BU Mines/SEPA – 2 Route de Lavaugrasse – 87250 Bessines sur Gartempe, France

step of the process. The Fe/U massic ratio must be lower than 0.15% in the purified uranium to fulfill the ASTM criteria.

Recently, bifunctional extracting molecules which combine both cationic exchanger and neutral donor functions on the same molecule have been designed by the CEA and a patent has been filed by AREVA and CEA¹⁰. Several new amidophosphonic ligands were synthesized and tested for the selective separation of uranium from phosphoric acid¹¹. After screening, DEHCNPB or butyl-N,N-bis(EthylHexyl)-carbamoylnonyl phosphonate (Figure 1) appears to be the best candidate to extract uranium from 5M H₃PO₄ solutions with very high selectivity towards Fe(III) and other cationic impurities ($SF_{U/Fe} \approx 2800$)¹².

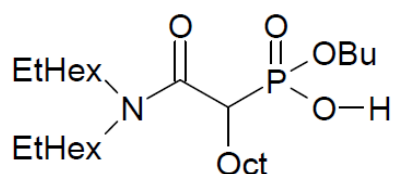


Figure 1: Structure of DEHCNPB

This paper presents the experimental work done to develop a full liquid-liquid extraction process with this molecule and to elaborate a phenomenological model from parametric laboratory studies. This model was then implemented in the CEA PAREX code in order to design a flowsheet, which was tested on the PROUST platform in Marcoule to demonstrate the scientific feasibility of the selective extraction of uranium from an industrial phosphoric acid solution.

2 – Laboratory parametric studies

2 –1 Preparation of solutions and distribution ratio measurements

DEHCNPB ligand was synthesised by Pharmasynthese according to the previous published synthesis¹². Organic solution is prepared by dilution of the extractant at 0.1 M in n-dodecane and the accurate concentration was titrated by sodium hydroxide. The addition of a phase modifier is not necessary with this extractant.

Synthetic aqueous solutions of phosphoric acid were prepared by mixing concentrated solutions of phosphoric acid, uranium and iron phosphates. Uranium and iron distribution ratios were measured in batch conditions to evaluate the efficiency of U and Fe extraction and the U/Fe selectivity. In order to improve the detection limits of iron in organic phase, aqueous solutions were spiked with ⁵⁹Fe and iron distribution ratios were determined by gamma spectrometry. Equal volumes of aqueous and organic solutions were vigorously shaken to obtain a good emulsion, during thirty minutes for equilibrium distribution measurements. The concentrations of uranium and iron in aqueous phase, before and after contact, were measured by Inductively Coupled Plasma with atomic emission spectroscopy (ICP-AES). The cation concentrations in the organic phase were also determined by ICP-AES after two successive stripping with ammonium oxalate and 0.5 M ammonium carbonate.

2 –3 Equilibrium studies

The influence of the concentration of DEHCNPB on uranium and iron extraction as well as the impact of uranium loading were studied in order to characterize the stoichiometry of the complexes formed in organic phase and to model the extraction equilibriums.

2 –3 –1 Influence of the DEHCNPB concentration on uranium extraction

The distribution coefficient of uranium(VI), D_U , was measured at 5M H₃PO₄ at different concentrations of DEHCNPB varying from 0.01 to 0.1 mol/L. The plot of $\log D_U$ versus $\log [DEHCNPB]_{free}$ is linear with a slope of 2 which confirms that UO_2^{2+}

is extracted by two molecules of DEHCNPB corresponding to the release of 2 protons in aqueous phase.

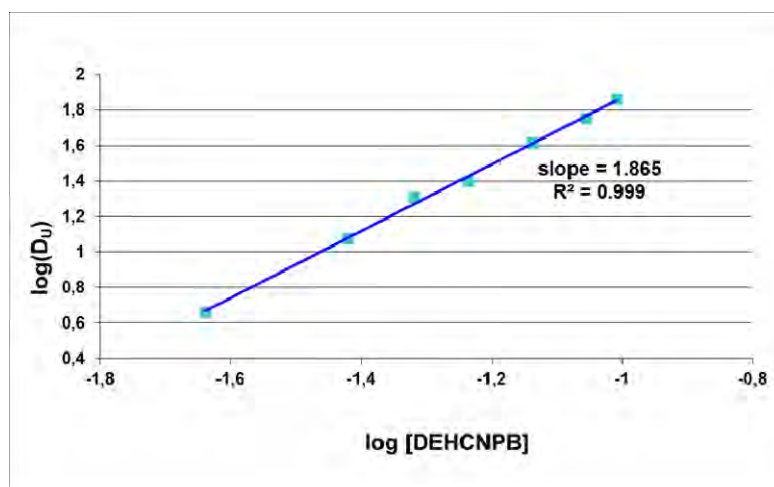


Figure 2: Influence of the initial concentration of DEHCNPB on D_U at 5 M H_3PO_4 at 23°C

2 –3 –2 Influence of the DEHCNPB concentration on iron extraction

The distribution coefficient of iron(III) (spiked with ^{59}Fe), D_{Fe} , was measured at 5 M H_3PO_4 at different concentrations of DEHCNPB varying from 0.01 to 0.1 mole/L. The plot of $\log D_{Fe}$ versus $\log [DEHCNPB]_{free}$ is linear with a slope of 1.6. The extraction of Fe(III) by 1 and 2 molecules of DEHCNPB was thus assumed in organic phase.

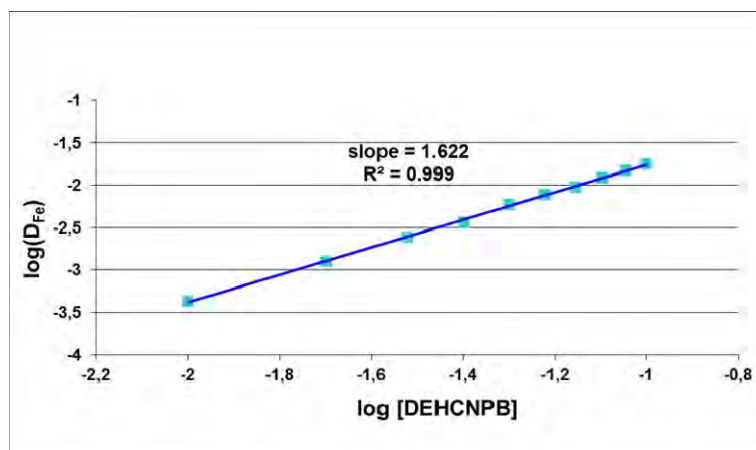


Figure 3: Influence of the initial concentration of DEHCNPB on D_{Fe} at 5 M H_3PO_4 at 23°C

2 –3 –3 Influence of uranium loading

0.1M DEHCNPB solutions were contacted with increasing concentrations of uranium at 5 M H_3PO_4 . It was possible to load up to 5.5 g/L of uranium in organic phase with 0.1M of extractant diluted in n-dodecane without forming any third phase. The molar DEHCNPB/U ratio at saturation seems to show that 4 or 5 molecules of extractant are needed to extract U(VI) which indicates that 2 dimers of DEHCNPB would coordinate uranium in the complex. However, this hypothesis will have to be confirmed by further SAXS, SANS or NMR measurements.

2 –3 –4 Test with a genuine industrial phosphoric acid solution

The performances of extraction were evaluated with a genuine solution of industrial phosphoric acid whose initial composition is given in Table 1.

The results are very close to those obtained with synthetic solutions and confirm the great selectivity of DEHCNPB for uranium. Among all the other cations present in the genuine solution, only molybdenum is slightly extracted ($D_{Mo} = 0.15$) but the selectivity remains large enough ($SF_{U/Mo} > 600$).

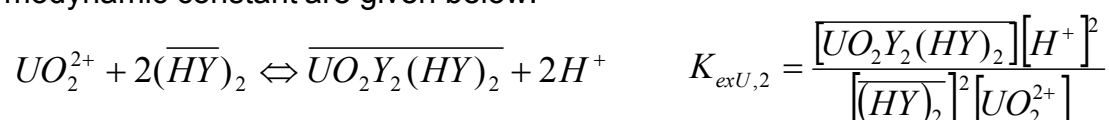
Elements	U	Fe	Mo	Cr	Zn	Cd	Al	V	Ti	Zr
Conc. (mg/L)	155	2470	6	276	393	19	1880	264	55	44
D_M	>100	0.02	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 1: Initial composition of an industrial phosphoric acid solution and distributions ratios measured with 0.1M DEHCNPB at 23°C

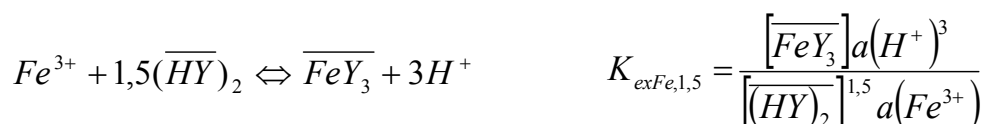
3 – Modelling of the extraction with DEHCNPB

Extraction mechanisms have been proposed based on the experimental data acquired with this new solvent. The goal of the modelling is to determine the thermodynamic constants associated with the different steps of the process: extraction, iron scrubbing and uranium stripping.

A cationic exchange between uranium and DEHCNPB, named HY, is considered in its proton-dimer form. The global form of this equilibrium and the associated thermodynamic constant are given below:



In aqueous phase, environment effects are almost constants and as phosphoric acid is poorly dissociated, the activity coefficients were not considered to take into account deviations from ideality. The proposed mechanism for the extraction of iron is also a cationic exchange mechanism. The global form of this equilibrium and the associated thermodynamic constant are given below:



The experimental study of the influence of the DEHCNPB concentration on Fe(III) distribution ratios shows a slope of 1.6. It was thus proposed that a dimer and a monomer would bind iron in the organic complex. Several extraction equilibrium were proposed and their constants were optimized by minimizing the differences between experimental and calculated organic concentrations after application of the mass action law. Mass balances were resolved in both phases in order to determine the free concentrations according to the optimization procedure computed in the Scilab calculation software. The aim of this algorithm is to minimize the root mean square deviation between calculated and experimental distribution ratios.

The comparison between experimental and calculated data for the isotherm of uranium extraction is represented in Figure 4.

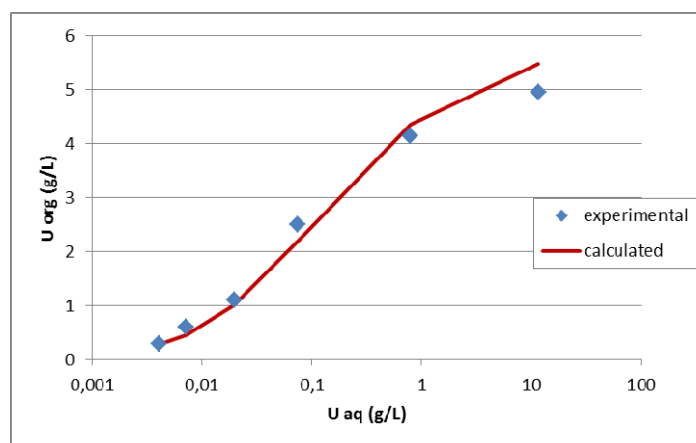


Figure 4: Comparison of experimental and calculated isotherm of extraction of U with 0.1 M DEHCNPB/TPH and 5 M H_3PO_4 at 25°C

4 – Flowsheet design and counter-current test

The model was implemented into the PAREX¹³ simulation code to calculate a flowsheet in order to perform a counter current laboratory run, depicted in Figure 5:

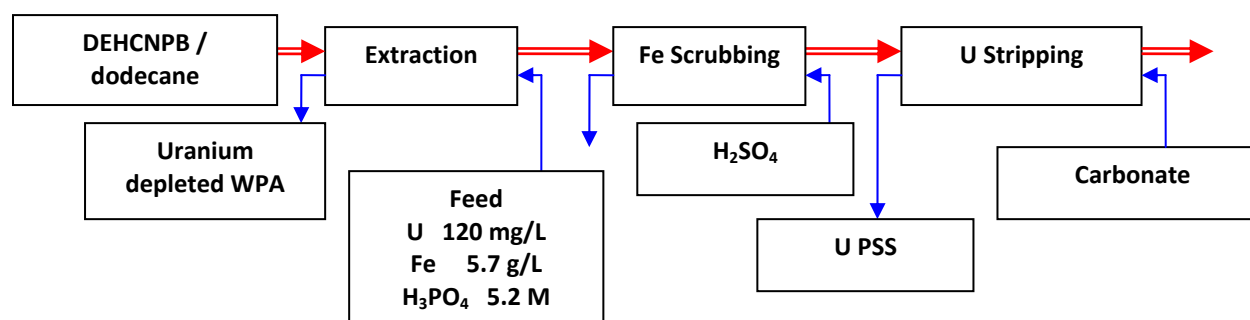


Figure 5: Flowsheet tested for the extraction of uranium by a genuine phosphoric acid on the PROUST platform

This flowsheet was tested on the PROUST platform in Marcoule. Liquid-liquid contacting equipment were Poly(methyl methacrylate) (PMMA) lab-scale mixer settler, heated at 35°C for the extraction step and at 45°C for the iron scrubbing and the uranium stripping steps. Perforated stainless steel blades were used for mixing.

The test was very successful as more than 91% of uranium was recovered, concentrated from 0.12 to 5.6 g/L and very well decontaminated from iron and other impurities. The proportion of iron in the uranium output was found to be lower than 0.043% that meets the American Society for Testing and Materials (ASTM) specification ($Fe/U < 0.15\%$). Furthermore, no cruds were observed in the stripping section and the hydrodynamic behaviour was good throughout the test.

Concentrations profiles were measured in aqueous and organic phases at the end of the test and were compared to the values calculated with the PAREX code. Figure 6 shows the good agreement between experimental and calculated profiles of uranium which validate the extraction model developed in this study.

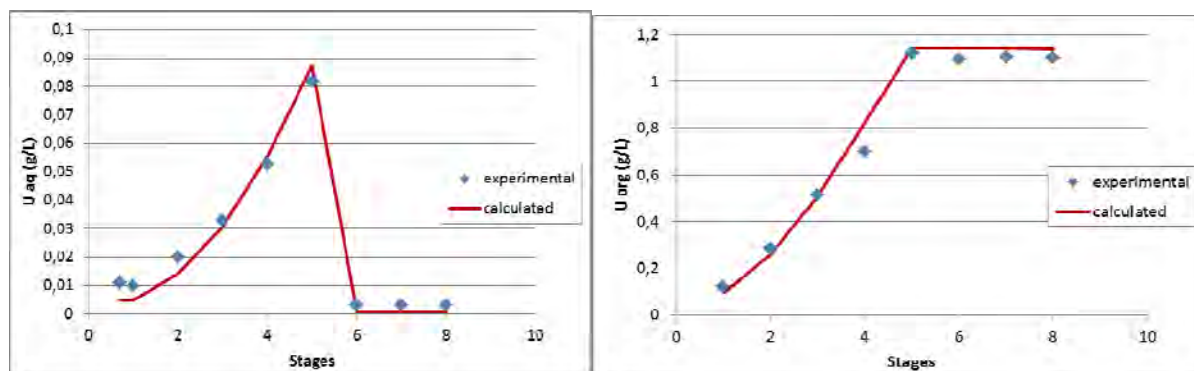


Figure 6: Comparison of experimental and calculated uranium aqueous (left) and organic (right) profiles after the counter-current test with an industrial phosphoric acid

5 – Conclusions

The amidophosphonate DEHCNPB molecule is very selective for the extraction of uranium from phosphoric acid even in presence of high concentrations of iron (3 to 5 g/L) in the genuine phosphoric acid solution. Parametric studies of the impact of the concentrations of extractant and uranium were used to characterize the stoichiometry of the extracted complex in the organic phase and to propose extraction mechanisms. From these experimental results, a model was developed and implemented in the PAREX code in order to calculate a flowsheet. This process flowsheet was implemented in the PROUST platform in G1 facility during 2012, to treat an industrial phosphoric acid solution in laboratory-scale mixer-settlers. The performances of the run are very promising as most of the uranium was recovered with less than 0.043% of iron in the uranium output. Mass balances determined during the test showed that stationary point was achieved. The experimental and calculated profiles of uranium and iron were in good agreement which validates the extraction model. Experiments are now in progress to optimize this flowsheet in order to develop a more compact and efficient process for uranium recovery from phosphoric acid.

References

1. P. Michel, Les Tech. Ind. Min. – Hydrometallurgie Vol. 2, décembre 2006
2. S. Gabriel, A. Baschwitz, G. Mathonniere, T. Elouet, F. Fizaine, Annals of Nuclear Energy 2013, 58, 213-220
3. F. J. Hurst, D.J. Course, U. S. Patent 3 711 591, Janvier 1973
4. F. Hurst, K. Brown, D. Crouse, Ind. Eng. Chem. Process Des. Dev., 1972, 11, 122-128
5. COGEMA APC, French Patent 77-20552, Juillet 1977
6. F. J. Hurst, D.J. Crouse, Ind. Eng. Chem. Process Des. Dev., 1974, 13, 286-291
7. W.L. Mc-Cready, J.A. Wethington, F.J. Hurst, Nucl. Technol., 1981, 53, 344-353
8. G. Lyaudet, P. Du Penhoat, A. Textoris, Ind. Minerale Mines Carrieres Tech., 1989, 71, 168
9. A. Textoris, G. Lyaudet, A. Bathelier, US Patent 5,017,344 (1991)
10. G. Arrachart, N. Aychet, G. Bernier, F. Burdet, A. Leydier, M. Miguiditchian, S. Pellet-Rostaing, G. Plancque, R. Turgis, E. Zekri, (CEA/ICSM) Patent WO 2013/167516 A1 (AREVA Mines)
11. R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguiditchian, S. Pellet-Rostaing, Solv. Ext. And Ion Exch, 2014, accepted
12. R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguiditchian, S. Pellet-Rostaing, 214, submitted
13. C. Sorel, M. Montuir, C. Balaguer, P. Baron, B. Dinh, X. Heres, V. Pacary, H. Roussel, Proceedings of the ISEC 2011 conference, Santiago, Chile, 3-6, 2011

New Thermodynamics Data related to actinides separation

*MC. Charbonnel, N. Boubals, F. Rodrigues, L. Berthon, P. Guilbaud, CEA Marcoule,
DEN/DRCP/SMCS/LILA, Bagnos-sur-Ceze, France*

In the field of reprocessing of the nuclear fuel, different actinide recycling options are considered to reduce the volume and the toxicity of ultimate waste. Different strategies have been tested to separate minor actinides, alone or with other actinides. For each way, specific molecules were designed and relevant ligands were selected with several criteria, among them of course the performance in terms of chemical affinity and selectivity towards the actinide target. The design of new ligands and/or the modelisation of extraction processes need a deeper understanding of actinides distribution. To obtain this knowledge studies have been performed at molecular scale with both structural and thermodynamic approaches.

The presentation will focus on new thermodynamic properties (free energy ΔG° , enthalpy ΔH° and entropy ΔS°) related to the complexation and extraction of actinides and lanthanides with selected ligands and extractants.

Two examples will be presented to illustrate the interest of such knowledge:

- A first example in aqueous phase with the complexation of lanthanides and actinides with hydrophilic diglycolamides, with the presence of several $M(DGA)_n^{3+}$ complexes (system selected for the EXAM process dedicated to the extraction of Am(III)),
- A second example with the extraction of U(VI) and Pu(IV) by several dialkylamides (ligand of interest in the first step of GANEX process, dedicated to the extraction of actinides).

To study the appropriate equilibriums, the speciation has been checked with different spectroscopic methods and molecular dynamics. Then dedicated studies were performed to determine the stability constants and the related enthalpy variations. The interest of calorimetry (alone or coupled with Van t'Hoff method) will be detailed. Discussions will be undertaken about the evolution in series (inside the lanthanide family with two DGAs in the first example and inside the amide family for the second one).

By providing basic information on the structure of complexes and on the energetics related to their formation, this study helps to support the modelisation of the related liquid-liquid process but also to design new efficient molecules.

Extraction Chromatographic Separation of Am(III) and Eu(III) by Porous Silica coating TPPEN-NIPA Gel (1) ---- Gel Synthesis and Temperature Effect ----

Kenji Takeshita and Yusuke Inaba, Tokyo institute of Technology, Tokyo, Japan;
Tsuyoshi Yaita and Shin-ichi Suzuki, Japan Atomic Energy Agency, Tokai, Japan;
Atsunori Mori, Kobe University, Kobe, Japan

N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) is a podand-type ligand with six nitrogen-donors and recognizes the slight difference in the softness between trivalent MA (minor actinide) and Ln (lanthanide). Co-polymer gels with a TPEN derivative, *N,N,N',N'*-tetrakis(4-propenyloxy-2-pyridylmethyl)ethylenediamine (TPPEN), and acrylic monomer were applied to the separation of MA from Ln. Four copolymer gels with different acrylic monomers, such as *N*-isopropylacrylamide (NIPA), acrylic acid (AAc), methyl methacrylate (MMA), and *N,N*-dimethylacrylamide (DMAAm), were synthesized. The chemical structures of TPPEN and the acrylic monomers were shown in Fig.1. The batch extraction tests of typical trivalent MA ($^{241}\text{Am(III)}$) and Ln ($^{152}\text{Eu(III)}$) into these gels were carried out, as shown in Fig.2. In weakly acidic solutions at pH 4 to 5, TPPEN-NIPA gel and TPPEN-DMAAm gel showed high separation factors of Am(III) over Eu(III), which were evaluated to be 26 and 18, respectively. These results indicate that the MA separation performance is improved by using poly-acrylamide as a backbone polymer and TPPEN-NIPA gel is the most suitable for the MA/Ln separation.

TPPEN-NIPA gel is a thermosensitive polymer (LCST: 32°C), which is swollen at 298K and shrunken at 313K. To understand the extraction behavior of metal ion in the gel, the temperature dependence of the extraction of metal ion into TPPEN-NIPA gel was studied by both the batch extraction tests and the X-ray absorption fine structure (XAFS) analysis. The complexation of metal ion with TPPEN was very weak at 298K, because of the hydration complex formation of metal ion. Eu(III) was not interacted with TPPEN and only Am(III) was complexed weakly. On the other hand, the complexation of metal ion with TPPEN was improved at 313K. Then Eu(III) was complexed weakly with TPPEN and Am(III) made a strong complex with TPPEN. The unique temperature effect of TPPEN-NIPA gel, which occurs by the hydration and dehydration of poly-NIPA, is available for the establishment of a new MA/Ln separation process with temperature operation. Temperature above LCST can be used for the recovery of MA from waste solution and that below LCST for the isolation of MA (i.e. the purification of MA).

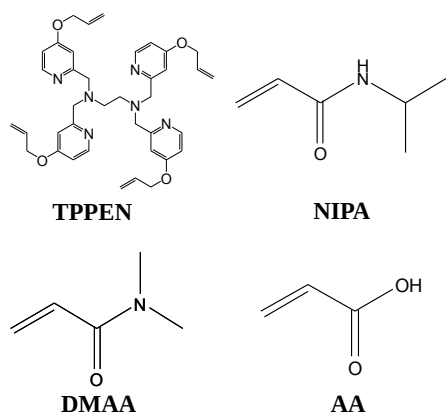


Fig.1 Chemical structure of monomers.

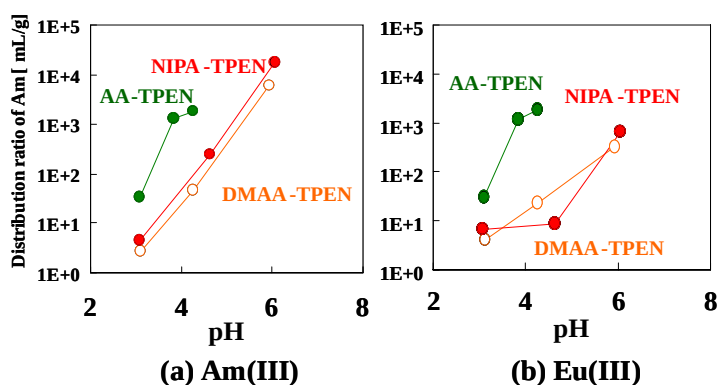


Fig.2 Extraction of Am(III) and Eu(III) with TPPEN gels.

“TRU-SANEX”: a variation on the EURO-GANEX process for heterogeneous recycling scenarios

K. Bell, J. Brown, C. Campbell, M. Carrot, C. Gregson, J. Holt, C. Maher, C. Mason, M. Sarsfield, R. Taylor

National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, UK

GANEX (grouped actinide extraction) processes, that simultaneously co-separate all transuranic (TRU) actinide elements (Np, Pu, Am, and Cm) are under consideration in Europe for recycling scenarios in which “Generation IV” reactor fuels are homogeneously loaded with minor actinides. The GANEX process comprises an initial separation of U from irradiated fuel in the first solvent extraction cycle; transuranic elements are then co-separated in the 2nd cycle. The first cycle has been successfully hot tested at the CEA.¹ Recently, a 2nd cycle process, termed EURO-GANEX, has been developed and successfully tested as part of the European 7th Framework “ACSEPT” project.²

To handle high Pu content (fast reactor and thermal mixed oxide) fuels a solvent composed of 0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in Exxsol D80 is used in the EURO-GANEX process. TRU elements are co-stripped from the solvent loaded with TRU and lanthanides by a solution of a sulphonated bis-triazinyl pyridine complexing agent (SO₃-Ph-BTP)³ and aceto-hydroxamic acid (AHA) in HNO₃. Excellent recoveries of actinides and decontamination from lanthanides were obtained in a EURO-GANEX hot test.

However, whilst there are some potential advantages related to proliferation resistance and process simplification, one significant disadvantage of homogeneous recycling and thus the GANEX process is the presence of curium in the relatively large plutonium containing TRU product. This then necessitates remote handling in the downstream fuel manufacturing plant.

Here, we report the results of a spiked test of a variation of the EURO-GANEX process that is designed for heterogeneous recycling of TRU actinides. The process produces separate (U), (Np,Pu) and (Am,Cm) products. Whilst it is a variation of the EURO-GANEX process, this flowsheet has been termed a “TRU-SANEX” process since it resembles the innovative-SANEX process⁴, designed for the heterogeneous recycling of minor actinides (Am, Cm) following the PUREX process, but with separation of Np and Pu as well as Am and Cm. Testing was performed in a 32 stage glove box housed centrifugal contactor rig and good recoveries of TRU actinides were obtained. The reported results will be compared to the results from spiked and hot testing of the EURO-GANEX process.

¹ M. Miguiditchian et al., Proc. Internat. Conf. GLOBAL 2009, Paris, 6–11 September 2009

² R. Malmbeck et al., ISEC 2014 abstract.

³ A. Geist et al., Solvent Extr. Ion Exch. 2012, 30, 433–444

⁴ G. Modolo et al. Progress in Nuclear Energy, 2013. In print.

Fluorinated malonamides for L/L extraction of *f*-elements

M.C. Dul¹, D. Bourgeois^{*1}, S. Dourdain¹, S. Pellet-Rostaing¹, D. Meyer¹

Summary: Extraction of a metal ion into an organic layer is governed by molecular interactions (complexation of the metal) and supramolecular ordering (aggregation of the extractant). Recently, we proposed fluorinated malonamides (F-malonamides) as efficient extractants for the L/L extraction of lanthanides in fluorinated solvents. Their comparison with classical hydrocarbon extractants (H-malonamides) enabled us to evaluate the relative importance of both factors, and led to the demonstration that supramolecular ordering can in some cases prevail and direct result of L/L extraction. All the results will be presented and discussed in detail.

Context: L/L extraction of *f*-elements in fluorous solvents

Recovery of *f*-elements is a research subject of fast growing importance, with the need for efficient recycling of several rare earth metals, commonly used in optical, electronic, and magnetic devices. Interestingly, as fluorous chemistry proved its efficiency in various fields including liquid-liquid (L/L) extraction and purification of organic and inorganic compounds [1], scarce research work deals with the adaptation of this technology for the separation of *d*- or *f*-elements. Malonamides are neutral extractants, with general formula (MeR'NCO)₂CHR (see Figure 1), and were developed in the frame of *f*-elements extraction and minor actinides separation [2]. Recently, we demonstrated that fluorinated malonamides (F-malonamides, Figure 1) can lead to an efficient L/L extraction of lanthanides in fluorinated solvents [3].

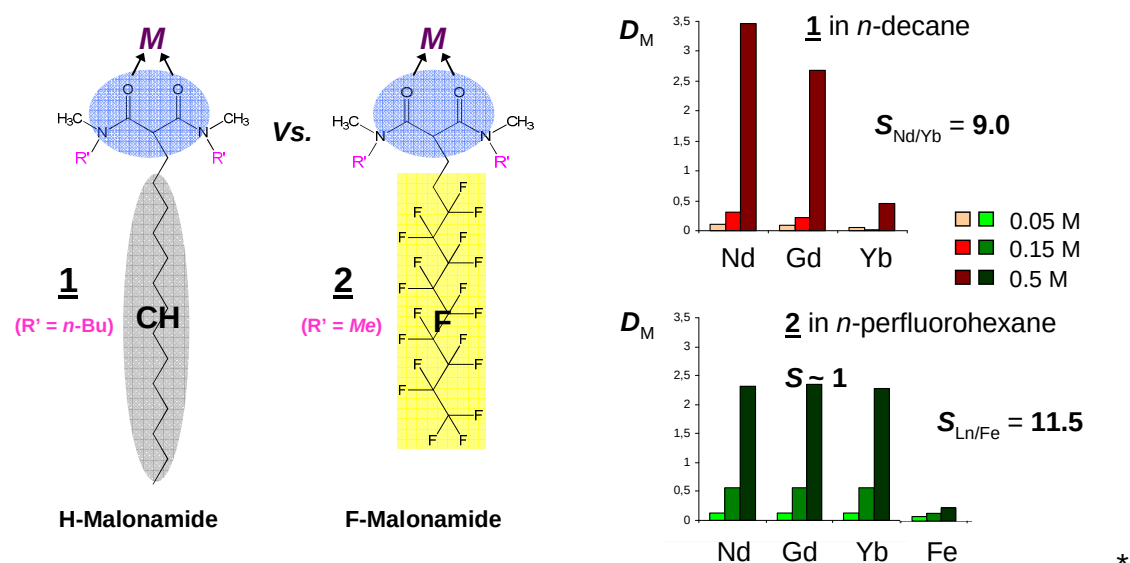


Figure 1: Structure of H- and F-malonamides, and some L/L extraction results with both systems

This new class of compounds was synthesized in good yields on multigram scale, and their L/L extracting abilities were studied on neodymium salts. We proved that the stabilization of Nd(III) salts in fluorinated solvents does not require the fluorophilic

¹ Institute for Separative Chemistry (ICSM), BP17171, Site de Marcoule, F-30207 BAGNOLS SUR CEZE, FRANCE –

* Corresponding Author, damien.bourgeois@cea.fr

triflate counter-ion, and that F-malonamide **2** in perfluorohexane shows comparable efficiency to H-malonamide **1** in *n*-decane. We observed no selectivity within the lanthanide series, but some selectivity between lanthanide(III) and iron(III) (Figure 1).

Factors governing L/L extraction of metallic cations

Understanding the balance of interactions which govern the selectivity of L/L extraction is an ongoing research topic, of key importance in the frame of the recycling of rare earth metals (separation of lanthanides) or the retreatment of nuclear fuel wastes (actinides/lanthanides separation). In these cases, the difficulty results from the tiny differences between the metals to separate (ionic radii between light and heavy lanthanides, softness of the cation between actinides and lanthanides). The supramolecular ordering of the organic layers is supposed to play an important role during these processes [4], but its importance relative to molecular coordination remains largely unknown (Figure 2).

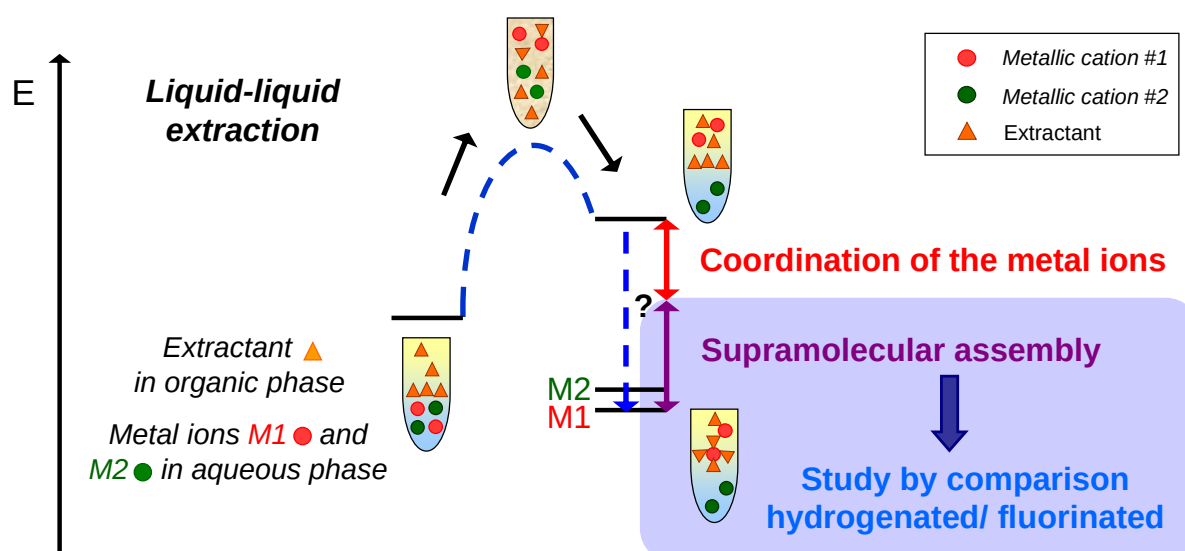


Figure 2: Driving forces of L/L extraction

The purpose of the research project we develop in our team is to prepare and study model compounds where the only parameters that will differ is the strength of the Van der Waals forces, involved in the supramolecular ordering. Our key idea is to compare homologous extractants, bearing either a hydrocarbonated (H-chain) or a perfluorinated (F-chain) hydrophobic side-chain (Figure 3).

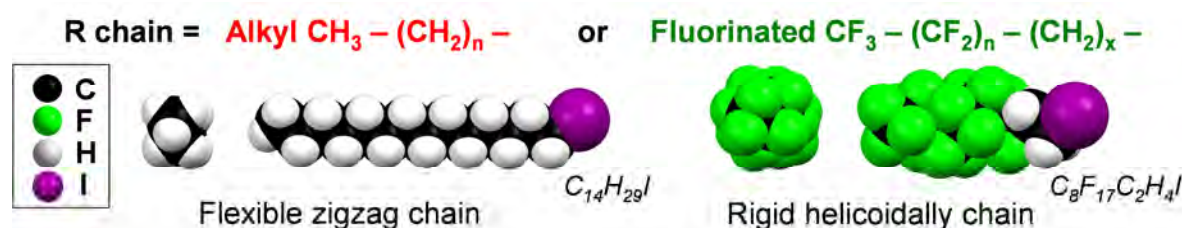


Figure 3: Structure of H- and F-chains

Comparison between H- and F-malonamides

Thus, the malonamide compounds **1** and **2** (Figure 1) prepared at our laboratory possess a similar complexing head, and different hydrophobic tails. Interestingly, in dichloromethane (CH_2Cl_2), their behavior is completely different: whereas the H-malonamide **1** exhibits good extracting capability, as previously reported in the literature, F-malonamide **2** does not lead to L/L extraction (Figure 4). Furthermore, we set in evidence that the amount of water extracted in both cases is very different.

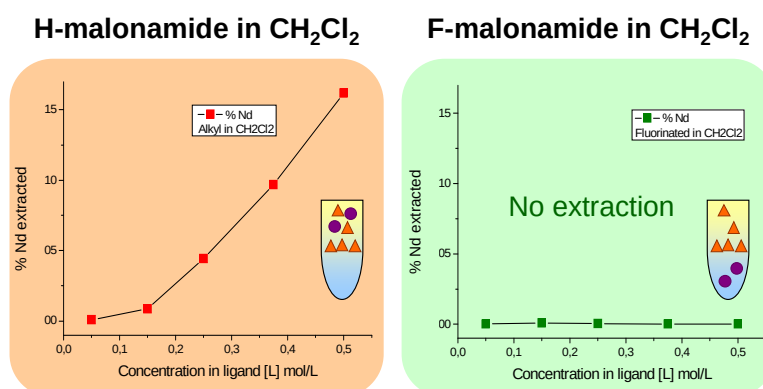


Figure 4: Extraction results of Nd(III) from aqueous HNO_3 solution into CH_2Cl_2 with various H- and F-malonamide organic concentrations.

Therefore, we prepared at the laboratory several controlled organic phases, varying the concentration, the nature of the metallic cation, the nature of the malonamide, the nature of the solvent and the content in water. We performed a systematic structural analysis of these samples with classical techniques such as nuclear magnetic resonance (NMR, 1D and DOSY), IR and UV/vis, and we also studied the supramolecular speciation of the same samples with dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS), to determine the factors which govern the critical aggregation concentration. Latter studies were complemented with small-angle neutron scattering (SANS) experiments, so that we now have a complete image of the molecular and the supramolecular aspects of organic phases in both cases (Figure 5).

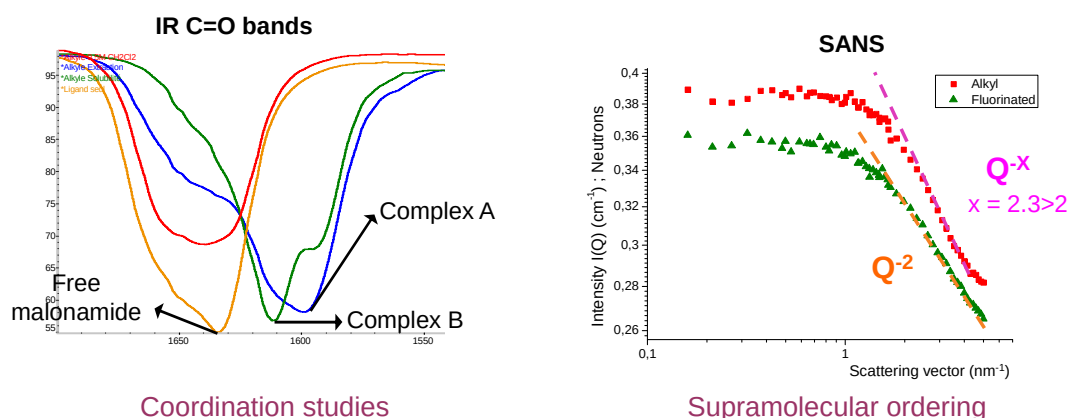


Figure 5: Molecular and supramolecular studies on malonamides **1** and **2**

We propose as a justification for the different behavior of H- and F-systems that the nature of the aggregates formed in the organic layer is different: reverse aggregates, as classically observed, in the case of the H-malonamide, vs direct aggregates, with a fluorous core, in the case of the F-malonamide. [5]

Conclusion: consequences for efficient *f*-elements L/L extraction

During this study, we demonstrated that L/L extraction ability is very sensitive to the nitrogen atoms substitution pattern, and that the most efficient F-malonamide bears a N-methyl substituent, whereas the best H-malonamide bears a N-*n*Bu substituent (Figure 6).

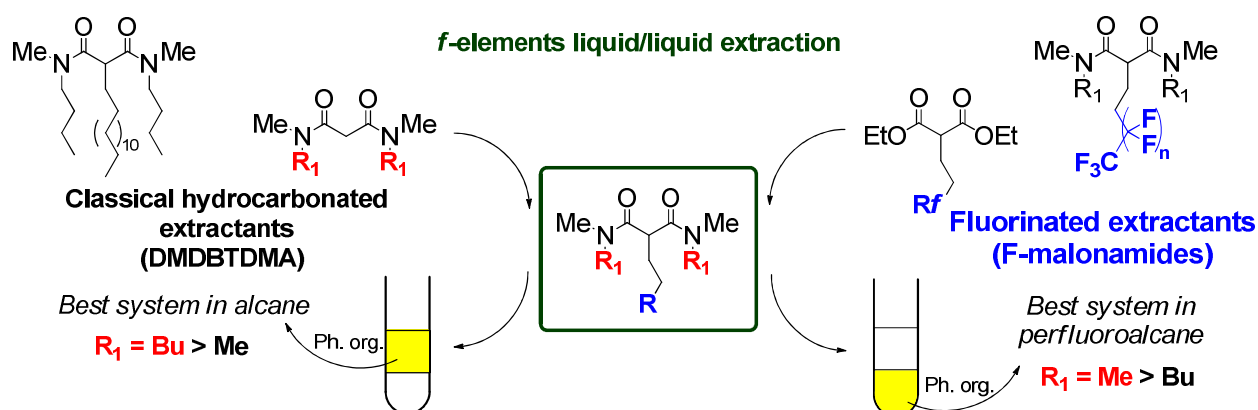


Figure 6: Rational design of H- and F-malonamides for L/L extraction of *f*-elements

We also found general results regarding the relative influence of molecular (complexation) vs supramolecular (aggregation) effects which intervene during L/L extraction. All the results will be presented and discussed in detail.

References

1. J.A. Gladysz, D.P. Curran, I.T. Horváth, Handbook of Fluorous Chemistry; Wiley-VCH, Weinheim, 2004, pp. 1-595.
2. (a) C. Cuillerdier, P. Hoel, C. Musikas, L. Nigond, Eur. Pat. Appl. EP 505277 A1 19920923, 1992; (b) V.K. Manchanda, P.N. Pathak, *Sep. Purif. Technol.* **2004**, 35, 85-103.
3. MC. Dul, D. Bourgeois, J. Maynadié, D. Meyer, *Tetrahedron Lett.* **2013**, 54, 6271-6274.
4. (a) R. Chiarizia, M.P. Jensen, P.G. Rickert, Z. Kolarik, M. Borkowski, P. Thiyagarajan, *Langmuir* **2004**, 20, 10798-10806; (b) P. Bauduin, F. Testard, L. Berthon, T. Zemb, *Phys. Chem. Chem. Phys.* **2007**, 9, 3776-3783.
5. MC. Dul, D. Bourgeois, S. Dourdain, D. Meyer, S. Pellet-Rostaing, *manuscript in preparation*.

Liquid-liquid extraction of Rh(III) from chloride medium using tetralkyl phosphonium salts as extractants

J. Y. Mendez-Quezada¹, D. Cholico-Gonzalez^{1,2}, S. Gutiérrez-Granados¹, Pilar Gonzalez¹, Ricardo Navarro¹, Imelda Saucedo¹; C. Ponce de León³, M. Avila-Rodriguez^{1*}

¹ Chemistry Department, Universidad de Guanajuato, Guanajuato Gto., Mexico

²Universidad de Guadalajara, Energy Group, ³Electrochemical Engineering Laboratory, School of Engineering Sciences, University of Southampton, UK

SUMMARY

The extreme long reaction time and the lack of selectivity of the methods for the recovery of Rh(III) are some significant disadvantages, which limit the recycling of this metal ion from waste solutions. In this paper a fast and efficient liquid-liquid extraction system of Rh(III) using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) and Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) as extractants is reported. A systematic study was carried out varying parameters as concentration of chlorides and extractant as well as the time of extraction. In the case of the Cyphos IL 104, the results obtained show high percentage of Rh(III) extraction (> 99%) and a very fast mass transfer from the aqueous phase to the organic phase (less than 5 minutes of contact between the phases).

KEYWORDS

Ionic liquids, Cyphos IL 101, Cyphos IL 104, rhodium.

INTRODUCTION

Platinum group metals (PGM) have shown high catalytic activity to oxidize unburned organic compounds found in the exhaust gases of internal combustion engines. This helps to diminish air pollution, however, the production process of these catalytic converters leave solutions containing significant amounts of PGM that can be recovered. There are different separation techniques that allow recovering PGM among which are electrochemical methods, precipitation and liquid – liquid extraction, liquid membranes, ionic exchange, impregnated resins and electrodialysis [1-4]. In the case of rhodium recovery, different methods have been reported such as: reduction using sodium formate or sodium borohydride and liquid-liquid extraction with neutral extractants (Cyanex 921) from halides and thiocyanates solutions. In such studies, difficulty to separate Rh(III) due to the slow kinetic has been showed. However, ionic Liquids (room temperature melted salts), a new kind of extractants, have not been tested and might prove to be effective in the recovery of this element. Because of their exceptional physicochemical properties, ionic liquids have seen a remarkable increase in the interest for their applications in the past decade [5-8]. Then, in this paper results the results obtained in the study of Rh(III) extraction from chloride medium by quaternary alkylphosphonium salts (ionic liquids) are reported. Distribution curves of Rh(III) as a function of HCl concentration and as a function of the concentration of each tested extractant and the extraction's kinetics are showed. An important contribution of this work is that the extraction rate of the Rh(III) in the studied systems is very high.

EXPERIMENTAL

All reagents used were analytical grade. The extractants used in the solvent extraction processes were tetradecyl(trihexyl)phosphonium chloride (Cyphos IL 101) and tetradecyl(trihexyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104, kindly supplied by Cytec Canada Inc.), and used without prior purification. Cyphos IL 101 and Cyphos IL 104 are phosphonium salts (see Figure 1) having purity around 95%, less dense than water and slightly viscous. For the liquid-liquid extraction experiments, the organic phase consisted of Cyphos IL 101 or Cyphos IL 104 diluted at various concentrations (mol L^{-1}) in kerosene (Aldrich US, boiling point $175\text{--}315\text{ }^{\circ}\text{C}$, with low aromatic content), and 1-decanol (Aldrich) 10%v/v as modifier. The aqueous phase consisted of Rh(III) 10 mg L^{-1} and HCl at different concentrations as will be noted in each case. The ratio of volumes of the organic phase (Vorg) and aqueous phase (Vaq) was in every case one ($V_{\text{aq}} = V_{\text{org}} = 10\text{ mL}$). The solutions (aqueous phase/organic phase) were shaken with a ping-pong shaker (Cole Palmer 51502) at 90 rpm at 25°C for 120 min, which was enough time to reach equilibrium. Once it was attained, the phases were separated and the Rh(III) concentration in the aqueous phase was determined by spectrometry of atomic absorption of flame (AAF) with a Perkim Elmer AAnalyst 200 spectrophotometer. The concentration of Rh(III) in the organic phase was calculated by mass balance.

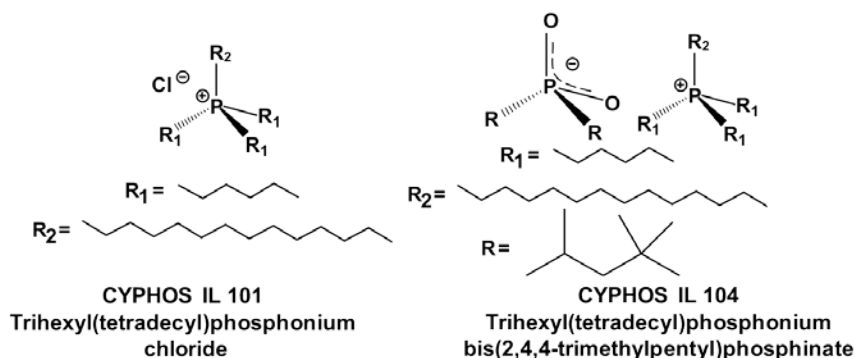


Figure 1. Chemical Structures of Cyphos IL 101 and Cyphos IL 104 extractants.

Results and Discussion

Extractant concentration effect on the recovery of Rh(III)

Figure 2 shows the Rh(III) extraction percentage variation as a function of Cyphos IL 101 (Figure 2A) and Cyphos IL 104 (Figure 2B) concentrations when the HCl concentration in the aqueous phase is 0.1 mol L^{-1} .

When a Cyphos IL 101 concentration of 0.01 mol L^{-1} is used, the recovery of Rh(III) reaches 55% but when increasing the extractant concentration, a unusual behavior is observed. At first, extraction of Rh (III) diminish but after a 0.2 mol L^{-1} concentration of Cyphos IL 101 is used, recovery increases up until 57% for a 1.68 mol L^{-1} concentration of extractant (concentrated extractant). This behavior indicates a

change of the extracted specie in the organic phase due to the generation of chloride ions in the aqueous phase coming from Cyphos IL 101 along the extraction procedure.

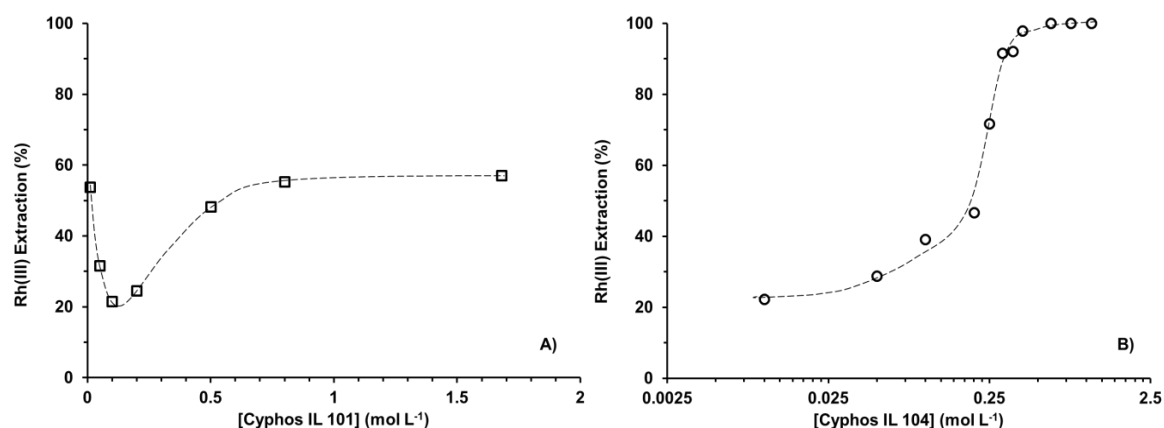


Figure 2. Rh (III) percentage extraction variation as a function of the concentration of extractant (Cyphos IL 101) ($\diamond$) and Cyphos IL 104 ($\square$)

In the case of the extraction with Cyphos IL 104, the observed behavior corresponds to the normal extraction process on which the recovery increases with the augmentation in the presence of the extractant. Rh(III) recovery is highly favored, reaching an efficiency close to 100% for Cyphos IL 104 concentrations starting in 0.4 mol L⁻¹. The difference in behavior between the extractants can be explained if it is considered that Cyphos IL 104 doesn't have chloride ions in its structure and therefore the extracted complex is the same throughout the entire studied concentration range of the extractant.

HCl concentration effect on the recovery of Rh(III)

The variation of the extraction percentage of Rh (III) transferred to the organic phase in relation to the concentration of HCl, using Cyphos IL 101 and Cyphos IL 104 as extractant are showed in Figure 3.

It can be observed that in the case of the Cyphos IL 101 extraction (Figure 3A), the extraction percentage of Rh(III) stays almost unaltered up to an HCl concentration of 2 mol L⁻¹. From this point forward, the Rh(III) extraction percentage decreases. On the other hand, in the case of the extraction with Cyphos IL 104, for low HCl concentrations (0.1 mol L⁻¹) extraction percentage is close to 100% (Figure 3B). When increasing the HCl concentration, there is a shape descent in curve of the extraction percentage. However, between a HCl concentration of 1.0 mol L⁻¹ and 2.0 mol L⁻¹, extraction percentage increases, falling again for higher concentration of the acid, as it happens in the extraction with Cyphos IL 101.

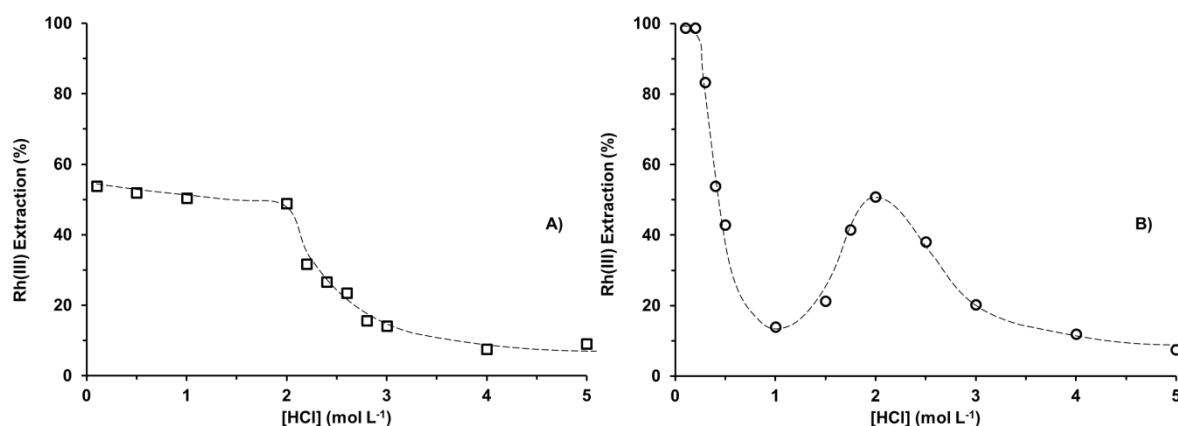


Figure 3. Extraction percentage of Rh (III) as a function of the HCl concentration. Organic phase: A) Cyphos IL 101 0.01 mol L⁻¹ (Δ) and 0.025 mol L⁻¹ ($\circ$). B) Cyphos IL 104 1.07 mol L⁻¹. Aqueous phase: Rh(III) 10 mg L⁻¹ in different HCl concentrations.

This behavior can be explained if we take into account the nature of the extractants. Cyphos IL 101 is a quaternary phosphonium salt with a chloride as counter-ion, then extraction of Rh(III) is expected to occur by an anionic exchange mechanism with the Rh(III)/Cl⁻ complexes that are formed in the aqueous phase. Figure 4 shows the different complexes of Rh(III) and Cl⁻, where it is possible to see that at values of HCl from 0.35 to 2 mol L⁻¹ the complex RhCl_5^{2-} is predominant. When the HCl concentration is higher than 2 mol L⁻¹, the RhCl_6^{3-} is now the predominant complex. From this value the percentage of Rh(III) extracted starts to diminish.

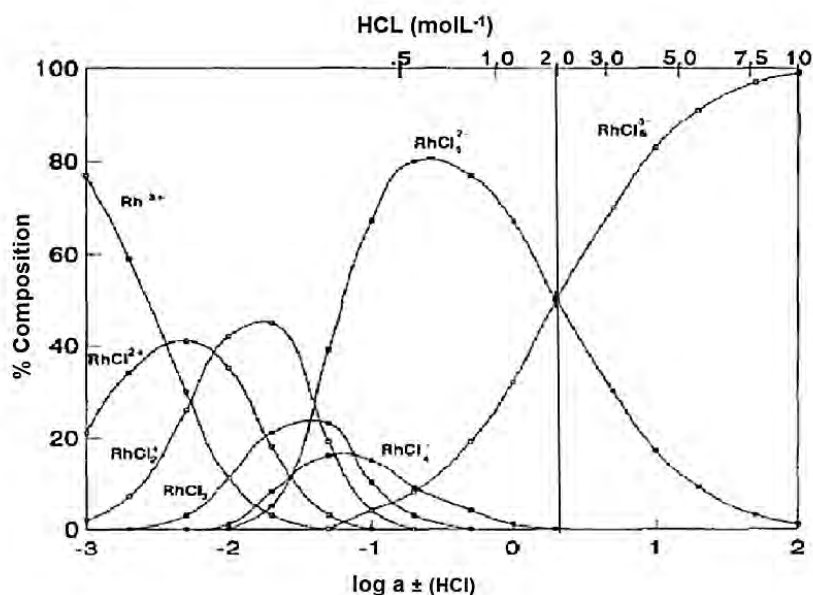


Figure 4. Rhodium chloride speciation diagram (from refe 1) at 25 °C.

On the other hand, Cyphos IL 104 has as counter-ion the bis(2,4,4 trimethylpenthyl)phosphinate, which is well known by its extractive properties with metal ions. At low HCl concentrations, Rh(III) is extracted by the phosphinate by means of a complex formation mechanism. When increasing acidity, the phosphinate acquires a proton and logically, the extraction percentage of Rh(III) is

reduced. With the increase of the chloride presence in the aqueous phase (HCl concentration between 1.0 and 2.0 mol L⁻¹), the anionic complex formation is preferred (see Figure 4). In these conditions, the extraction mechanism is similar to the case of Cyphos IL 101.

Slope analyses of the variation of log D as a function of log a_{Cl^-} of the Rh(III) extraction with both extractants have been made. The slope obtained was close to 3 in the case of extraction with Cyphos IL 104 for concentrations of HCl up to 1 mol L⁻¹. When the concentration of HCl is higher than 2 mol L⁻¹ the slope obtained was close to 4, that is a similar value obtained in the case of Rh(III) extraction by Cyphos IL 101.

Rh(III) equilibrium extraction time.

The obtained results of the extraction percentage variation of Rh(III) as a function of the contact time of the phases are showed in Figure 4A for both extractants.

In both cases it is observed that the extraction kinetic is very fast, achieving the equilibrium in less of 10 minutes.

Because Cyphos IL 104 yielded best extraction results, kinetics for different extractant concentrations was evaluated (Figure 4B). It can be seen for Cyphos IL 104 concentrated, the extraction's kinetic is low, reaching equilibria only after 30 minutes. The latter can be due to the increase in the viscosity in the organic phase that comes with increasing the concentration of the extractant causing a slowdown in the recovery of Rh(III). When an organic phase with the Cyphos IL 104 1.07 mol L⁻¹ is used, the extraction percentage increases to almost 100% while for the 0.4 mol L⁻¹, extraction only reaches 93%, achieving equilibrium in only 5 minutes.

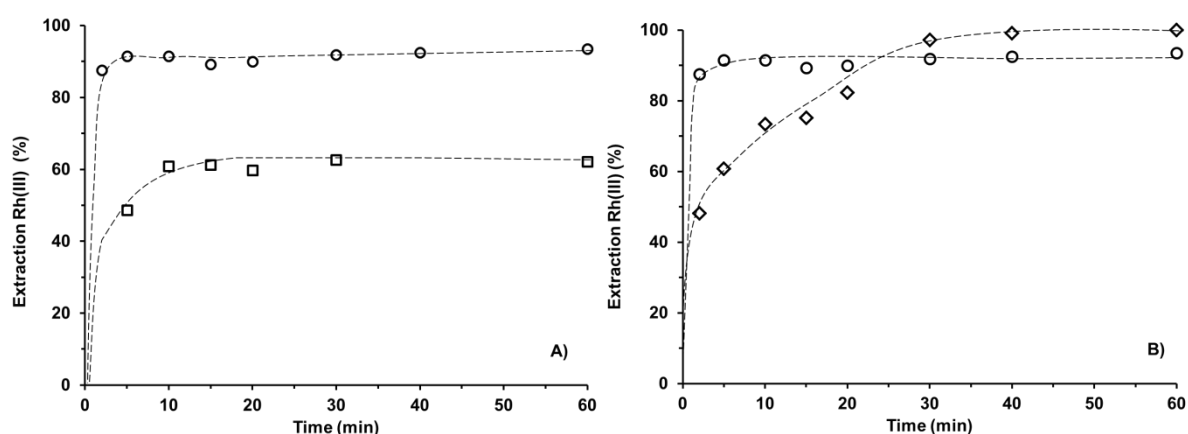


Figure 4. Extraction percentage of Rh(III) as a function of time. A) Organic phase: Cyphos IL 101 0.1 mol L⁻¹ (◇) and Cyphos IL 104 (□) diluted in kerosene and 10%v/v 1-decanol. B) Organic Phase: Cyphos IL 104 1.07 mol L⁻¹ (○) and 0.4 mol L⁻¹ (△). Aqueous phase: Rh(III) 10 mg L⁻¹ in HCl 0.1 mol L⁻¹.

CONCLUSIONS

Based on the obtained results, the Rh(III) extraction from HCl media using quaternary alkylphosphonium salts as extractants (ionic liquids) appears to be viable, showing a greater affinity for the Cyphos IL 104 than to the Cyphos IL 101. Influence of the contact time between the phases was evaluated, showing that equilibrium is reached in 10 minutes when the Cyphos IL 101 is used as extractant, whilst for the Cyphos IL 104 the equilibrium was completed after 5 minutes. On the other hand, using Cyphos IL 104 concentrated (1.07 mol L^{-1}), the equilibrium was achieved in 30 minutes. Results showed that for a low HCl concentration, Rh(III) extraction is high for Cyphos IL 104 and Cyphos IL 101. The best results were obtained for an HCl concentration of 0.1 mol L^{-1} and Cyphos IL 104 as extractant because when increasing its concentration, the extraction percentage increases remarkably too. Under these conditions, it's possible to recover close to 100% of Rh(III) from the aqueous phase. .

ACKNOWLEDGMENTS

Jéssica Yadira Méndez Quezada wishes to thank the received support by the PROMEP (Mexico) Networks Project 'Recovery of Precious Metals'. Authors would like to thank to CYTEC for the kindly supply of Cyphos IL 101 and Cyphos IL 104.

REFERENCES

1. Benguerel E., Demopoulos G. P., Harris G. B., *Hydrometallurgy*, 40, 135 (1994).
2. Bernardis F. L., Grant R. A., & Sherrington D. C., *Reactive & Functional Polymers*, 65, 205 (2005).
3. Cleare M. J., Charlesworth P. and Bryson D. J., *Journal of Chemical Technology and Biotechnology*, 29, 210 (1979).
4. Levitin G., Schmuckler G., *Reactive & Functional Polymers*, 54 149–154 (2003)
5. Renne J. Soukup-Hein, Molly M. Warnke, Daniel W. Armstrong. *Annual Review of Analytical Chemistry*. 2, 145-168 (2009).
6. Dietz, M.L. *Separation Science and Technology*, 41(10) 2047-2063 (2006).
7. Fraser K.J., MacFarlane D., *Australian Journal of Chemistry*, 62(4), 309-321 (2009).
8. Holbrey J.D., Seddon K., *Clean Technologies and Environmental Policy*, 1(4) 223-236 (1999).

Investigation of Carriers for Supported Liquid Membrane Extraction of Rare Earth Elements

Maryam Mohammadi, Department of Chemical Engineering and Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden;

Maryam Mohammadi¹, Joaquin Martínez¹, Kerstin Forsberg¹, Ake Rasmuson^{1,2}

¹ Department of Chemical Engineering and Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

²Department of Chemical and Environmental Science, Materials and Surface Science Institute, Solid State Pharmaceutical Cluster, University of Limerick, Limerick, Ireland.

The global demand of rare earth elements (REE) has increased significantly in recent years due to their unique spectroscopic and magnetic properties, which make them suitable for a wide variety of products such as catalysts, rechargeable batteries, plasma televisions, and catalytic converters. Accordingly, there is a need for efficient processes for recovery and selective separation of REE, which is difficult to achieve due to their similar chemical characteristics. Among novel technologies for separation of REE, supported liquid membrane (SLM) extraction is a promising technique because of its potentially high selectivity, and the combination of extraction and stripping in one step. The carrier in the liquid membrane is known as a key parameter for the separation efficiency, and is the focus of the present study. In this study, the synergistic extraction of trivalent rare earth elements (Nd, Dy, and Y) from hydrochloric acid solution by mixtures of di-(2-ethylhexyl) phosphoric acid (D2EHPA) with 2-ethylhexylphosphonic acid mono-2-ethyl hexyl ester (EHEHPA) or tributyl phosphate (TBP) has been studied. The influence of the acidity of the solution and concentration of the extractants and REE on the distribution ratio and separation factor is investigated, and the equilibrium constants are determined.

Key words: Solvent Extraction, Rare Earth Elements, D2EHPA, EHEHPA, Equilibrium Constant

Intermittent counter-current extraction in continuous downstream processing

Peter Hewitson, Ian Sutherland, Svetlana Ignatova

*Advanced Bioprocessing Centre, Brunel Institute for Bioengineering, Brunel
University, Uxbridge, UK*

The pharmaceutical, food and cosmetics industries require high throughput, lower solvent usage extraction, separation and purification methods to reduce both costs and environmental impact.

Intermittent Counter-current extraction (ICcE) has been demonstrated as a potential liquid-liquid extraction method for high throughput, continuous separation of compounds into two product streams and for the isolation, concentration and enrichment of a low abundance target compound [1]. Scale up, using industrial type instruments supplied by Dynamic Extractions Limited, has also been successfully demonstrated [2]. An equilibrium cell model has been proposed to describe the operation of the ICcE method [3].

Both theory and methodology for determining optimal operating parameters will be presented. Experimental results include the scaling of ICcE separations across a range of instruments from the analytical instrument (22 mL column volume) to pilot scale instrument (18 L) using a model mixture of pharmaceutical compounds. Examples of extractions from two different solid plant materials by ICcE will be demonstrated. Throughput and solvent usage will be compared for both ICcE and batch extractions.

[1] P. Hewitson, S. Ignatova, H. Ye, L. Chen I. Sutherland, J. Chromatogr. A 1216 (2009) 4187

[2] P. Hewitson, S. Ignatova, I. Sutherland, J. Chromatogr. A 1218 (2011) 6072

[3] P. Hewitson, I. Sutherland, A. Kostanian, A Voshkin, S. Ignatova, J. Chromatogr. A 1303 (2013) 18

Investigations of water-soluble Schiff base ligands for the separation of actinyl and non-actinyl cations

Cory A. Hawkins,^{*1} Christian G. Bustillos,^{1,2} I. May,² R. Copping,² and M. Nilsson¹

Abstract

The competitive solvent extraction of U(VI) and Eu(III) by HDEHP in toluene was studied in the presence of an aqueous soluble Schiff base, *N,N'*-bis(5-sulfonatosalicylidene)-diaminoethane ($\text{H}_2\text{salen-SO}_3$). Reversal of the metal ion separation factors has been attributed to the selective aqueous phase complexation of the U(VI) ion by $\text{H}_2\text{salen-SO}_3$.

Introduction

Current systems for the separation of actinide and lanthanide cations often employ organophosphorus reagents in combination or in sequence with anionic extractants under acidic conditions [1]. However, because organophosphorous reagents do not often display large selectivity between trivalent actinides and lanthanides, separation of the two groups often requires the addition of soft donor ligands [2, 3]. Alternative approaches to these separations include those that exploit differences in the available oxidation states of An and Ln elements [4]. Namely, several of the actinides (U through Am) have higher oxidation states (e.g., V and VI) available under conditions in which they exist as linear dioxo cations. Under this configuration the actinides behave significantly different from trivalent lanthanides. The stability of these oxidation states can be a challenge for some transuranic actinides under acidic conditions. Studies suggest, however, that these oxidation states may be stabilized by coordination of ligands to the equatorial plane of the actinyl ion. For example, recent studies indicate that Schiff bases have been able to stabilize U(V) [5,6]. Furthermore, there are numerous structural studies that show that ' N_2O_2 ' Schiff base ligands can bind to trivalent lanthanide cations. Multifarious structural motifs have been observed, including tetradentate coordination through all four donor atoms and coordination just through phenolic oxygens [7]. Yet, there is also evidence that, under comparable reaction conditions, U(VI) will more readily coordinate to such ligand sets than Ln(III) [8]. In light of these reports we are investigating Schiff base ligands for the selective complexation and solvent extraction of An(V/VI)-cations. A 1:1 $\text{UO}_2(\text{salen-SO}_3)$ complex has been verified in solid state by X-ray crystallography and IR spectroscopy [9]. Likewise, a 1:1 $\text{UO}_2(\text{salen-SO}_3)$ complex has been confirmed in aqueous solution by ^1H NMR and UV-vis spectroscopy [9]. This report is from our preliminary studies employing a water soluble tetradentate Schiff base as a selective holdback reagent for uranyl(VI).

^{*1} University of California Irvine, Department of Chemical Engineering and Materials Science & Contact

² Science, Technology and Engineering, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.

Experimental

Materials

All chemicals used in these procedures were certified reagent grade or higher and used without further purification, unless noted otherwise. Water deionized from was obtained from a deionized feed such that the resistivity was at least $18 \text{ M}\Omega\cdot\text{cm}^{-1}$. For the solution spectroscopy and solvent extraction experiments a $0.010 \text{ M UO}_2(\text{NO}_3)_2$ working stock solution was prepared from a commercial ICP standard solution of depleted ($0.2\% \text{ }^{235}\text{U}$) uranyl nitrate (1000 ppm, Inorganic Ventures, Christiansburg, VA, USA) by diluting with deionized water and adjusting the pH to 4.0 dropwise with a KOH solution. The europium nitrate stock solution was prepared from the oxide (Michigan Metals & Manufacturing, Inc., West Bloomfield, MI, 99.99%) by dissolving in concentrated nitric acid. Excess nitric acid was removed by diluting in deionized water and evaporating to dryness in several cycles. The final solutions were reconstituted to 0.1 M with $1 \times 10^{-3} \text{ M HNO}_3$ and the concentrations were verified by ion-exchange titration or ICP-MS. HDEHP (Di(2-ethylhexyl)phosphate, 95%, ACROS Organics, Geel, Belgium) was purified using the Cu(II) complexation method [10]. The synthesis of 5-sulfo-salicylaldehyde sodium salt and the desired ligand structure shown in Figure 1, *N,N'*-bis(salicylidene-5-sulfonato)-diaminoethane disodium salt, were adapted from previously published procedures [11,12]. Ethanol of crystallization was difficult to remove and consisted of 0.5-2% by weight. The abbreviation used in this paper, $\text{H}_2\text{salen-SO}_3$, indicates the two phenolic protons (H_2) and the sulfonated salicylidene groups (salen-SO_3). Acid and base solutions were standardized and solution pH and pC_H ($-\log [\text{H}^+]$) were measured by potentiometry using a semi-micro refillable electrode (Beckman-Coulter, Indianapolis, IN), which was filled with 3 M KCl and calibrated by standard pH solutions (Fisher Scientific,) and by Gran titration.

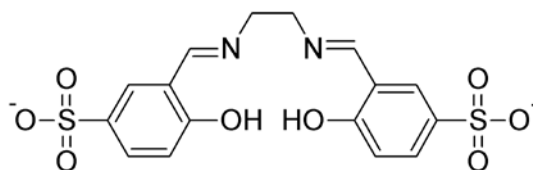


Figure 1. *N,N'*-bis(5-sulfonatosalicylidene)-diaminoethane ($\text{H}_2\text{salen-SO}_3$), synthesized as the disodium salt.

Continuous Contact Extractions

Extraction studies were conducted using 0.01 M HDEHP in toluene as the organic phase and $0.01 \text{ M H}_2\text{salen-SO}_3$ in 0.1 M KNO_3 with 0.01 M acetic acid (equilibrium $\text{pC}_\text{H} = 5.5$) to investigate the partitioning behavior of U(VI) and Eu(III). The aqueous phase was prepared by dissolving $0.0236 \text{ g H}_2\text{salen-SO}_3$ ($5.00 \times 10^{-5} \text{ mol}$) in 0.1 M KNO_3 $\text{pC}_\text{H} 4.4$ containing $1 \times 10^{-4} \text{ M UO}_2(\text{NO}_3)_2$ and adjusting the pC_H to 5.3 using 0.2 cm^{-3} of 0.2 M acetic acid. For Eu(III) partitioning, the tracer was added to this aqueous solution prior extraction. The experiments employed continuous contact between 5 cm^{-3} of the organic phase pre-equilibrated with the aqueous phase without metal ion present and 5 mL the aqueous phase containing the metal ions. The time-

dependent partitioning of $\{\text{UO}_2\}^{2+}$ (1×10^{-4} M) and Eu^{3+} (1×10^{-5} M radiotracer + carrier) in the presence of $\{\text{UO}_2\}^{2+}$ (1×10^{-4} M) were examined in two separate experiments by rapid stirring with a magnetic stir bar to generate an emulsion. The concentration of $\{\text{UO}_2\}^{2+}$ was chosen to provide sufficient count rates after neutron activation of the samples. Specific activity of the lanthanide radiotracer was high enough to maintain a concentration of 1×10^{-5} M Eu(III) and 3×10^{-4} M for all metal ions in order to avoid exceeding the metal cation capacity of the organic phase and mitigate the formation of polymeric species. At each timepoint, the phases were disengaged by centrifugation and equal volume aliquots of the phases were removed and sampled in triplicates of 100 μL for analysis. Comparison to extraction without the holdback reagent was made possible by preparing a similar system without $\text{H}_2\text{SalenSO}_3$ present and contacting for 30 min. The extent of extraction was calculated as a distribution ratio (ratio of gamma counts rate in equilibrated organic phase to that in the aqueous phase).

The $^{152/154}\text{Eu}$ tracer was prepared by irradiating a 0.001 M solution of $\text{Eu}(\text{NO}_3)_2$ at the UC Irvine Mark I TRIGA reactor (estimate thermal neutron flux of $5 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, 10 hours). Uranium samples were transferred to 1.4 mL neutron activation analysis (NAA) polytubes (L&A plastic Molding, Yorba Linda, CA) and a 8 mL NAA polytube was used for secondary containing and was heat sealed as well. These samples were irradiated in the “lazy Susan” of the UC Irvine Mark I TRIGA nuclear reactor for 1 hour at 250 kW (estimated neutron flux of $8 \times 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$). The ^{239}U ($t_{1/2} = 23.45$ minutes) was allowed to decay, whereupon the ^{239}Np ($t_{1/2} = 2.36$ days) delayed gamma rays (spectral region: 95.9– 110.1 keV; values in order of E_γ (keV), $\gamma(\%)$, mode: 99.52, 15.0, Pu $K_{\alpha 2}$; 103.73, 23.9, Pu $K_{\alpha 1}$; 106.13, 22.7, $\gamma\text{E1} + 0.3\%\text{M2}$) were counted using a Canberra HPGe detector operated with GenieTM 2000 (v. 3.2.1) gamma acquisition and analysis software [13]. Count rates were normalized to the reactor scram time and counting errors were calculated by the software. Europium samples were analyzed in gamma counting polytubes by a Packard Cobra IITM series automatic gamma counter. Overall uncertainties in the measurements were reported as the sum of the relative counting errors relative standard deviations from triplicate samples at the 95% confidence interval. Mass balance recoveries (all between 94% and 111%) were determined by the ratio of the sum of count rates in both phases post-phase contact to the count rate for the metal ion-spiked aqueous solution used in the extraction.

Results and Discussion

Continuous Contact Extraction of U(VI) and Eu(III)

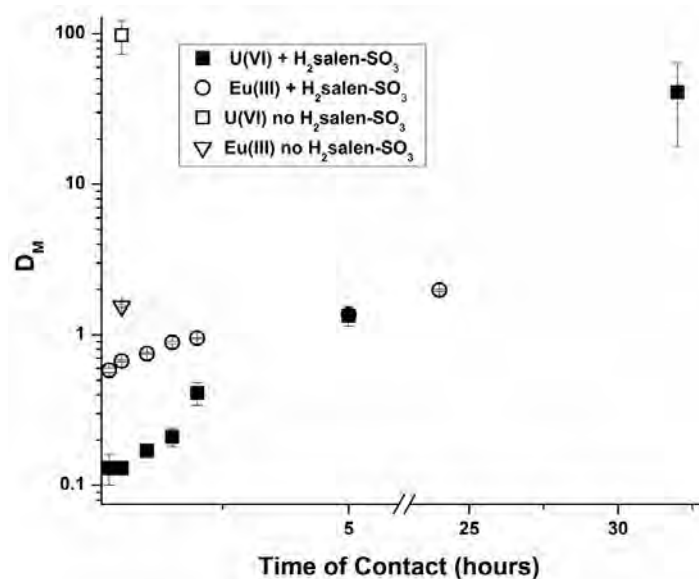


Figure 2. Competitive extraction of uranyl(VI) (10^{-4} M), and Eu(III) (10^{-5} M total) in the presence of uranyl(VI) (10^{-4} M), from 0.01 M H₂salen-SO₃ in 0.1 M KNO₃ and 0.01 M acetic acid at equilibrium pC_H of 5.3 by 0.01 M HDEHP in toluene. Error bars consist of uncertainties calculated from the combination of counting statistics and triplicate analysis at the 95% confidence interval.

The distribution ratios for the partitioning of U(VI) and Eu(III) between a 0.1 M solution of HDEHP in toluene and 0.1 M KNO₃ without H₂salen-SO₃ after 30 minutes of contact are shown in Figure 2 as the open square and open triangle. Separation factors are consistent with those calculated from previously published extraction constants in similar systems, demonstrating that, in the absence of masking reagents, D_U is nearly two orders of magnitude higher than D_{Eu} [14, 15]. In the presence of 0.01 M H₂salen-SO₃ at 30 minutes of contact, however, there is an almost three orders of magnitude decrease in D_U . At the same time, D_{Eu} decreases by only a factor of three, indicating that Eu(III) exhibits weaker complexation with the Schiff base under these conditions. Although there is an increasing trend in the distribution ratios for both Eu(III) and U(VI) when H₂salen-SO₃ is present, the behaviour in the first 30 minutes of contact is most likely representative of conditions that would exist in a process [16]. Accordingly, holdback factors (ratio of the extent of extraction in the absence of holdback reagent to that in its presence, D_0/D) decrease with increasing contact time. It is encouraging that holdback factors for U(VI) range between 750 and 70 from 0.25 to 5 hours of contact time, and those for Eu(III) vary from 3 to 1. The increasing trend in the distribution ratios in the presence of H₂salen-SO₃ may be due to phase transfer kinetics, ligand degradation, or both. No significant loss of metal ions from precipitation or other effects were detected, as mass balances for the extraction remained close to 100% ($\pm 10\%$) for all experiments. However, the apparently low distribution ratios at such high pH

(compared to those predicted by the ion-exchange reaction) may be due to the formation of unextractable, yet soluble, hydrolysis products, particularly for Ln(III) ions [17]. These and other matters are the subjects of on-going study.

Conclusions

By combining the quasiplanar geometry of a Schiff base N_2O_2 binding site with the charged sulfonate groups, a new class of selective holdback reagents has been demonstrated. To our knowledge, this is first description of the reversal of actinide/lanthanide solvent extraction selectivity using a water soluble tetradentate Schiff base. While ligand stability is a critical issue to explore, the results from continuous extraction of U(VI) and Eu(III) are proof-of-principle that a similar ligand architecture may be employed in f-element separations. Possible improvements in Ln/An separation factors may afford the design of separation systems under conditions not commonly considered for nuclear fuel and waste effluent processing.

Acknowledgements

This work was supported by the University of California under the UCOP Grant ID# 12-LF- 237294.

References

1. Lumetta, G. J.; Neiner, D.; Sinkov, S. I.; Carter, J. C.; Braley, J. C.; Latesky, S. L.; Gelis, A. V.; Tkac, P.; Vandegrift, G. F. "Combining Neutral and Acidic Extractants for Recovering Transuranic Elements from Nuclear Fuel", Proceedings of the 19th International Solvent Extraction Conference, ISEC 2011; Valenzuela, F. L.; Moyer, B. A., Eds.; Gecamin Ltd: Santiago de Chile, Chile, October 3–7, 2011; Paper No.68.
2. Y. Zhu, J. Chen, R. Jiao, "Extraction of Am(III) and Eu(III) from Nitrate Solution with Purified Cyanex 301", *Solv. Extr. Ion Exch.*, **14**(1), 61-68, 1996.
3. D.R. Peterman Proceedings of the 19th International Solvent Extraction Conference, "Separation of Minor Actinides from Lanthanides by Dithiophosphinic Acid Extractants", ISEC 2008; Moyer, B. A., Ed.; Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Quebec, Canada, Volume II, 1427-1432.
4. K.L. Nash, G.R. Choppin, "Separations Chemistry for Actinide Elements: Recent Developments and Historical Perspective", *Sep. Sci. Technol.*, **32**(1-4), 255-274, 1997.
5. K. Takao, M. Kato, S. Takao, A. Nagasawa, G. Bernhard, C. Hennig and Y. Ikeda, "Molecular Structure and Electrochemical Behavior of Uranyl(VI) Complex with Pentadentate Schiff Base Ligand: Prevention of Uranyl(V) Cation–Cation Interaction by Fully Chelating Equatorial Coordination Sites", *Inorg. Chem.*, **49**(5), 2349-2359, 2010.
6. V. Mougel, J. Pecaut and M. Mazzanti, "New polynuclear U(IV)–U(V) complexes from U(IV) mediated uranyl(V) disproportionation", *Chem. Commun.*, **48**, 868, 2012.
7. See, for recent examples, a) X. Zou, M. Li, P. Yan, J. Zhang, G. Hou and G. Li, "Systematic study on the structures of salen type lanthanide complexes tuned by lanthanide contraction and corresponding luminescence", *Dalton Trans.*, **42**, 9482-9489, 2013. b) B.H. Koo, K.S. Lim, D.W. Ryu, W.R. Lee, E.K. Koh and C.S. Hong, "A unique tetranuclear ErIII₄ cluster exhibiting field-induced single-molecule magnetism", *Chem. Commun.* **48**, 2519-2521, 2012.

- c) P.-H. Lin, W.-B. Sun, M.-F. Yu, G.-M. Li, P.-F. Yan and M. Murugesu, "An unsymmetrical coordination environment leading to two slow relaxation modes in a Dy₂ single-molecule magnet", *Chem. Commun.* **47**, 10993-10995, 2011. d) E.M. Broderick, N. Guo, T. Wu, C.S. Vogel, C. Xu, J. Sutter, J.T. Miller, K. Meyer, T. Cantat and P.L. Diaconescu, "Redox control of a polymerization catalyst by changing the oxidation state of the metal center", *Chem. Commun.* **47**, 9897-9899, 2011.
8. a) X. Wu, M.S. Bharara, T.H. Bray, B.K. Tate, A.E.V. Gorden, "Synthesis and characterization of 2-quinoxalinol Schiff-base metal complexes", *Inorg. Chim. Acta*, **362**(6) 1847-1854, 2009. b) R. Kannappan, S. Tanase, D.M. Tooke, A.L. Spek, I. Mutikainen, U. Turpeine, J. Reedijk, "Separation of actinides and lanthanides: crystal and molecular structures of N,N'-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine and its uranium complex", *Polyhedron*, **23**(14), 2285-2291, 2004.
9. Data unpublished as of 18 March 2014.
10. J.A. Partridge, R.C. Jensen, "Purification of di-(2-ethylhexyl)phosphoric acid by precipitation of copper(II) di-(2-ethylhexyl)phosphate", *J. Inorg. Nucl. Chem.*, **31**(8), 2587- 2589, 1969.
11. M. Botsivali, D. F. Evans, P. H. Missen, M. W. Upton, Studies on singlet oxygen in aqueous solution. Part 2. Water-soluble square-planar nickel complexes as quenchers, *J. Chem Soc., Dalton Trans.*, 1147-1149, 1985.
12. D. F. Evans, P. H. Missen, "Some water-soluble Schiff-base complexes of nickel(II) - the role of water", *J. Chem. Soc., Dalton Trans.*, 1451-1454, 1985.
13. E. Browne, R.B. Firestone, *Table of Radioactive Isotopes*, Wiley-Interscience, New York, USA, 1986, p. 329-2.
14. J. Sary. "Separation of Transplutonium Elements", *Talanta*, **13**(3), 421-436, 1966.
15. C.A. Blake, D. J. Crouse, C.F. Coleman, K.B. Brown, A.D. Kelmers, "Progress report : further studies of the dialkylphosphoric acid extraction (Dapex) process for uranium", ORNL Progress Report, ORNL-2172, 1957.
16. D. Magnessun, R. Malmbeck, "Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors", *Solv. Extr. Ion Exch.*, **30**(2), 115-126, 2012.
17. B. Weaver, F.A. Kappelmann, "Preferential extraction of lanthanides over trivalent actinides by monoacidic organophosphates from carboxylic acids and from mixtures of carboxylic and aminopolyacetic acids", *J. Inorg. Nucl. Chem.*, **30**(1), 261-272, 1968.

Analyzing the Sedimentation and Coalescence Behavior of Polydisperse Droplets in Opaque Systems Using Ultrasonic Technique

Pornprapa Chuttrakul, Andreas Pfennig, Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria

Liquid-liquid dispersions which are occurring in petrochemical and chemical industry are commonly separated in gravity settlers. To improve settler design, phase separation of dispersions was studied. The parameters having the greatest effect on phase separation under gravity are drop size, drop-size distribution, as well as driving-force parameters for sedimentation and coalescence, namely density difference, viscosity and interfacial tension.

The phase separation experiments are usually carried out in optical cells, but this method is not applicable for nontransparent systems. Therefore, ultrasonic spectroscopy was used in this work to determine the behavior of the droplets in emulsion systems.

The effect of the driving-force parameters on coalescence and sedimentation was characterized experimentally using ultrasonic technique. The viscosity of the aqueous phase was increased by adding polyethylene glycol. This is not only changing viscosity but also interfacial tension, having a significant impact on drop size. In high-viscosity systems the settling speed of swarm droplets will significantly slow down and droplet size will be smaller.

Settling in polydisperse emulsions has been investigated as well. Ultrasonic investigation allows an exact determination of the boundary between the close-packed dispersion and the settling zone, which cannot be detected by any optical method even for very transparent systems. It additionally allows quantitative evaluation of local hold-up in opaque systems.

Novel Magnetic and Optical Measurements of Liquid-Liquid Interfacial Reactions

Hitoshi Watarai^{*1}

Magnetophoretic velocity analysis was applied to determine the change of magnetic susceptibility of organic droplets due to the reaction at the liquid-liquid interface. It was demonstrated that the interfacial reaction forming paramagnetic metal complex could be detected by this method. Furthermore, the optical method to determine the chirality of chiral molecules was developed by using interfacial nano-aggregation of porphyrin in microemulsion systems.

Introduction

Developments of new characterization method of emulsion and microemulsion systems, which contain substantial interfacial area exhibiting unique functions, are crucially important for the innovation of solvent extraction systems. Various types of molecular spectroscopic methods have been investigated and demonstrated their utility for the purpose of analysis of such systems. However, there will be still some alternative approaches to extend the applicability of optical method, for example by combining with magnetic field and circularly polarized light. In the present study, the magnetophoretic detection of interfacial reaction in the emulsion droplets and the chiral optical detection in microemulsion systems are examined.

Magnetophoretic detection of interfacial reaction

Magnetic force applied to a droplet in emulsion system can migrate the droplet with a characteristic velocity depending on the difference in the magnetic susceptibilities of the droplet and the surrounding medium (1). Therefore, from the measurement of the magnetophoretic velocity of the droplet in the emulsion, the magnetic susceptibility of the droplet can be determined (2). When the one dimensional migration to x direction is considered, the magnetophoretic velocity, v , can be represented by,

$$v = \frac{2(\chi_p - \chi_m)}{9\mu_0\eta} r^2 B \frac{dB}{dx} \quad (1)$$

where χ_p and χ_m are the volume magnetic susceptibilities of droplet and medium, respectively, μ_0 is the vacuum magnetic permeability, η is the viscosity of the medium, r is the radius of the droplet, B is the magnetic flux density, and dB/dx is its gradient. It is important to note that the magnetophoretic velocity can be observed even for a diamagnetic droplet (e.g. a toluene droplet with volume magnetic

^{*1} Corresponding Author, Institute for NanoScience Design, Osaka University, Toyonaka, Osaka, Japan

watarai@chem.sci.osaka-u.ac.jp

susceptibility of -7.95×10^{-6}) in a diamagnetic medium (e.g., an aqueous solution with volume magnetic susceptibility of -9.12×10^{-6}).

In the present study, a new method to measure the magnetic susceptibility of a micro-droplet in emulsion has been constructed by using a small magnetic circuit (3 cm x 4 cm x 5 cm, 2.82 T) with a high magnetic field gradient at the central pole piece edges ($B(dB/dx) = 3900 \text{ T}^2/\text{m}$). Figure 1 shows the small magnetic circuit which was built originally. It has a pair of pole pieces in the center of the circuit and the high magnetic gradient was generated at the corner of the pole piece.

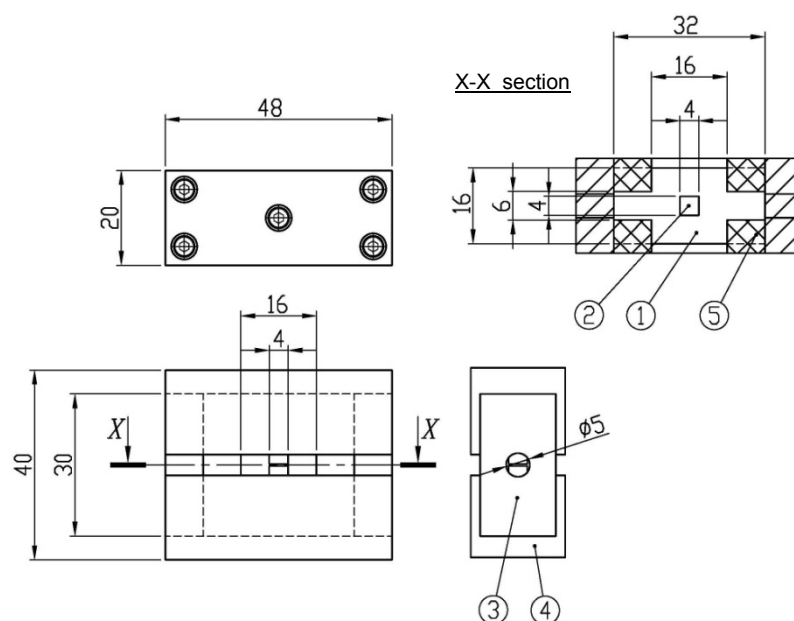


Figure 1. Dimensions (mm) of a small magnetic circuit (2.82 T) for microscopic magnetophoretic measurement of single droplets; ①magnet, ②pole piece with 0.6 mm gap, ③yoke, ④frame, and ⑤spacer.

The square glass capillary cell (Polymicro Technologies, Phoenix, AZ, USA) which had $100 \mu\text{m} \times 100 \mu\text{m}$ inner section and $300 \mu\text{m} \times 300 \mu\text{m}$ outer section, was inserted into the gap of pole pieces. The capillary cell was fixed vertically to the magnetic circuit through a PTFE adapter. A sample solution was introduced spontaneously into the square capillary cell by the capillary force, when the surface of sample solution touched at the bottom end of the capillary. The sample introduction period was about 5 seconds, and then the migration behaviour of organic droplets in the solution near the edge of pole piece was observed by an objective (10 $\times$) with a CCD camera (WAT-221S, Watec, Yamagata, Japan). The microscope images were analyzed using the image processing software (ImageJ) with a personal computer. The migration velocity and the size of droplets were measured from the images. After finishing an experiment, the sample solution in the capillary was rinsed using water in a syringe. The volume magnetic susceptibilities of organic solutions and the aqueous

medium and the molar magnetic susceptibility of Prussian blue were measured by a magnetic balance (MSB-AUTO, Sharewood Scientific, Cambridge, U.K.) These measurements were performed in a thermostated room at $25 \pm 1^\circ\text{C}$.

The magnetophoretic velocity of a toluene droplet with ferrocene dispersed in 1 M HCl aqueous solution including $\text{K}_3[\text{Fe(III)(CN)}_6]$, Fe(III)Cl_3 and cetyltrimethylammonium bromide (CTAB) was measured and the volume magnetic susceptibility of droplets was determined. From the dependence of the magnetic susceptibility on the radius of the droplets, the interfacial magnetic susceptibility of the droplets adsorbed by Prussian blue aggregates was obtained. The interfacial concentration of Prussian blue of individual droplet calculated from the observed magnetic susceptibility indicated that the interfacial concentration of Prussian blue are different even in similar sized droplets, suggesting nonuniform formation of interfacial aggregate in droplets.

Chiral recognition with nano-J-aggregate of porphyrin in microemulsion

Circular dichroism (CD) spectral measurement of the liquid-liquid interface has been attained by using a centrifugal liquid membrane (CLM) method and the chiral determination of some 2-alcohols with nano-J-aggregate of porphyrin was demonstrated (3). However, the CD signal of the nano-aggregate at the interface was not stable and diminished after 30 min due to the coagulation of the interfacial aggregates. Therefore, it was suggested that only nanometre sized aggregates have the ability to recognize the molecular chirality of 2-alcohol at the dodecane-water interface. In the present study, the chiral recognition ability of the nano-J-aggregates of protonated tetraphenylporphyrin ($\text{H}_4\text{TPP}^{2+}$) was examined in Triton X-100-toluene-sulfuric acid o/w microemulsion, since the reaction in microemulsion is expected to be controlled by the limited nanometre sized region of individual microemulsion droplets. The chiral recognition ability of the nano-J-aggregate in the microemulsion system was clearly observed as shown in Fig. 2, where (R)-(-)-2-nonanol and (S)-(+)-2-nonanol exhibited the corresponding CD spectra with opposite sign. The observed chiral signal was stable and the intensity depended on the concentration of 2-alcohol. The absorption band of the J-aggregate was observed at 473 nm as shown in Fig. 2, though the absorbance is smaller than that of the monomer of $\text{H}_4\text{TPP}^{2+}$ observed at 438 nm. The DLS measurement of the microemulsion droplet suggested that the effective size of the droplet to show the definite chiral signal was 50-100 nm in diameter, though the size of the droplet depended on the concentration of H_2SO_4 significantly. The optimized concentration of H_2SO_4 , which gave substantial CD intensity, was 3-4 M. The mechanism of the generation of CD signal was discussed by postulating the formation of the nanometer sized J-aggregate at the microemulsion interface, where the conformation of the aggregates should be affected by the presence of the chiral alcohol molecule. The generation of optical chirality of such aggregate is usually discussed considering an exciton coupling

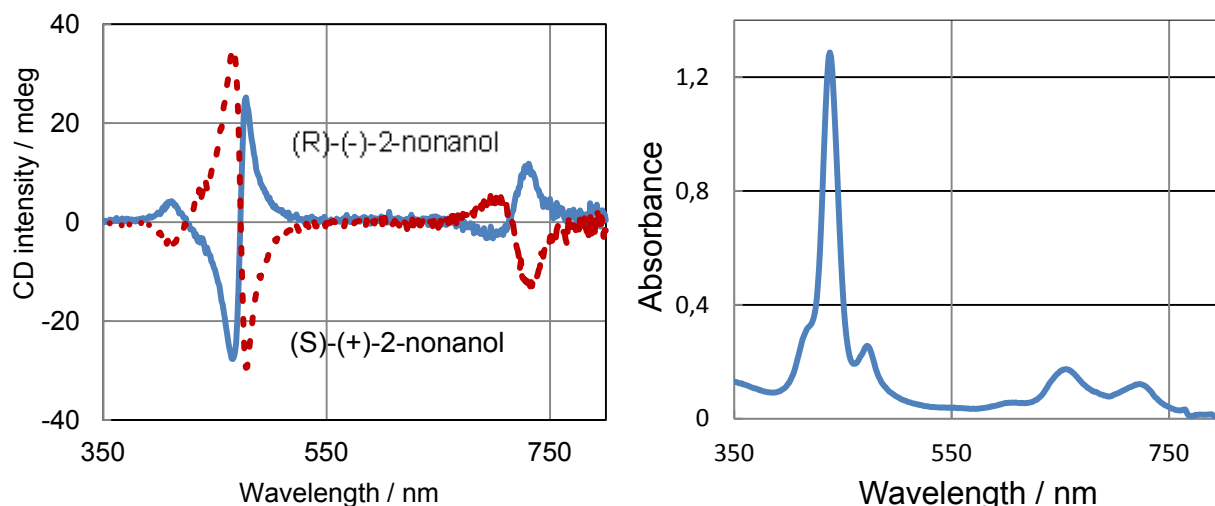


Figure 2. Circular dichroism spectra (left) and absorption spectrum (right) of microemulsion system including 0.038 M (R)-(-)-2-nonanol and (S)-(+)-2-nonanol with J-aggregate of 5.0×10^{-6} M H_4TPP^{2+} ; 0.055 M Triton X-100 in 4M H_2SO_4 solution.

theory. However, the present system may not necessarily need such explanation. Recently, it was observed that the sign of CD spectra of the concentrated interfacial aggregates of H_4TPP^{2+} in a CLM cell depended on the rotation direction of the cell, even if the system did not include any chiral compounds. Theoretical analysis suggested that the origin of the rotation direction dependent CD spectra was attributable to the overlapping of linear polarization spectra of the J-aggregates of H_4TPP^{2+} formed at the front and back interfaces in the rotating cell (4). This means that CD spectra can be produced from the overlapped but separated two aggregates with some angle, regardless of the distance between them. The present results should help understanding of the optical chirality due to the conformational changes in microemulsion systems.

Acknowledgements

The author thanks Dr. Shigeki Egami and Ms. Fumie Hiraoka for their contribution in experiments. The study was supported in part by a Grant-in-Aid for Scientific Research (A212450220) of MEXT, Japan.

Reference

1. H. Watarai, *Annu. Rev. Anal. Chem.*, **2013**, 6, 353.
2. M. Suwa and H. Watarai, *J. Chromatogr., A*, **2003**, 1013, 3.
3. H. Watarai, K. Mitani, N. Morooka, and H. Takechi, *Analyst*, **2012**, 137, 3238.
4. H. Takechi, A. Canillas, J. M. Ribo, and H. Watarai, *Langmuir*, **2013**, 29, 7249.

Zinc(II) Ions Recovery from Multimetal Acidic Chloride Solutions Using Pyridinium Ketoximes

Karolina Wieszczycka¹, Aleksandra Wojciechowska, Marta Krupa

Summary

Our studies indicated that the extraction from the multimetal solutions improved the efficiency of the zinc separation and the best results of the metal recovery over cobalt(II) and nickel(II) ions were observed for the aqueous acidic solutions containing 2.5-3 mol/L HCl, wherein the amount of extracted copper(II) and iron(II) ions was not higher than 0.005 and 0.02 g/L, respectively.

Introduction

Over the last few years the extraction of metals ions from chloride, ammonia, sulphate and chloride/sulphate aqueous solutions by hydrophobic 2-, 3- and 4-pyridylketoximes has been widely investigated [1-8]. However, the most selective and effective extractant (1-(2-pyridyl)tridecan-1-one oxime) could not be proposed as a ligand for a metal extraction from a strong acidic solution. Our recent studies indicated that 1-(3-pyridyl)undecan-1-one oxime can be applied as an effective and selective extractant of zinc(II) ions from the hydrochloric acid solutions [8]. The main disadvantages of process are - the efficiency of the zinc(II) extraction process by 3-pyridylketoxime depending mainly on the contact area, contact time of the two phases and the concentration of a protonated form of the ligand, which creates in the initial stage of the extraction. Moreover, the protonated form of the ligand decomposes after a contact with the stripping agent and the next extraction stage also requires a high concentration of hydrochloric acid in the aqueous feed. As expected, these problems have been solved by the structure modification from 3-pyridylketoxime to quaternary 3-pyridinium ketoxime [9], however, the selectivity of the zinc extraction have not been studied in detail.

Therefore, the goal of the research was to study the selective zinc(II) ions extraction from acidic chloride solutions containing also iron(III), nickel(II), cobalt(II), and copper(II) ions using as an extractant a hydrophobic quaternary 3-pyridinium ketoxime. The influence of the composition of an aqueous phase, especially concentration of metals or chloride and hydrogen ions, on the selectivity of the zinc(II) extraction were analysed.

Experimental

Reagents

¹ e-mail: karolina.wieszczycka@put.poznan.pl, Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

All reagents used in this study were of reagent grade. Toluene (POCH, Poland) and decan-1-ol (Merck, Germany) were used as components of the organic phase. Sodium chloride (Chempur, Poland), sodium nitrate(V) (Sigma-Aldrich, Germany), hydrochloric acid (38%) (POCH, Poland), nitric acid (70%) (POCH, Poland), zinc(II) chloride (anhydrous) (Sigma-Aldrich, Germany), iron(III) chloride (hexahydrate), copper(II) chloride (hexahydrate) cobalt(II) chloride (hexahydrate) and nickel(II) chloride (hexahydrate) (Sigma-Aldrich, Germany) were used to compose the aqueous phase. The principal extractant was 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide which was synthesised in a three stage reaction (Fig. 1). In the first stage 1-(3-pyridyl)undecan-1-one was synthesised by treating 3-pyridylcarbonitrile with decylmagnesium bromide. In the second stage, the synthesised ketone was treated with hydroxylamine hydrochloride in the presence of sodium hydroxide (at pH = 7). In the third stage the synthesised oxime was stirred and heated (60 ° C) for 12 h with propyl bromide in ethanol as a diluent to give the pyridinium ketoxime. ^1H NMR (CDCl_3) δ in ppm: 9.22 (s); 8.90 (s); 8.50 (d); 7.90 (t); 7.29 (d); 3.60 (t); 2.78 (t); 1.51 (q); 1.31-1.19 (m); 0.81 (m); ^{13}C NMR (CDCl_3) δ in ppm: 156.2; 148.9; 147.1; 133.8; 132.3; 123.4; 62.5; 32.6; 31.7; 29.7; 29.5; 29.4; 29.1; 26.1; 25.7; 22.5; 18.1; 14.0; 10.3.

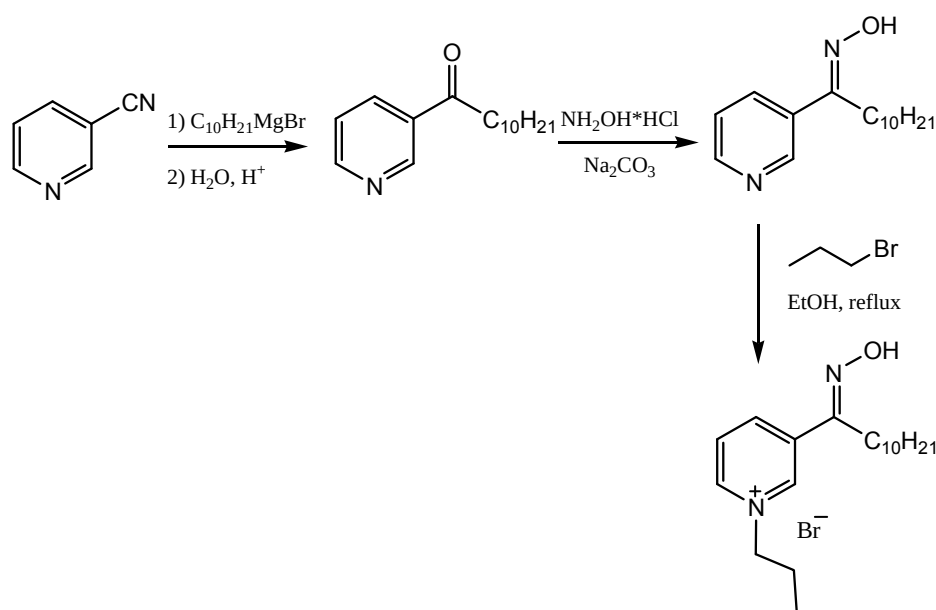


Fig. 1 Scheme of pyridinium ketoxime synthesis.

Extraction studies

Extraction studies of individual metals were carried out in a test tube using organic to aqueous volume ratio (O/W) equal to 1. Both phases were shaken for 30 minutes at room temperature (21-23 °C) using a bio-mix BWR04. Aqueous feed solutions were prepared by dissolving the appropriate amounts of the chloride or nitrate salts of zinc(II), sodium and lithium in ultrapure water. The research was carried out at a constant chloride ion concentration (4 mol/L) and various hydrochloric acid concentrations (from 0 to 4 mol/L), or at a constant mineral acid concentration (HCl or HNO_3 ; 0.5 mol/L) and various chloride ions concentrations (from 0 to 4 mol/L). The

ionic strength of the aqueous solutions was constant at 4 mol/L. The selectivity test was performed using an aqueous feed solution containing 1 g/L of Zn(II), Cu(II), Fe(III), Cu(II) and Ni(II) ions and 1 or 4 mol/L HCl. Cumulative concentration of chloride ions was equal 4 mol/L. An organic phase used in the extraction studies contained 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide and toluene with 10% (v/v) addition of decan-1-ol. The concentration of the extractant was 0.2 mol/L. The metals concentration was determined by the atomic absorption spectrometry using Z8200 (Hitachi) apparatus.

Calculation

The metal content in the organic phase was determined by a mass balance between the concentration of a metal in the aqueous phases before and after the extraction. Distribution coefficient (D), percentage extraction (%E) and separation factor (β) were calculated from equations:

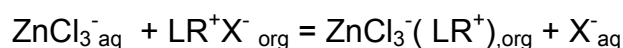
$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \quad \%E = \frac{[M]_{\text{aq}}}{[M]_{\text{o,aq}}} \quad \beta_{Zn/M} = \frac{D_{Zn}}{D_M}$$

where $[M]_{\text{o,aq}}$ represents the initial concentration of metal ions, $[M]_{\text{aq}}$ and $[M]_{\text{org}}$ are the metal concentration after the extraction in the aqueous and organic phases, respectively.

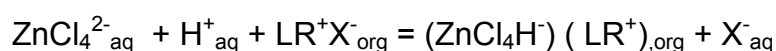
Results and discussion

The hydrophobic extractant containing a pyridinium cation can mainly form the complexes with metals ions through the ion-exchange, ion-pair mechanism and simultaneous combination of these.

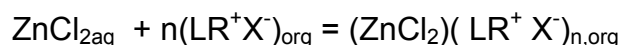
The ion-exchange mechanism can be represented as:



or



But the ion-pair mechanism does not require the anionic form of the metal species to be present in the aqueous phase and it implies that a neutral metal containing species is transferred to the organic phase.



The presence of both a quaternary pyridinium ring and oxime substituent in the extractant structure, have not changed the mechanism of the metal complexation, however, the location of the substituent at pyridinium ring could have influenced the selectivity of the extraction. Recent studies have indicated that the zinc(II) extraction with 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide depends on the concentration of chloride ions as well as the acidity of the aqueous phase [9]. For example, under the acidic conditions the rate of the extraction increases linearly along with the increase of the chloride ions concentration up to 2 mol/L and either

remains fairly constant upon further addition of Cl^- . Moreover, the stoichiometry studies indicated that mainly ZnCl_4^{2-} ions were extracted and one of the ligand molecule was replaced by hydrogen cation forming complex of composition $(\text{LR}^+)(\text{HZnCl}_4^-)$. Similar relation of extraction efficiently with chloride ions concentration has been observed for the weak acidic aqueous solutions, however, under these conditions the zinc extraction was combined with ZnCl_3^- ions coordination. The affinity of the 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide to anionic species of zinc(II) chloride enabled us to predict the high selectivity the zinc extraction over copper(II) and nickel(II) ions. In case of nickel(II) chloride, the speciation analysis showed that most nickel is present as Ni^{+2} and NiCl^+ but at high concentration of chloride ions and at higher temperature the small amounts of NiCl_2 can also be observed. However, the diagram of a distribution of the copper-chloride species in the aqueous chloride solutions showed a dominant of cationic copper-chloride species at lower concentration of Cl^- , a linear increase CuCl_2 with the increase of Cl^- concentration and an insignificant content of CuCl_3^- achieving maximum 9% at 4 mol/L Cl^- . As predicted, in case of both nickel(II) and copper(II) ions the transport of the metal ions from aqueous chloride solutions containing from 0.01 to 1 mol/L Cl^- to the organic phase was not observed. Further increase of chloride ions concentration caused a slight extraction of nickel(II) ions (in the range 0.1-1%) and more visible transport of copper(II) (from 1% at 1 mol/L Cl^- to 5% at 4 mol/L Cl^-) (Fig. 2). Also, the increase of HCl concentration in the aqueous solutions containing constant concentration of chloride ions did not cause the extraction of copper(II) and nickel(II) ions more efficient.

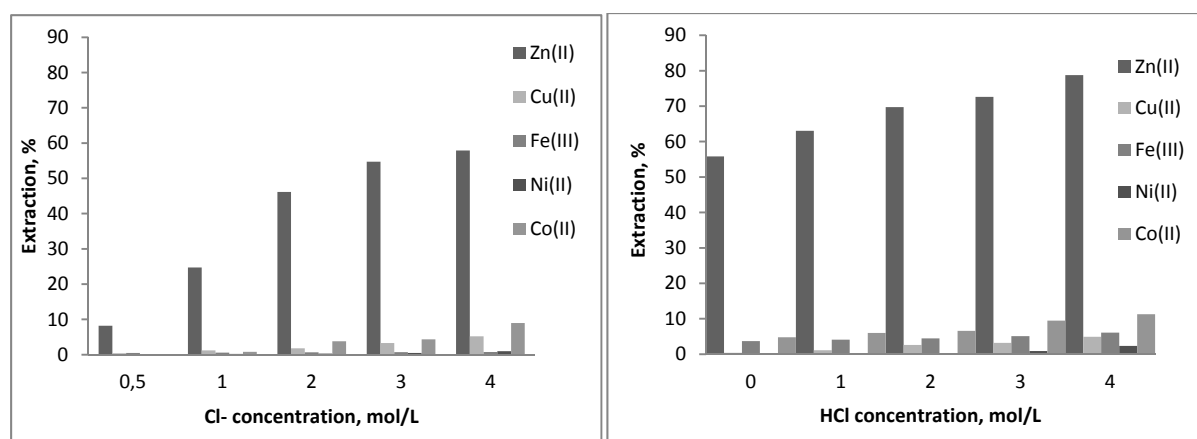


Fig. 2. Zinc(II) extraction studies carried out at constant mineral acid concentration (0.5 mol/L) and various chloride ions concentrations (from 0 to 4 mol/L) (A) and at constant chloride ion concentration (4 mol/L) and various hydrochloric acid concentrations (from 0 to 4 mol/L) and (B) ($[\text{Zn(II)}] = 1\text{g/L}$; $I = 4\text{ mol/L}$; $[\text{extractant}] = 0.1\text{ mol/L}$)

Iron(II) ions had no ability to form anionic chloro-complexes even at 4 mol/L of chloride ions, however, in that case the extraction was observed and it increased from 0.3 to 0.7% with the increasing chloride ions concentration from 1 to 4 mol/L Cl^- ,

respectively and from 1 to 6% with the increasing HCl concentration at constant 4 mol/L Cl^- . In case of cobalt(II) chloride, wherein the majority of the ions exists as Co^{2+} (up to 2 mol/L HCl concentration) and CoCl^+ remained constant, the mole fraction of CoCl_2 , CoCl_3^- and CoCl_4^{2-} increased with the HCl concentration. Therefore, the composition should enable a cobalt complexation as it has been observed for ternary amines or Alamine 336 [10]. Unfortunately, as it is shown in Figure 2, the maximum cobalt(II) ions extraction reached 11%, even from strong acidic chloride solutions.

The selectivity of 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide dissolved in toluene with 10% (v/v) addition of decan-1-ol was determined by contacting the organic phase with the fresh aqueous solution containing: constant concentration of Zn(II) ions 1g/L of Fe(III), Cu(II), Co(II) and Ni(II), various hydrochloric acid concentrations (from 0 to 3.9 mol/L) at constant ionic strength $I = 4$ mol/L. The studies confirmed that the increase of hydrochloric acid concentration decreased the zinc(II) selectivity over the copper(II) and iron(III) ions, for nickel(II) and cobalt(II) this parameter increased achieving maximum for solution containing 3 mol/L HCl and after that decreased giving even 7% extraction of the nickel(II) ions (Table 1.).

Table 1. Extraction of metals from synthetic solutions containing 1 g/L of Fe(III), Cu(II), Co(II) and Ni(II) ($[\text{HCl}] = 0.5\text{--}3.9$; $I = 4$ mol/L[extractant] = 0.1 mol/L)

HCl mol/L	Metal extraction, %					Separation factor			
	Zn(II)	Cu(II)	Fe(III)	Ni(II)	Co(II)	$\beta_{\text{Zn/Cu}}$	$\beta_{\text{Zn/Fe}}$	$\beta_{\text{Zn/Ni}}$	$\beta_{\text{Zn/Co}}$
0.5	6.1	0.0	0.1	0.3	0.1	1247.7	125.4	20.4	55.8
1.0	10.6	0.0	0.1	0.1	0.1	750.3	113.0	81.4	50.3
1.5	20.9	0.0	0.1	0.1	0.2	831.8	41.8	237.5	237.5
2.0	47.5	0.1	0.6	0.1	0.1	862.7	97.1	840.1	840.1
2.5	60.3	0.2	0.9	0.1	0.1	804.8	107.8	1311.0	1442.3
3.0	69.6	0.5	1.6	0.0	0.1	651.3	106.8	31521.5	3149.0
3.5	69.3	1.1	3.1	3.3	0.1	396.4	121.0	125.8	190.8
3.9	69.0	4.3	3.4	6.9	2.2	85.9	59.7	51.5	121.9

The effect of a ligand structure on zinc(II) extraction and its selectivity was also examined using quaternary pyridinium ketoximes containing a different structure of the alkyl halide attached to the pyridinium nitrogen (1-ethyl-3-[1-(hydroxyl-imino)undecyl]pyridinium bromide, 1-butyl-3-[1-(hydroxyimino)undecyl]pyridinium bromide and 3-[1-(hydroxyimino)undecyl]-1-pentylpyridinium bromide). The extraction process was carried out with the aqueous solutions containing 3 mol/L HCl at constant ionic strength $I = 4$ mol/L. The results showed that the zinc(II) and the competitive metals extraction decreased with the decreasing length of the alkyl chain, however, the highest extraction percentage and a good selectivity were observed for the quaternary pyridinium ketoxime containing propyl or pentyl bromide attached to the pyridinium nitrogen.

Conclusions

The present investigations have resulted in proposing the quaternary pyridinium ketoxime as the extractant for separation of zinc(II) ions from acidic chloride solutions containing other metals ions such as copper(II), iron(III), nickel(II) and cobalt(II). The obtained results showed that the best extraction efficiency (77-80%) was observed for strong acidic aqueous solutions containing constant concentration of chloride ions, however, for these solutions the extractions of other metals were also observed. Our studies also indicated that the extraction from the multimetal solutions improved the efficiency of the zinc separation and the best results of the metal recovery over cobalt(II) and nickel(II) ions were observed from the aqueous solutions containing 2.5-3.0 mol/L HCl at the constant ionic strength $I = 4$ mol/L, wherein the amount of extracted copper(II) and iron(II) ions was not higher than 0.005 and 0.02 g/L, respectively.

Acknowledgements

This research was supported with 32-374/14 DS-PB grant and realised in the frame of Polish-Portuguese scientific and technological co-operation for the years 2013-2014 „Selective extractants for the removal of minor metallic elements from chloride spent pickling baths”.

Reference

1. K. Klonowska – Wieszczycka, A. Olszanowski, A. Parus B. Zydorczak; Solvent Extr. Ion Exch. 27 (1), 50-62, (2009)
2. A. Parus, K. Wieszczycka, A. Olszanowski; Sep. Sci. Technol. 46(1) 87-93 (2011)
3. A. Parus, K. Wieszczycka, A. Olszanowski, Hydrometallurgy 105, 284–289 (2011)
4. K. Wieszczycka, M. Kaczerewska, M. Krupa, A. Parus, A. Olszanowski, Sep. Purif. Technol. 95, 157-164 (2012)
5. A. Parus, K. Wieszczycka, A. Olszanowski, Sep. Sci. Technol. 48(2), 319-327 (2012)
6. K. Wieszczycka, M. Krupa, A. Olszanowski, Sep. Sci. Technol. 47(9), 1278-1284 (2012)
7. K. Wieszczycka, M. Krupa, A. Wojciechowska, A. Olszanowski, Solvent Extr. Ion Exch. (2014) DOI:10.1080/07366299.2013.850334
8. K. Wieszczycka, Sep. Purif. Technol. 114, 17-23 (2013)
9. K. Wieszczycka, A. Wojciechowska, M. Krupa, R. Kordala-Markiewicz, J. Chem. Eng. Data 58(11), 3207–3215 (2013)
10. M. Filiz, N.A. Sayar, A.A. Sayar, Hydrometallurgy 81,167-173 (2006)

Synthesis of a new extractant with phenylphosphinic acid and selective extraction of In(III) and Ga(III) over Zn(II) from acidic media

Yoshinari Baba^{*1}, Naoki Matsuo¹, Yuji Sasaki¹, Tatsuya Oshima¹

Summary

[Bis(2-ethylhexyl)amino]methylphenylphosphinic acid (BEAPP) as a novel extraction reagent was synthesized to develop a selective extractant for In(III) and Ga(III) in acidic media containing Zn(II). The extraction selectivity for In(III), Ga(III) and Zn(II) was examined from 1M aqueous ammonium nitrate solution with BEAPP in toluene. BEAPP was successful in the mutual separation of In(III), Ga(III) and Zn(II) although their separation could not be achieved with the commercial acid extractants such as D2EHPA, PC-88A and Versatic 10. The extraction selectivity of BEAPP for their metal ions was in the following order: In(III) > Ga(III) > Zn(II). In order to elucidate their selectivity, the extraction equilibria for In(III), Ga(III), and Zn(II) with BEAPP were quantitatively investigated by a batchwise method at 303 K. In(III), Ga(III) and Zn(II) were extracted with BEAPP (HR) according to the following reactions, respectively: $\text{In}^{3+} + 2(\overline{\text{HR}})_2 \rightleftharpoons \overline{\text{InR}_3(\text{HR})} + 3\text{H}^+$, $\text{Ga}^{3+} + 1.5(\overline{\text{HR}})_2 + \text{NO}_3^- \rightleftharpoons \overline{\text{GaR}_2(\text{HR})(\text{NO}_3)} + 2\text{H}^+$, and $\text{Zn}^{2+} + 2(\overline{\text{HR}})_2 \rightleftharpoons \overline{\text{ZnR}_2(\text{HR})_2} + 2\text{H}^+$. The extraction equilibrium constants of In(III), Ga(III) and Zn(II) with BEAPP were determined to be $K_{\text{ex,M}} = 1.70 \times 10^4 \text{ [mol dm}^{-3}\text{]}$, 4.17 $[(\text{mol dm}^{-3})^{-0.5}]$ and $1.55 \times 10^{-2} [-]$, respectively.

Introduction

In recent years, the demand for indium and gallium has increased more and more as semiconductor materials such as InP and GaAs in the field of electronic devices. In addition, these metals also are used in solar panels and have emerged as important strategic metals since they are essential elements for the electronic industry. However, indium and gallium is not produced from ore, but they have been generally recovered as by-products in the zinc refinery residues. For these stable supplies of worldwide concerns, electronic wastes that contain indium or gallium have been highlighted as possible secondary resources [1]. Therefore, the development of effective techniques for the separation and recovery of these metals is an important issue for Japan where natural resources are not abundant.

The solvent extraction is one of the major separation techniques for metal ions. Hence, a large number of extractants for In(III) and Ga(III) have been already developed and reported, including phosphoric acid [2-6], phosphinic acid [7-8] oximes [9], carboxyl acid [10], amines [11]. In addition, the synergistic extraction of In (III) and Ga (III) has been reported [12-14]. However, there are some problems, for examples, the extraction equilibrium time of oximes series were so long, and the solubility to aqueous phase of carboxyl acid series and amines series were high. On the other hand, the extractants of phosphoric acid series have low solubility to

^{*}Corresponding Author: Yoshinari. Baba, Tel.: +81-985-58-7307, E-mail address: t0g202u@cc.miyazaki-u.ac.jp

¹ Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, Miyazaki, JAPAN

aqueous and resistance properties for hydrolysis. Therefore, a phosphoric acid series is being set to mainstream for extraction of In(III) and Ga(III). In particular, di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexylphosphoric acid mono 2-ethylhexyl ester (PC-88A) have been used as selective extractants for In(III) and Ga(III). However, it is very difficult to mutually separate these metals by one step extraction using any industrial extractants (D2EHPA, PC-88A, and Versatic10) as mentioned above. It is desired to develop the selective separation technique for In(III) and/or Ga(III) from lots of Zn(II) because these metals show similar chemical properties. In order to do that, first of all, it is very important to develop a new selective extractant for mutual separation of In(III)/Ga(III)/Zn(II).

In this study, a new extractant with a phenylphosphinic acid group was synthesized for the mutual separation of In(III), Ga(III) and Zn(II). Since the extractant have the tertiary amine moiety along with phosphinic acid group as shown in Fig.1, it is expected that the extraction selectivity for these metal ions is different from those of commercial phosphorus acid extractants. The extraction selectivity of the new extractant (BEAPP) for metal ions was compared with those of the commercially available acidic extractants, D2EHPA and Versatic 10. The extraction equilibria of In(III), Ga(III) and Zn(II) were examined in detail in order to determine their extracted species and extraction equilibrium constants.

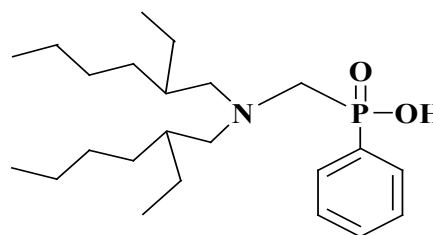


Fig.1 Chemical structure of BEAPP

Experimental

Materials and reagents

Metal nitrates of analytical grade (Wako Pure Chemical Ind. Ltd.) were used to prepare test solutions containing metal ion. Phenylphosphinic acid (Tokyo Kasei Kogyo Co.), bis(2-ethylhexyl)amine (Wako Pure Chemical Ind. Ltd.), and paraformaldehyde (Sigma-Aldrich Co. LLC.) were used as raw materials without further purification. All other reagents and solvents were of analytical grade and were used as received. All aqueous solutions were prepared with distilled and deionized water. [Bis(2-ethylhexyl)amino]methylphenylphosphinic acid (BEAPP) was synthesized by Mannich reaction with 85% yield in our laboratory[15], and BEAPP was identified using $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C), FT-IR and elemental analysis.

Extraction procedures

To evaluate extractability of BEAPP, liquid-liquid extraction was carried out using 1.0 M (mol dm^{-3}) aqueous ammonium nitrate solution containing 1 mM metal ions. The pH was adjusted with concentrated HNO_3 or NH_3 . Toluene was used for the organic phase containing BEAPP. In an Erlenmeyer flask, the equal volumes (10 cm^3) of the aqueous phase and the organic phase were shaken mechanically 24 hours at 303 K. After the phase separation, the pH of the aqueous solution was measured with pH meter and was determined by the acid-base titration in lower pH region than 0.5. The

metal concentration in the aqueous solution was determined by atomic absorption spectrophotometry FAAS or ICP. The metal ion concentration in the organic phase was calculated from the mass balance between the aqueous and organic phases. Extraction percentage ($E\%$) and metal distribution ratio (D) were calculated according to Eqs. (1) and (2), respectively.

$$E\% = \frac{[M]_{org,eq}}{[M]_{aq,init}} \times 100 = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,init}} \times 100 \quad (1) \quad D = \frac{[M]_{org,eq}}{[M]_{aq,eq}} = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,eq}} \quad (2)$$

where $[M]_{aq,init}$ represents the initial concentration of metal ion in the aqueous phase. $[M]_{aq,eq}$ and $[M]_{org,eq}$ are the total concentrations of metal ion in the aqueous and organic phases at equilibrium, respectively.

Results and discussion

Selective extraction of In(III), Ga(III) and Zn(II) with BEAPP

The extraction of In(III), Ga(III) and Zn(II) from the aqueous phase with the conventional industrial extractants in toluene is shown in (a), (b) and (c) in Fig. 2 as a function of aqueous phase equilibrium pH. As shown in Fig. 2 (a), the organo-phosphorus extractant, D2EHPA, preferentially extracted In(III) over Ga(III) and Zn(II) however, Ga(III) and Zn(II) was extracted at the same pH region. This indicates that these metals were not able to mutually separate with D2EHPA. On the other hand, the carboxylic acid extractant series, Versatic10 and 2-[(4-octylphenyl)amino]acetic acid (AN) [16] extracted selectively In(III) and Ga(III) over Zn(II) as is shown in Fig. 3 (b) and (c), respectively. However, In(III) and Ga(III) cannot be separated mutually with these extractants because these metals are extracted at the same pH region.

The extraction selectivity of BEAPP was examined using metal ions such as In(III), Ga(III), and Zn(II). Figure 3 (d) shows the effect of equilibrium pH on the extraction percentage of metal ions with BEAPP. As seen in this result, the extraction order for metal ions with BEAPP was $\text{In(III)} > \text{Ga(III)} > \text{Zn(II)}$. The extraction selectivity of BEAPP for In(III), Ga(III) and Zn(II) is different from that of the extractants such as PC-88A, D2EHPA, Versatic10 and AC. This suggested that the different extraction behavior of In (III), Ga (III) and Zn (II) was due to steric hindrance of the phenyl group or the presence of amine group in BEAPP. These mutual separations with BEAPP allow selective recovery of In(III), Ga(III) from zinc refinery residues by the one-step extraction.

The extraction selectivity of In(III) and Ga(III) was examined from mixture solution of Ga(III)/In(III) and Zn(II)/Ga(II), respectively, using BEAPP. From Ga(III)/In(III) mixture, In(III) was selectively extracted with BEAPP even in the presence of a 100-fold excess of Ga(III). In addition, Ga(III) was selectively extracted with BEAPP even in the presence of a 130-fold excess of Zn(II). The high selectivity for In(III), Ga(III) and Zn(II) with BEAPP may be attributed to chelate formation by the tertiary amine moiety

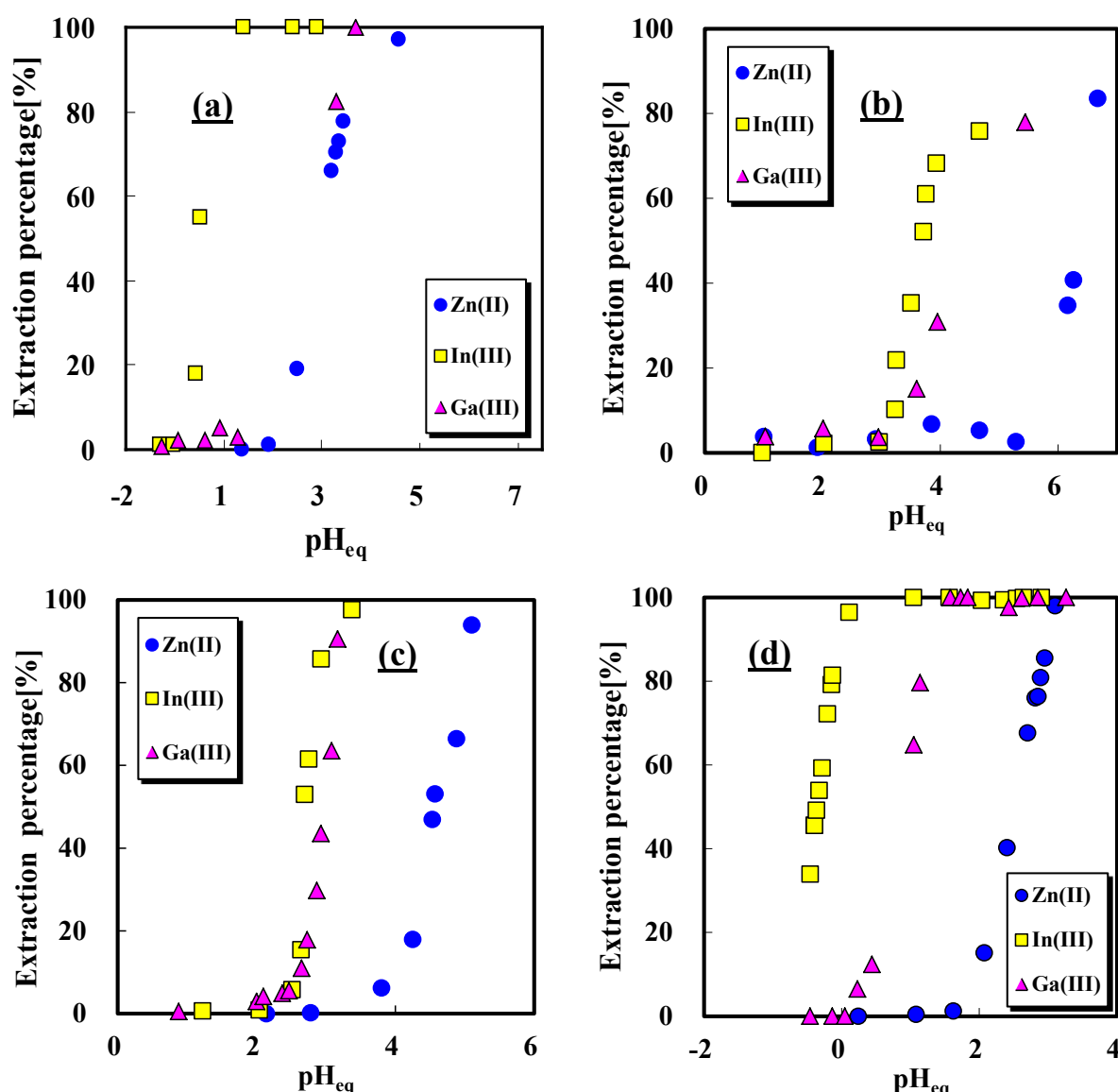


Fig.2 Effect of hydrogen concentration on extraction percentage with D2EHPA (a), Versatic10 (b), AN (c) and BEAPP (d) from 1 M aqueous ammonium nitrate solution.

(=N-) and phosphoric acid in addition to the steric hindrance of phenyl moiety in BEAPP. To our knowledge, this is the first report discussing the achievement of the mutual separation of In(III), Ga(III) and Zn(II) with high efficiency by solvent extraction with a single extractant.

Figure 3 shows the dependencies of the concentration of hydrogen ion on the distribution ratio of In(III), Ga(III) and Zn(II). As seen from this figure, the straight lines with slopes of 3, 2, and 2 were obtained for In(III), Ga(III), and Zn(II), respectively. This indicates that

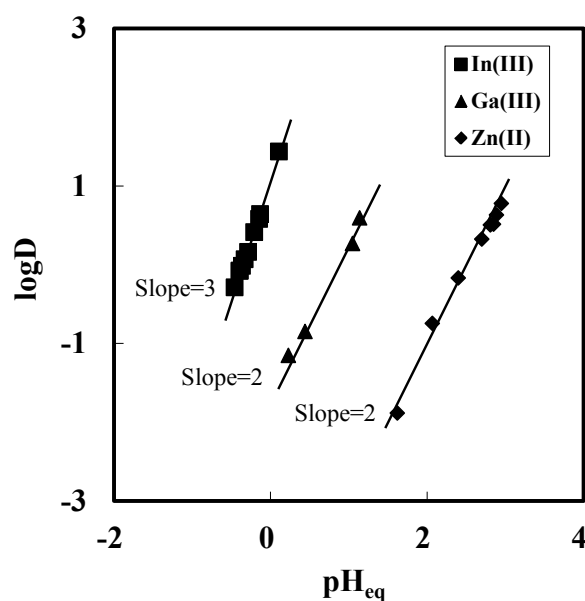
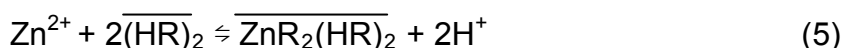
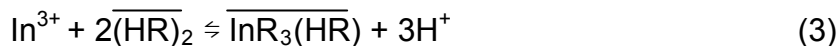


Fig.3 Effect of pH on $\log D$ with BEAPP

three hydrogen ions participate in the extraction of In(III), and two hydrogen ions are related to the extraction of Ga(III) and Zn(II). In addition, the effect of pH and nitrate anion on the distribution ratio of these metals was similarly examined in order to elucidate their extraction equilibria. The extraction equilibria of their metal ions with BEAPP are expressed by Eqs. (3)-(5):



Back extraction of In(III), Ga(III) and Zn(II)

The back extraction of In(III), Ga (III) and Zn(II) from the loaded organic phase was examined using HCl, HNO₃ and EDTA. The chelating agent EDTA, HCl and HNO₃ effectively stripped Zn(II) from the organic phase. High back extraction percentage of In(III) was achieved using 5M HNO₃, while back extraction of Ga(III) was not effective very much even using various back extraction agents.

Conclusions

The newly prepared extractant, [bis(2-ethylhexyl)amino]methylphenylphosphinic acid (BEAPP), was found to be efficient for selective extraction of In(III), Ga(III) and Zn(II) ions. It was found that the mutual separation ability of BEAPP for In(III), Ga(III) and Zn(II) was highly superior to that of commercial acidic extractants. This is probably due to the steric hinderance by the phenyl moiety and chelating effect by the amine moiety and phosphinic acid in BEAPP. The high selectivity of In(III) and Ga(III) with BEAPP was confirmed by extracting mutually In(III), Ga(III) and Zn(II) from the mixture containing these metal ions. The stoichiometries in the extraction reactions of In(III), Ga(III) and Zn(II) with BEAPP were determined by the slope analysis based on the experimental results. Moreover, the back extraction of the extracted In(III), Ga(III) and Zn(II) from the organic phase was achieved using 5 M HNO₃.

Acknowledgement

We thank The Environment Research and Technology Development Fund (ERTDF) in the Ministry of the Environment in Japan for financial support of this research.

References

1. T. Suzuki, T. Nakamura, Y. Inoue, M. Niinae, J. Shibata, *Sep. Purif. Technol.*, **98** (2012), 396-401.
2. J.S. Liu, H. Chen, X.Y. Chen, Z.L. Guo, Y.C. Hu, C.P. Liu, Y.Z. Sun, Extraction and separation of In(III), Ga(III) and Zn(II) from sulfate solution using extraction resin, *Hydrometallurgy*, **82** (2006) 137-143.

3. J. Jayachandran, P. Dhadke, Solvent extraction separation of gallium(III) with 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A), *Hydrometallurgy*, 50 (1998) 117-124.
4. S. Nishihama, T. Hirai, I. Komasaawa, Separation and Recovery Gallium and Indium from Simulated Zinc Residue by Liquid-Liquid Extraction, *Ind. Eng. Chem. Res.*, 38 (1999) 1032-1039.
5. S. Nishihama, A. Hino, T. Hirai, I. Komasaawa, Extraction and Separation of Gallium and Indium from Aqueous Chloride Solution Using Several Organophosphorus Compounds as Extractants, *J. Chem. Eng. Japan*, 31 (1998) 818-827.
6. S. Virolainen, D. Ibane, E. Paatero, Recovery of indium from indium tin oxide by solvent extraction, *Hydrometallurgy*, 107 (2011) 56-61.
7. B. Gupta, N. Mudhar, I. Singh, Separations and recovery of indium and gallium using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), *Sep. Purif. Technol.*, 57 (2007) 294-303.
8. B. Gupta, A. Deep, P. Malik, Liquid-Liquid extraction and recovery of indium using Cyanex 923, *Anal. Chim. Acta.*, 513 (2004) 463-471.
9. F.J. Alguacil, Solvent extraction of indium (III) by LIX 973N, *Hydrometallurgy*, 51 (1999) 97-102.
10. X. Zhang, G. Yin, Z. Hu, Extraction and separation of gallium, indium and thallium with several carboxylic acids from chloride media, *Talanta*, 59 (2003) 905-912.
11. I. S. EL-Yamani, E. I. Shabana, STUDIES ON EXTRACTION OF INDIUM(III) CHLORIDE COMPLEXES BY LONG-CHAIN AMINES, *J. Radioanal. Nucl. Chem.*, 88 (1985) 217-223.
12. S. Fan, Q. Jia, N. Song, R. Su, W. Liao, Synergistic extraction study of indium from chloride medium by mixtures of sec-nonylphenoxy acetic acid and trialkyl amine, *Sep. Purif. Technol.*, 75 (2010) 76-70.
13. H. Imura, A. Oshiro, K. Ohashi, Synergistic Extraction of Gallium(III) and Indium(III) with 2,4-Pentanedione and 3,5-Dichlorophenol on the Basis of Outer-sphere Complexation, *Anal. Sci.*, 14 (1998) 1093-1098.
14. H. Ma, Y. Lei, Q. Jia, W. Liao, L. Lin, An extraction study of gallium, indium, and zinc with mixtures of sec-octylphenoxyacetic acid and primary amine N1923, *Sep. Purif. Technol.*, 80 (2011) 351-355.
15. Y. Sasaki, N. Matsuo, T. Oshima, and Y. Baba, to be submitted to *Sep. Purif. Technol.*
16. C. Kai, T. Oshima and Y. Baba, *Solv. Extr. Res. Develop. Japan*, 17, 175-185 (2010)

Phase Equilibria of Innovative Solvent Systems for Homogenous Catalysis

Ole Riechert¹, Tim Zeiner², Gabriele Sadowski¹

¹Laboratory of Thermodynamics, Technische Universität Dortmund Emil-Figge-Str. 70, 44227 Dortmund, Germany

²Laboratory of Fluid Separations, Technische Universität Dortmund Emil-Figge-Str. 70, 44227 Dortmund, Germany

Homogenous catalyzed hydroamination provides a powerful, atom-economic reaction pathway to alkyl amines on the basis of renewable feedstock. Using this type of catalyst, the reaction runs under mild conditions with high selectivity. One major drawback in homogenous catalysis is the challenge of catalyst recycling which can be covered by the application of innovative thermomorphic solvent systems (TMS). Those systems are homogenous at reaction temperature and heterogeneous at separation temperature. This property can be used for catalyst recycling and product recovery in one extraction step to achieve a resource- and money-saving process design.

Renewable feedstock, such as terpenes gain significant interest in chemical industry due to the natural limitation of fossil feedstock. In particular, β -myrcene is an interesting raw material and can be converted by homogenous catalyzed hydroamination with an amine, e.g. morpholine, to alkyl amines. This reaction can be carried out in a mixture of acetonitrile and *n*-alkanes, which show a temperature-dependent miscibility gap as mentioned above.

So far, solvents for TMS were selected based on the liquid-liquid equilibria (LLE) of the potential solvent systems only. The influence of reactants on the LLE was not considered within this context, yet. Hence, this study focuses on investigating the thermodynamics of the reactants, β -myrcene and morpholine, in solvent systems composed of acetonitrile and *n*-alkanes.

Binary systems' LLE of acetonitrile, *n*-alkanes and binary vapor-liquid equilibria (VLE) of systems composed of one of the solvents and a reactants, β -myrcene or morpholine, were measured and successfully modeled using PC-SAFT [1]. Based on that, ternary systems' LLE composed of the solvent system and a reactant were predicted and found in good agreement with experimental data. Additionally, a generalized approach was developed accounting for the dependence of the LLE on the chain-length of the *n*-alkanes. This allows for predicting systems containing alkanes of different chain lengths in good accordance with experimental data in binary as well as ternary systems' LLE.

The thermodynamic modeling of the TMS allows a predictive design of the product and catalyst separation by extraction. By application of the thermodynamic model a rigorous optimization of the process is feasible. Moreover, this approach provides a strategy for application of extractive separation of the catalyst and product by reducing the experimental effort.

[1] Gross, J.; Sadowski, G. (2001); Ind. Eng. Chem. Res. 40 (4), p. 1244–1260

Recycling metals by controlled transfer of ionic species between complex fluids

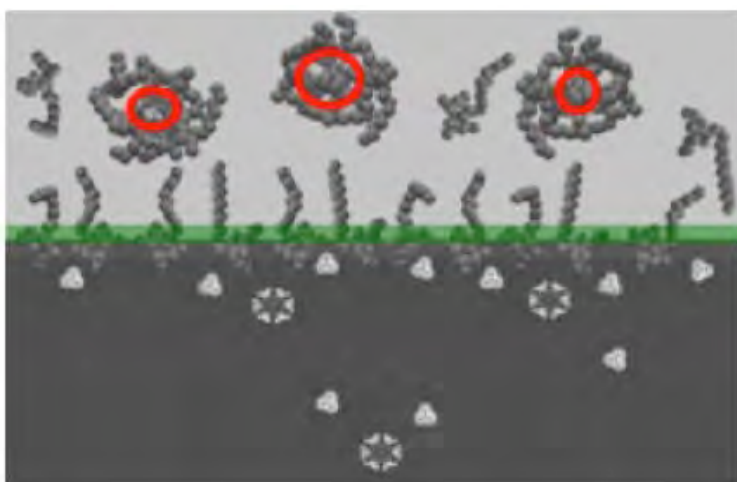
C. Bauer, Ch. Déjugnat, O. Diat, J.-F. Dufrêche, S. Dourdain, M. Duvail, D. Meyer, S. Pellet-Rostaing and Th. Zemb

Institute for Separation Chemistry of Marcoule , Bagnols sur Ceze, France

We illustrate here a colloidal approach of the transfer of ions between two phases, involving a macroscopic oil-water interface as well as divided polar/apolar interface developed whenever extractant molecules organize as reverse aggregates. Simultaneous statistical thermodynamics and elucidation of micellar-like structures and corresponding phase diagrams involved allows to rationalize in an unified model:

- *the phase transition responsible of “third phase accidents” and the corresponding variations in viscosity ,*
- *The differences in free energies of transfer associated to ion transfer between phases that are the origin of selectivities and their relation with solvent formulation.*
- *The origin of synergy peaks occurring with ceratin molde fractions of extracatnst as well as “modifiers”*

By analogy of electronics in nanostructures, this “ienaic” approach deals with ions and their nearest nieghbours in equilibrium between fluid nanostructures generalizes the classical multiple chemical equilibrium models, and requires only a few measurable parameters to model a complete liquid-liquid extraction implying equilibrium between a concentrated slurry and an emulsified water-poor microemeulsion, as shown in the figure. Ions are adsorbed on the flexible interface shown (shown in red) , while efficiency depends on the transfer through the macroscopic interface (shown in green).



Polymer/ionic liquid composite membranes for olefin selective separation

*Daniel Gorri¹, Raúl Zarca¹, Alfredo Ortiz¹, Inmaculada Ortiz^{*1}*

Summary

Currently the separation of propylene from propane on a commercial scale is performed almost exclusively by distillation in refineries and petrochemical industries. Since this technology is highly energy intensive, there is a strong economic incentive to explore alternative separation technologies with lower energy consumption. Novel facilitated transport composite membranes including ionic liquids have been proposed by our research group to carry out the separation of olefin/paraffin gas mixtures. In this work, a comparative study has been performed by using ionic liquids with the same anion (tetrafluoroborate) and different organic cations, testing the effect of the alkyl chain length of the cation. Based upon the experimental results, ionic liquids based on imidazolium cations with less and shorter alkyl substituents improve the selective separation of these mixtures.

Introduction

The separation of propylene from propane is a task of primary importance in the petrochemical industry. Traditionally this separation is being performed by distillation in a single or double column with 150-200 trays. The columns usually operate at high pressures (16-26 bar) and room temperature or moderate pressures and low temperatures (183-233 K) working at high reflux ratios between 12 and 20. Therefore the process not only requires high capital investment, but also it is one of the most highly energy demanding processes in the petrochemical industry [1]. In fact, it was estimated that 0.12 Quads of energy (1 Quad = 10^{15} BTU) were used yearly only for olefin/paraffin distillation [2]. Thus, the conventional separation process certainly holds an enormous potential for capital and energy cost savings which provide an incentive to develop new separation technologies for olefin/paraffin separation.

The use of membranes that play an active role in the olefin/paraffin separation has been extensively reported in the literature [3]. The separation mechanism is based either on selective physicochemical interactions between olefin and the membrane material, in molecular sieving effects or in a combination of both. Membrane technology holds a great potential for energy and capital saving in the separation process of olefins from paraffins. The criteria for selecting the most suitable membrane for a given application are complex; nonetheless, durability, mechanical and thermal stability at the operating conditions, productivity and separation efficiency and costs are important stipulations that must be considered. Among these requirements selectivity and permeation rate are clearly the most basic, while the relative importance of the rest varies with the application. Recently the use of polymer/ionic liquid composite membranes with enhanced separation properties is becoming increasingly important.

1

* Corresponding Author: Inmaculada Ortiz, Dep. Chemical and Biomolecular Engineering, University of Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain. Email: ortizi@unican.es

In a previous work by our research group, novel facilitated transport composite membranes were proposed to carry out the separation of olefin/paraffin gas mixtures [4]. The pair ionic liquid-silver salt used in that case was 1-butyl 3-methylimidazolium tetrafluoroborate-silver tetrafluoroborate, showing very promising results in terms of separation selectivity and propylene permeability. In the present work the study has been extended to other ionic liquids with the same anion (tetrafluoroborate) and different organic cations, testing the effect of the alkyl chain length of the cation.

Experimental

Materials

Propylene and propane gas were purchased from Praxair with a minimum purity of 99.5%. The polymer PVDF-HFP (CAS number 9011-17-0) was supplied by Sigma Aldrich. The ionic liquids (IL) BMImBF₄ and EMImBF₄ were provided by Iolitec, with a minimum purity of 99% and residual halide content less than 500 ppm. The silver salt used was silver tetrafluoroborate of 99% purity purchased from Apollo Scientific Ltd. Tetrahydrofuran (THF) supplied by Panreac was used as a solvent to prepare the membranes.

Membrane preparation

The PVDF-HFP/IL/Ag⁺ composite membranes were prepared by the solvent casting technique. First of all the polymer is dissolved in 10 mL of THF at 40°C for 8 hours in a closed vial to avoid the evaporation of the solvent. Once the polymer has been dissolved, it is mixed with the ionic liquid (IL) and the silver salt and stirred for 5 minutes. Finally the membrane precursor mixture is placed in a Petri dish and the solvent is evaporated at 25 °C and 300 mbar under dark conditions for 24 h. For better understanding of the results presented in this work, it would be appropriate to clarify that the silver content of the membranes is expressed as a percentage of the silver salt weight compared with the weight of the membrane without silver AgBF₄/(PVDF-HFP + IL).

Gas permeation experiments

Once the polymer-IL membrane has been prepared ($A = 39.6 \text{ cm}^2$) it is placed into a permeation cell inside a water bath in order to control the temperature. The flow rate of each gas is adjusted by a mass flow controller and before starting the experiment the composition of the feed stream is analyzed by gas chromatography. The feed stream flows through the upper chamber, while the nitrogen used as sweep gas flows through the permeate side. The pressure of both streams is controlled using two micrometric valves. The flow rate of the permeate stream is measured using a mass flowmeter (as the sum of permeate and sweep gas) and at the cell outlet the composition of both, the feed stream and the permeate stream are analyzed by gas chromatography. The analysis was performed in a gas chromatograph HP 6890 equipped with a thermal conductivity detector (TCD)

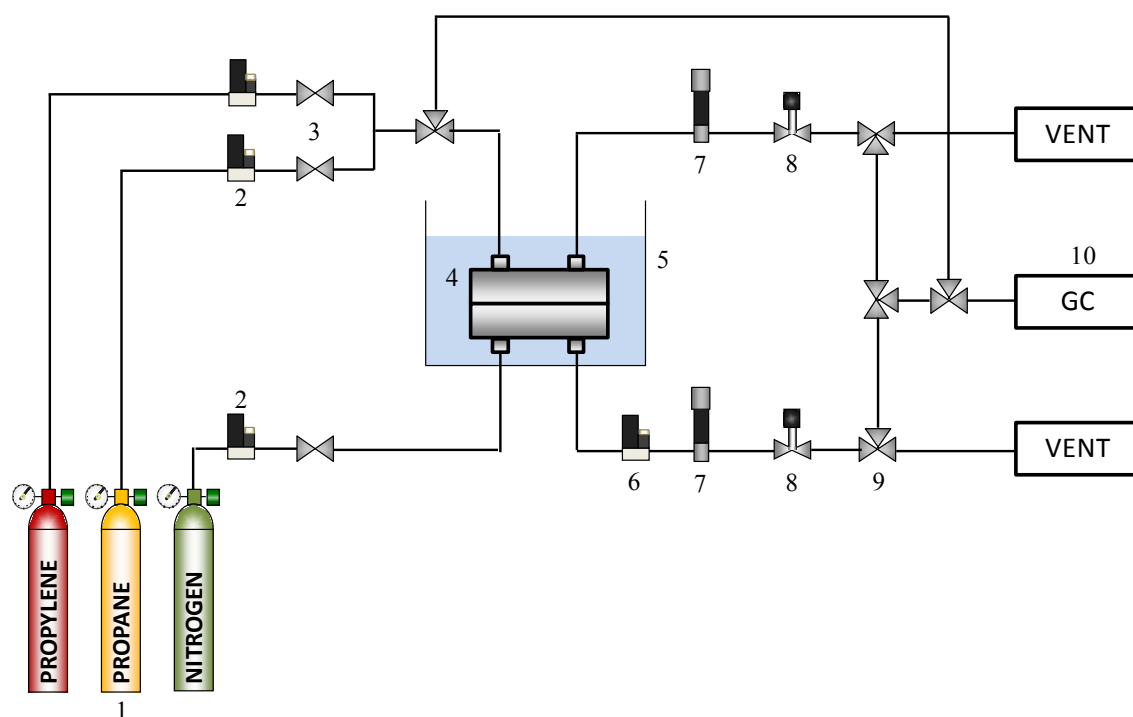


Figure 1: Diagram of the experimental setup: 1-Gas bottles, 2-Mass flow controllers, 3- Two way valves, 4- Permeation cell, 5- Water bath 6- Mass flowmeter, 7- Pressure transducer, 8- Micrometric valve, 9-Three way valves, 10- Gas chromatograph.

The experimental permeabilities of each gas are calculated according to eq.1:

$$J_i = P_{m,i} \frac{\Delta P_i}{\delta} \quad (1)$$

where J_i is the flux of the specie i across the membrane, $P_{m,i}$ is the permeability of each gas, ΔP_i difference in the partial pressure of the gas between both sides of the membrane and δ is the thickness of the membrane measured using a digital micrometer Mitutoyo Digmatic Series 369.

Results

Gas mixture permeation experiments were carried out in order to measure gas permeabilities and determine the C_3H_6/C_3H_8 separation selectivity. The selectivity of the membrane (α) is given by eq. 2 and is equal to the ratio of the permeabilities of the two permeating species:

$$\alpha = \frac{P_{m,propylene}}{P_{m,propane}} \quad (2)$$

The influence of the membrane composition as well as the different operational conditions such as the sweep gas flow rate, gas partial pressure and temperature on the separation of propane/propylene gas mixtures was studied.

Figure 2 illustrates the effect of temperature on the propylene permeability and selectivity for a membrane with composition 80% PVDF-HFP/20% BMImBF₄/80%AgBF₄. As expected, the membrane with 80% AgBF₄ exhibits high fluxes of propylene because the facilitated transport mechanism takes place. Regarding the effect of temperature the results show that a higher operating temperature increases gas permeability. This can be explained because at higher temperatures two simultaneous effects take place, i) the polymer chain mobility increases and ii) the viscosity of the ionic liquid drastically decreases. These two phenomena lead to higher diffusion coefficients for both C₃H₈ and C₃H₆. However, C₃H₈ is affected to a larger extent over C₃H₆ that already had a very fast permeation due to facilitated transport. As a consequence, the higher temperature decreases the permeation advantage of propylene over propane resulting in lower separation selectivities.

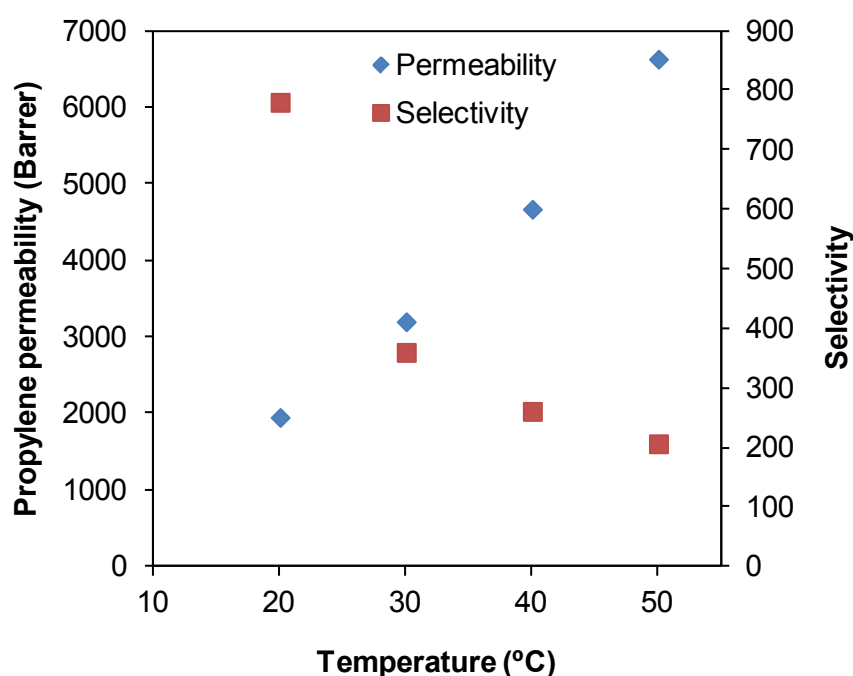


Figure 2. Experimental propylene permeabilities and selectivities for a polymer-ionic liquid (80% PVDF-HFP/20% BMImBF₄/80%AgBF₄) composite membrane

In Table 1 preliminary results obtained with composite membranes containing the EMImBF₄ ionic liquid are compared with the results obtained previously with the BMImBF₄ ionic liquid. In each case, the composition of the membranes was: 0.4 g ionic liquid + 0.4 g polymer + 80% AgBF₄. These membranes were tested with 50/50%v/v C₃H₈/C₃H₆ mixtures at 293 K and 1 bar of feed pressure, and nitrogen as sweep gas at the permeate side.

With regard to selectivity, the experimental results show that best results are obtained when the EMImBF₄ ionic liquid was used in membrane preparation, although the permeabilities of both gases is slightly higher in the membrane containing the BMImBF₄ ionic Liquid. This is because shorter alkyl chains provide lower physical solubility of both gases, and therefore the separation process is dominated by the

effect of the chemical reaction. These results are in agreement with previous results on the solubility of these gases in ionic liquids and their mixtures with silver salts [5]. Additionally short alkyl chain imidazolium ionic liquids have lower viscosity and hence enhance facilitated transport through the liquid phase entrapped in the polymer matrix. Therefore, based upon the experimental results, ionic liquids based on imidazolium cations with less and shorter alkyl substituents improve the selective separation of these mixtures.

Table 1. Comparison of performance for membranes containing different ionic liquids

	Membrane containing EMImBF ₄	Membrane containing BMImBF ₄
Propylene permeability (Barrer)	2028	2070
Propane permeability (Barrer)	27	28
Selectivity	76.5	73.4

Acknowledgements: The Ministry of Education and Science (Spain) financially supported this research under projects CTQ2012-31639 (MINECO, Spain-FEDER 2007-2013) and ENE 2010–15585.

References

- [1] D.E. Gottschlich, D.L. Roberts, Energy minimization of separation processes using conventional/membrane hybrid systems. Energy minimization of separation processes using conventional/membrane hybrid systems. Report No. DOE/ID-10301 (1990).
- [2] R.B. Eldridge, Olefin/paraffin separation technology: A review, *Ind. Eng. Chem. Res.* 32 (1993) 2208-2212.
- [3] R. Faiz, K. Li, Polymeric membranes for light olefin/paraffin separation, *Desalination*. 287 (2012) 82-97.
- [4] M. Fallanza, A. Ortiz, D. Gorri, I. Ortiz, Polymer-ionic liquid composite membranes for propane/propylene separation by facilitated transport, *J. Membr. Sci.* 444 (2013) 164-172.
- [5] M. Fallanza, A. Ortiz, D. Gorri, I. Ortiz, Propylene and propane solubility in imidazolium, pyridinium, and tetralkylammonium based ionic liquids containing a silver salt, *J. Chem. Eng. Data*. 58 (2013) 2147-2153.

Process development of enantioselective extraction of aromatic acids in intensified lab columns

Alexander Holbach; Julia Godde; Norbert Kockmann / TU Dortmund / Germany

The most common techniques to separate racemic mixtures are today crystallization and chromatography. But the processes are cost intensive and difficult to scale up. A well promising alternative is the enantioselective liquid-liquid extraction (ELLE). The principle behind this technique is a selective recognition of one enantiomer with a selector molecule. Steensma [1] and Schuur [2] demonstrated that a separation of amino alcohols in counter-current equipment is possible, using membrane modules and centrifugal extractors, respectively. Due to the low selectivity many counter-current extraction stages are necessary. The equipment needs a good mass transfer, small hold up and low investment cost. We developed a new process intensified extraction column, which can realize high specific surfaces and thus good mass transport rates [3]. The low volume flow rates (2 – 15 ml/min) and the low hold up (350 ml) is ideal for the process development for pharmaceutical products. With the EFCE test system n-butylacetate / acetone / water we could realize 25 theoretical stages per meter. This is more than twice as already achieved in other miniplant columns.

It could be demonstrated that the enantioselective extraction of (R/S)-cyclohexyl-mandelic acid inside this columns is possible. We separated a racemic mixture with hydroxypropyl- β -cyclodextrine as selector molecule ($\alpha_{op} \sim 1.4$). The enantiomeric excess was measured up to 50 % of (R)-cyclohexyl-mandelic acid inside the lab ($H_{ac} = 1.1$ m). This was the first time that the enantioselective extraction could be realized inside counter-current extraction columns. With larger active extraction sections, more theoretical stages and therefore a better performance can be realized. Based on experimental data a downstream process for the separation of aromatic acids is proposed. The downstream process includes, beside the fractional extraction of racemic mixtures, the back extraction of the selector molecule, product precipitation, and recovery of the side products.

[1] Steensma, PhD thesis, Enschede, 2005

[2] Schuur; et al.; Organic & Biomolecular Chemistry, 9, 36-51, 2011

[3] Holbach, et al., CIT 85, 9, 1385-1386, 2013

A flat channel membrane microcontactor for liquid-liquid extraction

Jonas Hereijgers, Vrije Universiteit Brussel, Brussels, Belgium; Tom Breugelmans, University of Antwerp, Antwerp, Belgium; Wim De Malsche, Vrije Universiteit Brussel, Brussels, Belgium.

A disadvantage of extraction is that a given settling time or some sort of de-mixing step is required afterwards. Membrane based extraction devices avoid this by using a membrane as an interface stabilizer. Hollow fibers have been the traditional format to integrate the membrane into the channel. A fundamental limitation of hollow fibers is that the extraction kinetics are adversely affected when aiming at a larger column cross section with a concomitant increase in diffusion distances. A possible approach consists of minimizing the fiber diameter and maximizing the number of hollow fibers in a module. The occurrence of dead zones, backmixing, bypassing and channeling causing irregular mass transfer along the module thereby present however serious drawbacks. Therefore, a flat channel membrane microcontactor (MMC) with channel depths ranging from 50 to 200 μm was constructed (Fig. 1a). Using a distributor at the beginning and the end of the channel, the width could be easily varied from 1 to 20 cm. Hence allowing to construct larger cross sections for downstream processing in a mini-plant without the above mentioned drawbacks. Mass transfer experiments (Fig. 1b) showed that equilibrium is reached in 2 min, making it also possible to test every 10 minutes a different parameter condition (e.g. solvent). The challenge in such membrane devices consists of avoiding breakthrough of one of the solvents through the pores. Breakthrough, described by the Laplace pressure (Fig. 1c), often occurs when using typical extraction solvents due to the low interfacial tension. To tackle this problem and to create a robust system, an innovative channel design was developed and backpressure regulation was performed, which allowed to keep pressure differences below the Laplace pressure independent of the flow rate.

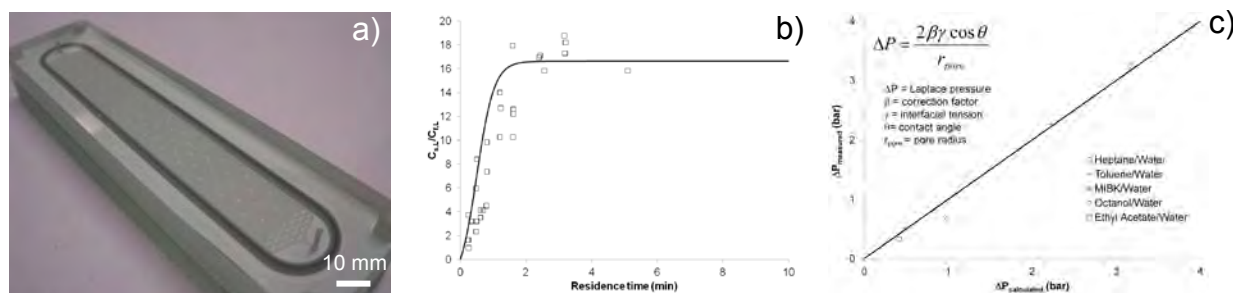


Fig. 1: a) Channel design of the MMC. b) Concentration ratio feed/solvent at the outlet of the MMC. c) Breakthrough pressures of a Teflon membrane (Frisenette, pore size = 100nm, $\beta = 0,3$).

Process intensification of high-phase-ratio extraction with gas-liquid-liquid microdispersion system

Jing Tan^{*}, Jianhong Xu, and Guangsheng Luo^{*}

The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, 100084, China

Mass transfer in extraction with high phase ratio (higher than 50:1) is low and process intensification of high-phase-ratio extractions shows great importance in reducing equipment size and compacting separation processes. In this study, gas-liquid-liquid microdispersion systems were designed to realize microbubble-agitated extraction processes for process intensification. Series of membrane dispersion modules with microfiltration membranes as dispersion mediums were developed to generating gas-liquid-liquid microdispersion systems with three different microdispersion modes. N-butyl alcohol- succinic acid / water system was chosen as the model system. In the experiment, the effects of mass transfer direction, dispersion mode, dispersion size, phase ratio and flow rates on dispersion sizes as well as mass transfer coefficient were studied. The results show that with gas-liquid-liquid microdispersion system, the overall volumetric mass transfer coefficient can reach more than 10 times greater than the extraction process without gas addition. Physical and mathematical model was established for the mechanism study. Experimental data and calculation result show good coincidence. This study helps the development of new extraction processes and devices.

Intensification of mass transfer by coupling membrane dispersion and microbeads packed column for high two-phase ratio system

Guotao Liu, Tsinghua University, Beijing, China PR; Jing Tan, Tsinghua University, Beijing, China PR; Guangsheng Luo, Tsinghua University, Beijing, China PR

Recently, membrane dispersion devices and microextractors have shown great potential for intensification of solvent extraction process. But few of the research published is related to operation carried out with high large two-phase ratio system which is common in industry, such as wet process phosphoric acid purification. Previous research of our group showed that extraction efficiency in a membrane dispersion device began to decrease when two-phase ratio increased. Still effective technique for intensification of mass transfer performance for high two phase ratio system has not been reported. Here, we couple the membrane dispersion and microbeads packed column to enhance mass transfer performance. Three working systems of n-butanol / succinic acid / H₂O, 30%TBP-kerosene / HNO₃ / H₂O and MIBK / H₃PO₄ / H₂O were used to test the mass transfer and phase separation characteristics. Influence of the flow rate, two-phase ratio and column parameters were studied. The results show that extraction efficiency of those with a microbeads packed bed is higher than that with only membrane dispersion. Finally, a model for mass transfer coefficient prediction of these membrane dispersion and packed column combination units is established

Keywords:

Mass transfer; microbeads packed column; large two-phase ratio

Influence of plate wettability on the performance of a Pulsed Disc and Doughnut Column

T. Grabin¹, K. Smith¹, K. Mumford¹, Y. Wang¹ and G. Stevens¹

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia.

Corresponding author email address: gstevens@unimelb.edu.au

Summary

The hydrodynamic performance of a Pulsed Disc and Doughnut solvent extraction column with different internal plate materials has been presented to examine how the column performance changes with the wetting characteristics of the plates. Teflon, Nylon and Stainless Steel plates have been used to simulate a change in the wetting behaviour of the plate material. The liquid-liquid system studied was TOA-kerosene-water with sulphuric acid as the solute. Results show that there are significant changes in the measured holdup and operational regimes at low agitation intensities, including phase inversion by insufficient pulsation when the organic phase is dispersed. It was therefore concluded that the hydrodynamic performance of the column is dependent on the plate wettability.

Introduction

Solvent extraction is used as a separation and purification process for a large number of chemical and metallurgical industries. Several types of contactors have been developed with different agitation systems and different internal geometries such as mixer-settlers, pulsed plate columns and Karr reciprocating plate columns. Recently the Pulsed Disc and Doughnut Column has received a lot of attention due to its versatility and low cost. The industrial operation of a contactor can deteriorate due to changes in the wetting characteristics of the plates caused by aging of the material, adsorption of contaminants or crud formation. In designing a solvent extraction column, the rule of thumb suggests that the plates be wetted by the continuous phase, however contradictory results have been reported for the pulsed perforated plate column [1]. In this study the effect of plate wettability on holdup and droplet size are compared at similar operational conditions with three different plate materials with distinct wetting characteristics.

Experimental

The pulsed disc and doughnut column used in this study consists of a 1.0 m long precision bore glass column with internal diameter of 72.5 mm. A t-section is placed on top of the main column which allows the light phase (organic) to overflow and an expanded glass section is present below the main column to allow the aqueous phase to separate from the organic phase before exiting from the bottom of the column. The pulsation was controlled by a piston-type unit which consists of a motor, variable speed unit (controls the frequency) and eccentric drive head (controls the amplitude). Both phases entered the column through distributors, the organic phase

located at bottom and aqueous phase located at top of the column. The interface was kept below the distributor to ensure the organic phase was continuous. Experimental measurements were done with mass transfer of sulphuric acid from the dispersed aqueous phase to the continuous organic phase. Table 1 summarizes the geometries associated with each plate material including measured contact angle. Physical properties of the liquid system are shown in Table 2.

Table 1. Summary of column internal geometries

	Teflon	Nylon	Stainless Steel
Effective column height, H_c	815 mm	791 mm	790 mm
Effective column Volume, V_e	3,365 cm ³	3,265 cm ³	3,261 cm ³
Number of pairs (of discs & doughnuts), N	32	32	29
Plate thickness, E	3 mm	3 mm	1.6 mm
Disc diameter, d_d	62.4 mm	62.4 mm	63.5 mm
Doughnut aperture, d_a	36.9 mm	36.9 mm	35.0 mm
Plate spacing, h	9.73 mm	9.36 mm	12.02 mm
Compartment height, h_c	25.47 mm	24.72 mm	27.24 mm
Plate free area, S	25.9 %	25.9 %	23.3 %
Voidage, ϵ	82.55 %	82.02 %	90.99 %
Advancing contact angle, θ_a	179°	118.7°	95.3°
$1+\cos\theta_a$	1.52×10^{-4}	0.520	0.908

Table 2. Physical properties of the liquid-liquid system used

Physical property	phase	Density (kg/m ³)	Viscosity (Pa.s)	Interfacial tension (N/m)
Continuous organic phase	TOA-Kerosene	805	0.00185	0.011
Dispersed aqueous phase	0.4% H ₂ SO ₄	998	0.0001	

Procedures

The dispersed phase holdup was measured via the drainage technique [2] and is represented in terms of the characteristic velocity developed by Gayler and Pratt [3] according to equation (1). Droplet size was measured via a photographic method [4] and expressed in terms of the Sauter mean diameter, d_{32} , as defined by equation (2). The advancing contact angle was measured via the captive needle approach [5] with the liquid-liquid-solid system and expressed in terms of $1+\cos\theta_a$ (refer to Table 1). The range of operating parameters investigated in this study is given in Table 3.

$$V_d + \frac{V_c x_d}{1-x_d} = \epsilon \bar{v}_o x_d (1 - x_d) \quad (1)$$

$$d_{32} = \frac{\sum_{i=0}^n n_i d_i^3}{\sum_{i=0}^n n_i d_i^2} \quad (2)$$

Table 3. Range of operating parameters

	Teflon & Nylon	Stainless Steel
Frequency, f	1.7 – 2.0 – 2.3 Hz	1.5 – 1.8 – 2.1 Hz
Amplitude, A	0.9 cm	1.2 cm
Pulsation rate, Af	1.53 – 1.8 – 2.07 cm/s	1.8 – 2.16 – 2.52 cm/s
Dispersed phase velocity, V_d	0.05 – 0.1 cm/s	
Continuous phase velocity, V_c	0.04 & 0.05 cm/s	
Phase flow ratio, V_c/V_d	0.37 – 1.06	

Results and Discussion

Operational regimes

The three different plate materials, Teflon (super hydrophobic), Nylon (intermediate hydrophobicity) and stainless steel (hydrophilic), showed similar operating regimes. When the dispersed phase wet the plates (ie. aqueous dispersed and stainless steel plates or organic dispersed and Teflon plates), the dispersed phase formed a film around the plates at low pulsation intensities. Despite the presence of the film, the stainless steel plates at 1.5 Hz maintained distinct dispersed aqueous droplets in the emulsion regime while for Teflon plates the continuous aqueous phase became dispersed within the film. When the films from two adjacent plates coalesced, chain coalescence occurred resulting in phase inversion. Table 4 shows the operating regimes at different pulsation frequencies for both dispersed aqueous and dispersed organic.

Table 4. Operating regimes at different pulsation frequencies

Dispersed phase	Plate material	1 Hz	1.25 Hz	1.5 Hz	1.75 Hz	2.0 Hz
Aqueous	Teflon	M-S	M-S	T	E	E
	Nylon	M-S	M-S	T	E	E
	Stainless steel	M-S	T	E	E	E
Organic	Teflon	P-I	P-I	P-I	E	E
	Nylon	M-S	M-S	E	E	E
	Stainless steel	M-S	T	E	E	E

M-S: Mixer-Settler; T: Transition; E: Emulsion; P-I: Phase-Inversion

Holdup

Characteristic velocity plots for a range of pulsation intensities have been provided for Teflon, Nylon and Stainless steel plates in Figure 1, Figure 2 and Figure 3 respectively. The characteristic velocity calculated from these plots had good accuracy with $R^2 > 0.996$ for all data. A summary of the characteristic velocities and pulsation rates for the three different plate materials can be found in Table 5. It was found that characteristic velocity decreased as agitation rate increased for each plate material.

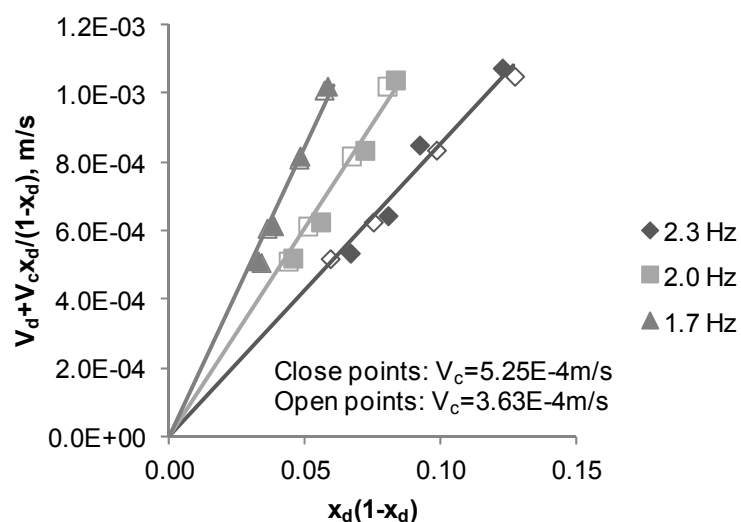


Figure 1. Characteristic velocity plot over a range of operating conditions for Teflon plates

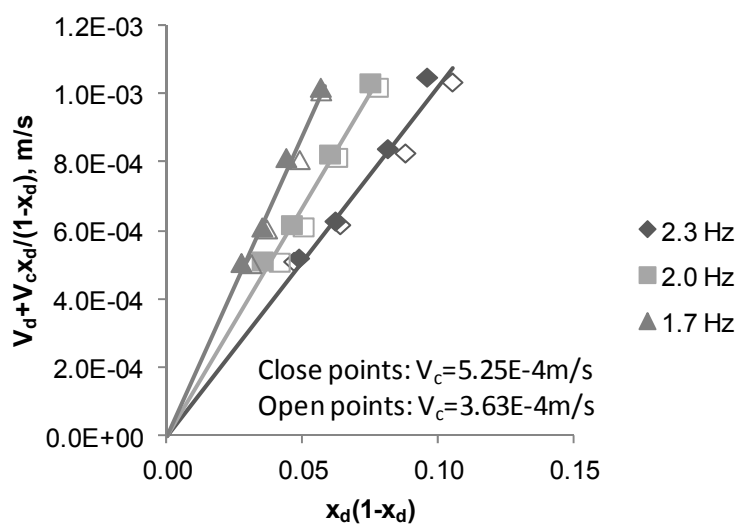


Figure 2. Characteristic velocity plot over a range of operating conditions for Nylon plates

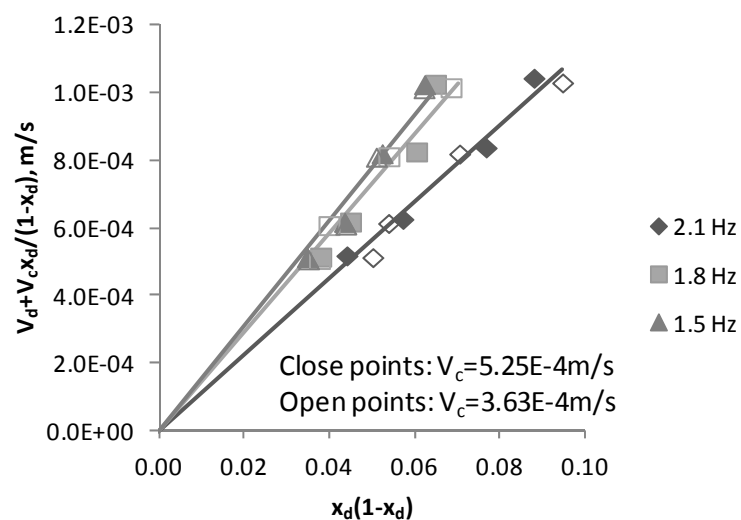


Figure3. Characteristic velocity plot over a range of operating conditions for Stainless steel plates

Table 5. Summary of characteristic velocity

Plate material	A_f (cm/s)	ev_o (cm/s)
Teflon	2.07	0.851
	1.80	1.208
	1.53	1.691
Nylon	2.07	1.018
	1.80	1.330
	1.53	1.755
Stainless steel	2.52	1.123
	2.16	1.462
	1.80	1.552

When the aqueous phase was dispersed, the increase in hydrophilicity of the plate material ($1+\cos\theta_a$) resulted in reduced holdup at similar agitation rates for high and intermediate agitation intensities, hence increasing the characteristic velocity. At low agitation intensity the film formed around the stainless steel plates resulting in noticeably increased holdup.

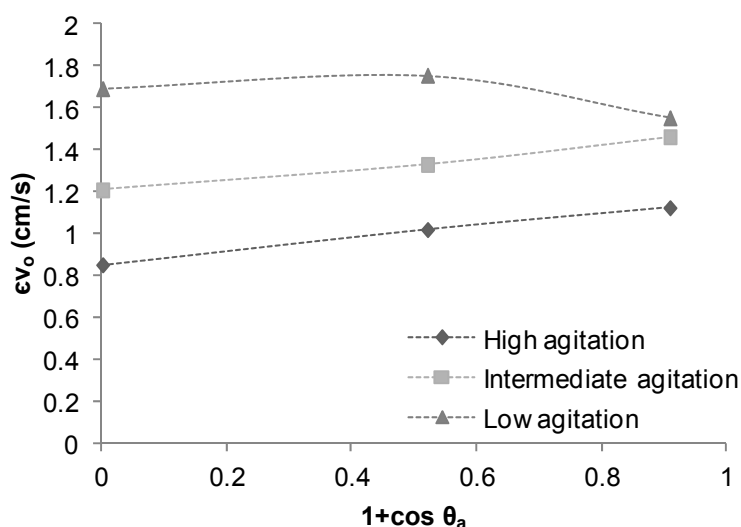


Figure 4. Effect of plate wettability on characteristic velocity at different agitation rates

Droplet size

The droplet size distribution, measured in terms of the Sauter mean diameter, d_{32} , was averaged over the phase flow rates and appeared to be unaffected by the plate wettability at high and intermediate agitation intensities (given a standard deviation of around 0.05 mm). At low agitation rates each plate showed different behaviours: Nylon had the lowest d_{32} with a similar standard deviation as before while the standard deviation for Teflon doubled and Stainless steel increased the standard deviation to 0.13.

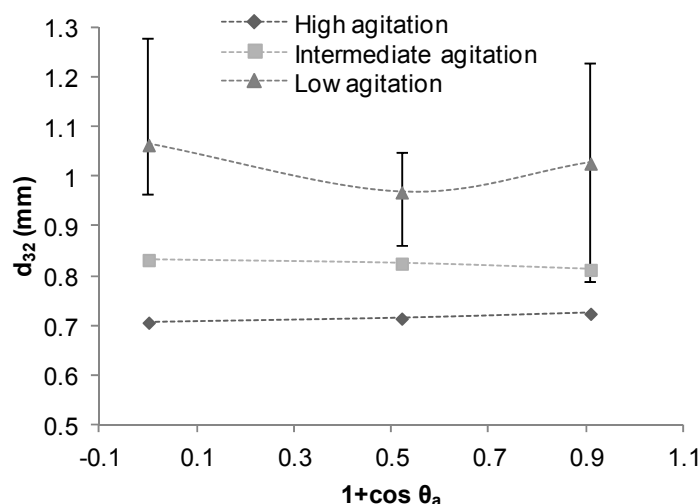


Figure 5. Affect of plates wettability on Sauter mean diameter, d_{32} at different agitation rates

The stainless steel plates at low agitation rate showed distinct behaviour. The aqueous film detached from the plate by forming ligaments among smaller droplets resulting in a low d_{32} . As the dispersed flow rate increased, large and irregular shaped drops were formed and due to their lack of sphericity these drops were neglected in the d_{32} calculation. A further increase in flow rate reduced the presence of large and irregular drops and the system was more stable.

Conclusions

The hydrodynamic performance of a Pulsed Disc and Doughnut Column has been presented over a range of operating conditions for three different plate materials: super hydrophobic (Teflon), intermediate (Nylon) and hydrophilic (Stainless steel). The characteristic velocity was found to increase with an increase in hydrophilicity of the plate material while the drop size distribution remained unchanged at high and intermediate agitation intensities with the different plate materials. At low agitation when the dispersed phase wet the plate material, a dispersed phase film formed and greatly increased the holdup. Therefore it can be concluded that the operational regime and holdup are influenced by the wettability of the plates while droplet size is only influenced by plate wettability at low agitation intensities.

Acknowledgements

Thank you to the Particulate Fluids Processing Centre, a Special Research Centre of the Australian Research Council, for infrastructure support.

Literature

1. Ikeda, H. and A. Suzuki, Plate wettability and droplet diameter in a pulsed perforated-plate extraction column. *The Canadian Journal of Chemical Engineering*, 1992. **70**(2): p. 232-236.
2. Gayler, R. and Pratt, Liquid-Liquid Extraction part II. Hold-up and Pressure Drop in Packed Columns. 1951.
3. Gayler, R. and H.R.C. Pratt, Liquid-Liquid Extraction part IV. A Further Study of Hold-up in Packed Columns. *Trans. Instn Chem. Engrs.*, 1953. **31**: p. 57-68.
4. Azzopardi, B.J., Measurement of drop sizes. *International Journal of Heat and Mass Transfer*, 1979. **22**(9): p. 1245-1279.
5. Berg, J.C., Wettability 1993.

Cesium Separations with Crown Ether Derivatives Containing Aromatic Groups

Y. Miyazaki, T. Kobayashi, S. Suzuki, H. Shiwaku, M.R. Awual, Y. Okamoto,

R. Motokawa, T. Yaita,

Actinide Coordination Chemistry Group, Quantum Beam Science Directorate, Japan

Atomic Energy Agency (SPring-8), Hyogo-679-5148, Japan

In order to solve the environmental pollution problem derived from the Fukushima Dai-ichi nuclear power plant accident, the development of decontamination methods for environmental materials is very important. We have developed crown ether derivative compounds for cesium separation, and furthermore studied the relationship between structure and complexation ability for Cs.

The crown ether can generally recognize the alkali metal ions corresponding to the ring size of an ether chain. Although the interaction between cesium and oxygen in crown ether is dominant interaction for Cs ligation, the ring size suitable for cesium would be key function for appearance of selectivity Cs. On the basis of these ideas, various crown ether derivatives have been designed for development of promising adsorbents selective and sensitive for cesium.

In this present study, the developed benzo-crown ethers were simple structures, but relatively high Cs selectivity than K was observed. The DFT calculation result suggested that π donation from aromatic ring would also enhance Cs selectivity and we are re-considering the model for Cs selectivity. The other coordination properties of these crown ether derivatives with Cs were studied by NMR, UV-Vis spectroscopy and so on, and will be presented in this talk.

Lanthanide Separations by Functionalized Mesoporous Silica-Transportations and Coordination

Md. Rabiul Awual, Tohru Kobayashi, Hideaki Shiwaku, Yuji Miyazaki, Ryuhei

Motokawa, Shinichi Suzuki, Yoshihiro Okamoto, Tsuyoshi Yaita

Actinide Coordination Chemistry Group, Quantum Beam Science Directorate, Japan

Atomic Energy Agency (SPring-8), Hyogo 679-5148, JAPAN

The progress has been made in the technology industry and the demand for highly pure rare metals (lanthanides (Ln^{3+})) has increased dramatically. There is no doubt that solvent extraction is one of the most useful techniques for separation of Ln^{3+} but several disadvantages such as high consumption of reagents, organic solvent and costly have been highlighted. Therefore, the extraction systems to solid-liquid processes have been used as second-generation extraction materials where include a high selective ligand for Ln^{3+} . The novel separation technology can extract the pure Ln^{3+} and the amount of Ln^{3+} adsorption is controlled by the materials cage cavities and stable complexation mechanism.

In this study, a novel separation material for Ln^{3+} was designed using O- and N-donor ligand immobilized mesoporous silica. **Fig. 1** shows the structure of O- and N- donor ligand (A) and TEM images of mesoporous silica (B,C). The straight channel material provides to face the donor atoms of the immobilized ligand to the metals toward a target ion, and thus, facilitates the entering and diffusion of Ln^{3+} . The specific Ln^{3+} transportation based on solution pH, sorption capacity, and recovery by stripping agents was performed. The interaction mechanism and Ln^{3+} coordination after adsorption of specific Ln^{3+} at the solid interface have been studied by EXAFS.

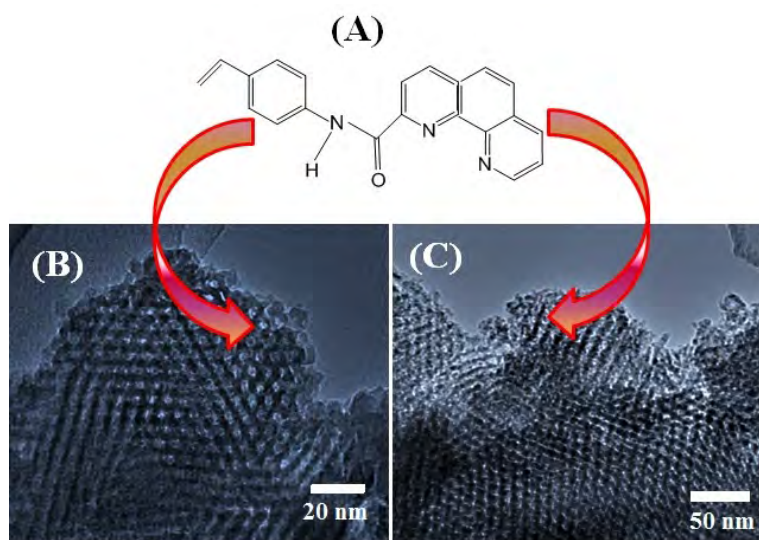


Fig. 1: Structure of O- and N- donor ligand (A) and TEM images of straight channel ordered mesoporous Silica (B,C).

The proposed materials possessed sufficient loading and releasing capacities for specific Ln^{3+} in repeated processes after sorption-recovery operations. The successful development of potential materials can serve as promising applications and time- and cost-effective tool for selective Ln^{3+} sorption and recovery in separation technologies on an industrial scale.

Process Intensification of Light Rare Earth Metals Extraction via Gas-liquid-liquid Membrane Micro-dispersion System

Jing Liu¹; Jing Tan¹; Hailong Hou²; Yundong Wang^{1*}; Jianhong Xu¹; Guangsheng Luo¹

Summary

A gas-liquid-liquid membrane micro-dispersion system was designed to achieve a bubble-agitated extraction process for intensification of extraction with high phase ratio. The process with the phase ratio larger than 30 for light rare earth metals, such as La, Ce, Pr and Nd extraction was taken as a typical case. A micro-dispersion system with 5 μm pore size microfiltration membrane as the dispersion medium was developed to generate the gas-liquid-liquid micro-dispersion system. Overall volumetric mass transfer coefficient of gas-liquid-liquid micro-dispersion system was 10-30 times higher than that the extraction process without gas introduction. A mathematical model was developed to predict the mass transfer in liquid-liquid micro-dispersion extraction processes with/without gas introduction.

Keywords: process intensification, extraction, light rare earth metals, gas-liquid-liquid micro-dispersion

1. Introduction

Aiming to be more eco-friendly and getting larger profit, process intensification has played a more and more important role in chemical engineering. As a result, there comes up many ways to intensify the process such as developing new devices and process integration[1, 2]. Solvent extraction was widely used in the extraction and separation of rare earths[3]. The liquid-liquid and gas-liquid-liquid membrane micro-dispersion systems were designed and researched for the other extraction systems in previous work[4] and the mass transfer efficiency had an obviously improvement.

In this study, these two systems were applied to extract Pr^{3+} with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester(EHPNA) and saponified EHPNA. The influences of the flow rate of water phase, the residence time and the flow rate of added gas were studied, and a unified equation was achieved which can predict the mass transfer performance of the liquid-liquid micro-dispersion extraction process.

^{1*}Corresponding Author, The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University Beijing 100084, P. R. China, E-mail: wangyd@tsinghua.edu.cn.

²School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, P. R. China

2. Experimental section

2.1 Experimental set-up

The experimental set-up is shown in Fig.1. The continuous phase was pumped into the top side of the membrane while the dispersed phase was pumped into buffer reservoir. Due to the pressure difference, the dispersed phase passed through the membrane and formed a micro-dispersion system. Then the micro-dispersion system flowed along the capillary till to the phase separator. In the capillary, there were efficient time for mass transfer. In the end, the micro-dispersion system separated into two phases in the separating funnel. As showed in Fig.2., the gas phase was dispersed into the organic phase firstly and then the gas-organic membrane micro-dispersion system was dispersed into the water phase(the continuous phase) and formed a gas-liquid-liquid membrane micro-dispersion system.

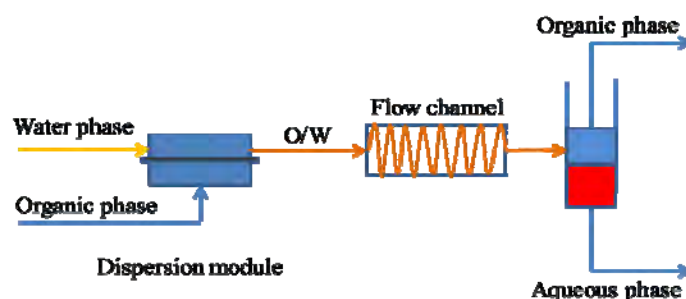


Fig. 1. Liquid-liquid extraction process.

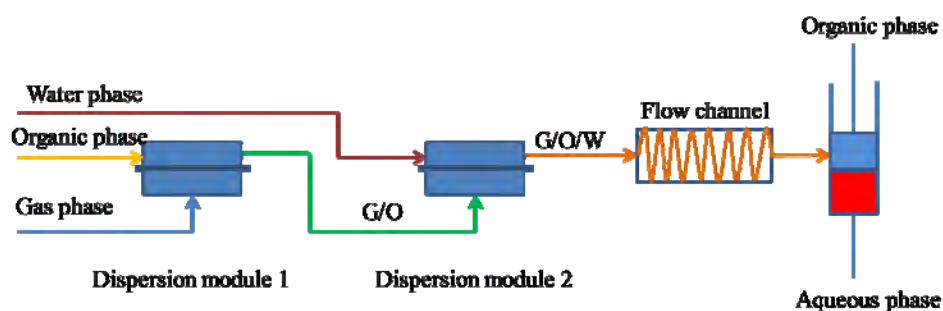


Fig. 2. Gas-liquid-liquid extraction process.

2.2 Materials

EHPNA (industrial pure) was provided by Luoyang Aoda Chemical Co., Ltd. Sulfonated kerosene was provided by Hubei Xingyinhe Chemical Co., Ltd. Praseodymium chloride aqueous solution and Neodymium chloride aqueous solution were made by rare-earth chloride(4N) desolved in hydrochloric acid aqueous solution with cetain pH, and the rare-earth chloride was provided by Beijing Baimu Alloy co., LTD. Ammonium hydroxide and hydrochloric acid were all analytically pure.

2.3 Analysis

The liquid product was analyzed with ICP-OES. The concentration of rare-earth irons in organic phase was determined by law of conservation of mass.

3. Experimental results

3.1 Liquid-liquid micro-dispersion extraction process

All the experiments were carried out at atmospheric pressure and room temperature(25°C).

We used cappillary pipes with different lengths to control the residence time. The residence time is calculated by Eq. (1):

$$T = \frac{V_{\text{Pipe}}}{Q_{\text{Total}}} \times 100\% \quad (1)$$

where T stands for the residence time, s; V_{Pipe} stands for the volume of the pipe, ml; Q_{Total} stands for the superficial velocity of the total fluid in the pipe, mL/s.

After the extraction process, the Murphree efficiency is calculated by Eq.(2):

$$E = \frac{C_0 - C'}{C_0 - C^*} \times 100\% \quad (2)$$

where E stands for the Murphree efficiency, %; C_0 stands for the initial concentration of rare-earth in the water phase, mol/L; C' stands for the concentration of rare-earth in the water phase after extraction, mol/L; C^* stands for the equilibrium concentration of rare-earth in the water phase, mol/L, which was obtained through the equilibrium extraction experiment.

Fig.3. shows the effect of Q_W in a saponification system. The flow rate of the water phase, on the Murphree efficiency for a certain phase ratio. In this liquid-liquid system, the Murphree efficiency reaches almost 100% when $Q_W = 80$ mL/min because of the good dispersion and adequate residence time. As Q_W decreases from 80 mL/min to 70 mL/min, the Murphree efficiency decreases from 100% to 84%. The residence time doesn't increase very apparently, the decrease of Murphree efficiency may be caused by the decrease of turbulence. As Q_W decreases from 70 mL/min to 5 mL/min, the Murphree efficiency increases from 84% to 96%. The residence time increases significantly especially when Q_W decreases from 40 mL/min to 5 mL/min. So the increase of Murphree efficiency may be due to the increase of the residence time.

Fig. 4. shows the effect of the Q_W on the overall volume mass transfer coefficient for a certain phase ratio. With the increase of Q_W , the overall volume mass transfer coefficient K_{oa} increases apparently. Combined figure 3 with 4, we could conclude that setting Q_W 80 mL/min could obtain not only a high Murphree efficiency but also a

big K_{oa} value in a very short residence time for about 5 seconds when the phase ratio was 1:1.

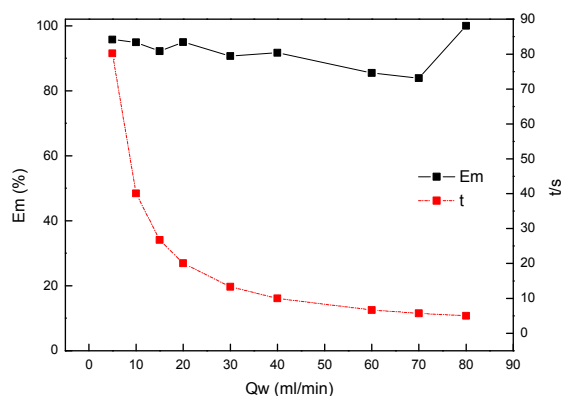


Fig. 3. Effect on water flow rate on Murphree efficiency ($Q_o:Q_w=1:1$).

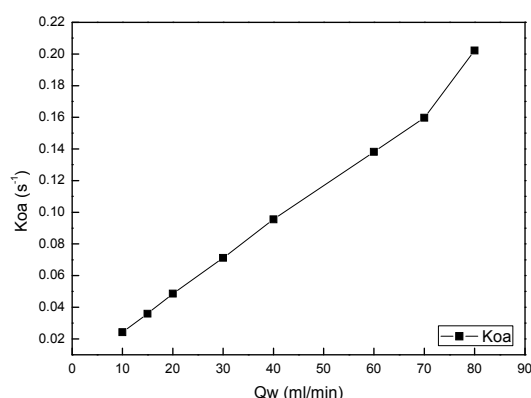


Fig. 4. Effect on water flow rate on the overall volume mass transfer coefficient K_{oa} ($Q_o:Q_w=1:1$).

3.2 Gas-liquid-liquid micro-dispersion extraction process

For higher phase ratio, the extraction process becomes more difficult, so an inert gas was introduced to the liquid-liquid micro-dispersion system to intensify the extraction process. But the system of saponified EHPNA-HCl- Pr^{3+} appears emulsion easily, so we choose the unsaponified EHPNA to extract Pr^{3+} .

As showed in Fig. 5., for a constant phase ratio 10:100, the Murphree efficiency increases sharply with the gas flow increasing from 0 ml/min to 50 ml/min and then increases slowly until getting the value of almost 100%. With a outlet pipe of 2m, the residence time was about 7.7s that we can make sure that there're enough residence time for the extraction process.

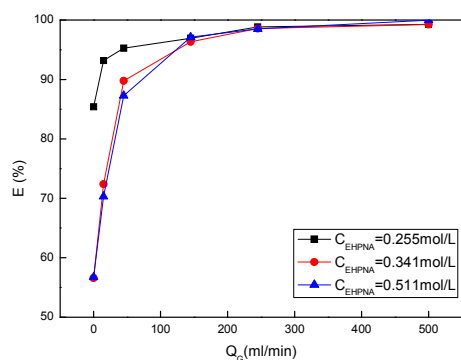


Fig. 5. Effect on gas flow rate on Murphree efficiency ($Q_o:Q_w=10:100$).

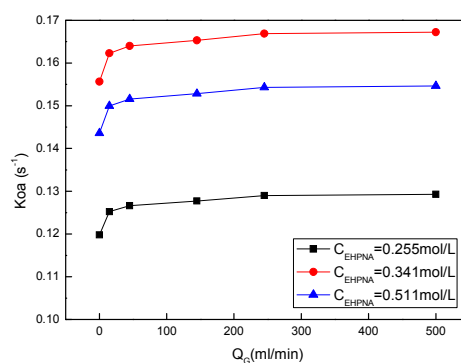


Fig. 6. Effect on gas flow rate on the overall volume mass transfer coefficient K_{oa} ($Q_o:Q_w=10:100$).

Extracted by EHPNA of different concentrations, the $K_o a$ value has different value ranges. In Fig.6., reacting with EHPNA of different concentrations, the overall mass transfer coefficient ranges in $0.120\text{--}0.130\text{ s}^{-1}$, $0.156\text{--}0.167\text{ s}^{-1}$ and $0.143\text{--}0.155\text{ s}^{-1}$ respectively.

4. Mathematical model and discussion

To correlate $K_o a$, the dimensionless numbers of We and Φ are needed. The Weber number, We , and the flow-rate fraction of dispersion phase, Φ , are defined as follows:

$$We = \frac{\rho u_c^2 d}{\gamma} \quad (3)$$

$$\Phi = \frac{Q_D}{Q_D + Q_C} \quad (4)$$

where ρ is the density of the water phase, kg/m^3 ; u_c is the superficial velocity of the water phase, m/s ; d is the inner diameter of the flowing tube, m ; γ is the interfacial tension of organic phase and water phase, N/m ; Q_D is the flow rate of the dispersed phase, also the organic phase here, mL/min ; Q_C is the flow rate of the continuous phase, also the water phase here, mL/min .

For phase ratio of 1:1, Φ is constant. In the liquid-liquid micro-dispersion system with saponified EHPNA extracting Pr^{3+} , The correlation equation is determined as

$$K_o a = 0.0187 We_e^{0.496} \quad (5)$$

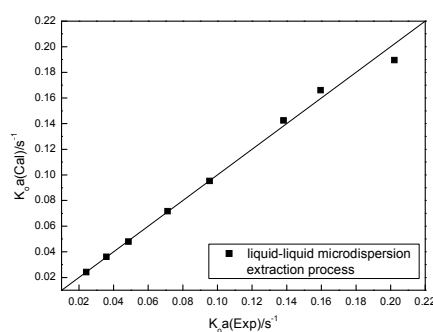


Fig. 7. The comparison of $K_o a$ between experiment values and calculated values by Eq. (5).

As shown in Fig. 7., the correlation as eq. (5) shows good coincidence with experimental values. Due to inducing the gas phase into the liquid-liquid system, the $K_o a$ value could be improved from 0.032 s^{-1} to 0.15 s^{-1} .

5. Conclusions

In this paper, micro-extractors was used to intensify the extraction of light rare earth with EHPNA and saponified EHPNA. For a short residence time of about 5s, high murphree of almost 100% could be achieved. Besides, K_{0a} and Murphree efficiency increased with Q_W and Q_G . A unified mathematical model in the form of $K_{0a} = 0.0187W_e^{0.496}$ was proposed and the calculated results agreed with the experimental results well. Compared the K_{0a} value in the liquid-liquid system with that in the gas-liquid-liquid system, a gas-liquid-liquid system is an effective method to intensify the extraction process with high phase ratio.

Acknowledgments

This research was carried out under the of National Key Basic Research Program of China (No. 2012CBA01203) and the Specialized Research Fund for Doctoral Programme of Higher Education of MOE of China (No. 20130002110018) in the State Key Laboratory of Chemical Engineering of Tsinghua University, Beijing, P. R. China. The authors gratefully acknowledge these grants.

References

- [1]. Bart, H. J., C. Drumm and M. M. Attarakih, Process intensification with reactive extraction columns. *Chemical Engineering and Processing: Process Intensification*, 2008. 47(5): 745-754.
- [2]. Drioli, E., A. I. Stankiewicz and F. Macedonio, Membrane engineering in process intensification—An overview. *Journal of Membrane Science*, 2011. 380(1-2): p. 1-8.
- [3]. Thakur, N. V., Separation of Rare Earths by Solvent Extraction. *Mineral Processing and Extractive Metallurgy Review*, 2000. 21(1-5): 277-306.
- [4]. Tan, J., et al., Process intensification of H_2O_2 extraction using gas-liquid-liquid micro-dispersion system. *Separation and Purification Technology*, 2011. 80(2): 225-234.

Liquid-liquid microflow patterns and mass transfer of two radionuclides: uranium (VI) and europium (III)

*Gwendolyne Hellé^{*1}, Sean Robertson², Siméon Cavadias², Clarisse Mariet¹, Gérard Cote³*

One of the most important separation techniques in radiochemical procedures is solvent extraction. Its use in microsystem with multiphase micro-flows attracts an increasing attention because such systems allow a good control of the interface area between aqueous and organic phases as well as of the contact time of the two phases. In order to design a microfluidic device for an extraction process, it is necessary to understand in detail the fundamental mechanisms involved in fluid flow and the dependence of mass transfer between the aqueous and the organic phase on the chemical (kinetic and hydrodynamic) and transport properties of the phases. In this study, flow patterns of the aqueous-organic binary systems in a double Y-shape micro-channel and the kinetic mass transfer in the two-phase micro flow systems are discussed, both for a liquid anion exchanger (extraction of uranium in HCl by Aliquat 336[®]) and a neutral extractant (extraction of europium in HNO₃ by the N,N'-dimethyl N,N'-dibutyl tetradecylmalonamide). Thanks to the momentum balance equation, we determined the effect of viscosity and the operating conditions on flow patterns. After an optimization of the flow of the two phases, the extraction reactions of U(VI) and Eu(III) were investigated in the microflow channel. Extractions were performed for the same range of acidities as at macroscale. To elucidate the extraction kinetics of each system in the micro-channel, the flows were laminar, and the liquid-liquid interface was formed parallel to its sidewall. From the dimensions of the two-phase flow section in the micro-channel, the flow rate was converted to the contact time of both phases. The extraction reaction in the presence of a large excess of ligand can be regarded as a simple mass transfer from the aqueous phase to the organic phase with an apparent rate constant k_{app} . For U(VI) and Eu(III), k_{app} is equal to $(0.55 \pm 0.03) \text{ s}^{-1}$ and $(2.9 \pm 0.2) \cdot 10^{-3} \text{ s}^{-1}$, respectively.

^{*1} CEA Saclay, DEN/DANS/DPC/SEARS/LANIE 91191 Gif-sur-Yvette cedex, France, gwendolyne.helle@cea.fr

² Chimie ParisTech, Laboratoire de Génie des Procédés Plasmas et Traitements de Surfaces-EA 3492, Université Pierre et Marie Curie, 11 rue Pierre & Marie Curie, 75231 Paris Cedex – France

³ Chimie ParisTech, IRCP – UMR CNRS 8247, 11 rue Pierre & Marie Curie, 75231 Paris Cedex – France

I. Introduction

Solvent extraction is one of the most important separation techniques applied in radiochemical procedures. Many researchers studied the multiphase micro-flows because of their effectiveness for solvent extraction [1-4]. These works showed that micro flow channels allow a better control of the interface area between aqueous and organic phases than many macroscale devices. Another attractive feature of a microfluidic device is the ability to precisely control the contact time of the two phases, especially short contact times, or the distribution rate between the aqueous and the organic phases. In order to design a microfluidic device for an extraction process, it is necessary to understand in detail the fundamental mechanisms involved in fluid flow and the dependence of mass transfer between the aqueous and the organic phases on the chemical (kinetic and thermodynamic) and transport properties of the phases [5]. In this study, flow patterns of the aqueous-organic binary systems in the microchannel and the kinetic mass transfer in the two-phase microflow systems are discussed for two extraction systems, involving a liquid anion exchanger and a neutral extractant, respectively.

II. Methodology

The microsystem used was a double Y-shape glass chip previously described [5]. The extraction of uranium (VI) from HCl solutions by Aliquat 336[®] diluted in *n*-dodecane constitutes the liquid anion exchanger system whereas the extraction of europium (III) from HNO₃ solutions by the *N,N'*-dimethyl *N,N'*-dibutyl tetradecylmalonamide extractant (DMDBDMA) diluted in *n*-dodecane is the neutral one [6]. All aqueous solutions were prepared with 18-MΩ deionized water produced by a Milli-Q water purification system (Millipore, Bedford, MA). Eu(NO₃)₃(H₂O)_n, HNO₃ 68 % and HCl Ultrex 37 % were from Sigma Aldrich. Uranyl nitrate solution was prepared from a 10 000 mg.kg⁻¹ SPEX solution (Jobin Yvon). DMDBDMA (98.8 %) was synthesized by Pharmasynthese SAS. Aliquat 336[®] (98 %) was from Alfa Aesar. Aqueous and organic phases were mutually pre-saturated by contact under shaking for 3 h. The extraction of the analyte was monitored by inductively coupled plasma mass spectrometry (ICP-MS) measurements.

III. Results and discussion

A. Optimization of the chemical conditions with batch extractions

In order to optimize the chemical conditions of the extraction, the extraction performances were first determined in batch. The distribution ratio ($\mathcal{D}_M$) and the extraction efficiency (% E_M) of the metal M were calculated from the equations (1) and (2) for the same volume of the two phases $V_a = V_o$. The subscripts a and o refer to the aqueous and organic phases respectively. i refers to the initial state.

$$\mathcal{D}_M = \frac{[M]_o}{[M]_a} = \frac{[M]_{a,i} - [M]_a}{[M]_a} \quad (1) \quad \text{and} \quad \% E_M = 100 \times \left(\frac{[M]_{a,i} - [M]_a}{[M]_{a,i}} \right) \quad (2)$$

The optimized conditions for the neutral extractant are $[\text{DMDBTDMA}] = 1 \text{ mol.L}^{-1}$ in *n*-dodecane for the organic phase and $[\text{Eu(III)}] = 10^{-2} \text{ mol.L}^{-1}$ in $[\text{HNO}_3] = 4 \text{ mol.L}^{-1}$ for the aqueous one. Under these optimized conditions, a distribution ratio $\mathcal{D}_{\text{Eu(III)}} = 9.1 \pm 0.3$ and an extraction yield equal to $\%E_{\text{Eu(III)}} = 90.1 \pm 0.3$ were obtained. In the case of the anion exchanger, the optimized conditions are $[\text{R}_4\text{NCl}] = 10^{-2} \text{ mol.L}^{-1}$ in 1 % (v/v) 1-decanol/*n*-dodecane for the organic phase and $[\text{U(VI)}] = 10^{-5} \text{ mol.L}^{-1}$ in $[\text{HCl}] = 5 \text{ mol.L}^{-1}$ for the aqueous one. Under these conditions, the distribution ratio is $\mathcal{D}_{\text{U(VI)}} = 5.9 \pm 0.5$ corresponding to an extraction efficiency equal to $\%E_{\text{U(VI)}} = 85.4 \pm 1.2$.

B. Flow patterns of the aqueous-organic binary systems in the micro-channel

For each chemical system and for the optimized chemical conditions determined in batch experiments, the flow regime was established to obtain a stratified flow in order to easily separate the two immiscible fluids exiting the micro-channel.

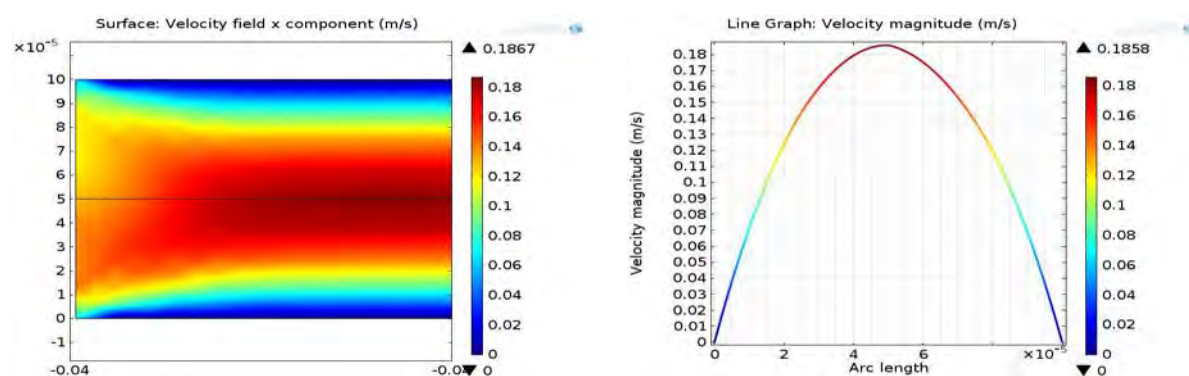


Figure 1: Analytically calculated velocity profile at the entrance of the y-junction for the stratified flow system $[\text{Aliquat 336}^{\text{®}}] = 10^{-2} \text{ M}$ diluted in *n*-dodecane modified by 1% v/v decanol, $[\text{U(VI)}] = 10^{-5} \text{ M}$, $[\text{HCl}] = 5 \text{ M}$, ($\mu_a=1.27 \text{ mPa.s}$, $\mu_o=1.48 \text{ mPa.s}$) and $Q_a = 1.0 \text{ mL/h}$, $Q_o = 0.85 \text{ mL/h}$.

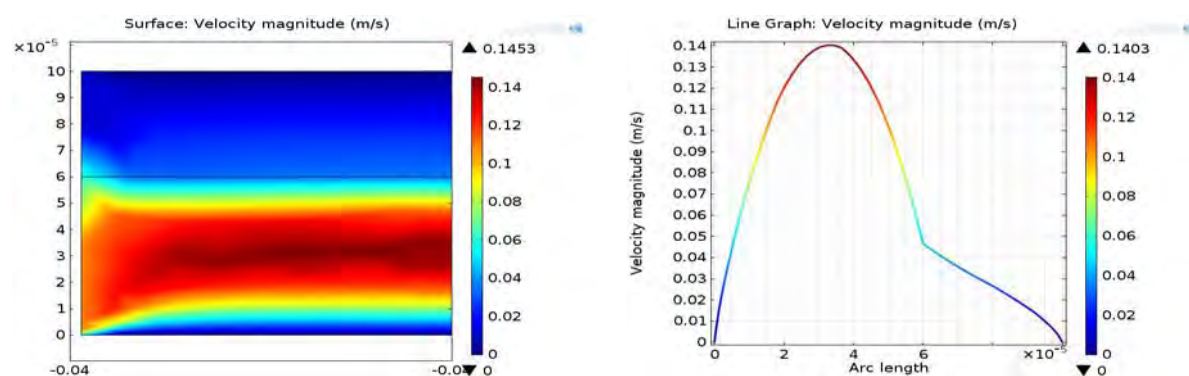


Figure 2: Analytically calculated velocity profile at the entrance of the y-junction for the stratified flow system $[\text{DMDBTDMA}] = 1 \text{ M}$ diluted in *n*-dodecane, $[\text{Eu(III)}] = 10^{-2} \text{ M}$, $[\text{HNO}_3] = 4 \text{ M}$, ($\mu_a=1.18 \text{ mPa.s}$, $\mu_o=18.11 \text{ mPa.s}$) and $Q_a = 1.0 \text{ mL/h}$, $Q_o = 0.06 \text{ mL/h}$.

Flow rates ratios are considerably different for the two chemical systems. This is due to the difference of viscosities between the aqueous and organic phases. In particular, for the system $\text{Eu(III)}/\text{DMDBTDMA}$, the viscosity of the organic phase

(18.11 ± 0.02 mPa.s) is about fifteen times larger than the aqueous one (1.186 ± 0.001 mPa.s).

Thanks to the momentum balance equation, we determined the effect of viscosity (μ) and the operating conditions on flow patterns with COMSOL software (Figures 1 and 2).

C. Flow kinetic studies in the two-phase micro flow systems and optimization of the extraction in microchip

To evaluate the extraction kinetics of the Eu(III)/HNO₃/DMDBTDMA and U(VI)/HCl/Aliquat 336[®] systems, the two-phase microflow system was employed with the optimal chemical conditions previously determined for each system. On the other hand, the contact times calculated [6] according to the relation (3) were fixed by setting flow rates compatible with laminar flow and separated aqueous and organic phases at the outlets of the microchip. h is the position of the interface between the aqueous and the organic phases, W the width, the H the height and L the length of the microchannel.

$$t_o = \frac{(H-h) W L}{Q_o} \quad (3) \quad \text{and} \quad \ln \left(\frac{[\bar{M}]_{eq} - [\bar{M}]_{t_o}}{[\bar{M}]_{eq}} \right) = -k_{app} t_o \quad (4)$$

For an analyte M initially present in the aqueous phase and extracted into the organic phase, the apparent rate constant k_{app} was determined for a first order rate reaction. Here, k_{app} is an averaged value and it depends on both hydrodynamics (interfacial area and volumes ratio of the two phases) and/or chemistry of extraction (extractant concentration...). According to equation (4), the plot of $\ln ([\bar{M}]_{eq} - [\bar{M}]_{t_o} / [\bar{M}]_{eq})$ versus organic contact time should give a straight line with a slope equals to $-k_{app}$ and passing through the origin. In this way (Figure 3), we determined an apparent rate constant equal to $k_{app} = (0.55 \pm 0.04) \text{ s}^{-1}$ for the system U(VI)/Aliquat 336[®] and $(2.9 \pm 0.2) \cdot 10^{-3} \text{ s}^{-1}$ for Eu(III)/DMDBTDMA. It is of interest that the values of k_{app} are very different, as expected from the nature of the two considered systems.

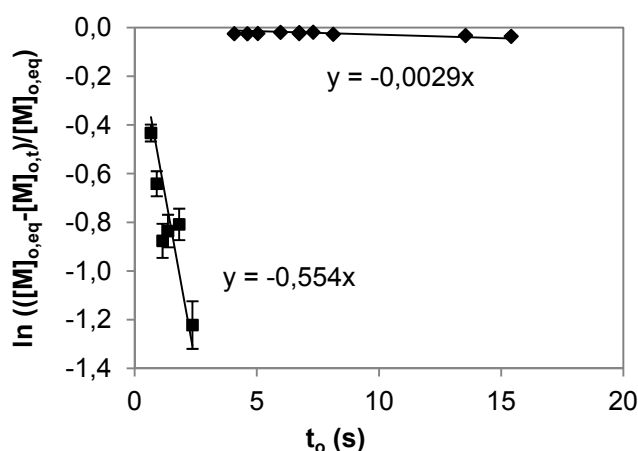


Figure 3: Relationship between $\ln ([\bar{M}]_{eq} - [\bar{M}]_{t_o} / [\bar{M}]_{eq})$ and the organic contact time for the two chemical systems: ($\blacklozenge$) $\{[Eu(III)] = 10^{-2} \text{ mol.L}^{-1}$ in $[HNO_3] = 4 \text{ mol.L}^{-1}$ and $[DMDBTDMA] = 1 \text{ mol.L}^{-1}$ in n -dodecane} and ($\blacksquare$) $\{[U(VI)] = 10^{-5} \text{ mol.L}^{-1}$ in $[HCl] = 5 \text{ mol.L}^{-1}$ and $[Aliquat 336^{\text{®}}] = 10^{-2} \text{ mol.L}^{-1}$ in n -dodecane modified by 1 % v/v 1-decanol in the microsystem.

To optimize the extraction in the microchip, the effects of the flow rates of both phases were investigated. An increase in the concentration of U(VI) or Eu(III) in the organic phase is observed by decreasing the aqueous flow rate from 1.0 mL.h⁻¹ to 0.1 mL.h⁻¹ for the system U(VI)/Aliquat 336[®] (Figure 4) and from 1.4 mL.h⁻¹ to 0.5 mL.h⁻¹ for the system Eu(III)/DMDBTDMA (Figure 5) (for this chemical system, there is a limitation of the flow rates due to instabilities at aqueous flow rate lower than 0.5 mL.h⁻¹).

In microsystem, the distribution ratios $\mathcal{D}_{M,\text{microsystem}}$ are calculated according to the following relation (5) where $[M]_{a,i}$ and $[M]_a$ refer to the initial concentration of M in aqueous phase and its concentration in aqueous phase at the outlet of the microchip, and Q_a and Q_o denote the flow rate of the aqueous and organic phases, respectively.

$$\mathcal{D}_{M,\text{microsystem}} = \left(\frac{[M]_{a,i}}{[M]_a} - 1 \right) \frac{Q_a}{Q_o} \quad (5)$$

Thus, whatever the system considered here, the extraction efficiency increases with an increase in the contact times of the two phases. In the case of the extraction of U(VI) by the Aliquat 336[®], the best extraction efficiency equal to $(76.3 \pm 1.1) \%$ was obtained corresponding to a distribution ratio $\mathcal{D}_{U,\text{microsystem}} = 4.0 \pm 0.1$ for $Q_a = 0.1$ mL.h⁻¹ and $Q_o = 0.08$ mL.h⁻¹. For the system Eu(III)/DMDBTDMA, the best extraction efficiency obtained is equal to $(26.2 \pm 1.0) \%$ corresponding to a distribution ratio $\mathcal{D}_{Eu,\text{microsystem}} = 5.9 \pm 0.3$ for $Q_a = 0.50$ mL.h⁻¹ and $Q_o = 0.03$ mL.h⁻¹. In the case of the extraction of Eu(III) by DMDBTDMA, it is of interest to note that these results can be improved by optimizing the geometry of the chip, for instance, by increasing the channel length leading to an increase in the contact times of the two phases.

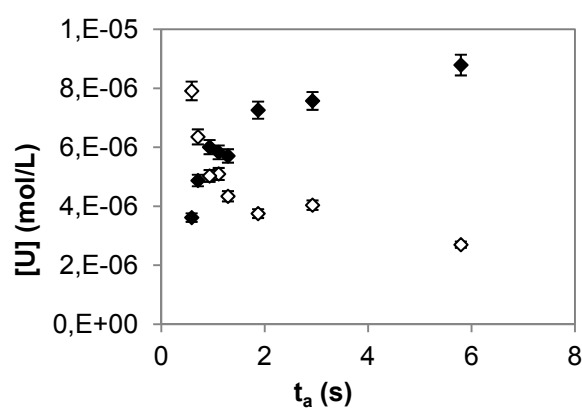


Figure 4: Evolution of the concentration of U as a function of the aqueous contact time for the aqueous phase ($\diamond$) and for the organic phase ($\blacklozenge$) during the extraction of U in microsystem with the chemical system $\{[U(VI)] = 10^{-5} \text{ mol.L}^{-1}$ in $[HCl] = 5 \text{ mol.L}^{-1}$ and $[Aliquat 336^{\text{®}}] = 10^{-2} \text{ mol.L}^{-1}$ in 1 % 1-decanol/n-dodecane (v/v)}.

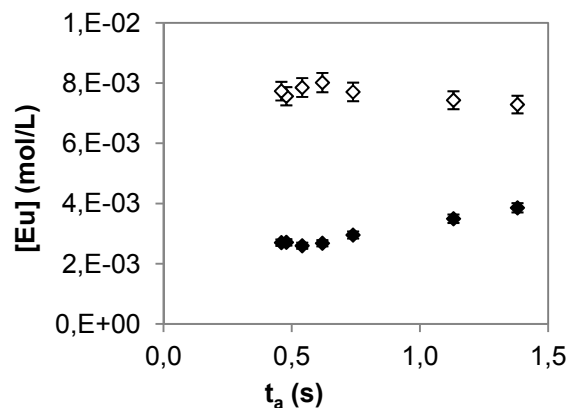


Figure 5: Evolution of the concentration of Eu as a function of the aqueous contact time for the aqueous phase ($\diamond$) and for the organic phase ($\blacklozenge$) during the extraction in microsystem with the chemical system $\{[Eu(III)] = 10^{-2} \text{ mol.L}^{-1}$ in $[HNO_3] = 4 \text{ mol.L}^{-1}$ and $[DMDBTDMA] = 1 \text{ mol.L}^{-1}$ in n-dodecane}.

IV. Conclusion

Liquid-liquid microflow patterns of two different extraction systems, with different physical characteristics, such as viscosities, were studied to obtain a stratified flow in order to easily separate the two immiscible liquid phases exiting the double Y-shape microchip. The extraction of uranium (VI) from HCl solutions by Aliquat 336[®] diluted in *n*-dodecane modified by 1% v/v decanol was chosen as a liquid anion exchanger system whereas the extraction of europium (III) from HNO₃ solutions by the N,N'-dimethyl N,N'-dibutyl tetradecylmalonamide extractant (DMDBTDMA) diluted in *n*-dodecane was selected as a neutral one. The kinetic evaluation, quantified by the determination of an apparent rate extraction constant k_{app} , was performed by using the two-phase micro flow system. As expected, it was found that the mass transfer is much more rapid (about 200 times) in the case of the extraction uranium (VI) by Aliquat 336[®] than in the case of the extraction of europium (III) by DMDBTDMA. This illustrates that microsystems provide an easy access to the kinetics of fast systems.

References

- [1] M. Tokeshi, T. Minagawa and T. Kitamori, "Integration of a microextraction system on a glass chip: ion-pair solvent extraction of Fe(II) with 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid and tri-*n*-octylmethylammonium chloride", *Anal. Chem.*, vol. 72, pp. 1711-1714, 2000.
- [2] M. Tokeshi and T. Kitamori, "Continuous flow chemical processing on a microchip using operations and a multiphase flow network". *Progress in Nuclear Energy*, vol. 47(1-4), pp. 434-438, 2005.
- [3] A. Aota, M. Nonaka, A. Hibara and T. Kitamori, "Countercurrent laminar microflow for highly efficient solvent extraction". *Angew. Chem.*, vol. 119, pp. 896–898, 2007
- [4] F. Kubota, J.-I. Uchida and M. Goto, "Extraction and separation of rare earth metals by a microreactor". *Solvent Extr. Res. Dev., Jpn.*, vol. 10, pp. 93-102, 2003.
- [5] G. Hellé, C. Mariet and G. Cote, "Microfluidic tools for the liquid-liquid extraction of radionuclides in analytical procedures.", *Procedia Chem.*, vol. 7, pp. 679-684, 2013.
- [6] H. Yang, E. Lee, J. Lim, D. Chung and K. Kim, "Extraction of americium(III) and europium(III) using a gamma pre-irradiated solution of N,N'-dimethyl-N,N'-dibutyltetradecyl malonamide in *n*-dodecane modified with N,N'-dihexyloctanamide", *J. Radioanal. Nucl. Chem* vol. 280, pp. 495-502, 2009.

Comprehensive Numerical and Experimental Analysis of Copper Solvent Extraction in Y-Y Microreactors

Pedro Ribeiro Martins Bento, Department of Metallurgical Engineering, University of Utah, Salt Lake City, USA; Omid Kazemi, Department of Material Science and Engineering, Amirkabir University of Technology, Tehran, Iran; Sanja Miskovic, Department of Metallurgical Engineering, University of Utah, Salt Lake City, USA

Abstract

Microfluidic or microreactor solvent extraction (SX) is a high-throughput metal extraction method, which has proven to be a promising alternative to conventional large-scale mixer-settler SX process. Within the microreactor, the extraction process is performed through a non-dispersive manner, under laminar conditions, when the reactant phases are brought into contact and form an interface through which the mass transfer occurs. Through this work, a comprehensive numerical and experimental study, by using computational fluid dynamics (CFD) approach on a series of Y-Y microreactors, is performed. The extraction efficiency of all tested microreactors is investigated by varying several key operational parameters including: phases contact time, microchannel length, interphase liquid/liquid contact surface area, microchannel cross-sectional profile, temperature, and copper concentration of the aqueous phase at the inlet. For the purpose of experimental analysis, both standard copper aqueous solutions and copper leach solutions are used. A pregnant copper leach solution is produced by sulfuric acid from a flotation copper concentrate composed of chalcopyrite-chalcocite-bornite minerals. The predicted copper concentration gradient and outlet copper concentration of both aqueous and organic phases are validated experimentally by in-line spectrometer. The results show that the contact time has significant impact on the extraction efficiency; as the contact time increases, separation efficiency improves. Furthermore, for constant flow rates, the efficiency is shown to increase with the solvent to aqueous volumetric ratio increase over the lower range of volumetric ratios. After the critical point is achieved, this trend is found to be reversed for the volumetric ratios higher than the critical value. Finally, it is found that presence of other materials (impurities) reduce the diffusion rate and consequently reduce the efficiency.

Extraction and throughput for micro-solvent extraction of platinum using a single chip and a multi-chip module

*F.H. Kriel¹, C. Priest^{*1}, J. Ralston¹, L. Parkinson¹, S. Woollam², N. Plint², R.A. Grant³, P. Ash³*

Summary

Platinum extraction was studied using a microfluidic solvent extraction (μ SX) chip for three different organic to aqueous flow rate ratios. Equilibrium was achieved within ~ 2 s for two of the designs and more than 5 s for the third, in agreement with fast kinetics expected for the ion exchange mechanism. The first steps towards higher throughput are demonstrated using a three-chip μ SX module. The flow and kinetics are unchanged from a single chip. An expression for the relationship between the number of chips and flowrate is given, which accounts for upstream and downstream pressure drops. This is the first occasion that the principle of numbering-up has been demonstrated for μ SX.

Introduction

Microfluidic systems boast very high surface-to-volume ratios, which can be exploited in a wide variety of applications^{1,2,3}. These “lab-on-a-chip” technologies, named for their miniaturization of bench-scale chemistry and biology, are very attractive when using rare or expensive samples because μ L to pL of fluid may be sufficient. This, however, is not the only advantage of miniaturized fluidics. Reynolds numbers are typically very small, yielding laminar flow. Fluid dimensions are small, which allows fast mass transfer via diffusion. Surface tension forces are large relative to fluid mass and viscous forces and can be exploited to control the fluids (droplet formation⁴, Laplace valves⁵, guiding flow⁶). A branch of microfluidics has focused on multiphase systems, where flow of more than one fluid is controlled within microfluidic channels. The perceived applications of multiphase microfluidics are many. Some examples from our own studies include emulsification⁷, encapsulation⁸, droplet reactors⁹, lenses¹⁰, and rapid extraction of metal ions¹¹. The latter is our focus here.

Although traditionally a small-volume technology, the advantages of microfluidic systems are equally attractive, or perhaps more so, for higher throughput applications, where modest increases in process efficiency can mean a significant economic advantage. For this reason, this study focused on high concentration platinum solutions. In earlier studies, we demonstrated microfluidic solvent extraction, μ SX, of copper(II) from leach solutions derived from CuO ore^{11, 12}. This study also showed that stream-based μ SX is capable of handling particle-laden leach solutions (i.e., loaded with sub-micron silica particles), without forming crud or blocking the fluidic chip.¹²

¹ Ian Wark Research Institute, University of South Australia, Mawson Lakes, Australia;

* Corresponding author: craig.priest@unisa.edu.au

² Anglo American's Technical Solutions, Johannesburg, South Africa

³ Johnson Matthey Technology Centre, Sonning Common, Reading, United Kingdom

In recent work, Yin et al.¹³ followed our μ SX approach to extract very low concentrations (< 20 mg/L) of precious metals using 5% Alamine 336 in kerosene. Their results suggest that extraction proceeds extremely quickly (more than 99% recovery of Pt is achieved after only 1 s contact time in the chip) but the extraction kinetics is not resolved due to lack of data at shorter times. Here, we determine the extraction of Pt from high concentration solutions (24 g/L) over a range of contact times from 0.5 to 5 s and examine the effect of organic/aqueous ratio on the extraction using a tailored chip design. We also demonstrate the principle of numbering-up of μ SX chips, where many chips operate in parallel to achieve higher throughputs, and provide a fundamental relationship between the number of chips and increased throughput for a given feed pressure. This is the first occasion that the principle of numbering up has been demonstrated for stream-based μ SX.

Results and Discussion

The chip design chosen for this study is shown in Fig. 1. Key features are the etch depth for each channel, d_{aq} and d_{org} , meniscus height, h , and contact length between the two channels, L . Based on these dimensions and any given flow rate, the contact time, t , available for extraction can be calculated. Tuning the respective etch depths of the channels allows the flow rate ratio, R , to be varied, as shown elsewhere.¹⁴ At the same time, the contact area ($A = hL$) of the liquid-liquid interface is altered. Table 1 gives actual and calculated A , R , and the surface-to-volume ratio for the three chips, based on ideal (isotropic) wet etching.

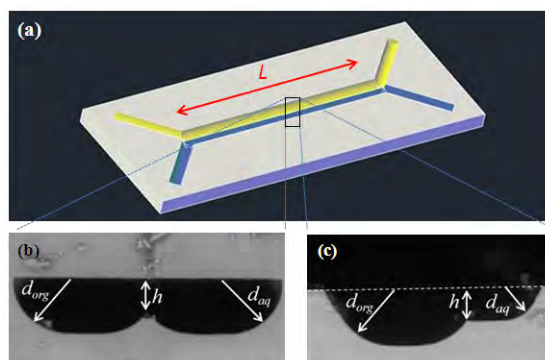


Figure 1. (a) An Illustration of the borosilicate glass microchip used in this study, with (b) symmetrical channel cross-section and (c) tuned to control the flow rate ratio.

Assuming laminar flow, which is certainly the case here, the flow rate ratio, R , can be estimated using the Hagen-Poiseuille equation;

$$P = \frac{8\mu_{aq}L}{\pi r_{aq}^4} Q_{aq} = \frac{8\mu_{org}L}{\pi r_{org}^4} Q_{org} \quad (1)$$

where Q is volumetric flow rate, μ is dynamic viscosity, L is the length of the contact zone, r is the effective radius of a cylindrical channel, and P is the hydrodynamic pressure drop in the liquid over the length L . Subscripts aq and org refer to the aqueous and organic phases, respectively. Equating the feed pressures gives

$$R = \frac{\mu_{aq}}{\mu_{org}} \times \frac{r_{org}^4}{r_{aq}^4} \quad (2)$$

As our channel cross-section is not cylindrical, we employ an effective radius based on the hydraulic diameter of the channels and assume a rectangular cross-section, i.e., $r = \frac{xy}{x+y}$, where x and y are the width and height of the channel. This approach yields $R = 0.56$, 2.05 , and 7.10 for the three chips. As the isotropic etching of the channels leads to a rather consistent geometry, we can define $x \cong 2y$ for sufficiently large etch depths. It follows that $r \cong \frac{2}{3}y$, which is a useful approximation for the effective radii in Eqn. 2. In our experiments, we achieved $R = 0.56$, 2.0 , and 5.7 for designs 1, 2, and 3 (see Table 1), in good agreement with the estimated values, despite the sensitivity of R to small differences in etch depths.

Table 1. Estimated and actual organic/aqueous flow rate ratios, R , and equilibrium contact times, t_{eqm} .

Design	Contact area A (mm ²)	Surface/volume ratio (mm ⁻¹)	Estimated R	Actual R	Estimated t_{eqm} (s)	Actual t_{eqm} (s)
1	4.8	10.7	0.56	0.56	1.2 [#]	~ 2
2	4.1	10.8	2.05	2.00	1.2 [#]	> 5
3	3.2	14.5	7.10	5.70	0.7 [#]	~ 2

[#]based on $D = 10^{-9}$ m²/s and $L = (10 + 2r_a)$ μm.

Extraction – Single Chip

Solvent extraction of platinum was carried out using the three different microchannel designs for t from 0.5 to 8 s. The progress of the extraction is shown in Fig. 2 for each R and can be described well by fitting an exponential decay curve in the form of $[Pt] = \alpha e^{-kt} + \beta$, where β is the equilibrium concentration of Pt, t is the contact time, k is the pseudo-first-order rate constant, and α is the maximum change in concentration at equilibrium. In Table 1, the actual and estimated contact times required to achieve equilibrium, t_{eqm} , are given for each design. The estimated times are calculated assuming a diffusion length equal to the aqueous stream width, i.e., $10 \mu\text{m} + 2r_a$, and a diffusion coefficient, $D = 7 \times 10^{-9}$ m²/s.¹⁵ The actual t_{eqm} is in reasonable good agreement for the chip designs 1 ($R = 0.56$) and 3 ($R = 5.70$), although the diffusion times appear to underestimate the actual contact times required. For chip design 2 ($R = 2.0$), the actual and estimated t_{eqm} are very different and the reason for this difference is presently unclear. Nonetheless, the timescales involved are consistent with rapid, diffusion-limited kinetics which are characteristic of the ion exchange mechanism. Bulk experiments were carried out in parallel to compare the raffinate concentration of Pt with that achieved in the microchip. The raffinate $[Pt]$ after 20 s bulk mixing (i.e. at equilibrium) for $R = 0.6$, 2.0 , and 6.0 was 15.8 , 0.9 , and 0.14 g/L, respectively, which agrees with the μSX results shown in Fig. 2. This result is entirely consistent with our expectation that the physical chemistry of the extraction is unchanged by confinement in the microchannel.

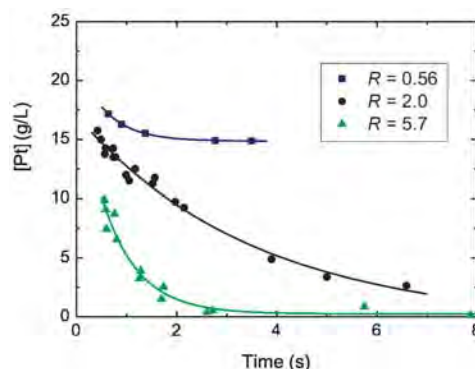


Figure 2. Extraction versus time for three organic/aqueous flow rate ratios. Exponential decay fitting to the data in the form of $[Pt] = \alpha e^{-kt} + \beta$ is shown (curves).

Numbering-Up

The viability of μ SX for higher throughput applications, including for refining of Precious Metals, will depend on the ability to scale-up volumetric throughput while maintaining the microscopic dimensions of the liquid-liquid contact. So-called ‘numbering-up’ could be achieved through massive parallelization of individual extraction chips but, to our knowledge, this has not been demonstrated for co-flowing streams of immiscible liquids. To take the first steps towards high throughput μ SX, we assembled three chips in parallel with a single inlet for the aqueous phase and another for the organic phase. These inlet ports are large (0.6 mm diameter) and continue through the entire ~ 15 mm thick ‘stack’ of chips, so that the hydrodynamic resistance along the inlet port is negligible (six orders of magnitude smaller) compared to that along the microchannel itself. In this configuration, we expect even partitioning of the flow to all channels in the module.

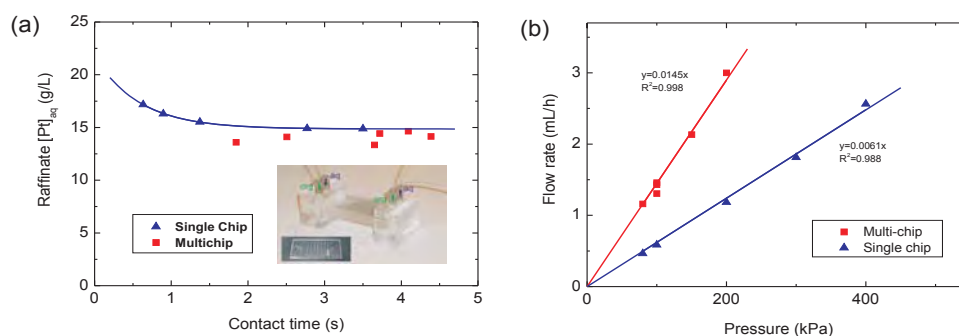


Figure 3. (a) Pt concentration in the raffinate versus contact time for a single chip and 3-chip module showing good agreement. Inset: Image of the 3-chip module. (b) Flow rate versus feed pressure for a single chip and multi-chip module, showing a 2.34x increase in throughput for the multichip module.

The flow behavior, extraction efficiency, and throughput in the multichip module was determined for contact times between 1.5 and 4.5 s. Due to the spatial separation of the chips within the stack, we were able to use optical microscopy to focus through the upper chips and observe the flow stability and phase disengagement. No visual difference between the flow behavior in the top, middle, and lower chip was observed with respect to the single chip experiments. Fig. 3(a) gives the raffinate [Pt]

concentration versus contact time for the single chip and multichip module. The results are in good agreement over the range of contact times studied, as one would expect for even and stable partitioning of the liquids.

Fig. 3(b) plots the flow rate against the feed pressure from the pumps. Clearly, the flow rates achieved are much higher in the multichip module; however, from the slopes of the linear fits, we found that the flow rate increases by a factor of 2.34, rather than 3, for a given feed pressure and switching from a single chip to multichip module. This behavior is related to the flow resistance caused by increased flow rates in the inlet/outlet tubing. For a given feed pressure, the relationship between the number of chips in the module, n , and ratio between the aqueous phase flow rate in the module and single chip, $\gamma = \frac{Q_{aq}(multichip)}{Q_{aq}(single\ chip)}$, is given by:

$$n = \frac{\gamma k}{\gamma - k + 1} \quad (3)$$

where $k = \left(\frac{L_2}{r_2^4}\right) / \left(\frac{L_1+L_3}{r_{tube}^4}\right)$. The constant k accounts for the hydrodynamic resistance in the channels, $\left(\frac{L_2}{r_2^4}\right)$, and in the tubing, $\left(\frac{L_1+L_3}{r_{tube}^4}\right)$. For the module, with $L_1 + L_3 = 75$ mm and $r_{tube} = 125$ μ m, Eqn. (3) gives $\gamma = 2.5$, which is close to the experimental value of 2.34. The choice of inlet/outlet tubing (total length and diameter), is clearly an important engineering consideration for numbering-up. For the microbore tubing used here, there is a practical limit of $\gamma \sim 10$ where adding more chips doesn't improve the total flow rate significantly. In contrast, a small increase of r_{tube} to 500 μ m, permits $\gamma \rightarrow 1000$, or ~ 1 L/h, before this limit is reached.

Conclusion

Platinum extraction using Amberlite LA-2 in Solvesso 150 was investigated for a range of organic/aqueous phase ratios (0.56, 2.0, and 5.7) in a μ SX chip. Pseudo-first-order kinetics was observed, governed by diffusion of ions to the liquid-liquid interface. The characteristic diffusion time was calculated to be ~ 1 s for PtCl_6^{2-} . Slightly longer times were required to reach equilibrium (2 s for $R = 0.56$ and 5.7; > 5 s for $R = 2.0$). Numbering-up of μ SX was demonstrated for the first time. The relationship between the number of chips and total flow rate was given with respect to a single chip, based on known parameters and for a given feed pressure.

Acknowledgements

The authors thank Anglo American Platinum and Johnson Matthey for financial and technical support, and granting the authors permission to publish. Part of this work was performed at the SA node of the Australian National Fabrication Facility.

Experimental

Aqueous platinum solutions (24 g/L) were prepared by dissolving sodium hexachloroplatinate (IV) (Johnson Matthey) in 0.5 M HCl. Pt^{4+} was extracted using 78

g/L Amberlite LA-2 in Solvesso 150 (ASCC). Bulk SX was carried out in a 5 mL glass vial by vigorously shaking the organic and aqueous phases together for 20 s and leaving them to separate. Microfluidic SXs were carried out as described elsewhere^{11, 12} use custom fabricated microchips (ANFF-SA, Australia). Two microchannels (dimensions given in discussion) merge at a Y-junction to form a single microchannel that is divided into two by a guide structure which helps stabilize the co-flowing streams. This is where extraction takes place. The contact length in this channel, L , was 129 mm (single chip) or 155 mm (multichip). Phase disengagement occurred at a downstream Y-junction. The volumetric ratios, R , was achieved by wet etching the two channels for different times to achieve the channel profiles shown in Fig. 1, as described by Hibara et al.¹⁴. Flow was driven by pressure pumps (Mitos P-pump, Dolomite) between 400 and 50 kPa. Flow stability in the microchip was monitored using optical microscopy (Olympus, BH2-UMA). UV-vis absorption (Ocean Optics QE65000) was used to determine the concentration of Pt^{4+} using a Z-Flow Cell (2.5 mm path length, quartz windows). Absorbance was measured at 259 nm for the Pt^{4+} and used according to Beer's law.

References

1. Gardeniers, J. G. E.; van den Berg, A., *Anal Bioanal Chem* 2004, 378, 1700-1703.
2. Elvira, K. S.; Solvas, X. C.; Wootton, R. C. R.; deMello, A. J., *Nat Chem* 2013, 5, 905-915.
3. Al Lawati, H. A. J., *Luminescence* 2013, 28, 618-627.
4. Surenjav, E.; Herminghaus, S.; Priest, C.; Seemann, R., *Applied Physics Letters* 2009, 95, 154104.
5. Takei, G.; Nonogi, M.; Hibara, A.; Kitamori, T.; Kim, H.-B., *Lab Chip* 2007, 7, 596.
6. Zhao, B.; Moore, J.; Beebe, D. J., *Science* 2001, 291, 1023.
7. Priest, C.; Herminghaus, S.; Seemann, R., *Applied Physics Letters* 2006, 88, 024106.
8. Priest, C.; Quinn, A.; Postma, A.; Zelikin, A. N.; Ralston, J.; Caruso, F., *Lab on a Chip* 2008, 8, 2182-2187.
9. Evans, H. M.; Surenjav, E.; Priest, C.; Herminghaus, S.; Seemann, R.; Pfohl, T., *Lab on a Chip* 2009, 9, 1933-1941.
10. Iwashita, Y.; Bahr, C.; Priest, C.; Herminghaus, S.; Seemann, R., *Houille Blanche-Revue Internationale De L Eau* 2009, 6, 129-134.
11. Priest, C.; Zhou, J. F.; Klink, S.; Sedev, R.; Ralston, J., Solutions Containing Nanoparticles. *Chemical Engineering & Technology* 2012, 35, 1312-1319.
12. Priest, C.; Zhou, J. F.; Sedev, R.; Ralston, J.; Aota, A.; Mawatari, K.; Kitamori, T., *International Journal of Mineral Processing* 2011, 98, 168-173.
13. Yin, C.-Y.; Nikoloski, A. N.; Wang, M., *Minerals Engineering* 2013, 45, 18-21.
14. Hibara, A.; Iwayama, S.; Matsuoka, S.; Ueno, M.; Kikutani, Y.; Tokeshi, M.; Kitamori, T., *Anal. Chem.* 2005, 77, 943.
15. Nama, D.; Anil Kumar, P. G.; Pregosin, P. S., *Magnetic Resonance in Chemistry* 2005, 43, 246-250.

Membrane microcontactors for multi-stage countercurrent extraction

Jonas Hereijgers, Vrije Universiteit Brussel, Brussels, Belgium; Tom Breugelmans, University of Antwerp, Antwerp, Belgium; Wim De Malsche, Vrije Universiteit Brussel, Brussels, Belgium.

The technological ability to decrease diffusive distances has led to a number of promising approaches to perform e.g. liquid-liquid extractions in segmented flow and stratified flow configurations to provide large surface to volume ratios, but with limited operational ranges in flow rates and phase compositions [1]. A more robust configuration consists of a membrane stabilized flow with preferential wetting by one phase, which by capillary action stabilizes the position of the interface between two immiscible liquids [2]. Furthermore, the need to perform a phase separation is omitted in this approach. A membrane microcontactor with channel depths of 50 to 200 μm was developed with the possibility of varying the channel width from 1 to 20 cm (Fig. 1). A high performance and dispersion-free operation was enabled by using a distributor at the beginning and the end of the channel. By placing multiple of such membrane microcontactor devices, a continuous multi-stage countercurrent system has been constructed. Incorporating the device in a mini-plant system facilitates that real-life processes are mimicked and examined. With these microchannels equilibrium is reached in a matter of minutes and much lower sample volumes are consumed in comparison to traditional (centrifugal) extractors. By regulating the pressure with control valves and additional pumps between each membrane microcontactor a sheer unlimited range of flow rates is achieved at each side of the membrane.

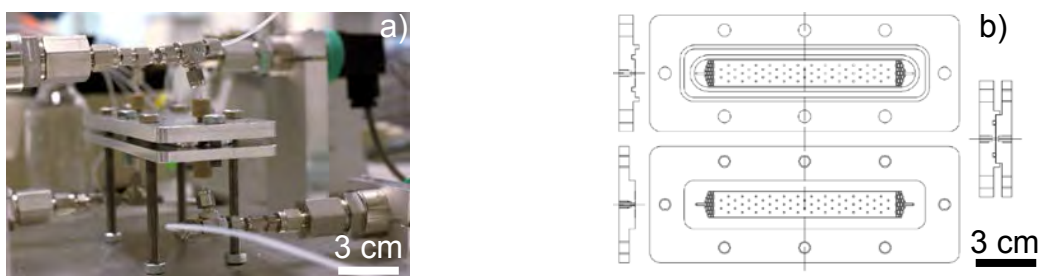


Fig. 1: a) Set-up of a single unit membrane microcontactor system with pressure sensors. b) Scheme of membrane microcontactor.

References:

- [1] J. Kralj, H.R. Sahoo and K.F. Jensen, Integrated Continuous Microfluidic Liquid-Liquid Extraction, *Lab Chip*, 7 (2007) 256-263.
- [2] Cai Z. X., Fang Q., Chen H. W., Fang Z. L., A microfluidic chip based liquid-liquid extraction system with microporous membrane, *Analytica Chimica Acta* 556 (2006), pp.151-156.

Recovery of Minor Metals from Secondary Sources Using Solvent Extraction

*Erkki Paatero^{*1}, Sami Virolainen²*

Summary

A review is presented for the known and potential applications of solvent extraction to recover minor metals from secondary sources. The utilization of SX is also discussed in relation to other viable options. The examples in the presentation are based on the authors' own experiences.

Zn ores contain typically In, Ga and Ge, which often end up in residues or landfills, but these elements can be recovered by SX from the process stream as by-products. In the Cu industry, Au, Ag and PGMs are the main valuable by-products but the minor metals Mo, Re, Se, Te and W are also worth recovering. The recovery of Mo from a Cu SX stream as well as that of Mo and Re from a shaft furnace residue are discussed. An example from the steel industry is the recovery of a Mo/Cr mixture by SX from leachates of steelmaking dust.

The most valuable consumer wastes are Waste Electrical and Electronic Equipment (WEEE). It is not the recovery methods that are the bottleneck, but gathering enough material in a place where it can be economically processed and preferably integrated to a larger metallurgical plant (as shown in the recent UNEP Metal Recycling: Opportunities, Limits, Infrastructure report).

Introduction

As a hydrometallurgical separation method, solvent extraction is an option for recovery of minor metals from secondary sources. In this presentation, the scope is broad and such raw materials can be by-products from metallurgical processes, metallurgical wastes or post-consumer wastes and products (End of Life, EoL products). These and other examples have been reported in the Doctoral Thesis by Virolainen (2013).

In nature, minor metals are mostly associated with host base metals which the minor metals follow in metallurgical processing. This has been visualized by Reuter *et al.* with the "Metal Wheel" (e.g. in the EU report on critical raw materials from 2010). The same authors have also introduced a "Metal Wheel for EoL" (Fig. 1) which is discussed in detail in a recent UNEP report (2013). In the EoL Metal Wheel, the first annulus from the core represents society's essential carrier metals. They are the extractive metallurgy's backbone in primary and recycling metallurgy. For instance, recycled steel also returns the alloy metals back to the industry together with the carrier metal iron. The metals in the second annulus in the Metal Wheel include metals that dissolve mainly in a carrier metal and can often be fractioned by pyrometallurgy. The metals in the following (white) annulus end up in a pyroprocess in dust, slime, speiss and slag, from which the valuable metals can be recovered by

^{1*} Outotec Oyj, Espoo, Finland

² Lappeenranta University of Technology, Lappeenranta, Finland

hydrometallurgy, for instance. The metals in the outermost annulus are usually lost from the system. The Fe segment is a process infrastructure, the steel route, where the minor metals are diluted during the recycling route. However, in the base metal segments (Cu, Zn and Pb), the minor metals are available for hydrometallurgical separation and for concentration to high-level products.

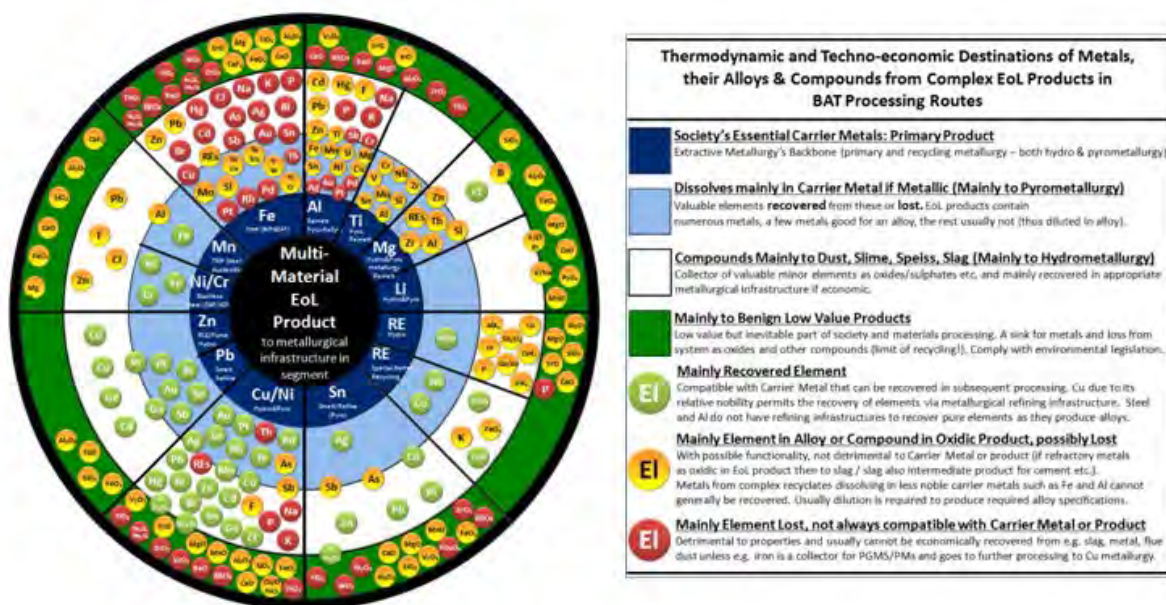


Figure 1. "The Metal Wheel" around the essential carrier metals in End of Life products. (Reproduced with the permission of M.A.Reuter)

Role of aqueous solution chemistry for separation

The following cases are examples of actual separations that utilize the possibilities offered by aqueous solution chemistry to make separation of the minor metals possible. These and other examples have been reported in the Doctoral Thesis by S. Virolainen (2013). Knowledge of the speciation at different Eh and pH values provides a general basis for the development of a hydrometallurgical separation but unfortunately the presence of other ions, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, complicates the systems. The figures in this presentation are calculated with MEDUSA software using its databank, with the exception of the Eh-pH diagram for Mo, which is based on other literature data.

Molybdenum from Copper SX

Mo (VI) exists in some copper ores. It is soluble to a certain degree in the leach acid and consequently enters the SX; values between 30 and 120 ppm have been reported by Cruz and Reghezza, 2007. The hydroxyoxime type extractants commonly used for copper SX are also known to coextract Mo either as H_2MoO_4 (molybdenic acid) and MoO_2^{2+} (molybdenyl) ion present in sulfuric acid (Fig. 2). The extracted Mo can be selectively scrubbed from the loaded organic phase using an aqueous solution with a high enough pH to obtain Mo in an oxoanionic form. The key

is to take into account the slow reaction kinetics in the transformations between the different Mo species in the neutral pH region, where Mo is present as polymeric anions. In addition, Mo heteropolymers may appear with e.g. Cu and Fe. Outotec has developed (Laitala *et al.*, 2009) a special wash tank which acts both as a loaded organic tank and a scrubber to remove molybdenum from the organic phase prior to Cu stripping. Mo is recovered as Ca molybdate.

Molybdenum and Rhenium from Copper shaft residue

In the late 70s, Outotec (formerly Outokumpu) developed a hydrometallurgical process for its Kokkola works in Finland to recover Mo and Re from an imported copper shaft residue, which contained 1.5% Mo in addition to Cu, Co, and Ni. According to the method, the residue is first leached with weak sulfuric acid followed by Fe, Cu, Co, and Ni removal. After that the solid residue is leached with alkaline and from the leach liquor Mo is extracted with a cation exchanger (D2EHPA) at low pH. Re is then extracted with an anion exchanger. As seen in Fig. 2, the speciation pattern of Re is very simple. The perrhenate anion (ReO_4^-) dominates over a wide pH range. However, many of the impurities (As, W, P) also exist as anions and again the Mo heteropolymers require very good pH control in different stages. In the process, Mo is recovered as Ca-molybdate and Re as ammonium perrhenate. The reader is advised to see the paper by Y. Bal *et al.* (2004) that describes the extremely complex chemistry of Mo in an SX process.

In the above example, Re is recovered as a by-product from a hydroprocess by SX. Ion exchange is an alternative and today it is in use for instance in Poland, Kazakhstan and the USA. The global mine production of Re in 2012 was about 52 tpa (USGS, 2003).

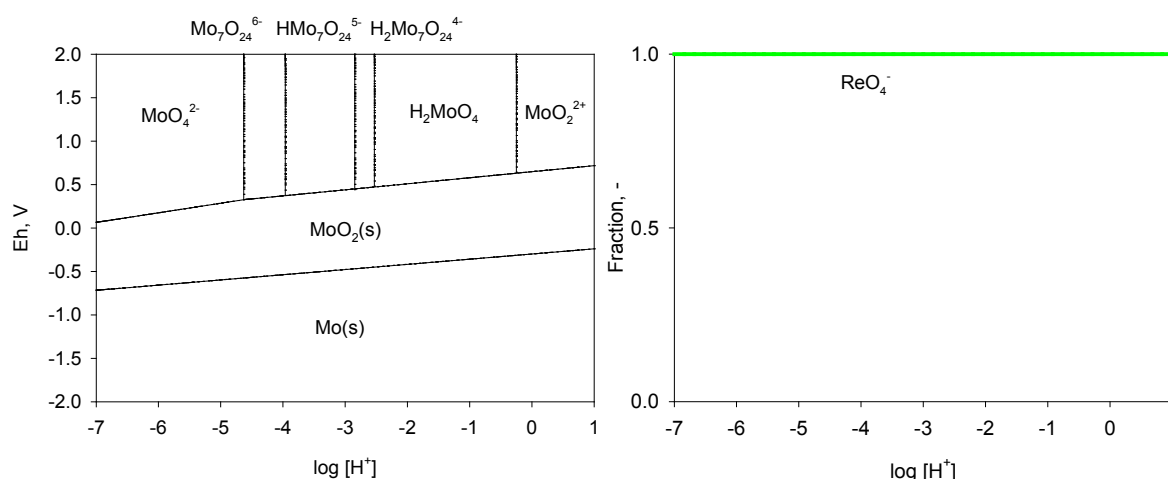


Figure 2. Eh-pH diagram of Mo(VI) and speciation of 1 mM Re(VII) in 0.5 M sulfate solution. $I_c = 1.0 \text{ M}$, $T = 25^\circ\text{C}$.

The recycling degree of Ge is obviously quite high due to its value and the fact that it has only a few main uses. Most Re is found in superalloys (e.g. in jet engines) and reforming catalysts which can be collected separately for recycling.

Molybdenum from steelmaking dusts

Argon oxygen decarburization (AOD) dusts are by-products in the steelmaking industry and may contain significant amounts of Mo. Due to the alkaline nature of the raw material, it can be leached with water. Since Mo occurs mostly as oxoanions from the alkaline side until approximately pH 2 (Fig. 2), amine extractants with anion exchange properties are suitable for the selective recovery of Mo from the water leachate. Most of the other leached metals, like Ca and K, occur as cationic species and thus they are not extracted. The only exception is Cr(VI), which occurs as CrO_4^{2-} anion on the alkaline side (Fig. 3) and is thus co-extracted. Despite this fact, the combination of water leaching and solvent extraction with an anion exchanger is seen as a simple and potential route to recover Mo from AOD dusts (Virolainen *et al.*, 2013).

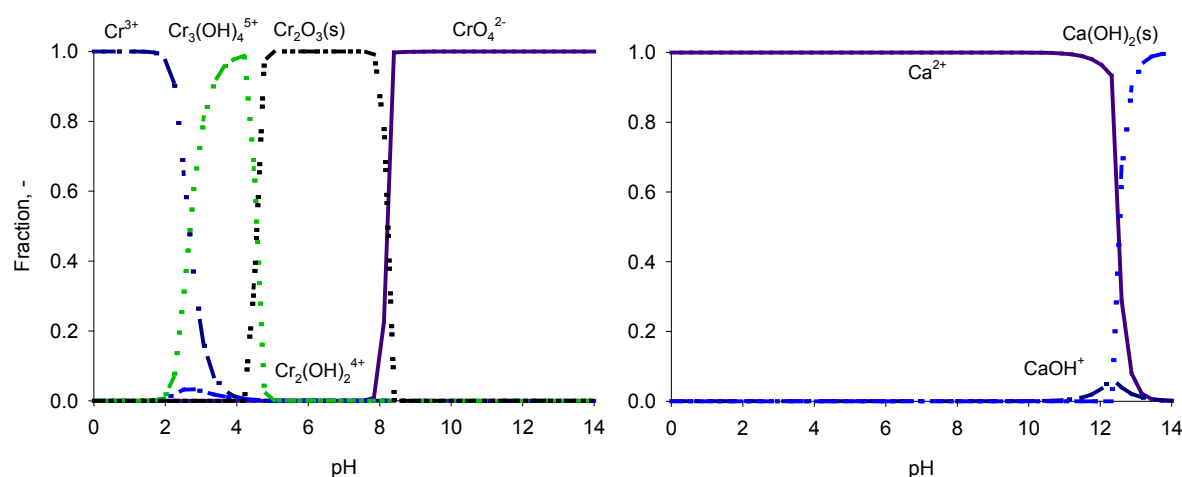


Figure 3. Speciation of Cr and Ca in water leachate. $[\text{Me}]_{\text{tot}} = 100 \text{ mM}$, $I_c = 1.0 \text{ M}$, $E_h = 0.5 \text{ V}$, $T = 25 \text{ }^\circ\text{C}$.

Indium from WEEE waste

Indium Tin Oxide (ITO) is used as an electrode material in LCD screens. ITO consists of 90% In_2O_3 and 10% SnO_2 . In recycling, the LCDs are dismantled and the ITO-containing glass panels are ground. According to one method (Virolainen *et al.*, 2011), this glass powder is leached with 1 M sulfuric acid from which both In and Sn are extracted with D2EHPA as extractant. The In/Sn separation is obtained by stripping with an 1.5 M HCl solution where indium appears predominantly as a chlorocomplex (Fig. 4). The indium capacity of D2EHPA is high enough to enable sufficient enrichment, although the amount of indium in LCD screens is very low.

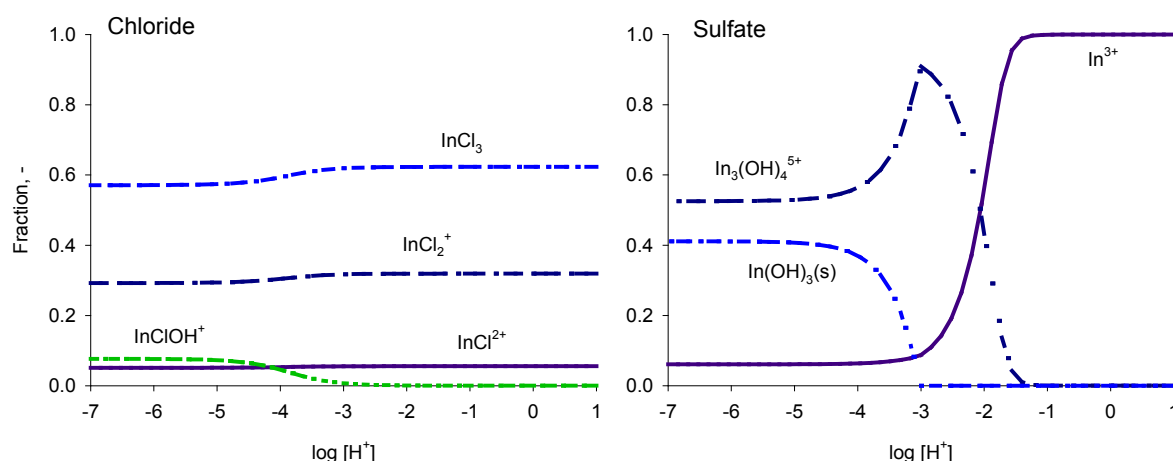


Figure 4. Speciation of In(III) in 1.0 M chloride and 0.5 M sulfate solutions $[In]_{tot} = 1 \text{ mM}$, $I_c = 1.0 \text{ M}$, $T = 25^\circ \text{C}$.

Indium, Gallium and Germanium as by-products

Zn ores contain typically In, Ga, and Ge which are today recovered by SX directly from the Zn process but often end up in residues or landfills. If the amount in such old landfills is high enough, the metals could be recovered by combining pyrometallurgical (e.g. with TSL technology, see Creedy et al., 2013) and hydrometallurgical treatment. If In, Ga, and Ge are in a sulfuric acid solution, the In and Ga can be extracted by cation exchange SX using e.g. D2EHPA as extractant. Ge has quite different speciation (Fig. 5) than In and Ga. At low pH germanic acid Ge(OH)_2 can be extracted with α -hydroxyoxime extractant, which can act through a solvating mechanism. However, adsorption using a resin with N-methylglucamine functional groups is a good alternative for the selective removal of Ge from acidic zinc sulfate solution although the possible presence of iron limits its usability (Virolainen et al., 2013).

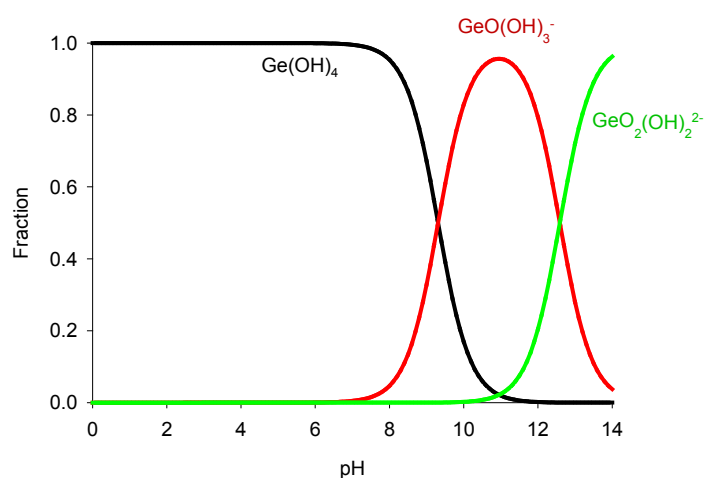


Figure 5. Speciation of Ge(IV) in sulfate solutions. $[Ge]_{tot} = 1 \text{ mM}$, $I_c = 2.0 \text{ M}$, $E_h = 0.5 \text{ V}$, $[SO_4^{2-}]_{tot} = 0.5 \text{ M}$, $T = 25^\circ \text{C}$.

Conclusions

Many of the minor metals are both high-value and high-tech metals, which are also classified as critical metals. The most optimal recycling method is to physically sort them without mixing them with other metals, as in the cases of In and Re. In recycling, the recovery methods are not the bottleneck, but gathering enough material to a place where it can be economically processed is the difficult leg. Processing should preferably take place integrated to a larger metallurgical base metal plant, where the metals in question already appear as potential by-products. Solvent extraction is a feasible method to separate and concentrate the minor metals and it could follow the fractionation of the materials in a furnace to dusts, speiss, and slag (e.g. with Outotec's Kaldo or TSL technologies).

References

1. Virolainen, S., Hydrometallurgical recovery of valuable metals from secondary raw materials, Thesis, Acta Universitatis Lappeenrantaensis 554, Lappeenranta 2013.
2. UNEP Expert report (lead author M.A.Reuter), Metal Recycling, Opportunities, Limits, Infrastructure, UNEP publications, 2013.
3. Bal, Y., Bal, K.-E., Cote, G. and Lallam, A., Characterization of the solid third phase that precipitates from the organic solutions of Aliquat 336 after extraction of molybdenum(VI) and vanadium(V), Hydrometallurgy 75(2004) 123-134.
4. USGS, Mineral Commodity Summaries, US Geological Survey, 2013.
5. Virolainen, S., Salmimies, R., Hasan, M., Häkkinen, A. and Sainio, T. Recovery of valuable metals from argon oxygen decarburization (AOD) dusts by leaching, filtration and solvent extraction, Hydrometallurgy 140 (2013) 181–189
6. Cruz, A. and Reghezza, A., Molybdenum: New by product at hydrometallurgical operations in Codelco North?, HydroCopper 2007, Viña del Mar, Chile May 16-18, 2007.
7. Laitala, H., Paatero, E., Nyman, B. and Ekman, E. Apparatus and method for removing impurities in connection with liquid-liquid extraction of copper, PCT Pat. WO2010109078 (priority 27.3.2009)
8. Virolainen, S., Ibanez, D. and Paatero, E., Recovery of indium from indium tin oxide by solvent extraction, Hydrometallurgy 107(2011) 56-61.
9. Creedy, S., Glinin, A., Matuszewicz, S., Hughes, S. and Reuter, M.A., Outotec Ausmelt technology for treating zinc, ERZMETALL 66(2013) 230-235.
10. Virolainen, S., Heinonen, J. and Paatero, E., Selective recovery of germanium with N-methyl-glucamine functional resin from sulfate solutions, Separation and Purification Technology 104(2013) 193-199.

Specific phenomena in extraction of organic acids with ionic liquids and formulation of solvents for extractive separations

Š. Schlosser, M. Blahušiak, J. Marták

Institute of Chemical and Environmental Engineering, Slovak University of Technology, Radlinského 9, 81237 Bratislava, Slovakia

Coordinating ionic liquids (ILs), especially phosphonium and ammonium ones, were found as good extractants of organic acids with better performance comparing to classical extractants [1-4]. Hydrophobic ILs have unique supramolecular structure. Contrary to molecular solvents which are homogenous liquids ILs can be regarded as structured nano-segregated liquids what influence much their properties. Structure of both parts of ILs, cation and anion, influence their properties but influence of anion is dominant [1-2]. Anions of water insoluble organic acids exhibit synergy effect and enhance extractive properties of ammonium and phosphonium ILs. Competitive extraction of BA and water occurs in these ILs. With increasing acid concentration in the solvent decreases water concentration in it and this dependence goes through minimum at BA loading of about 3 and surprisingly start to increase.

Pure coordinating ILs especially when dry are quite viscous liquids. Addition of molecular solvents, e. g. water and dodecane, strongly decreases viscosity of the solvent what can be used in the solvent formulation [3-5]. Viscosity of dodecane solution of IL exponentially increases with IL concentration and deviates from ideal mixing conditions.

Tested ILs were quite hydrophobic and insoluble in water. At the same time, in contact with aqueous solutions they exhibit high content of water with mass fraction above 14 mass%. In dynamic light scattering measurements, two different types of aggregates have been identified in the dry and water saturated solvents at lower content of phosphonium IL, with the mean size above 300 nm and 2 nm, respectively.

Most ILs as organic salts have practically negligible vapor pressure what enable effective regeneration of the solvent with volatile solutes by short path distillation. It is advantageous that free acid concentrate is recovered. This enables to design a hybrid fermentation-separation process for production of organic acids [6].

A hypothesis is suggested on formation of supramolecular structure with continuous polar channels where transport of acid is faster with probable hopping mechanism of acid molecules between acid chains at binding sites of IL.

Acknowledgment: Support of the Slovak grant VEGA 1/0757/14 is acknowledged.

References

- [1] Marták, J. and Schlosser, Š., Phosphonium ionic liquids as new, reactive extractants of lactic acid, *Chem. Pap.*, 60 (2006) 395-398.
- [2] Schlosser, Š. Marták, J., Separation of mixtures by pertraction or membrane based solvent extraction and new extractants, *Membranes: theory and practice*, N. Copernicus Univ., Toruń, 2009, pp. 123-152. Available at <http://www.chem.uni.torun.pl/FIZ/ChemZM/MTiP/MTiPIII/MTiPIII.html>
- [3] Marták, J. and Schlosser, Š., Extraction of lactic acid by phosphonium ionic liquids, *Sep. Purif. Technol.*, 57 (2007) 483-494.
- [4] Blahušiak, M., Schlosser, Š., and Marták, J., Extraction of butyric acid with a solvent containing ammonium ionic liquid, *Sep. Purif. Technol.*, 119 (2013) 102-111.
- [5] Blahušiak, M. and Schlosser, Š., Physical properties of phosphonium ionic liquid and its mixtures with dodecane and water, *J. Chem. Thermodyn.*, 72 (2014) 54-64.
- [6] Blahušiak, M., Schlosser, Š., and Cvengroš, J., Simulation of a new regeneration process of solvents with ionic liquid by short-path distillation, *Sep. Purif. Technol.*, 97 (2012) 186-194.

SPONGE-LIKE IONIC LIQUIDS.

A new platform for synthesis and pure product separation

Pedro Lozano^{*1}, Juana M. Bernal¹, Eduardo García-Verdugo², Gregorio Sánchez³,
M. Isabel Burguete² and Santiago V. Luis³

¹ *Departamento de Bioquímica y Biología Molecular. Facultad de Química, Universidad de Murcia, Murcia, Spain.*

² *Departamento de Química Inorgánica y Orgánica. Universidad Jaume I, Castellon, Spain.*

³ *Departamento de Química Inorgánica. Facultad de Química, Universidad de Murcia, Murcia, Spain.*

Summary

Hydrophobic ILs based on cations with long alkyl side-chains, e.g. N,N,N,N-hexadecyltrimethylammonium bis(trifluoromethylsulfonyl)imide, ([C₁₆tma][NTf₂]), are switchable ionic liquid/solid phases with temperature that behave as sponge-like systems (Sponge-Like Ionic Liquid, SLILs). Based on this new property, the SLILs have been used to develop straightforward and clean approaches for producing nearly pure synthetic compounds of added value (e.g. geranyl acetate, anisyl acetate, biodiesel, etc) in two steps: a catalytic step that occurs as monophasic liquid system, followed to a product separation step carried out by cooling/centrifugation of the solid reaction system, providing an upper SLIL-free liquid products and another bottom solid phase containing the SLIL.

Introduction

Sustainable chemistry is based on the use of safer solvents and reaction conditions, and encourages the use of environmentally benign non-aqueous solvents and efficient catalysts for chemical reactions and/or processes.¹ Enzymes are the catalysts of living systems, and clearly constitute powerful green tools for chemical synthesis, because of their high activity and selectivity (stereo-, chemo- and regioselectivity) for catalyzed reactions.² On the other side, solvents are key elements in chemical processes, where they acts as media for mass-transport, reaction and product separation. As responsible for a major part of the performance of chemical processes, solvents have a great impact on cost, safety and health. The search for new environmentally benign non-aqueous solvents, which can easily be recovered/recycled and which permit enzymes to operate efficiently in them, is a priority in the development of integral green chemical processes.³ In this context, the recent introduction of ionic liquids (ILs) in Chemistry could lead to a green revolution in industrial processes, because of their unique array of physico-chemical properties, headed by their very low vapor pressure, as well as their excellent suitability as non-aqueous reaction media for biocatalytic transformations.^{1,2,4}

The excellent suitability of hydrophobic ILs based on cations with long alkyl side-chains (e.g. 1-methyl-3-octadecylimidazolium bis(trifluoromethylsulfonyl)imide, [C₁₈mim][NTf₂]) for lipase-catalyzed biodiesel synthesis has been demonstrated.⁵ These ILs were able to dissolve both vegetable oil and methanol substrates at any concentration, providing monophasic reaction media of high efficiency for the biocatalytic process (e.g. up to 96% biodiesel yield in 6 h at 60°C, and enzyme reuse

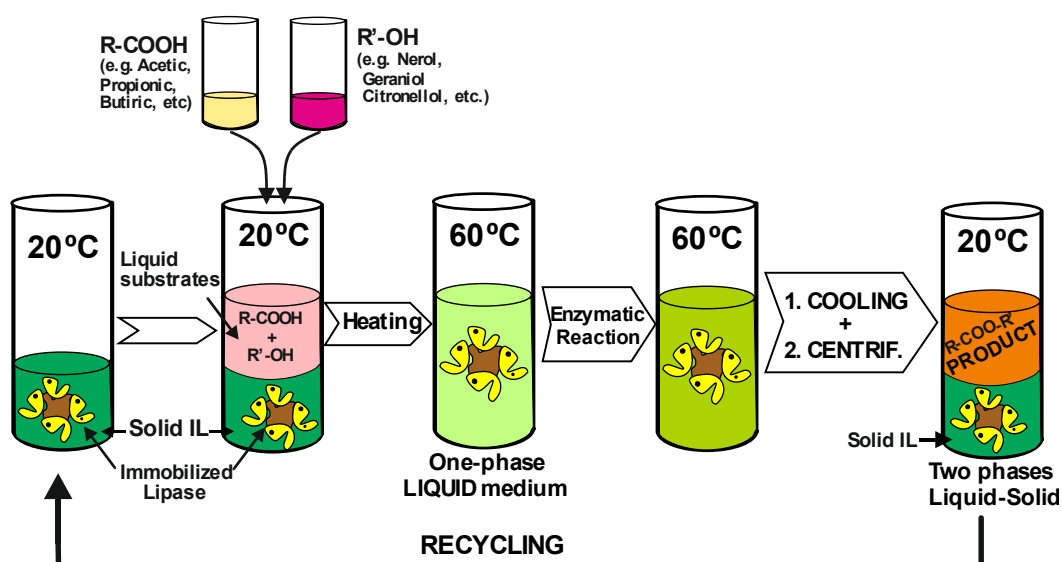


Figure 1. Green approach for enzyme-catalyzed ester synthesis by direct esterification in Sponge-Like Ionic Liquid (SLILs), and product separation by cooling and centrifugation, including full recovery and reuse of the enzyme–SLIL system.

without activity loss).^{6,7} Furthermore, it was observed how these ILs are switchable ionic liquid/solid phases with temperature that behave as sponge-like systems (Sponge-Like Ionic Liquid, SLILs). As liquid phases, these SLILs are excellent monophasic reaction media for the enzyme-catalyzed synthetic reactions that provided exceptional biocatalytic activity and stability. As solid phases, the reaction mixture can easily be fractionated by simple physical techniques (e.g. centrifugations at controlled temperature, etc) into different phases allowing an easy product separation, and the SLILs recovery.^{8,9}

The aim of this work is to demonstrate the exceptional suitability of SLILs, as a new green platform for performing both the enzymatic synthesis of high added value products, and their subsequent separation as nearly pure fractions by following straightforward and clean methodologies (e.g. centrifugation, see Fig.1). The influence of the nature of SLILs for several synthetic reactions (*i.e.* flavour esters and biodiesel), as well as several approaches for product separation, have been studied.

2. Biocatalytic production of flavour esters in Sponge-Like Ionic Liquids

Flavour esters of short-chain carboxylic acid (e.g. geranyl acetate, etc.) are among the most important fragrance compounds used in the food, cosmetic and pharmaceutical industries. The international legislations has meant that “natural” flavour substances can only be prepared either by physical processes (e.g. extraction) from natural sources, or by enzymatic or microbial transformation of precursors isolated from nature, without the use of organic solvents.¹⁰ In this context, enzyme-catalyzed direct esterification of a flavour alcohol and acetic acid in solvent-free media is the clearest way to obtain “natural” products. However, this approach provides moderate results because of the enzymes deactivation that occurs by direct contact with concentrated acids.¹¹

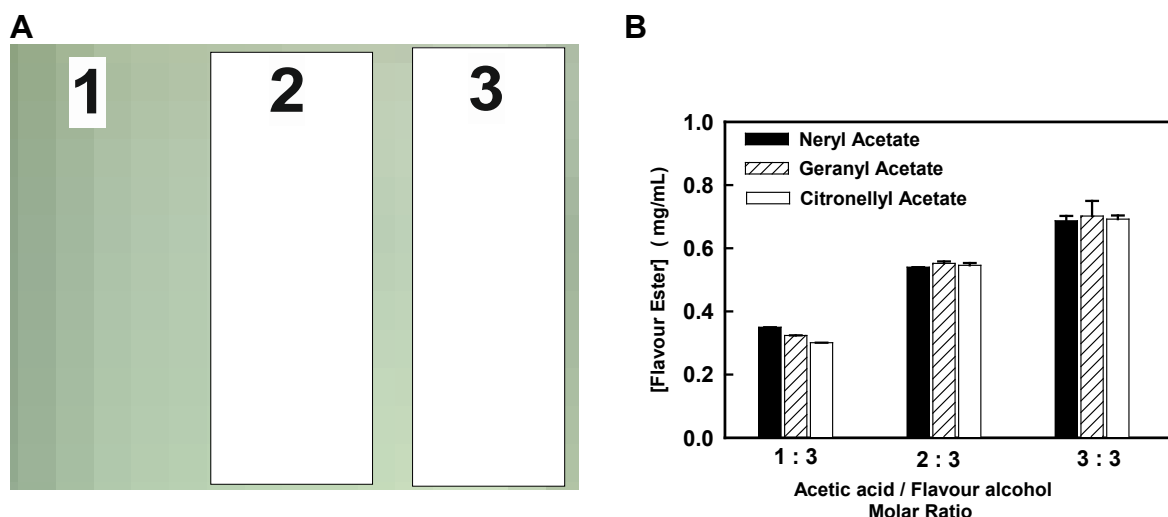


Figure 2. Novozym 435-catalyzed flavour ester synthesis by direct esterification between acetic acid and the corresponding flavour alcohol in 60% (w/w) $[C_{16}tma][NTf_2]$ SLIL at 50°C. **A.** Phase behavior of the reaction mixture containing geranyl acetate product at 50°C (1), 25°C (2), and after centrifugation at 14 000 rpm (30 min) and at 10°C (3). **B.** Effect of the acetic acid/flavour alcohol molar ratio on the flavour ester product obtained through the esterification reaction catalyzed by Novozym 435 in 60% (w/w) $[C_{16}tma][NTf_2]$ SLIL for 4 h reaction at 50°C.

The suitability of the $[C_{16}tma][NTf_2]$ SLIL as reaction media for carrying out the enzymatic synthesis of different terpene esters (*i.e.* neryl acetate, geranyl acetate and citronellyl acetate) by direct esterification of acetic acid and the corresponding alcohol was studied at 50°C. All the reactions were assayed at 60% (v/v) SLIL concentration, and at three different acetic acid/flavour alcohol molar ratio (*i.e.* 1/3, 2/3 and 3/3 mol/mol), being obtained product yields in the range 90-100% for all cases after 4h reactions. Using the geranyl acetate case as example in Fig. 2A, it was observed that reaction media were fully clear monophasic systems during enzymatic reaction at 50°C, then became monophasic solid systems after cooling to room temperature. Finally, each solid phase could be separated into two phases, an upper SLIL-free liquid (as determined by ^{19}F -NMR), and another bottom solid containing the IL by following the iterative centrifugation protocol detailed above (see Methods section). Fig. 2B shows the resulting product concentration at the upper SLIL-free phase for each reaction media, which was practically independent on the nature of the terpene alcohol at each assayed conditions.

Anisyl acetate is another fragrance ingredient used in many cosmetic and fine fragrance products. Although the enzymatic synthesis of anisyl acetate has never been reported, lipase-catalyzed direct esterification of acetic acid with anisyl alcohol in SILs media could be considered as the most straightforward way to obtain this fragrance ester. Also, the assistance of the reaction by microwave (MW) irradiation was also applied because enhancement in reaction rates for both chemical- and enzyme-catalyzed reactions.^{12,13} Fig. 3A depicts the time courses of the Novozym 435-catalyzed esterification of acetic acid with anisyl alcohol in 70% (w/w) $[C_{16}tma][NTf_2]$ SLIL at a 1/1 (mol/mol) acetic acid/anisyl alcohol ratio concentration, by using either MW irradiation (4W power) or conventional heating (50°C). The

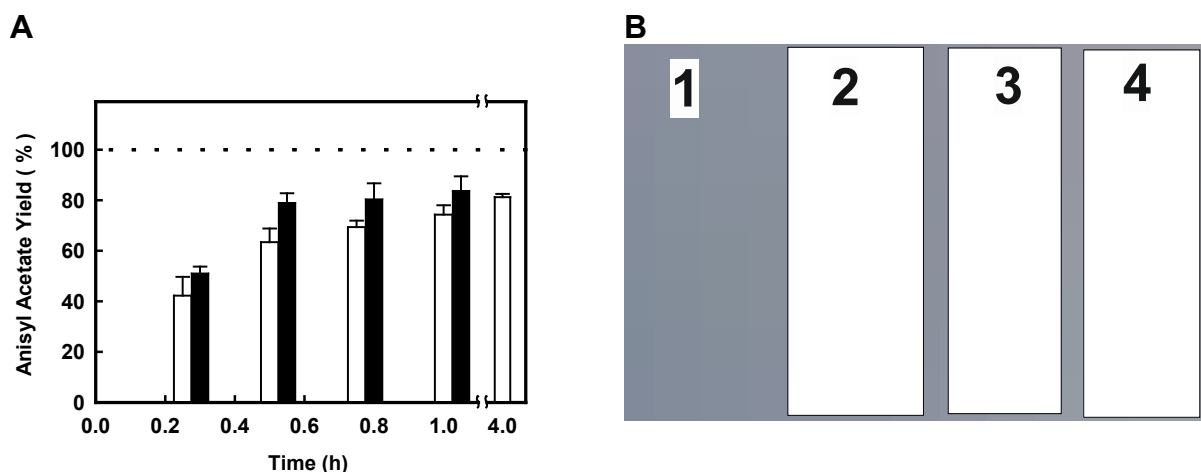


Figure 3. A. Time-course profiles shown by Novozym 435-catalyzed anisyl acetate synthesis by direct esterification of acetic acid with anisyl alcohol (1:1 molar ratio) in 70% (w/v) $[C_{16}tma][NTf_2]$ SLIL at 50°C conventional heating (white), or at 4W microwave irradiation (black). **B.** Pictures of the reaction mixture containing the anisyl acetate product at 50°C (1), 0°C (2), 0°C into a centrifugal filter, and after centrifugation at 14,000 rpm (10 min) and at 0°C (3).

enzyme was able to synthesize anisyl acetate in both cases, reaching up to 82% yield (with respect the initial acetic acid) in 1h under MW irradiation. Furthermore, the MW irradiation provides a slightly better anisyl acetate yield profile than conventional heating, which reached a similar product concentration as MW after 4h. Fig. 3B shows that the final reaction mixture was a fully clear monophasic system, and once again, it became solid by cooling down to room temperature. By using the previous centrifugation protocol at controlled temperatures on the solid reaction mixtures, the physical separation between both phases could not be adequately performed for product recovery, because the solid SLIL phase rapidly re-dissolved again into the anisyl acetate phase. Thus, a new fractionation approach based on the use of centrifugal nylon filter (0.2 μ m pore size) was assayed at 0°C. By this approach, the SLIL solid was retained above the nylon membrane, providing the filtration of the liquid anisyl acetate phase across the membrane to the bottom tube, behaving identically to a sponge wringing up. For this case, the observed synergism between MW irradiation and biocatalysis agreed with results obtained for different synthetic reactions, where the reaction rate improvements have been attributed to both thermal and non-thermal effects of this irradiation.^{13,14}

Nevertheless, the most exciting intriguing of these hydrophobic ILs is its ability to behave as sponge-like systems in solid phase, where products can easily separated from the IL by centrifugation and /or filtration. These features could be explained as being a function of the solid/liquid structural organization of ILs. For the case of pyrrolidinium-based ILs, it was reported how these ILs are organized as an intricately nanostructured net, where the ILs containing cations with shorter alkyl chain substituent form alternating cation–anion monolayer structures on confinement to a thin film, whereas a cation with a longer alkyl chain substituent leads to bilayer formation.¹⁵ In agreement with these studies, the nanostructural organization of the

liquid/solid temperature switchable SLIL phase may be described in term of ordered layers in which the alkyl side chains of the cations provide hydrophobic hole able for “housing” flavour molecules in solid phase.^{8,9} Then, the centrifugation step of the solid mixture across the filter allowed “to wring the soaked sponge” and so, recovering products. In this context, the ability these SLILs to melt at temperatures compatible with enzyme catalysis permitted development of an easy green method for flavour ester synthesis and clean separation products.¹⁴

3. Biocatalytic production of biodiesel in Sponge-Like Ionic Liquids.

The non-miscibility between vegetable oils and methanol is one of the most important limitations for catalytic production of biodiesel, leading to two-phase systems that reduces process efficiency, and for the case of biocatalysts, resulted in full enzyme deactivation by the direct contact with methanol. Several SLILs (e.g. $[C_{18}mim][NTf_2]$, etc.) are able to dissolve both triolein and methanol at any concentration, providing monophasic reaction media (see Fig. 4.1) with excellent suitability for the biocatalytic synthesis of biodiesel, i.e. up to 96% yield in 6 h at 60°C.^{6,7} Furthermore, this excellent suitability of SLILs can be extended to the protection of the enzyme against deactivation (up to 1370 days half life time at 60°C).¹⁶ However, any industrial application of this approach should involve a clean approach to extract the synthesized biodiesel with the full recovery and reuse of the SLIL.

For carrying out separation of both biodiesel and glycerol products from reaction media based on SLIL, a new cooling/centrifugation approach was developed, based on the previous addition of hot water (60°C) into the reaction medium (see Fig 4.2). By cooling down the reaction mixture up to 25°C, the system looks as a solid/liquid heterogeneous mixture (see Fig 4.3), which resulted in a three phases system after three consecutive centrifugation steps at 15,000 rpm (1 h) at room temperature, 23 and 15°C, respectively. Thus, it was obtained a upper pure biodiesel phase, a middle liquid aqueous phase containing the glycerol by-product, and a bottom solid containing the SLIL (see Fig. 4.4). Additionally, the presence of water, as green solvent non-miscible with biodiesel nor SLIL, improved the separation between phases in agreement with the density parameter (biodiesel < water < SLIL).¹⁶ The suitability of the proposed methodology for clean biodiesel separation is demonstrated. Increasing centrifugation time and/or speed of the protocol might improve the extraction yields, although the temperature at which centrifugation can be carried out is limited by the.

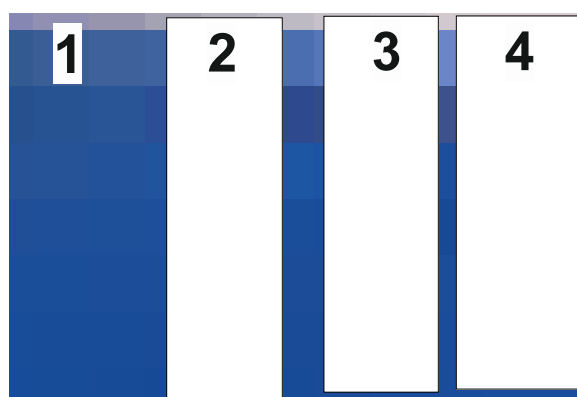


Figure 4. Phase behavior of the reaction mixture containing both biodiesel and glycerol products in 50% (w/w) $[C_{18}mim][NTf_2]$ at 60°C (1), 60°C after addition of water (2), 25°C (3), and after three consecutive centrifugation steps at 14,000 rpm (20 min) at 25, 23 and 15°C, respectively (4)

melting point of the fatty acid methyl esters present in the biodiesel. By approach, an easy way for separating both biodiesel and glycerol in different fractions is observed. Other proposed approaches based on liquid-liquid extraction with organic solvents (e.g. hexane), or supercritical fluid are less interesting for industrial application both from the economic and technical standpoint.^{1,5,6}

4. Conclusions.

This work shows a straightforward and green method for efficiently extracting organic compounds dissolved into an ionic liquid by simple cooling and centrifugation. This approach is opposite to the usual heating applied for classical separation process in Chemical Engineering (e.g. distillation). Furthermore, the low melting temperatures of SLILs (e.g. lower than 75°C) allowed us to develop two-step protocols for producing high added value compounds (i.e. flavour esters and biodiesel), as follows, (i) enzyme-catalyzed transesterification or esterification reactions with a product yield close to 100%, and (ii) clean separation of the reaction products by a cooling/centrifugation method. The unique ability of these Sponge-Like Ionic Liquids, as temperature switchable liquid/solid phase systems, opens up a new sustainable platform for chemical synthesis and product separation.

5. Acknowledgements. Work supported by MINECO, Spain (Ref: CTQ2011-28903).

6. References.

1. P. Lozano, E. García-Verdugo, S. V. Luis, M. Pucheault, M. Vaultier. *Curr. Org. Synth.* **2011**, *8*, 810–823.
2. P. Lozano. *Green Chem.* **2010**, *12*, 555-569.
3. J. H. Clark, S.J. Taverner. *Org. Process Res. Dev.* **2007**, *11*, 149-155.
4. P. Dominguez de Maria, *Angew. Chem. Int. Ed.* **2008**, *47*, 6960-6968.
5. P. Lozano, E. García-Verdugo, J. M. Bernal, D. F. Izquierdo, M. I. Burguete, G. Sanchez, S. V. Luis. *ChemSusChem*, **2012**, *5*, 790-798.
6. P. Lozano, J. M. Bernal, R. Piamtongkam, D. Fetzer, M. Vaultier, *ChemSusChem*, **2010**, *3*, 1359-1363
7. P. Lozano, J. M. Bernal, M. Vaultier. *Fuel*, **2011**, *90*, 3461-3467.
8. P. Lozano, J. M. Bernal, A. Navarro. *Green Chem.* **2012**, *14*, 3026-3033.
9. S. K. Ritter. *Chem. Eng. News*, **2013**, *91*, 34-35.
10. S. Serra, C. Fuganti, E. Brenna. *Trends Biotechnol.* **2005**, *23*, 193–198.
11. A. Guvenç, N. Kapucu, U. Mehmetoglu. *Process Biochem.* **2002**, *38*, 379-386
12. A. De la Hoz, A. Diaz-Ortiz, A. Moreno. *Chem. Soc. Rev.* **2005**, *34*, 164-178
13. D. F. Izquierdo, J. M. Bernal, M. I. Burguete, E. García-Verdugo, P. Lozano, S. V. Luis. *RSC Adv.* **2013**, *3*, 13123-13126.
14. P. Lozano, J. M. Bernal, A. Lajarin, D. Romera, E. Garcia-Verdugo, G. Sanchez-Gomez, M. Pucheault, M. Vaultier, M. I. Burguete, S. V. Luis. *Curr. Green Chem.* **2014**, *1*, DOI: 10.2174/2213346101666131113201434
15. A. M. Smith, K. R. J. Lovelock, N. N. Gosvami, P. Licence, A. Dolan, T. Welton, S. Perkin. *J. Phys. Chem. Lett.* **2013**, *4*, 378-382
16. P. Lozano, J. M. Bernal, G. Sanchez, G. Lopez, M. Vaultier. *Energ. Environ. Sci.* **2013**, *6*, 1328-1338.

Design of Novel Ionic Liquids Solvents for the Selective Recovery of Carbon Monoxide

*Gabriel Zarca, Inmaculada Ortiz, Ane Urtiaga*¹*

Research on the use of ionic liquids as solvents has extended to several fields due to their outstanding properties, e.g. solvent capacity, chemical and thermal stability, wide electrochemical window, non-flammability, etc. More recently, ionic liquids are becoming increasingly important for gas separation due to their negligible vapour pressure, which make them suitable for designing novel absorption separation processes with no solvent losses as well as preparing long-term stable supported ionic liquid membranes (SILMs) with enhanced separation properties over conventional polymers. In light of these facts, we have addressed the recovery of carbon monoxide from nitrogen-enriched gas mixtures. This is a very challenging separation since both gases have very similar solubilities and diffusivities in polymers, ionic liquids and molecular solvents; however, a CO-selective ionic liquid can be employed to that end. In this work, the Lewis acid-based 1-hexyl-3-methylimidazolium chlorocuprate(I) was prepared and its capacity to absorb CO has been studied as well as the absorption reaction kinetics between CO and the ionic liquid. Finally, supported ionic liquid membranes have also been prepared with this ionic liquid in order to assess their performance for CO/N₂ separation.

Introduction

This work explores a novel approach for the recovery of carbon monoxide from a nitrogen-rich gas stream, such as the flue gases released in some industrial processes after a partial combustion of hydrocarbons, by taking advantage of the outstanding properties of room temperature ionic liquids (RTILs) as a mean to overcome the main shortcomings of currently available industrial gas separation technologies, namely, cryogenic distillation, liquid absorption, and adsorption processes. Regarding these separation processes, cryogenic distillation is not suitable for large nitrogen contents, as it becomes inefficient due to the similar boiling point of both compounds and even more, if carbon dioxide is present in the feed stream, it has to be completely removed in order to avoid solid freeze up in the extremely cold environment [1]; in such conditions, the absorption processes can provide high purity CO regardless of N₂ concentration and therefore, they are preferred over other alternatives. Nevertheless, they are rarely employed owing to several concerns, typically, long-term deactivation and loss of stability of the absorbent and its relatively high energy and operational costs.

The reactive gas absorption in ionic liquids has been explored as a way to further increase the absorption capacity at low partial pressures of the target compound, principally in post-combustion CO₂ capture, whereas physical absorption in pure ionic liquids seems to be limited to high pressure applications [2]. Furthermore, when

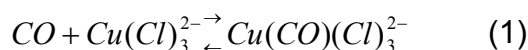
* Dep. Chemical and Biomolecular Engineering, Universidad de Cantabria, 39005, Santander, Spain.
Phone: +34 942 201587, E-mail: urtiaga@unican.es

considering the absorption of CO, this is a critical issue as the physical solubility in both molecular and ionic solvents is much lower than that of CO₂.

Reactive copper(I)-based ionic liquid for CO separation

Proven absorption/desorption technologies for separation of CO are based on the reversible complexation reaction between CO and *d*-block transition metals ions, namely copper(I), such as in the copper liquor process and COSORB process, where volatile ammonia and toluene are usually employed as solvents, respectively [3]. The π -complexation bonds formed are stronger than van der Waals interactions, but still weak enough to reverse the reaction in an economically attractive process.

Taking that into account, we proposed the system that comprises the ionic liquid 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]) and the salt cuprous chloride (CuCl) as an efficient non-volatile medium to provide an improved CO solubility over N₂. This ionic liquid, in contrast to traditional solvents, allows solubilising great amounts of CuCl, leading to a new Lewis acid-based ionic liquid that has the same imidazolium cation, but a series of copper(I) complexes $(CuCl)_x^{1-x-}$ as anion. In basic conditions, that is when the CuCl/[hmim][Cl] molar ratio is lower than one, the species preferentially formed is $(CuCl)_3^{2-}$. The latter anion selectively and reversibly binds CO molecules in a 1:1 ratio to form a copper(I)-CO adduct according to Eq. (1):



Ionic liquid properties

Ionic liquids are usually viscous liquids; therefore the mass transport might be limited in this type of solvents in contrast to conventional molecular solvents. The effect of temperature and copper(I) concentration on the chloride and chlorocuprate(I) ionic liquid viscosity were assessed. We found that the viscosity of the samples containing the highest amounts of CuCl suffered a drastic decrease thus both mass transport and CO capacity will be favoured in such conditions [4]. Regarding the influence of temperature, all the samples were affected in a very similar manner, i.e. exponential decrease with temperature, as can be appreciated from the almost parallel lines in the Arrhenius plot (Figure 1).

Another important finding is that the viscosity of these ionic liquids can be modified at elevated shear rates. As shown in Figure 2, a non-Newtonian shear thinning behaviour has been found in all cases, regardless of the temperature and CuCl concentration of the sample.

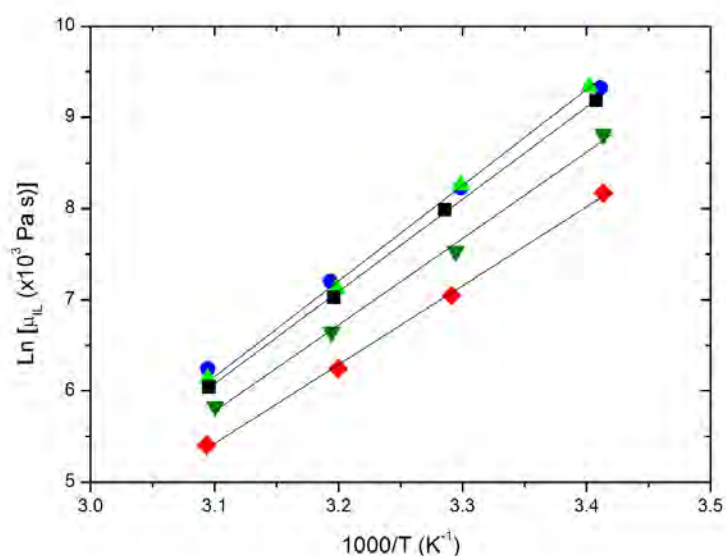


Figure 1. Ionic liquid viscosity as a function of temperature and copper(I) concentration: 0 (●), 0.25 (▲), 0.5 (■), 1 (▼) and 2 (◆) mol copper(I) L⁻¹. The solid lines are the linear fitting of the data.

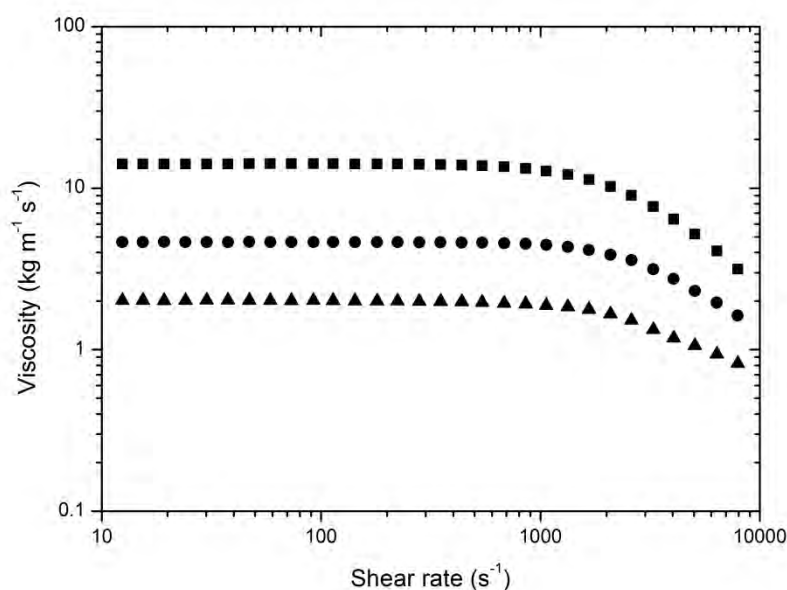


Figure 2. Non-Newtonian shear thinning viscosity of chlorocuprate(I)-based ionic liquid as a function of temperature: 293 (▲) 303 (●) and 313 K (■).

Carbon monoxide uptake

The thermodynamics as well as the kinetics of Eq. (1) have been characterised and the parameters that allow describing the CO selective separation process under different operational conditions in a stirred tank reactor obtained [5, 6]. The

absorption equilibrium study of CO and N₂ revealed that whereas both gases have similar physical solubility in the pure [hmim][Cl]; in the reactive chlorocuprate(I) ionic liquid, high CO/N₂ solubility-selectivities (up to 100) are achievable over a wide range of pressure, temperature, gas composition and CuCl concentration in the liquid phase. In addition, the long-term stability of the carrier was also demonstrated. As shown in Figure 3, the solubility of CO increased with increasing concentrations of copper(I) and pressure. The N₂ physical solubility in the reactive ionic liquid is also depicted for comparison purposes. However, since reaction 1 is exothermic, a decrease in CO solubility was observed when temperature was increased.

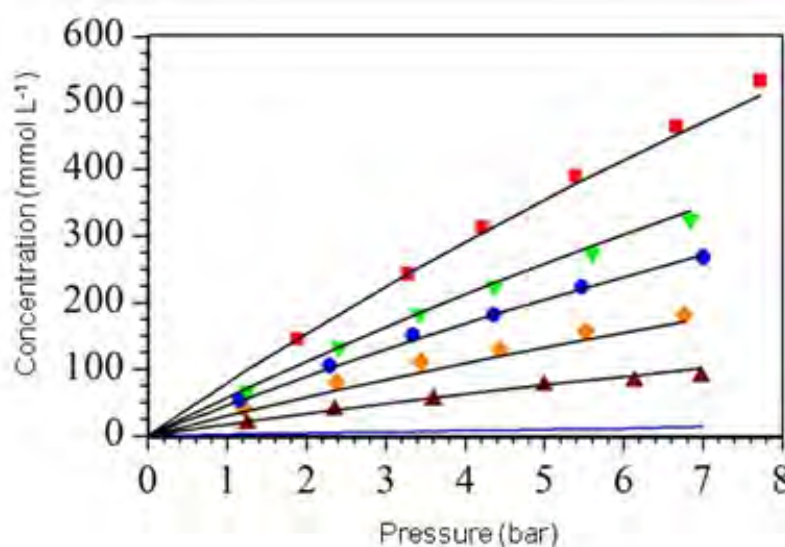


Figure 3. Comparison between total solubility of CO in 1-hexyl-3-methylimidazolium chlorocuprate(I) ionic liquid and N₂ physical solubility (blue solid line) at 303 K and several copper(I) concentrations: 0.6 (▲), 1 (◆), 1.6 (●), 2 (▼) and 4 mol copper(I) L⁻¹ (■).

Complementary to the thermodynamic study, the absorption reaction kinetics were also assessed in order to determine the kinetic constant of reaction as well as to describe the influence of temperature on this parameter. The kinetic constants obtained in this study can be employed to obtain the absorption fluxes as a function of the concentration of reactants and temperature. As shown in Figure 4, the carbon monoxide transport was enhanced in the chlorocuprate(I) ionic liquid with respect to the mass transport in the absence of reaction in the [hmim][Cl] ionic liquid by increasing the copper(I) concentration; on the contrary, only a minor influence of temperature on the absorption flux was observed, probably due to the trade-off between CO solubility and CO-copper(I) reaction that are affected in opposite ways by temperature.

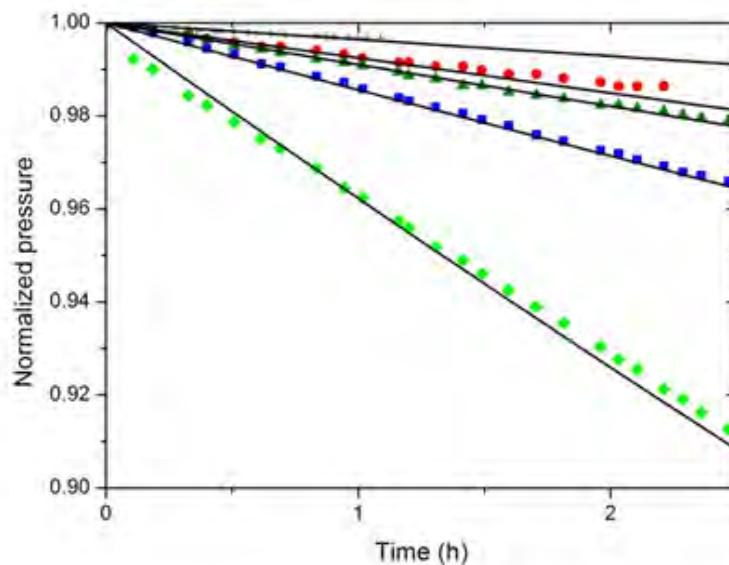


Figure 4. Carbon monoxide absorption fluxes in the non-reactive precursor [hmim][Cl] (+) and in 1-hexyl-3-methylimidazolium chlorocuprate(I): 0.25 (●), 0.5 (▲), 1 (■) and 2 mol copper(I) L⁻¹ (◆), at low CO partial pressures, 303 K and stirring rate of 100 rpm.

Ionic liquid-based gas separation membranes

Furthermore, this reactive system has been tested in the so-called supported ionic liquid membranes (SILMs) configuration [7, 8], since membrane technology is seen as a promising alternative to conventional gas separation processes owing to its relatively low investment and operating costs as well as energy requirements. The tested membranes showed that the permeability of CO was also improved in the presence of CuCl due to a carrier-mediated transport mechanism that increases the CO flux through the SILM. CO/N₂ selectivities increased with copper(I) concentration and temperature and values up to of 4 that cannot be achieved employing polymeric membranes were obtained. However, despite the promising results obtained with this approach, some critical issues were identified that require the exploration of different strategies so that this process can be regarded as a realistic alternative, namely, stabilization of the SILM at high pressures, where the difference in solubility between CO and N₂ becomes increasingly important.

Acknowledgements

Financial support to project ENE2010-15585 is acknowledged. G. Zarca is thankful to the Spanish Ministry of Economy and Competitiveness for the FPI postgraduate research grant (BES-2011-046279)

References

- [1] G.S. Patil, S. Baruah, N.N. Dutta, Facilitated transport of carbon monoxide: A review, *Gas Sep. Purif.* 5 (1991) 2-8.
- [2] J.A. Hogendoorn, W.P.M. van Swaaij, G.F. Versteeg, The absorption of carbon monoxide in COSORB solutions: Absorption rate and capacity, *Chem. Eng. J.* 59 (1995) 243-252.
- [3] J.E. Bara, D. Camper, D.L. Gin, R.D. Noble, Room-temperature ionic liquids and composite materials: Platform technologies for CO₂ capture, *Acc. Chem. Res.* 43 (2010) 152-159.
- [4] G. Zarca, I. Ortiz and A. Urtiaga, Carbon monoxide recovery from flue gases by reactive absorption in imidazolium chlorocuprate(I) ionic liquid: Mass transfer coefficients, Submitted to *Chinese J. Chem. Eng.* (2013)
- [5] O.C. David, G. Zarca, D. Gorri, A. Urtiaga and I. Ortiz, On the improved absorption of carbon monoxide in the ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate, *Sep. Purif. Technol.* 97 (2012) 65-72.
- [6] G. Zarca, I. Ortiz and A. Urtiaga, Kinetics of the carbon monoxide reactive uptake by an imidazolium chlorocuprate(I) ionic liquid, Submitted to *Chem. Eng. J.* (2014)
- [7] G. Zarca, I. Ortiz and A. Urtiaga, Copper(I)-containing supported ionic liquid membranes for carbon monoxide/nitrogen separation, *J. Membr. Sci.* 438 (2013) 38-45.
- [8] G. Zarca, I. Ortiz and A. Urtiaga, Facilitated-transport supported ionic liquid membranes for the simultaneous recovery of hydrogen and carbon monoxide from nitrogen-enriched gas mixtures, *Chem. Eng. Res. Des.* In press: <http://dx.doi.org/10.1016/j.cherd.2013.12.021> (2014)

The rational design of ionic liquid-based metal ion separation systems requires either that the ion transfer properties of these systems be predictable from the known behavior of conventional organic solvents or that the mechanism(s) of metal ion partitioning be understood at a fundamental level. With this in mind, we have examined the extraction of selected metal ions (e.g., alkaline earths and pertechnetate) from aqueous media into a series of N-alkylpyridinium and N,N'-dialkylimidazolium-based room-temperature ionic liquids (RTILs), either alone or in the presence of crown ethers. The results obtained indicate that although certain aspects of metal ion extraction into RTILs parallel the behavior of conventional solvents, ionic liquids frequently play a much more active role in the partitioning process, with ion exchange involving the cationic or anionic constituents of the ionic liquid comprising an important mode of ion transfer. In addition, the results suggest that the balance among the various possible pathways for metal ion extraction into these solvents is governed by contributions from a number of factors, among them the nature of the extracted ion, the hydrophobicity of the IL cation and anion, and the aqueous phase composition.

Kinetics and mechanism of enantioselective extraction of amino acid by organometallic complex

M. Gramblicka, University of Twente, Enschede, The Netherlands; S.R.A. Kersten, University of Twente, Enschede, The Netherlands; H.J. Heeres, University of Groningen, Groningen, The Netherlands; B. Schuur, University of Twente, Enschede, The Netherlands

Keywords: palladium-(S)-xylyl-binap, chiral, enantioselective liquid-liquid extraction, extraction kinetics, amino acid, organometallic

Abstract

Organometallic palladium complexes, widely popular as asymmetric catalysts, have recently shown to exhibit a broad versatility as enantioselective extractants of a range of amino acids in equilibrium enantioselective liquid-liquid extraction (ELLE) studies.[1] Because of the versatility of these enantioselective extractants, they are promising candidates to further develop the field of ELLE. In order to develop continuous extraction processes, not only the equilibrium selectivity and distribution are important, but also information on the kinetics should be known. The reactive extraction of tryptophan from aqueous solutions through enantioselective binding with dichloro[(S)-(-)-2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl]palladium(II) (PdCl₂-(S)-xylyl-BINAP) diluted in 1-octanol was selected as model ELLE system, and the kinetics of the extraction system was studied in detail. Hardly any ELLE-systems have been studied off-equilibrium, and kinetic studies in stirred cells have been proven difficult to elucidate on intrinsic kinetics in systems with fast complexation.[2] The system of interest for this study exhibited slow and very interesting kinetic behavior. Under the conditions of very intensive mixing of both phases (> 2000 rpm), tryptophan was extracted almost immediately in significant quantity, but with no enantioselectivity. In the course of following hours, the summed distribution of both tryptophan enantiomers did not change, but the selectivity did change. A fraction the less preferred L-enantiomer was slowly released back to the aqueous solution and replaced by the uptake of D-enantiomer. This resulted in a gradually increasing operational selectivity from unity in the initial non-selective extraction to 3 after >5 hours. The influence of operational parameters (concentrations, phase ratio, temperature) on the extraction was determined, and the extraction kinetics were fitted to the data using a mathematic model. Future work includes confirmation of the kinetic model by a detailed study on the mechanism of binding in the enantioselective organometallic complexes.

- [1] B.J.V. Verkuijl, B.Schuur, A.J. Minnaard, J.G. de Vries, B.L.Feringa, *Org Biomol Chem* 2010, 8, 3045
- [2] M. Steensma, N.J.M. Kuipers, A.B. de Haan, G. Kwant, *Chem Eng Sci* 2007, 62, 1395

Flow modification induced by the presence of droplets in Taylor-Couette flows

DHERBECOURT Diane^{a,b,1*}, NEMRI Marouan^{a,b}, CHARTON Sophie^a, CLIMENT Eric^b

^a CEA, DEN, DTEC, SGCS, F-30207 Bagnols-sur-Cèze, France.

^b Institut de Mécanique des Fluides, Université de Toulouse, CNRS-INPT-UPS, F-31400 Toulouse, France.

Keywords : Two-way coupling, Droplets, Dispersion

Aiming at the development and experimentation of nuclear fuel reprocessing, a miniaturized liquid-liquid extraction column has been designed and realized. The Taylor-Couette device is composed of two concentric cylinders (the inner is rotating while outer one is fixed). The two immiscible liquid phases flow oppositely and the disperse phase is generated by the flow shear stress in the gap, creating droplets whose area is adjustable with the mean velocity of the inner cylinder. The Taylor-Couette column exhibits separation performances comparable to an industrial pulsed column, at low flow rates and at small scale, and therefore became a relevant apparatus in the scope of R&D dedicated to extraction processes (Lanoë, 2002).

Under single phase flow conditions, mixing properties have recently been the aim of extensive studies at macroscopic scale (Residence Time Distribution) but also at microscopic scale, thanks to simultaneous Particle Image Velocimetry (PIV) and Planar Laser-Induced Fluorescence (PLIF) techniques (Nemri, 2012). This experimental study has been supplemented with numerical simulations based on the direct solution of the Navier-Stokes equations and Lagrangian tracking of fluid elements to characterize axial dispersion..

We move on now to the study of flow modulation by the presence of droplets. The column is now operated under two-phase flow conditions. As a first step, the dispersed phase is composed by small PMMA spherical particles, whose size and density are well known. The flow properties are investigated both at local and global (i.e. apparatus) scale. The particles effect on flow successive instabilities and transition thresholds between various flow regimes is investigated, prior to PIV measurements of the flow perturbations induced by particles. Particles size and concentration (i.e. holdup) representative of typical liquid-liquid extraction operations are investigated.

In addition, a simulation approach is developed to investigate further the coupling between the continuous phase flow and the droplets transport. This will allow us to predict the possible preferential accumulation of droplets and the residence time in the vortices, according to their size and density. This is an important issue in liquid-liquid extraction.

J.Y. Lanoë, 2002, "Performances d'une colonne d'extraction liquide-liquide miniature à écoulement de Taylor-Couette", Rapport scientifique ATALANTE 2002, pp. 245-251.

M. Nemri et al., 2012, « Experimental and numerical investigation on mixing and axial dispersion in Taylor-Couette flow patterns », doi:10.1016/j.cherd.2012.11.010.

1 Corresponding authors : dherbecourt.diane@cea.fr ; sophie.charton@cea.fr

A numerical investigation of the impact of Marangoni convection on oscillating rising droplets in liquid/liquid systems

*Roland F. Engberg¹, Mirco Wegener² Eugeny Y. Kenig^{*1}*

The impact of solutal Marangoni convection on fluid dynamics and mass transfer cannot be described by means of analytical methods, due to their inherently three-dimensional, highly unsteady and non-linear nature. Hence, experimental and – to an increasing degree – numerical efforts are needed to reveal the underlying phenomena. This paper presents three-dimensional numerical simulations of an oscillating single droplet rising in a quiescent ambient liquid with the Marangoni effect induced by the interfacial mass transfer of a solute. For the simulations, a CFD code based on the level set method was implemented in the open-source software OpenFOAM®. To obtain data for the validation of the numerical results, experiments in the oscillating droplet regime have been carried out with the toluene/acetone/water system for different initial solute concentrations. Comparisons between experimental and simulation results regarding the velocity and trajectories of a rising droplet show a good qualitative and quantitative agreement.

Introduction

In liquid-liquid extraction processes, one phase is usually dispersed in the form of rising or sedimenting droplets in a continuous phase. Therefore, the design of liquid-liquid extraction processes largely depends on mass transfer and fluid dynamic properties of droplet swarms. These properties are usually derived from correlations developed for single droplets. Consequently, a detailed knowledge of the underlying transport phenomena is essential for a physically meaningful derivation of correlations. In this respect, a combined numerical and experimental analysis seems to be a very promising approach. While numerical simulations provide an in-depth insight into transport phenomena and local data, thorough experiments are indispensable for model validation. Furthermore, experimental studies remain the primary basis for the description of the overall extraction process.

In some cases, the fluid dynamic behaviour of droplets is not influenced by interfacial mass transfer. However, this situation changes when mass transfer leads to gradients in the interfacial tension, evoking Marangoni convection. Previous works (Wegener et al., 2007, 2009a,b) in the spherical droplet regime with the toluene/acetone/water system have shown that Marangoni convection influences the fluid dynamic behaviour in a characteristic manner. Interfacial tension gradients induce additional shear stresses at the interface which disturb the development of internal circulations in the droplet and increase the drag coefficient. Thus, the droplet rises slower than a solute-free droplet. For non-oscillating droplets, it was observed that the higher the initial solute concentration was, the stronger was the Marangoni effect and the larger were deviations from the corresponding terminal rise velocity of

¹ Chair of Fluid Process Engineering, University of Paderborn

² Chair of Chemical & Process Engineering, Technische Universität Berlin

* Corresponding Author, eugen.y.kenig@upb.de

a solute-free droplet. For initial solute concentrations exceeding a certain critical value, the droplets accelerated only to a velocity level which corresponded to the terminal velocity of a comparable rigid sphere.

Due to the strong coupling of momentum and mass transfer, Marangoni effects are highly non-linear and unsteady. Generally, Marangoni convection is strongest in the beginning, when the droplet is being formed at and detached from a capillary, and large concentration gradients appear. With progressing mass transfer, Marangoni effects decrease. Once the Marangoni convection diminished, a reacceleration occurred which can be explained with the onset of a toroidal internal circulation and, consequently, the decrease of the drag coefficient.

In comparison with spherical droplets (or droplets with only slight deformations), the fluid dynamic behaviour of oscillating droplets is substantially different and less predictable, because the droplet shape is unsteady imposing different flow patterns by itself. It should be noted that, to the best of our knowledge, the impact of Marangoni convection on the fluid dynamic behavior of oscillating droplets has not been studied yet and that the literature regarding oscillating droplets is scarce.

In this work, the influence of Marangoni convection on the fluid dynamic behaviour was examined experimentally and numerically. Toluene droplets with a diameter of 5 mm rising in water were investigated. Marangoni convection was induced by the transferred component acetone, and the influence of the initial solute concentration was studied. In the experiments, the droplets were filmed with high-speed cameras, providing detailed insights into the fluid dynamic behaviour. For the simulations, a CFD code based on the level set method was developed and implemented in the open-source CFD-package OpenFOAM®. Droplets were simulated fully three-dimensional, and the results regarding droplet rise velocity and trajectories were compared with the experimental data.

Mathematical model and numerical method

Moving interface

The level set method (Osher and Sethian, 1988) employs a scalar function $\psi(x, t)$ to indicate whether a point x is located in the dispersed phase Ω_d or in the continuous phase Ω_c at time t :

$$\begin{aligned} \psi(x, t) &< 0 && \text{in the dispersed phase} \\ \psi(x, t) &> 0 && \text{in the continuous phase} \end{aligned} \quad (1)$$

Consequently, the interface $\partial\Omega = \partial\Omega_c \cap \partial\Omega_d$ is defined by the isocontour $\psi(x, t) = 0$. The movement of the interface can be described with a simple advection equation:

$$\frac{\partial\psi}{\partial t} + \mathbf{v} \cdot \nabla\psi = 0 \quad (2)$$

where $\mathbf{v}$ denotes the velocity field.

Fluid dynamics

The liquid phases considered in this study consist of toluene, water and acetone and are Newtonian. Consequently, the incompressible flow can be described with the mass continuity (3) and the Navier-Stokes equations (4):

$$\nabla \cdot \mathbf{v} = 0 \quad (3)$$

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] - \eta \Delta \mathbf{v} = -\nabla p + \rho \mathbf{g} + \mathbf{F}_\sigma \quad (4)$$

where ρ denotes density, η viscosity, p pressure and $\mathbf{g}$ gravitational acceleration. Regarding the interfacial forces $\mathbf{F}_\sigma$ induced by the interfacial tension σ , we have implemented different methods for the normal and the tangential components: The ghost fluid method (GFM) of Kang et al. (2000) was used for the normal components and the continuum surface force (CSF) model of Brackbill et al. (1994) was chosen for the tangential components.

Mass transfer

The interfacial boundary conditions for mass transfer are the thermodynamic equilibrium (5), which results in a concentration jump at the interface proportional to the distribution coefficient K , and the continuity of diffusional fluxes (6):

$$c_{Ad} = K c_{Ac} \quad (5)$$

$$D_{Ad} \mathbf{n} \cdot \nabla c_{Ad} = D_{Ac} \mathbf{n} \cdot \nabla c_{Ac} \quad (6)$$

Here, c is concentration, D is diffusivity, $\mathbf{n}$ is the interface unit normal, A is the transferred component acetone, and the subscripts c and d denote continuous phase and dispersed phase, respectively. Haroun et al. (2010) derived a single-field formulation for the mass transfer equation which was used in the present work. The mass transport in the entire computational domain is described in terms of the mixture concentration $C = H_\epsilon c_{Ac} + (1 - H_\epsilon) c_{Ad}$:

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C - D \Delta C = \nabla \cdot \left(D \frac{1-K}{H_\epsilon + K(1-H_\epsilon)} C \nabla H_\epsilon \right) \quad (7)$$

The term on the right-hand side accounts for the interfacial boundary conditions (Eqs. (5), (6)). H_ϵ is a smoothed Heaviside function defined as

$$H(\psi) = \begin{cases} 0 & \text{for } \psi < -\epsilon \\ \frac{1}{2} + \frac{\psi}{2\epsilon} + \frac{1}{2\pi} \sin\left(\frac{\pi\psi}{\epsilon}\right) & \text{for } |\psi| \leq \epsilon \\ 1 & \text{for } \psi > \epsilon \end{cases} \quad (8)$$

In terms of the grid spacing Δx , the smoothing parameter ϵ was set to $1.5 \Delta x$ for the computations.

Simulation

The governing equations were implemented in the open-source CFD-toolbox OpenFOAM®. Full three-dimensional simulations of toluene droplets with an initial diameter of $d_0 = 5$ mm rising in water were carried out. The transport direction was $d \rightarrow c$, and various initial concentrations of acetone were simulated. Except for the interfacial tension, the physical properties were assumed to be independent of the acetone concentration and, consequently, the properties of pure substances were employed. The physical properties (i.e. densities, viscosities and diffusivities) were taken from Misek et al. (1985). For the interfacial tension, an exponential function of the acetone concentration in toluene was fitted to the data of Misek et al. (1985). In accordance with previous studies (Wegener et al., 2009b; Engberg et al., 2014), a distribution coefficient $K = 0.63$ was used.

The computational domain was $12 d_0$ high and $8 d_0$ deep and wide. The grid consisted of cuboid cells and was refined to a grid spacing of $16 \mu\text{m}$ in the vicinity of the interface.

Further information regarding the numerical method used in this work can be found in Engberg and Kenig (2014) and Engberg et al. (2014).

Results

Simulation results for the transient rise velocity with three different initial concentrations are shown in Fig. 1 (left). In accordance with the experimental results, Marangoni convection reduces the rise velocity. Compared with the experimental data, however, the simulated rise velocities show only mild oscillations with lower amplitudes and higher frequencies. Nevertheless, it can be stated that the general trend is represented by the simulations, and the simulated characteristic rise velocities agree well with the according experimental data, as can be seen in Fig. 1 (right). It should be kept in mind that Marangoni convection leads to a strong coupling of momentum and mass transfer. The grid is too coarse to resolve the thin boundary layer of mass transfer properly and, consequently, the simulated mass transfer rates are significantly higher than in the experiments. It is likely that a finer grid would lead to a better quantitative agreement of the transient rise velocities. Due to the higher mass transfer rates, the rise time dominated by Marangoni convection is shorter than in the experiments.

Droplet trajectories obtained from experiments and simulations with two different initial concentrations are shown in Fig. 2. In all cases, the droplet deviates from the vertical rise path, and path oscillations can be observed. Regarding the time and length scale of the path oscillations, a good agreement of experimental and numerical results was achieved.

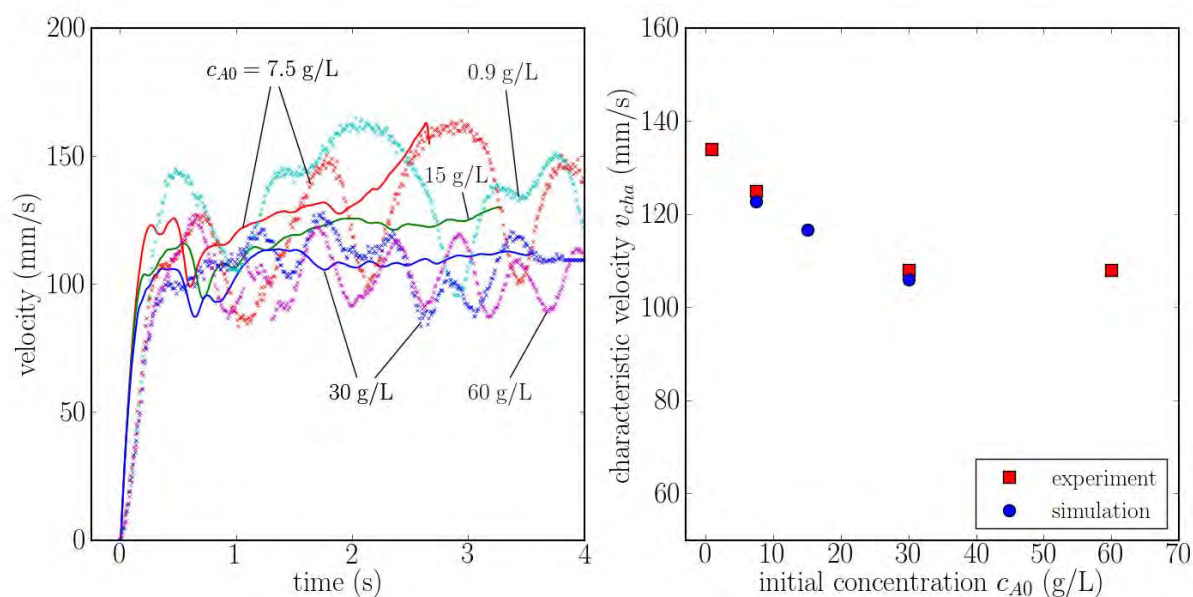


Figure 1: Experimental data (symbols) and numerical results (lines) for the transient rise velocity of toluene droplets in water with $d_0 = 5$ mm and various initial concentrations of acetone (left). The characteristic rise velocity as a function of the initial acetone concentration (right).

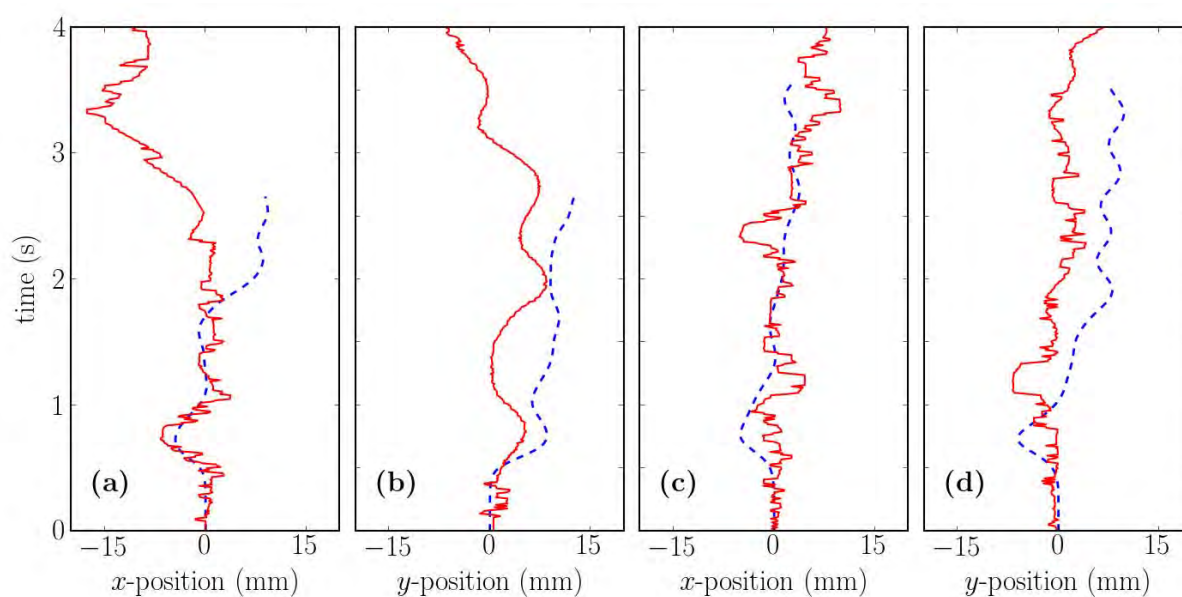


Figure 2: Droplet trajectories with Marangoni convection: Simulation results (dashed line) and experimental data (continuous line) for initial concentrations of $c_{A0} = 7.5$ g/L ((a) and (b)) and $c_{A0} = 30$ g/L ((c) and (d)).

Conclusions

In this work, the influence of Marangoni convection on the rise behavior of single oscillating droplets was studied experimentally and numerically. We focussed on toluene droplets with a diameter of 5 mm rising in water. Marangoni convection was induced by concentration differences of the transferred component acetone.

It was shown that Marangoni convection reduces the rise velocity, in accordance with the observations for smaller circulating droplets in previous studies. Furthermore, the

results reveal that this effect depends on the initial concentration of acetone. Even though the experimental rise velocities showed stronger oscillations, the experimental and the simulated data for the characteristic rise velocity were in very good accordance. A good agreement was found for the transient droplet trajectories.

References

- J. U. Brackbill, D. B. Kothe, C. Zemach, A continuum method for modeling surface tension, *J. Comput. Phys.* 100 (1992) 335-354.
- R. F. Engberg, M. Wegener, E. Y. Kenig, Numerische Simulation der konzentrations-induzierten Marangonikonvektion an Einzeltropfen mit verformbarer Phasengrenze, *Chem. Ing. Tech.* 86 (2014) 185-195.
- R. F. Engberg, E. Y. Kenig, Numerical simulation of rising droplets in liquid-liquid systems: A comparison of continuous and sharp interfacial force models, submitted to *Int. J. Heat Fluid Flow* (2014).
- Y. Haroun, D. Legendre, L. Raynal, Volume of fluid method for interfacial reactive mass transfer: Application to stable liquid film, *Chem. Eng. Sci.*, 65 (2010) 2896-2909.
- M. Kang, R. P. Fedkiw, X.-D. Liu, A boundary condition capture method for multiphase incompressible flow. *J. Sci. Comput.*, 15 (2000) 323-360.
- T. Misek, R. Berger, J. Schröter, Standard test systems for liquid extraction, *Inst. Chem. Eng.*, EFCE Publication Series, 46 (1985).
- S. Osher, J. Sethian, Fronts propagating with curvature-dependent speed: algorithms based on Hamilton-Jacobi formulations, *J. Comput. Phys.* 79 (1988) 12-49.
- M. Wegener, J. Grünig, J. Stüber, A. R. Paschedag, M. Kraume, Transient rise velocity and mass transfer of a single drop with interfacial instabilities - experimental investigations, *Chem. Eng. Sci.* 62 (2007) 2967-2978.
- M. Wegener, M. Fèvre, A. R. Paschedag, M. Kraume, Impact of Marangoni instabilities on the fluid dynamic behaviour of organic droplets, *Int. J. Heat Mass Transfer* 52 (2009a) 2543-2551.
- M. Wegener, T. Eppinger, K. Bäuml, M. Kraume, A. R. Paschedag, E. Bänsch, Transient rise velocity and mass transfer of a single drop with interfacial instabilities - Numerical investigations, *Chem. Eng. Sci.* 64 (2009b) 4835-4845.

Analysis of drop breakage in turbulent flow

Matthias Kraume, Stephanie Nachtigall

Technische Universität Berlin,

Chair of Chemical and Process Engineering,

Fraunhoferstr. 33-36, 10587 Berlin/Germany

Drop breakages occur in many liquid/liquid mixing applications in chemical, pharmaceutical or food industries. Besides the coalescence process, it directly influences the drop size distribution (DSD) which determines the efficiency of these processes.

It is widely accepted in literature that drop breakage happens when the external forces exerted on particles by the continuous phase exceed the internal forces which keep the particle together. Based on this assumption a multitude of theoretical models describing this process can be found in literature. Nevertheless, a reliable prediction of the DSD when varying for example material and process parameters is not possible even if coalescence is completely hindered. This leads to the conclusion that a deeper understanding of the drop breakage process is still needed.

In this work drop breakage in a turbulent flow comparable to the flow field in a stirred tank is investigated by high-speed imaging (see example pictures in Figure 1). A single stirrer blade, mimicking a part of a Rushton turbine is therefore mounted in a rectangular channel and induces drop breakage.

In order to describe the breakage event properly, the breakage probability, the breakage time as well as the deformations and oscillations leading to the breakage event are determined by automated image analysis. Additionally, the resulting Sauter mean diameter and the number and the size distribution of the daughter drops are evaluated.

To quantify the influence of the stabilizing forces, numerous different droplet substances with and without the addition of surfactants were investigated under the variation of the droplet diameter. Additionally, the fluid flow velocity of the continuous water phase was varied to also determine the influence of the external deforming forces.

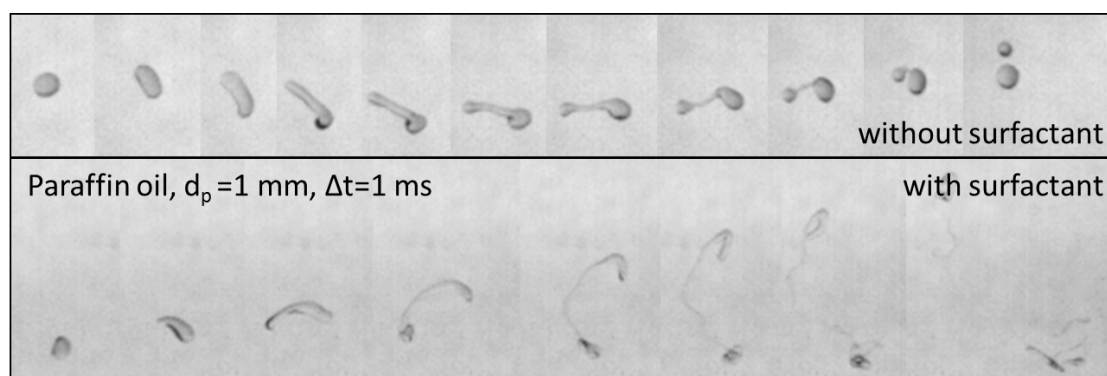


Figure 1: Breakage of a 1 mm paraffin oil droplet in a turbulent flow with different interfacial tensions.

The gained knowledge considering the breakage mechanisms should be scaled up to technical relevant mixing applications. Therefore, experiments in a standard lab scale stirred reactor (6-blade Rushton turbine, $d/T=0.33$, $H/T=1$) were conducted. Transient DSD were determined with an endoscope measurement technique and compared to the results of the single drop breakage investigations.

Interfacial dynamic in liquid/liquid extraction processes *probed by non-linear optics*

O. Diat, P.M. Gassin, J-F. Dufrêche, ICSM-UMR 5257 (CEA/CNRS/UM2, ENSCM) Bagnols sur Cèze, France; G. Martin-Gassin, ICGM, Univ. Montpellier II, France; F. Canto, L. Couston, CEA/DEN/DRCP/SE2A/LAMM, Bagnols sur Cèze ; E. Benichou, P.F. Brevet, ILM, UMR 5579, UCB Lyon 1, Villeurbanne, France

A non-linear optical technique namely second harmonic generation (SHG) is used to study the dynamics of an interfacial phenomena occurring during a liquid liquid extraction. The SHG, which consists in the conversion of two photons at the frequency ω in one photon at the doubled frequency 2ω , is a very sensitive surface technique because is forbidden in centrosymmetric media [1]. The studied system is made of a water/dodecane interface, with extractants monoamide (DEHiBA) or diamide (DMDBDMA) in an organic phase [2] and nitric ions in aqueous phase, in the frame of uranium ore or rare-earth elements extraction. We have shown for the first time that SHG measurements at equilibrium can be correlated with tensiometry measurements. Then, at out of equilibrium, a kinetic of ion transfer with different regimes as well as a dynamic highlighted through correlation function [3] were characterized as a function of the extractant concentration. Thanks to this technique, we show that extractant molecules could interact and form aggregate at the interface in a highly fluctuant way. This happens for an extractant concentration which is lower than those above which aggregates are detected (with SAXS) in the organic bulk phase. A deeper analysis [4] of this interfacial process permits to better understand the kinetics of ion transfer at a liquid/liquid interface and to be able to simulate it for industrial application.

References

- [1] S. Haslam et al, *Phys. Chem. Chem. Phys*, **2000**, 2, p.3235
- [2] V. Vidyalakshmi et al, *Solvent Extraction and Ion Exchange* **2003**, 21,p. 399; G. Martin-Gassin et al, *Phys. Chem. Chem. Phys*, 12(11) **2011**, 2138-44; G. Martin-Gassin et al, *Coll. Surf. A*, 413, **2012** pp 130–135.
- [3] X. Zhao and K. B. Eisenthal, *J. Chem. Phys.* **1995** 102, p. 5818
- [4] P-M. Gassin et al, *J. Phys.Chem C* 116 (24), **2012**, pp 13152-13160

Prediction of Interfacial Properties in Demixed Ternary Systems

*Sabine Enders^{*1}, Tommy Grunert²*

Interfacial properties, e.g. interfacial tension as well as interfacial concentration profiles, are actually not measurable in steady state working counterflow extraction columns. By neglecting the influence of the complex hydrodynamics in a column, the interfacial mass transfer is closely related to the coalescence behaviour. Additionally, relative enrichment in the interface can have a large impact on the interfacial mass transfer. Therefore, a theoretical method for the prediction of interfacial properties in ternary systems will be presented. While the prediction of interfacial tensions is in excellent agreement with experimental data, the theory will be applied on simulations for a counterflow extraction column by using the concept of equilibria stages. This procedure allows a detailed view on interfacial properties inside a counterflow extraction column and simultaneously an optimization respectively to interfacial properties and the efficiency of a column.

Introduction

While the liquid-liquid extraction processes are widely used, there are actually not fully understood. Interfacial mass transfer described by the two-layer theory [1] requires information about the concentrations in the interface, which is nowadays not accessible by measurements. Furthermore, coalescence behavior as well as Marangoni convection are strongly connected to the interfacial tension, which is not measurable in a working extraction column. For these reasons, a theoretical framework to predict interfacial properties in demixed ternary system is necessary. The focus in this work was setting on the prediction of interfacial properties with the help of a modified version of density gradient theory, which was originally developed by van der Waals [2] and rediscovered by Cahn and Hilliard [3]. Based on bulk phase data of the ternary liquid-liquid equilibrium and one experimental measuring point of the interfacial tension of the demixing binary subsystem, the interfacial tension of the demixed ternary system can be predicted. To compare the theoretical with experimental data, the reference system for extraction, namely water + acetone + toluene, was chosen. Additionally to the interfacial tension, the density gradient theory predicts the interfacial concentration profiles as well as the interfacial thickness. These results can be used for a detailed view inside a working extraction column, which is useful for further optimizations.

Theory

In order to calculate interfacial properties by using the density gradient theory, an expression for the grand thermodynamically potential is needed. Originally, Cahn and

^{*1} Corresponding Author, Technical University of Berlin, Chair of Thermodynamics and Thermal Separation Processes, BH 7-1, Ernst-Reuter-Platz 1, 10587 Berlin, Germany: sabine.enders@tu-berlin.de

² Technical University of Berlin, Chair of Thermodynamics and Thermal Separation Processes, BH 7-1, Ernst-Reuter-Platz 1, 10587 Berlin, Germany

Hilliard [3] used the Helmholtz free energy f to predict interfacial properties of a vapor-liquid equilibrium for pure substances, which is given in equation (1).

$$F = A \cdot N_V \cdot \int_{-\infty}^{+\infty} \left[f_0(\rho) + \kappa \cdot (\nabla \rho)^2 + \dots \right] dz \quad (1)$$

N_V is the Avogadro number, A is the area of the flat interface, κ the so-called influence parameter and z the local coordinate. Terms of higher order of the density gradient can be neglected. The difference between the actual free energy of the system and the free energy if the system is continuous is corresponding to the interfacial tension σ .

$$\sigma = N_V \cdot \int_{-\infty}^{+\infty} \left[f_0(\rho) + \kappa \cdot (\nabla \rho)^2 - \rho \cdot \mu^{Eq} \right] dz \quad (2)$$

The grand thermodynamically potential $\Delta\Omega(\rho)$ is by definition:

$$\Delta\Omega(\rho) = f_0(\rho) - \rho \cdot \mu^{Eq} \quad (3)$$

Insert equation (3) in (2) and using the concept of the Euler equation, equation (4) follows by changing the variable of integration from z to ρ .

$$\sigma = N_V \cdot \int_{\rho^L}^{\rho^V} \sqrt{2 \cdot \kappa \cdot \Delta\Omega(\rho)} d\rho \quad (4)$$

The influence parameter can adjusted to experimental data at one temperature and further used to predict interfacial properties. Comparing vapor-liquid equilibrium of a pure component and liquid-liquid equilibrium of an incompressible binary mixture, it is obvious that just one thermodynamically variable is changing continuously from bulk phase to bulk phase. The density changes in vapor-liquid equilibrium while the concentration changes in liquid-liquid equilibrium. Using the segment mole fraction Φ_i , equation (4) can be rewritten as:

$$\sigma = \int_{\Phi_1^I}^{\Phi_1^{II}} \sqrt{2 \cdot \kappa \cdot \Delta\Omega(\Phi_1)} d\Phi_1 \quad (5)$$

In this case the influence parameter κ loses its physical meaning, but it can be still used for an adjustment to experimental data. The grand thermodynamically potential for an incompressible binary mixture can be calculated using the Gibbs free energy:

$$\Delta\Omega(\Phi_1) = \Delta_{Mix} G(\Phi_1) / RT - \Phi_1 \cdot \mu_1^{Eq} - (1 - \Phi_1) \cdot \mu_2^{Eq} \quad (6)$$

For a binary demixing system the Gibbs energy (solid black line) and the so-called double-tangent (solid red line) is displayed in *Figure 1*. The grand thermodynamically potential is the area between the black and red line, starting and ending at the bulk phase segment mole fraction Φ_1^I and Φ_1^{II} .

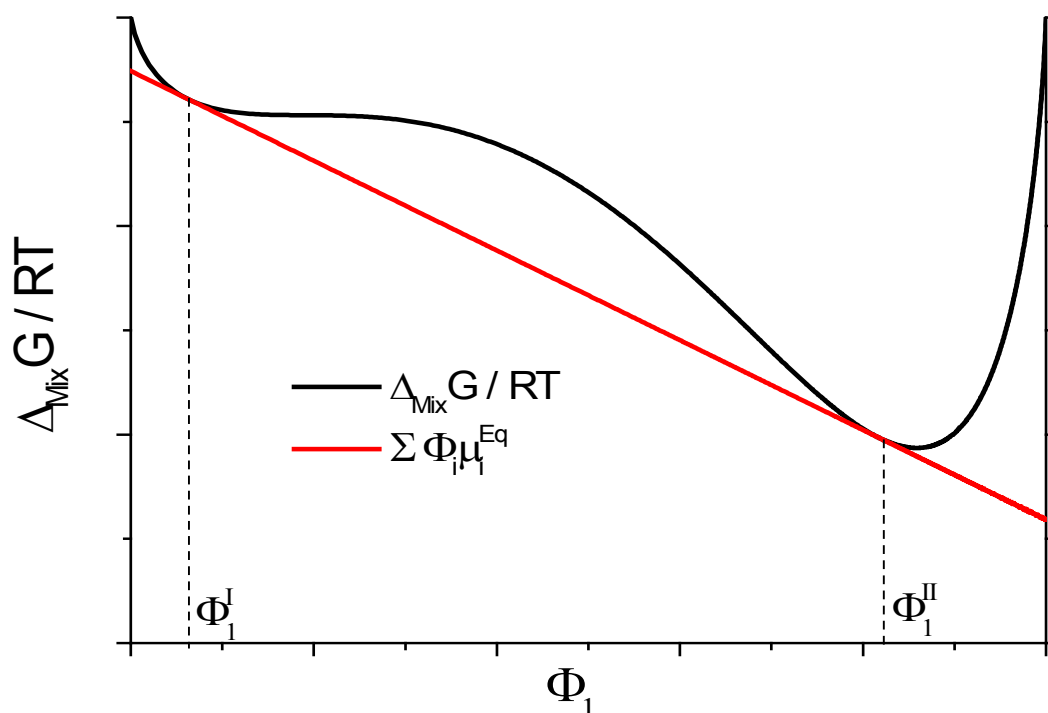


Figure 1: Gibbs energy of a demixing binary system.

For different temperatures, the grand thermodynamically potential (red filled areas) can be calculated and the result is plotted in Figure 2. Assuming an upper critical solution temperature (UCST) behaviour, the differences of bulk phases decrease by increasing the temperature from a lower level to a higher level. This leads simultaneously to a decreasing of the grand thermodynamically potential as well as interfacial tension. According to the work of Cahn and Hilliard [3], the interfacial concentration profiles and interfacial thickness can be calculated using the following expression:

$$z - z_0 = \int_{\Phi_1^I}^{\Phi_1^*} \sqrt{\frac{\kappa}{\Delta\Omega(\Phi_1)}} d\Phi_1 \quad (7)$$

z is the local coordinate corresponding to the local concentration Φ_1^* , while z_0 is the reference coordinate and can be set to zero. Switching from binary liquid-liquid equilibrium to ternary, the Gibbs energy of the mixture and the grand thermodynamically potential is calculated in the expanded procedure for ternary mixtures. Grunert *et. al.* [4] presents an expression for the interfacial tension for ternary systems with one binary demixing subsystems.

$$\sigma = \int_{\Phi_1^I}^{\Phi_1^{II}} \sqrt{2 \cdot \kappa' \cdot \Delta\Omega(\Phi_1, \Phi_2)} d\Phi_1 \quad (8)$$

The grand thermodynamically potential for a ternary mixture is given in Figure 3. It can be seen, that the grand thermodynamically potential decreases in a similar way as in the binary case by reaching the critical point (black filled star).

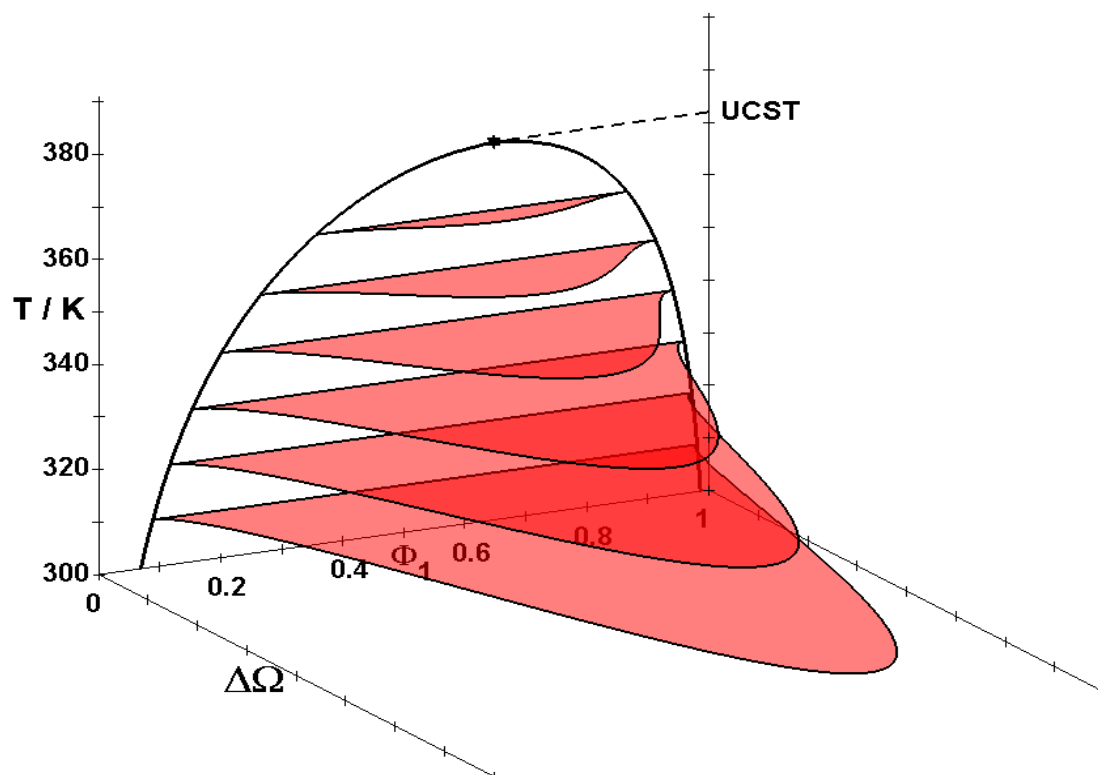


Figure 2: Grand thermodynamically potential in binary demixing system with UCST behaviour at different temperatures.

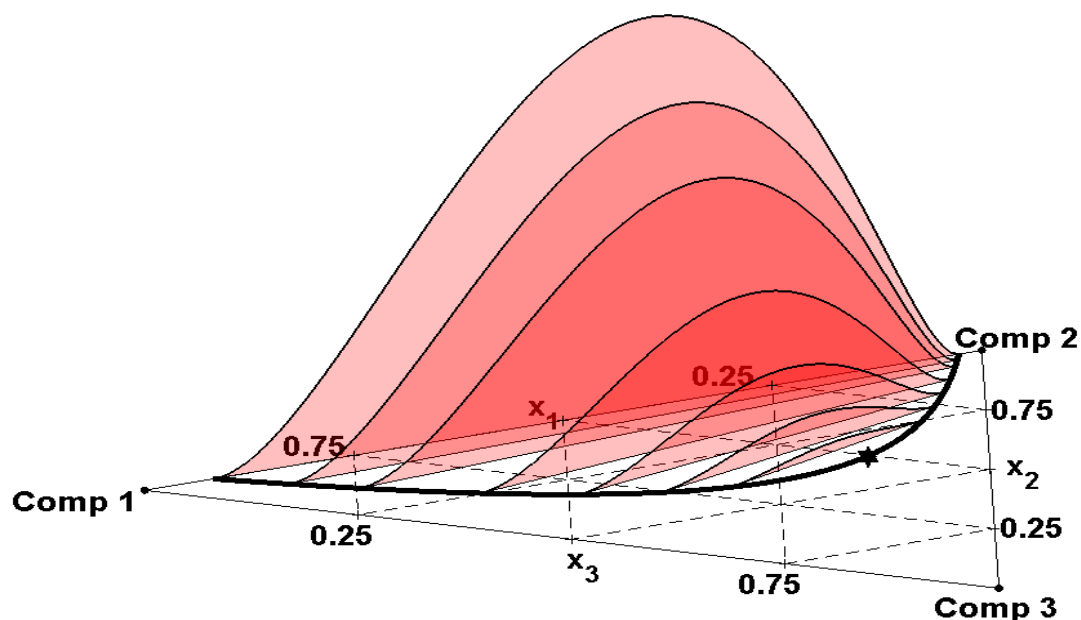


Figure 3: Grand thermodynamically potential in ternary demixing systems at a constant temperature.

The parameter κ' in equation (8) is according to the work of Poser and Sanchez [5] the influence of parameter of the ternary mixture. In case of ternary mixtures with one binary demixed subsystem, the parameter κ' is equal to the influence parameter κ of the binary demixed subsystem. This assumption allows a full prediction of the

interfacial properties of a ternary mixture, based on the bulk phase data obtained from a model for the Gibbs energy of the mixture and one experimental data point of the interfacial tension of the binary demixed subsystem.

Results and Discussion

A reference system for extraction contains water, acetone and toluene. For this reason the liquid-liquid equilibrium was calculated with a g^E -model and used for the prediction of the ternary interfacial tension.

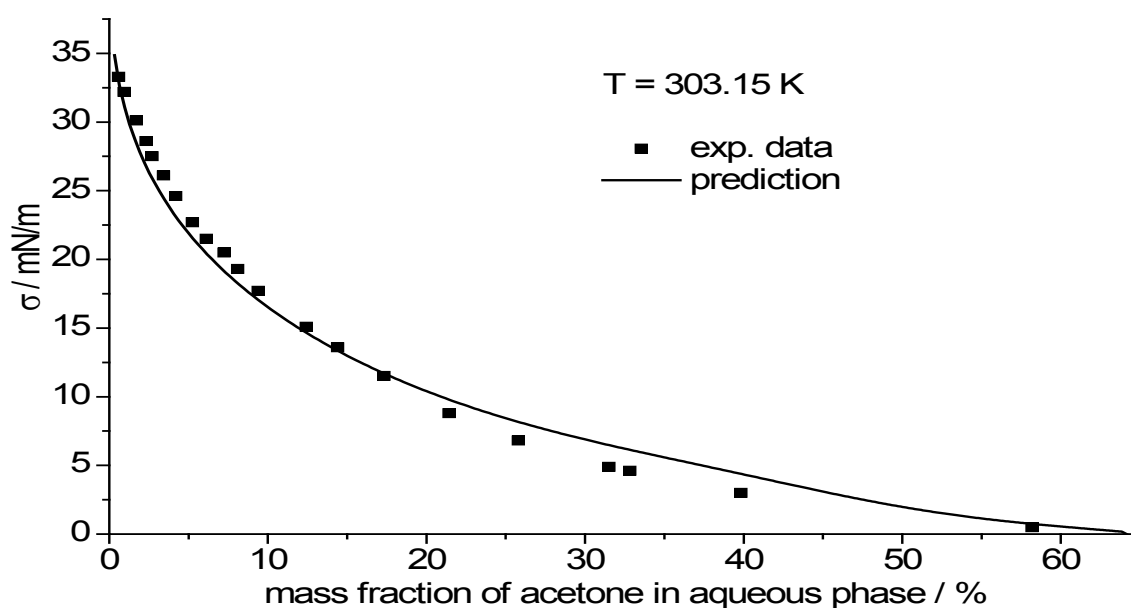


Figure 4: Predicted and measured interfacial tension of the system water + acetone + toluene at 303.15 K.

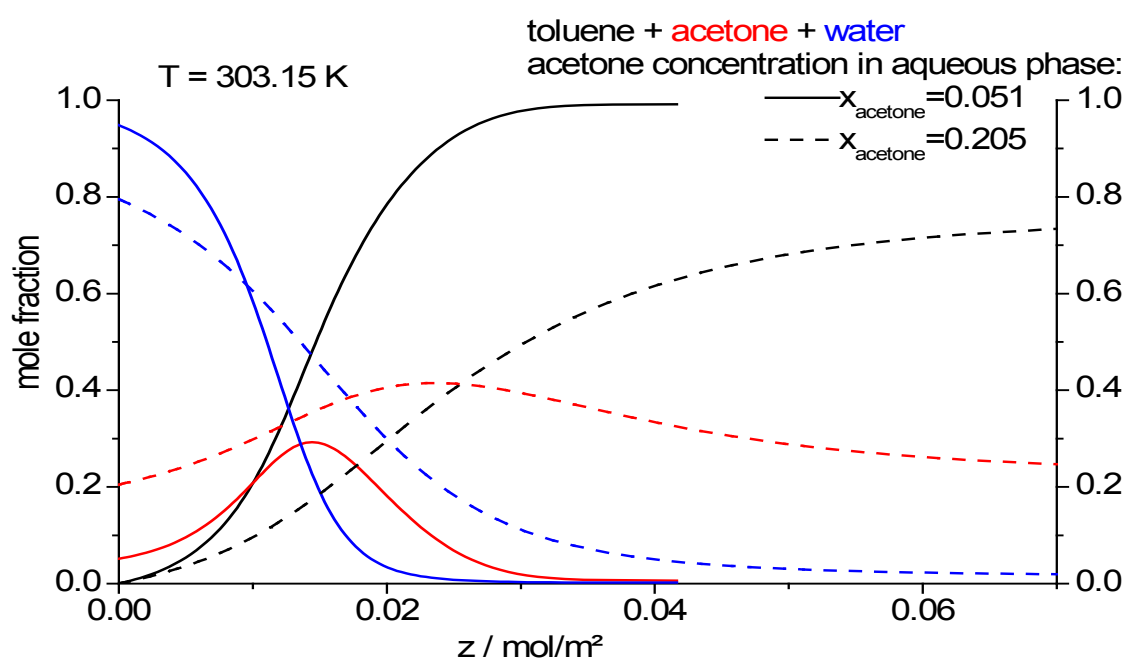


Figure 5: Interfacial concentration profiles of the system water + acetone + toluene at 303.15 K.

The influence parameter κ of the binary subsystem water + toluene was adjusted to $\kappa = 0.75 \text{ J} \cdot \text{mol} \cdot \text{m}^{-4}$ on experimental data from Prokop *et. al.* [6] at 293.15 K. *Figure 4* demonstrate the excellent accuracy of the prediction. For two different tie lines, the interfacial concentration profiles are displayed in *Figure 5*, which shows clearly enrichment behaviour of acetone inside the interface as well as larger interfacial thickness at higher acetone concentrations in the bulk phases. These information can be used to calculate the interfacial concentration profiles on each equilibrium stage in a counterflow extraction column simulation. Furthermore, the interfacial tension on each equilibrium stage can be calculated.

Summary and Outlook

The modified version of the density gradient theory in combination with a g^E - model is able to predict interfacial properties of ternary mixtures with excellent agreement to experimental data. Furthermore, the interfacial concentration profiles and interfacial tensions can be used in extraction column simulations to display thermodynamically properties on each equilibrium stage, which are actually not measureable. The next step is the extension to mixtures with more complex components as well as more complex miscibility gaps. The column simulations using the concept of equilibrium stages will give a detailed view in the interface inside a working extraction counterflow column at isothermal conditions as well as at non-isothermal conditions. Information about interfacial properties in a column can be used for its optimization or even better understanding of thermodynamically phenomena, for instance Marangoni convection, coalescence behavior or even interfacial mass transfer.

Acknowledgement

The author thanks the German research foundation (DFG) for financial support.

References

- 1 Sattler, K.; Feindt, H. J.; Thermal Separation Processes, VCH, Weinheim, 1995
- 2 van der Waals, J. D. , Doctoral Dissertation, Leiden University: Leiden, The Netherlands, 1873.
- 3 Cahn, J. W.; Hilliard, J. E., J. Chem. Phys. 1958, 28, 258-267.
- 4 Grunert, T.; Rudolph, H.; Enders, S., Z. Phys. Chem. 2013, 227, 269-284.
- 5 Poser, C. I.; Sanchez, I. C., Macromolecules 1981, 14, 361-370.
- 6 Prokop, R. M.; Hair, M. L.; Neumann, A. W., Macromolecules 1996, 29, 5902-5906.

Evaluation of a Hydrocyclone Technology for Separation of Industrial Extraction Systems

Esayas W. Barega^a, Edwin Zondervan^a, André B. de Haan^a, Wouter Hoek^b, Katarina Babic^c

^a. Eindhoven University of Technology, The Netherlands, ^b. Lyondell Basell, The Netherlands, ^c. DSM, The Netherlands

Summary

A hydrocyclone technology was experimentally evaluated for the separation of two industrial extraction systems; caprolactam-toluene-water, and ethyl benzene (EB)-methyl benzyl alcohol (MBA)-water. Preliminary experiments were performed up to a maximum continuous phase flowrate of 96 l/hr and at phase ratio of 10% v/v with the aqueous phase dispersed in the organic phase. For the caprolactam-toluene-water system, an entrainment of 8.8% v/v aqueous phase in the organic overflow was found. For the EB-MBA-water system, the entrainment increased to 14.3% v/v. The organic phase entrainment in the aqueous phase was 7.67% v/v and 27.9% v/v for the caprolactam-toluene-water and EB-MBA-water systems, respectively. Since satisfactory separation was not possible, the setup was modified to accommodate higher flowrates up to 1800 l/hr. Operation at high flowrates of 500-1500 l/hr and with 10% v/v phase ratio with phases recycling back to feed tanks did not result in the expected better separation. It rather caused in a quick accumulation of the aqueous phase in the feed organic stream due to re-entrainment. Therefore, operation of the hydrocyclone was performed at a low phase ratio of 1% v/v. For this phase ratio, an aqueous content in the organic overflow stream less than 2% v/v was achieved from the feed aqueous content of about 25% v/v for the caprolactam-toluene-water system. For the EB-MBA-water system, the separation efficiency was dependent on whether MBA is present. In the absence of MBA, an aqueous content in the organic overflow down to 200 ppm was obtained from the aqueous feed content of about 40% v/v. However, 7.7% v/v aqueous phase was entrained in the organic overflow, when MBA was present. In both investigated systems, there was a significant 20-30% v/v organic phase in the underflow aqueous stream.

1. Introduction

Hydrocyclones have commonly been used for a number of gas/solid and liquid/solid separations, where there is a significant density difference between phases (1). Applications are also reported for liquid/liquid separations, mainly in oil industry to remove the residual oil remaining in the water phase after the gravity settlers (2). In this research, a technical feasibility study was made to evaluate a hydrocyclone technology for the separation of two systems used in chemical industry, caprolactam-toluene-water and ethyl benzene (EB)- α -methyl benzyl alcohol (MBA)-water.

Hydrocyclones achieve separation using the energy of the fluid to generate a vortex, which induces a centrifugal acceleration up to 100x larger than a gravitational acceleration (3). The swirling flow reduces the residence time required to separate the micro droplets due to the centrifugal acceleration. As no external energy is used to create the vortex, the flowrate should be high enough to create sufficient centrifugal force (4). The dispersed particles are separated by moving either towards the wall or the core of the hydrocyclone based on their specific gravity relative to the continuous phase (5). Advantages of the hydrocyclone are small residence time required (1-2 s) for the separation compared to several minutes in a gravity settler, a simple structure, a smaller equipment size, and a lower investment and maintenance cost (4). Encountered challenges are also numerous. The density difference for liquid/liquid systems is small, compared to gas/liquid or solid/liquid systems, in the order of 200 kg/m³, thus, the separation becomes difficult and a lower separation efficiency is obtained. In addition, due to the sensitive nature of the dispersed phase in liquid/liquid sys-

tems, there is a possibility of further breakup of drops, which again lowers the efficiency of separation (6), (7). Furthermore, the separation efficiency is influenced by the split ratio (ratio of the underflow to the overflow), which is determined by whether the organic or aqueous phase is continuous, and therefore, can lead to loss of the organic phase to aqueous phase.

2. Materials and Methods

2.1. Materials

Toluene (purity >99%) was supplied by Merck Germany. ϵ -caprolactam (purity >99%), ethyl benzene (EB) (purity >99%), and α -methyl benzyl alcohol (MBA) (purity >99%) were supplied by Sigma-Aldrich (USA). Milli-Q super distilled water was used for all the experiments.

The set up used for the hydrocyclone experiments is depicted in Figure 1, for which flowrates up to 1800 l/hr could be used. The setup consists of two tanks for the organic and aqueous phases, two gear pumps for pumping each phase, two variable area flowmeters, a tee mixer followed by a pipe for mixing phases, and a hydrocyclone for the separation of phases. Tanks with a capacity of 50 l were used for the experiments. The aqueous and organic phase pumps have a capacity of 2 l/min and 30 l/min, respectively. The two phases were mixed in a pipe, which has an inner diameter of 19.05 mm and a length of 550 mm. The dispersion was then fed to the hydrocyclone, which has an outer diameter of 47 mm and a length of 927 mm.

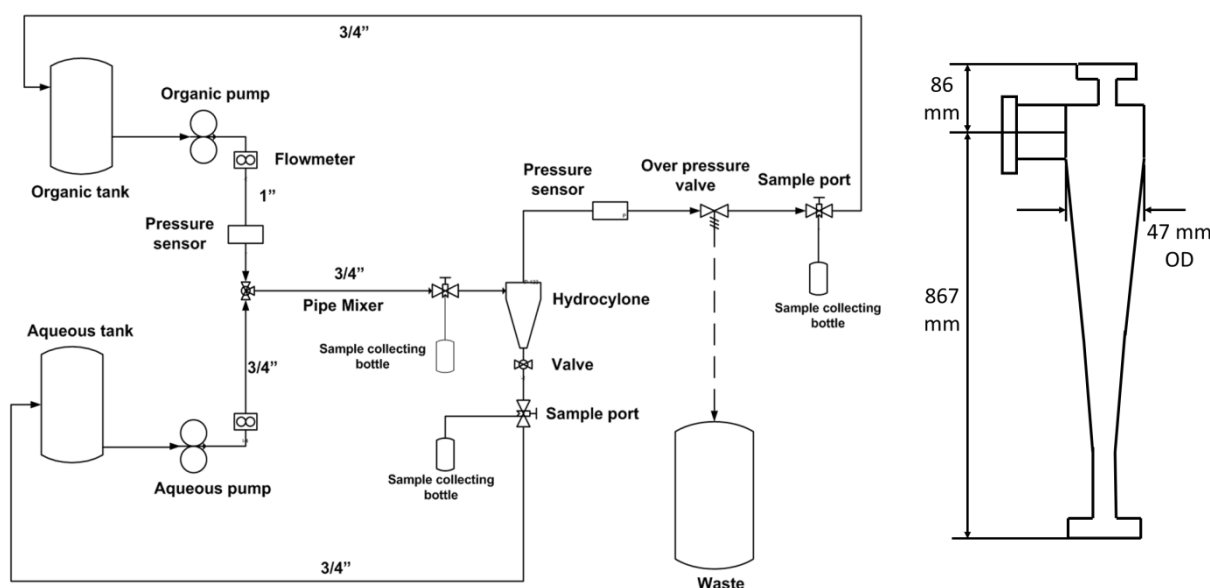


Figure 1: The hydrocyclone experimental setup for the separation of immiscible liquids

2.2 Methods

Prior to the experiments, the organic and aqueous phases were prepared for each system. For the caprolactam-toluene-water system, an equilibrated amount of caprolactam in toluene and Milli-Q water was prepared. A 28.51% (w/w) caprolactam concentration in the aqueous phase was used. For the EB-MBA-water system, 33% (v/v) of MBA in EB was used as organic phase and Milli-Q water as an aqueous phase.

The prepared organic and aqueous phases were fed to the tanks. Subsequently, they were first recirculated at a lower flowrate to ensure equilibrium. During hydrocyclone separation experiments, the organic pump flowrate was adjusted between 96 l/hr to 1800 l/hr whereas the aqueous flow was adjusted to 10% of the organic flowrate. For

both investigated systems, the aqueous phase was dispersed in the organic phase in similar manner to an industrial process. After steady operation was established, a 40 ml sample of the inlet stream to the hydrocyclone was taken through a sample port at the inlet. Additionally, 40 ml samples of organic and aqueous phases were taken from the overflow and underflow of the hydrocyclone, respectively. All the experiments were performed at a temperature of 20°C.

3. Results

3.1 Preliminary results at low flowrate

Figure 2 depicts the aqueous content in the organic overflow stream from the hydrocyclone for the caprolactam-toluene-water and EB-MBA-water systems at a continuous phase flowrate of 96 l/hr. For both systems, the complete separation was not possible. This can be concluded from a relatively large aqueous phase present (6.3-33.3% v/v) in the organic overflow stream. Additionally, Figure 2 clearly shows that the aqueous content in the organic overflow is lower for the caprolactam-toluene-water (6.3 and 8.3% v/v) compared to the EB-MBA-water system (14.3 and 33.3% v/v). This can be attributed to a higher continuous phase viscosity and a smaller density difference between phases for the EB-MBA-water system, which lowers the separation efficiency. Figure 2 further illustrates the influence of nozzle size on the separation. It can be observed the nozzle size barely have influence on the separation behavior for the caprolactam-toluene-water system. However, for the MBA-EB-water system, a significantly lower aqueous content in the organic stream was found with an overflow nozzle size of 3 mm compared to 5 mm. The comparison of organic phase content in the aqueous underflow stream is also shown in Figure 2. For both systems, especially for the EB-MBA-water system, there is considerable organic phase present in the aqueous underflow. Nevertheless, the organic content is much lower for the caprolactam system (6.7 and 7.7% v/v) compared to the EB-MBA-water system (27.9 and 42.9% v/v).

3.2 Results with modified setup

Since the aim is to reach ppm levels of the aqueous phase in the organic overflow stream, the separation results obtained from the preliminary experiments are not satisfactory. Therefore, the setup was redesigned and reconstructed to accommodate higher flowrates of the continuous phase up to 1800 l/hr as depicted in Figure 1 with the idea of establishing sufficient centrifugal force in the hydrocyclone and thereby improve the separation efficiency.

The comparison of product separation is shown in Figure 3 for overflow nozzle sizes of 3 mm and 5 mm, and at a continuous phase flowrate of 720 l/hr. It can be observed that the aqueous contents of the feed stream now lie between (20-25)% v/v compared to the previously obtained values of (>80% v/v) for both nozzle sizes.

For a 5 mm overflow nozzle, the aqueous content in the organic stream could be reduced from 24% v/v in the organic feed stream to 10% v/v in the organic overflow. For aqueous contents (22-24)% v/v in the feed, a considerably lower aqueous phase in the organic overflow of 0.5% v/v was found with a 3 mm overflow nozzle size compared to 10% v/v obtained with a nozzle size of 5 mm. This improvement of separation can be attributed to the reduction in the bypassing of the feed stream to the overflow. Nevertheless, decreasing the overflow nozzle size also increased the pressure drop thus limited the throughput that could be used. For the same flowrate of 720 l/hr, a pressure drop of 3.3 bar was measured with an overflow nozzle size of 3

mm. This is significantly higher compared to a pressure drop of only 0.5 bar, which was obtained with an overflow nozzle size of 5 mm.

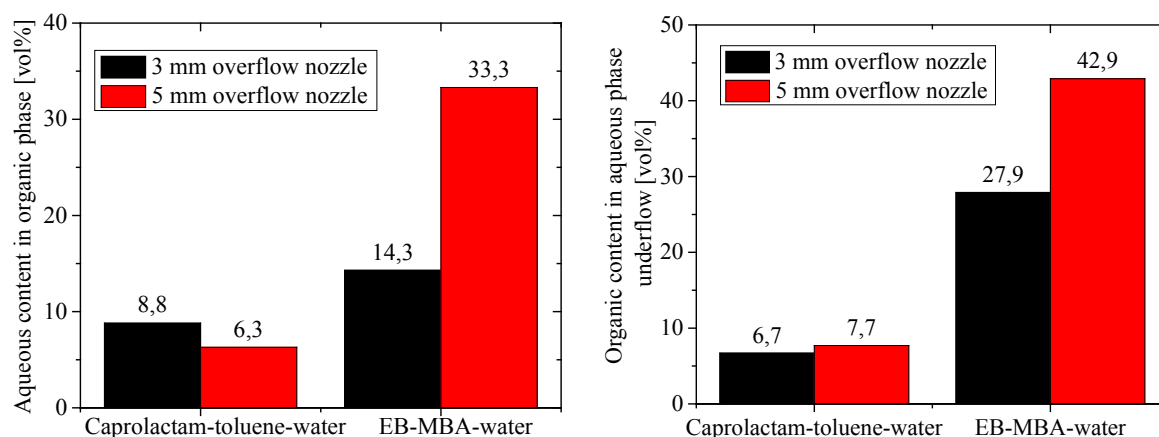


Figure 2: Left: Comparison of aqueous phase entrainment in the organic phase for the caprolactam-toluene-water and EB-MBA-water systems. Flowrate of continuous phase= 96 l/hr, phase ratio=10% v/v. Right: Comparison of organic phase entrainment in the aqueous phase for the caprolactam-toluene-water and EB-MBA-Water systems. Flowrate of continuous phase= 96 l/hr, phase ratio=10%

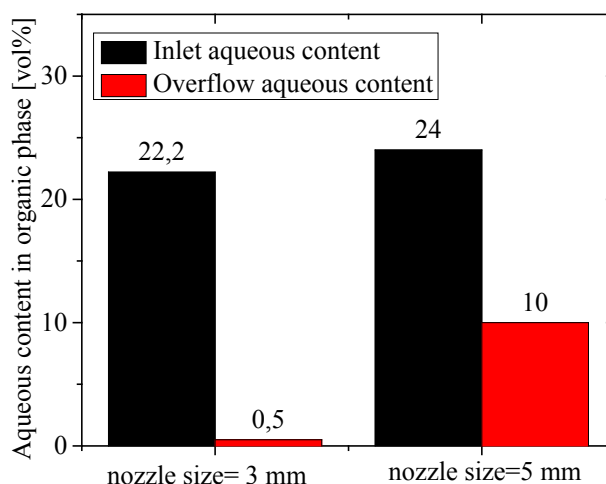


Figure 3: Effect of nozzle size on product stream separation by a hydrocyclone i.e., without aqueous phase pumped and product stream from previous streams with aqueous content >80% v/v for the caprolactam-toluene-water system

Preliminary experiments showed that continuous separation of the product without pumping any aqueous phase eventually leads to a low aqueous content organic feed to the hydrocyclone. Therefore, experiments were performed at an aqueous/organic phase ratio of 1% v/v and with recycling of both phases. This was done to maintain a relatively constant aqueous feed content to the hydrocyclone. The experiment was carried out with an overflow nozzle size of 3 mm and at a continuous phase flowrate of 720 l/hr. Sampling of the feed and overflow streams was performed at different times. Good separation could be obtained consistently as shown in Figure 4. For feed aqueous contents of 15-17% v/v, a separation efficiency greater than 90% was found. Thus, it can be concluded from Figures 3 and 4 that for the caprolactam-toluene-water system satisfactory separation could be obtained, when the aqueous content fed to the hydrocyclone is low <25% v/v. At higher water content regions, no separation was possible. This is because of the decrease of density difference between the phases and an increase in the viscosity of the dispersion with increased dispersed phase content, which reduced the separation efficiency.

The separation was evaluated for the MBA (33%)-EB(67%)-water system at flowrates of 540 l/hr and 720 l/hr, and with an overflow nozzle size of 3 mm. Figure 5 clearly shows that the separation with EB-water is much better than for EB-MBA-water case. The better separation obtained for the EB-water system can be attributed to its higher density difference with the aqueous water phase and its lower viscosity due to MBA absence. Moreover, it can be observed from Figure 5 that the separation efficiency is higher at a flowrate of 720 l/hr compared to 540 l/hr.

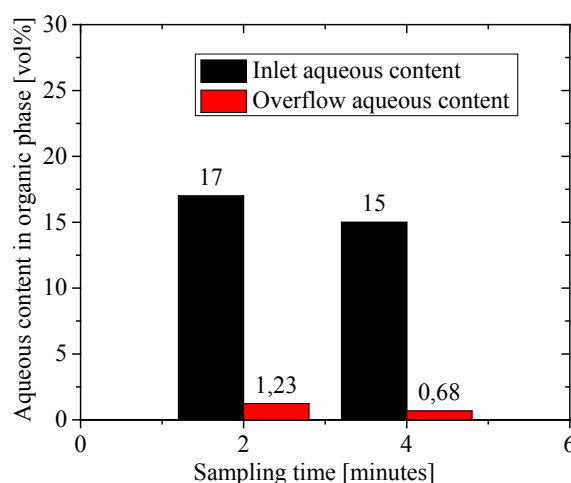


Figure 4: Aqueous content in the organic phase at the inlet and overflow of the hydrocyclone for a caprolactam-toluene-water system at two sampling times. The separation experiment was carried out by pumping both phases at aqueous/organic at a flow ratio of 1%. Flowrate of the continuous phase=720 l/hr, and nozzle size=3 mm

Furthermore, the organic content in the underflow aqueous phase was determined. Figure 6 reveals that depending on the flowrate, there is 20-30% v/v organic phase present in the aqueous underflow stream.

Therefore, as in the case of caprolactam-toluene-water, additional separation is needed to separate the lost organic phase from the aqueous underflow stream. In general, the separation efficiency obtained for the MBA-EB-water system was poor compared to the EB-water and caprolactam-toluene-water systems.

Thus, some strategies should be devised to increase the separation efficiency in case of the MBA-EB-water system. One option to do this could be for example by increasing the density difference between the phases using salts recycled from the process. Another option could be by increasing the density of aqueous phase using a more concentrated NaOH-water as an aqueous phase.

4. Conclusions

A hydrocyclone technology was experimentally evaluated for the separation of two industrial extraction systems; caprolactam-toluene-water, and EB-MBA-water. Complete separation of the organic and aqueous phases was not possible. The separation especially with an aqueous/organic phase ratio of 10% v/v and with phases recycled was poor, since it quickly built up the aqueous phase concentration in the organic feed stream to values greater than 80% v/v. However, much better separation was observed when operating at an aqueous/organic phase ratio of 1% v/v. This maintained feed aqueous contents in the organic phase of <25% v/v and <40% v/v for the caprolactam-toluene-water and EB-MBA-water system, respectively. Under these conditions, an aqueous content in the organic overflow down to 2% v/v and less than 200 ppm was obtained for the caprolactam-toluene-water and EB-water systems, respectively. For the MBA-EB-water system, the separation was poor and only a 60%

separation efficiency could be achieved. With respect to organic loss, a 20-30% v/v organic phase was present in an aqueous underflow for both investigated systems. The effect of flowrate and nozzle size on the separation efficiency was also investigated. Separation efficiencies of 60% and more than 90% were found with overflow nozzle sizes of 5 mm and 3 mm, respectively. The flowrate used should be high enough since the preliminary experiments with a maximum flowrate of 96 l/hr could not achieve the required purity levels of the overflow organic stream. Subsequent experiments with flowrates of 540 l/hr and 720 l/hr could get to low levels of aqueous content in the organic phase except for EB-MBA-water system.

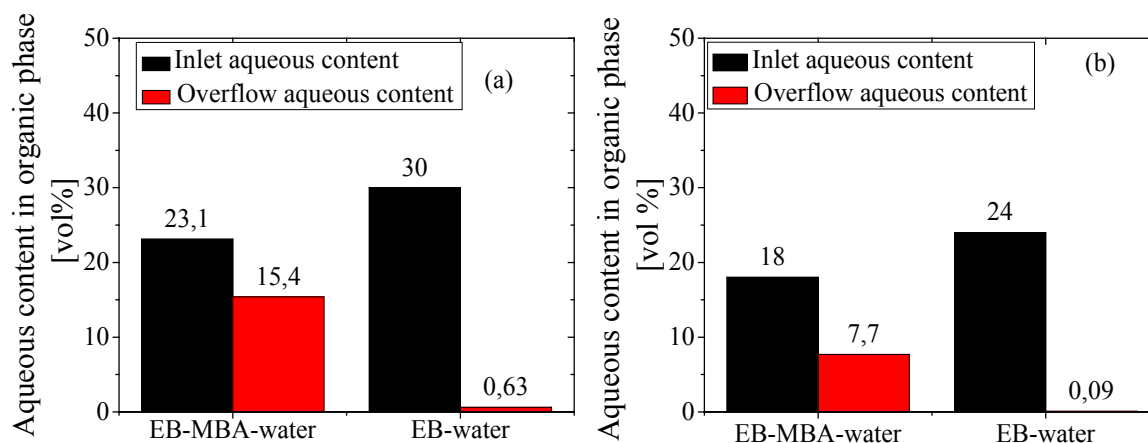


Figure 5: A comparison of aqueous content in the organic phase at the inlet and overflow of the hydrocyclone for EB-water and EB-MBA-water systems. The separation experiment was carried out by pumping both phases at aqueous/organic at a flow ratio of 1% v/v using an overflow nozzle size of 3 mm, and at a continuous phase flow rate of a) 540 l/hr, and b) 720 l/hr

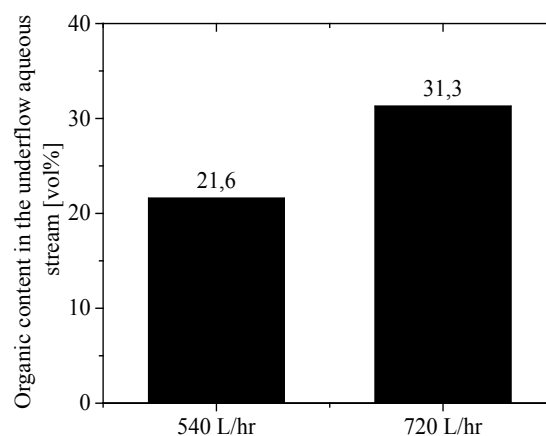


Figure 6: Organic content in the underflow aqueous stream from the hydrocyclone for EB-MBA-water system at continuous phase flowrates of 540 l/hr and 720 l/hr. The separation was carried out by pumping both phases at aqueous/organic flow ratio of 1% v/v using an overflow nozzle size of 3 mm

References

1. Ortega-Rivas, E. Hydrocyclones. *Ullmann's encyclopedia of industrial chemistry*. Weinheim : Wiley-VCH Verlag GmbH&Co, 2007.
2. Young, G.A.B., Wakeley, W.D., Taggart, S.L., Worrell, A.J.R. 1994, J.Pet.Sci.Eng., Vol. 11, p. 37.
3. Simkin, D.J. and Olney, R.B. 1956, AIChE J., Vol. 2, p. 545.
4. Husveg, T., Rambeau, O. Drengstig, T., Bilstad, T. 2007, Minerals Eng., Vol. 20, p. 368.
5. Bradley, D. *Hydrocyclones*. s.l. : Pergamon Press Ltd., 1965.
6. Schubert. *Liquid/Liquid Hydrocyclone*. 5,071,557 USA Patent, 1991.

7. *Hydrocyclone Performance with Complex Oil-Water Emulsions in the Feed.* **Belaidi, A. Thew, M.T., Munaweera, S.J.** 2003, *Canad. J. Chem. eng.*, Vol. 81, p. 1159.

Operating window of a multistage rotor-rotor spinning disc extractor

Job Vissers, Roy van Kouwen, Spinid BV, Eindhoven, The Netherlands; Katarina Babić, DSM, Geleen, The Netherlands; Jaap C. Schouten, John van der Schaaf, Eindhoven University of Technology, The Netherlands

The operating window of a novel multistage rotor-rotor spinning disc extractor (MSDE) is demonstrated here. The MSDE has a low inventory (0.1 L/stage), a short residence time (5-10 s/stage) and high mass transfer rates ($\sim 1-4$ 1/s). The MSDE comprises a series of contacting stages with an encasing as outer rotor and an impeller as inner rotor. These rotors co-rotate with a difference in rotation speed. The difference in inner/outer rotation speed emulsifies two immiscible liquids of different density. The joint rotation generates a centrifugal force that separates the light phase from the emulsion near the axis and the heavy phase at the rim of the outer rotor. Because of the special configuration of the inner rotor, the light liquid is pumped from left to right, whereas the heavy liquid flows from right to left by pressure force. Thus a countercurrent contacting mode is established from stage to stage. A high separation efficiency of the emulsion in each stage is vital for the performance of the MSDE. From experiments in a three stage MSDE with a water/heptane system, we identify an operating window of inner/outer rotation speeds that result in $>99.9\%$ separation efficiency as a function of heavy and light phase flow rates. On the left side of this window, the separation efficiency decreases because the difference in inner/outer rotation speed generates an emulsion that is too stable to be fully separated by centrifugal force. On the right side of this window the inner rotor's pumping capacity is too high and pumps the heavy phase out of the light phase outlet. An increase in water/heptane flow ratio shifts the right boundary of the window to the right, a decrease shifts the right boundary to the left. No effect of flow ratio on the left boundary of the window was observed. The operating window defines the capacity of the MSDE as a function of flow rates, flow ratio, and inner/outer rotation speeds for the water/heptane system. Furthermore, a rough prediction of the separation efficiency can be made for higher rotation speeds, for higher flow rates, and for other systems than water/heptane.

Investigation of the reactive extraction of terpenylamines with an acid-base reaction

Robin Schulz, Rebecca van den Bongard, Bartos Szemplinski, Tim Zeiner, Andrzej Górak

TU Dortmund University, Laboratory of Fluid Separations

Emil-Figge-Str. 70, 44227 Dortmund, Germany

Phone: +49 (0) 231 755-3034, E-Mail: robin.schulz@bci.tu-dortmund.de

Suggested theme: Process chemistry and engineering

Presentation preference: Oral presentation

Terpenylamines are a feedstock for production of polyamides based on renewable resources. They are made of terpenes, derived for example from tree resin. Thus, they do not compete with food production, like many other renewable resources and are already industrial available.

Terpenylamines are synthesized by a hydroamination of terpenes and a secondary amine. A model reaction is the conversion of β -myrcene with morpholine. Since morpholine is not soluble in myrcene it is provided from an aqueous phase, which forms a liquid-liquid-two-phase-system with myrcene. The reaction only takes place at the interface of these two phases. The product dissolves only in the organic phase and has to be purified in the following step.

Due to the comparable physical properties between terpenylamine and myrcene, purification is a challenge. In a solvent screening for extraction no suitable solvent was found. But if terpenylamine is protonated by an acid-base reaction it forms salt and dissolves in an aqueous phase. By neutralization an organic phase with terpenylamine it can be recovered.

To gain knowledge of the capability of protonating the terpenylamine with an acid a systematic investigation regarding the influencing parameters is necessary. First, a screening with different acid groups is carried out, and then different acids of the most suitable acid group are screened. Finally, the influence of temperature and concentration is investigated. For neutralization, the water and acid is evaporated and only organic residues remain in the solution.

The acid groups of hydrohalic acids, mineral acids, carboxylic acids, dicarboxylic acids and substituted carboxylic acids were examined. Only the group of carboxylic acids, exemplary investigated with acetic acid, works without decomposition of the terpenylamine. It was found that the temperature has no influence on the extraction, but the acid concentration has an influence on yield and selectivity. For higher acid concentration the equilibrium concentration of the acid-base reaction to the salt increases.

An acid can protonate the terpenylamine without destructing the molecular structure. Subsequently, the protonated terpenylamine can be extracted with the aqueous phase and an organic phase with almost pure terpenylamine is formed during neutralizing. The preferable acid for purification of the terpenylamine is acetic acid. The transferability to the industrial scale is shown by the investigation in a multi-stage mixer-settler-unit.

The project "Sustainable Chemical Synthesis (SusChemSys)" is co-financed by the European Regional Development Fund (ERDF) and the state of North Rhine-Westphalia, Germany, under the Operational Programme "Regional Competitiveness and Employment" 2007 - 2013.

Citric Acid Extraction by Liquid Surfactant Membranes in a Continuous Pilot Plant

*Adriane Salum^{*1}, Cibele Konzen¹, Juliana S. Barbosa¹, Estêvão M. R. Araújo¹, Julio C. Balarini¹, Tânia L. S. Miranda¹, Luiz Claudio Meira-Belo²*

Summary – In this work, citric acid was extracted from synthetic solutions by liquid surfactant membranes (LSM) in a mechanically agitated column similar to a Kühni-type. The experimental work was carried out using a continuous phase composed of synthetic solutions of citric acid at 10% w/v and a dispersed phase formed by primary emulsion composed of organic phase containing 20% w/w of Alamine 336, 2% w/w of Infineum 9268 and 78% w/w of Exxsol D 240/280 and aqueous inner phase containing sodium acetate and Li⁺ solutions (tracer) at 4.0 mol.L⁻¹ and 0.1 mol.L⁻¹, respectively. In order to study some hydrodynamic and mass transfer parameters of this system, the total hold-up ($\phi = 5.1\%$) was calculated from the mean local values. The globules distribution, mean Sauter diameter ($d_{32} \sim 1.0$ mm) and interfacial area ($134 \text{ m}^2.\text{m}^{-3}$) were obtained using a phase ratio dispersed/continuous equals to 1/1 (F_d/F_c), and total throughput $F_t = 2 \text{ L.h}^{-1}$, column impeller speed equals to 145 rpm and organic phase/stripping phase ratio equals to 3/1. At this operation condition, more than 50% of the citric acid could be recovered from the continuous phase using 20 extraction stages. From the obtained results, it was possible to estimate the mean slip velocity ($4.3 \times 10^{-3} \text{ m.s}^{-1}$) and the global mass transfer coefficient of the continuous phase ($1.3 \times 10^{-6} \text{ m.s}^{-1}$).

Introduction

The extraction process by liquid surfactant membranes comprises water-oil-water multiple emulsions which are used to separate and/or concentrate several organic or metallic species. Separation of organic acids by liquid surfactant technique, particularly of citric acid, from fermentation broths or synthetic solutions, at different concentrations, has been done for a few years, with promising results in bench scale¹⁻⁷.

The LSM process is closely similar to the solvent extraction (SX) technique, with changes in the extraction and stripping stages, which occur simultaneously due to the formation of a multiple emulsion. This emulsion is formed in two steps. In the first one, emulsification step, the stripping solution is finely dispersed into the solvent or membrane phase, producing the primary emulsion. It is important to note that the solvent phase, in addition to the carrier and diluent, usually contains a surfactant used to reduce the interfacial tension between the aqueous and organic phases to ensure the stability of the extraction system. In the second one, permeation step, the primary emulsion is dispersed into the feed phase, producing a double emulsion, which is composed of primary emulsion globules (dispersed phase) dispersed into

^{*1} Departamento de Engenharia Química, Escola de Engenharia, Universidade Federal de Minas Gerais - UFMG, Belo Horizonte - Brazil.

E-mail: salum@deg.ufmg.br. Phone number: +55 031 3409 -3678.

² Centro de Desenvolvimento da Tecnologia Nuclear – CDTN/CNEN, Belo Horizonte, Brazil

the feed phase (continuous phase). Two additional steps, settling and demulsification, finalise the separation process and they are employed to promote the phase separation and the recovery of the stripping solution containing the desired solute, respectively.

This similarity between both processes allows that equipment normally used in liquid-liquid extraction, particularly columns, be utilised in the LSM process with minimal or without change in its design. Thus, hydrodynamic and mass transfer parameters can be, in principle, measured and/or estimated by following the same procedure used in the SX technique.

In order to evaluate the citric acid extraction by liquid surfactant membranes in a continuous scale, a mechanically agitated column similar to a Kühni-type was used in LSM pilot plant and some hydrodynamic parameters and the global mass transfer of the feed phase were determined using aqueous synthetic solutions.

Experimental Work

The extraction experiments were performed using three synthetic solutions prepared according to the compositions presented in Table 1.

Tab. 1 – Composition of the extraction system used in the pilot unit

Phase	Composition	Concentration	Phase Ratio
Inner (I)	CH ₃ COONa	4.0 mol.L ⁻¹	1
	Li ₂ SO ₄	0.05 mol.L ⁻¹	
Membrane (II)	Alamine 336 (carrier)	20% w/w	3
	Infineum 9268 (surfactant)	2% w/w	
	Exxsol D 240/280 (diluent)	78% w/w	
Feed (III)	C ₆ H ₈ O ₇ (synthetic solution)	10% w/v	4

The emulsification step was carried out in a high shear homogenizer at 6.000 rpm and at room temperature. The permeation run and the settling were carried out in a similar Kühni-type column with 60 mm of internal diameter, free cross section of the stator plates equals to 30%, 20 extraction stages and 1.68 m of height. This run was performed using a phase ratio dispersed /continuous (primary emulsion/feed phase) equals to 1/1 (F_d/F_c), total throughput $F_t = 2 \text{ L.h}^{-1}$, column impeller speed equals to 145 rpm and room temperature. The demulsification was carried out in a continuous electrostatic demulsifier coupled to an A.C. high voltage source at 4.7 – 5.8 kHz.

The extraction concentration profiles were determined using six sampling points: at the top of the column, 4th, 8th, 14th and 18th extraction stages and at the bottom. The citric acid concentration in the samples was determined by complexometric titration with Cu²⁺ ions^{4,8}.

The local hold-up was determined by the calculation of the volume ratio between dispersed phase and total mixture volume collected at the sampling points. The total

hold-up (ϕ) was calculated from the mean local values. After determining the total hold-up, the slip velocity ($\bar{v}_s$) could be calculated from Equations (1)^{10,11} and (2)¹²:

$$\bar{v}_s = \frac{1}{C_R} \left(\frac{U_d}{\phi} + \frac{U_c}{(1-\phi)} \right) \quad (1)$$

$$C_R = 0.75 S_\phi + 0.25 \quad (2)$$

The globule size distribution (Φ_v), mean Sauter diameter (d_{32}) and interfacial area (a_{int}) were obtained from digital image registration of the multiple emulsion globules during the column operation. The diameters of the globules were estimated by the Hough Circle Detection software⁹ and globule size distribution was obtained using the maximum drop-size distribution¹³, as expressed in Equation 3:

$$\Phi_v(d) = \frac{\delta}{\pi^{1/2}} \exp(-\delta^2 w^2), \quad (3)$$

$$w = \ln[\beta d / (d_m - d)].$$

The mean Sauter diameter (d_{32}) and interfacial area (a_{int}) could be calculated from Equations (4)¹³ and (5)¹⁴, respectively:

$$d_{32} = \frac{d_m}{\left[1 + \beta \exp(1/4\delta^2) \right]}, \quad (4)$$

$$a_{int} = \frac{6C_R\phi}{d_{32}}. \quad (5)$$

The overall mean mass transfer coefficient of the feed phase was estimated by equation (6)^{4,14}:

$$\bar{k}_{oc} = \frac{F_c^{\text{in}} C_c^{\text{in}} - F_c^{\text{out}} C_c^{\text{out}}}{a_{int} \cdot A \cdot h_{col} (C_c^{\text{out}} - C^*)} \quad (6)$$

Results

The citric acid concentration profiles in the feed phase were obtained along the column operation and are presented in Figure 1. These profiles indicate that at low flow rates ($F_d = F_c = 1 \text{ L.h}^{-1}$), the steady state is reached after 5 hours of operation, in the mixture section. At the under settler, it would be necessary more than 6 hours to reach this condition because the homogenisation is slower and it is basically due to the descending flow of the aqueous phase from the column. The Figure 1 also shows that the citric acid concentration in the feed phase at the outlet of the column, in the steady state, is approximately 5% w/v, representing an extraction of at least 50% of the solute initially present in the continuous phase after 20 extraction stages.

The determination of the total hold-up indicated that 5.1% of the mixture volume into the column was composed by multiple emulsion globules. Higher hold-ups could be obtained increasing the flow rates. However, for this system, this is not indicated

because the settling of the loaded emulsion at the top of the column can be compromised by the reduction in the time for phase separation. Based on the obtained hold-up value, the slip velocity of the globules ($4.3 \times 10^{-3} \text{ m.s}^{-1}$) was estimated from Equation (1).

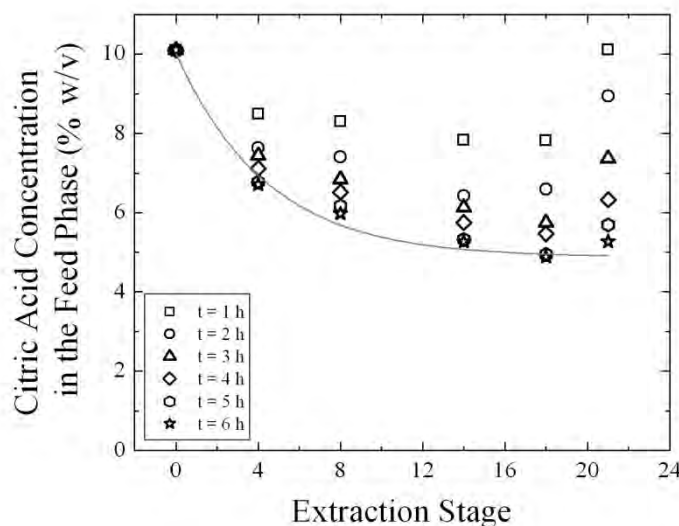


Fig. 1 – Citric acid concentration profiles along the column ($F_d = F_c = 1 \text{ L.h}^{-1}$)

The mean Sauter diameter and the interfacial area for mass transfer were determined using the maximum drop-size distribution to describe the experimental data, as presented in Figure 2. Diameters of about 400 globules were measured directly from the photographs to compose these data.

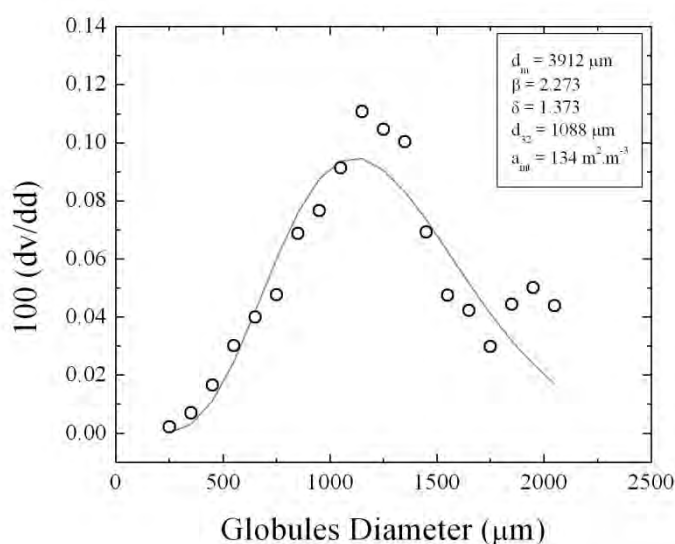


Fig. 2 – Volumetric differential distribution as a function of the globules diameter

According to this figure, the maximum diameter distribution gives a good fit. The experimental data present some dispersion, as expected, but the distribution parameters β (2.273) and δ (1.373), and the maximum globule diameter d_m

(3912 μm) could be easily determined using the methodology proposed by Mugele and Evans¹³ (1951). From these data, d_{32} was estimated in 1088 μm and the a_{int} in 134 $\text{m}^2.\text{m}^{-3}$.

The estimation of the mean Sauter diameter and the interfacial area is essential for determining the mass transfer coefficient. In this case, $\bar{k}_{\text{oc}}$ ($1.3 \times 10^{-6} \text{ m.s}^{-1}$) was calculated using Equation (6), which was based on the overall mass balance for the entire column for liquid-liquid extraction systems. Two main simplifications were done: the citric acid concentration at equilibrium was considered null, supposing that all solute is promptly stripped to the inner phase; and the mean k value was calculated instead of local one because the swelling produces volumetric changes in the continuous and dispersed flow rates. Thus, inlet and outlet flow rates were used as well as citric acid concentration at the feeding and at the bottom point. The column height was also used instead of compartment height to compose the global mass balance.

Conclusions

The citric acid extraction from aqueous synthetic solution was performed in a LSM pilot plant, using a mechanically agitated column similar to a Kühni-type. Promising results were obtained at the studied operation condition, in which more than 50% of the citric acid could be recovered from the continuous phase using 20 extraction stages. Some hydrodynamic parameters and the overall mass transfer coefficient of the feed phase were estimated.

This preliminary study in pilot plant showed that the LSM technique can be efficiently used to citric acid extraction. Other operation conditions should be still evaluated to provide more efficient separation conditions to recover this organic acid.

Nomenclature

a_{int}	interfacial area ($\text{m}^2.\text{m}^{-3}$)	<i>Greeks</i>	
A	column cross section (m^2)	β	size distribution parameter
C	citric acid concentration ($\text{kg}.\text{m}^{-3}$)	δ	size distribution parameter
C_R	constriction factor (dimensionless)	Γ	gamma function
d	globule diameter (μm)	ϕ	total hold-up
d_{32}	mean Sauter diameter (μm)	Φ_V	size distribution function
d_m	maximum globule size (μm)	<i>Superscripts and Subscripts</i>	
F	volumetric rate ($\text{m}^3.\text{s}^{-1}$)		
F_t	total throughput ($\text{m}^3.\text{s}^{-1}$)		
h_{col}	mixture section height of the column (m)	in	at the top column
$\bar{k}_o$	mean overall mass transfer coefficient ($\text{m}.\text{s}^{-1}$)	out	at the bottom column

S_ϕ	fractional free cross section of the stator plates (dimensionless)	*	equilibrium
U	volumetric flow ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	c	continuous
$\bar{V}_s$	slip velocity ($\text{m} \cdot \text{s}^{-1}$)	d	dispersed

References

1. Boey, S. C., Garcia Del Cerro, M. C., Pyle, D. L. Extraction of Citric Acid by Liquid Membrane Extraction. *Chem. Eng. Res. Des.*, v.65, p.218-223, 1987.
2. Del Cerro, C., Boey, D. Liquid Membrane Extraction. *Chem. Ind.*, p.681, 7 Nov., 1988.
3. Stoica-Guzun, A., Juncu, G. And Floarea, O. Batch Extraction of Citric Acid with Liquid Surfactant Membranes. *Chemical Engineering & Technology*, v.22, p.65-69, 1999.
4. Konzen, C., Estudo da Técnica de Extração por Membranas Líquidas Surfactantes Aplicada à Separação de Ácido Cítrico. Dissertação de mestrado, Universidade Federal de Minas Gerais (in portuguese), Belo Horizonte, 2000.
5. Mendes, E. G., Konzen, C., Salum, A., Miranda, T. L. S. Estudo de Caracterização do Sistema de Extração de Ácido Cítrico por Membranas Líquidas Surfactantes. *Anais do XVI Congresso Brasileiro de Engenharia Química – COBEQ 2002*. Natal: Abeq, 2002.
6. Manzak, A., Tutkun, O. Extraction of Citric Acid Through an Emulsion Liquid Membrane Containing Aliquat 336 as Carrier. *Separation Science and Technology*, v.39, n.10, p.2497-2512, 2004
7. Yordanov, B., Boyadzhiev, L. Pertraction of Citric Acid by Means of Emulsion Liquid Membranes. *Journal of Membrane Science*, v.238, p.191-197, 2004.
8. Graffmann, Von G., Domels, H., Sträter, M. L. Schnelle Bestimmung von Citratat in Wasch- und Reinigungsmitteln durch Titration mit Cu-Lösung. *Fette Seifen Anstrichmittel*, v.76, n.5, p.218-220, 1974.
9. Andersen, F. Hough Circle Detection: software livre, 2009. Disponível em: <<http://sourceforge.net/projects/circledetection/>>.
10. Weiss, J., Steiner, L., Hartland, S. Determination of Actual Drop Velocities in Agitated Extraction Columns. *Chemical Engineering Science*, v.50, n.2, p.255-261, 1995.
11. Kumar, A., Hartland, S. A Unified Correlation for the Prediction of Dispersed-Phase Hold-Up in Liquid-Liquid Extraction Columns. *Ind. Eng. Chem. Res.*, v.34, p.3925-3940, 1995.
12. Goldmann, G. *Ermittlung und Interpretation von Kennlinienfelder einer gerührten Extraktionskolonne*. München: Technische Universität München, 1986 (Ph.D. Thesis) apud KUMAR, A., HARTLAND, S. A Unified Correlation for the

- Prediction of Dispersed-Phase Hold-Up in Liquid-Liquid Extraction Columns. *Ind. Eng. Chem. Res.*, v.34, p.3925-3940, 1995.
13. Mugele, R. A., Evans, H. D. Droplet Size Distribution in Sprays. *Industrial & Engineering Chemistry*, v.43, n.6, p.1317-1324, 1951.
 14. Pratt, H. R. C., Stevens, G. W. Selection, Design, Pilot-Testing and Scale-up of Extraction Equipment/Axial Dispersion. In: THORNTON, J. D. *Science and Practice of Liquid-Liquid Extraction*. Oxford: Clarendon Press, 1992.

The use of option trees for the selection of solvents and reactive extractants for the design of biocompatible separation processes

Andreas Bednarz, RWTH Aachen University, AVT – Thermal Process Engineering, Aachen, Germany, Peter Scherübel, TU Graz, Institute of Chemical Engineering and Environmental Technology, Graz, Austria, Antje Spieß, RWTH Aachen University, AVT –Enzyme Process Engineering, Aachen, Germany, Andreas Pfennig, TU Graz, Institute of Chemical Engineering and Environmental Technology, Graz, Austria

Nowadays, organic value components are often produced through complex processes based on petrochemical raw materials. Biotechnological processes have not been able to compete in this field of production, mainly because of their raw-material price. The introduction of economically competitive bio-based products into the market is a current task for scientists and engineers. The development of biocompatible separation technologies for this objective has been investigated in the recent years.

To support the evaluation and decision process in process design challenges the variety of processes and downstream alternatives was structured with the help of a cascaded option tree in which the alternatives and corresponding process criteria are visualized and evaluated. From this option tree the project partners could easily infer the challenges and problems every possible process alternative presents, in order to derive the necessary experiments for proof of feasibility as well as process design. Preliminary investigation and experiments were performed with the focus on alternative downstream processes for the intermediate and product streams. Especially extraction and reactive extraction were investigated, focusing on the biocompatibility of the process. The successful preliminary investigations led to the selection of feasible systems with reactive extractant and diluent. These were followed by single-drop experiments on sedimentation and mass transfer to allow the modelling of the process with the simulation tool ReDrop. The fluid dynamics of the system were simultaneously investigated in column experiments to validate the accuracy of the model.

In the presentation, the results on the reactive extraction of an organic value component and the cascaded option tree generated in this project will be shown. The approach of solvent and reactive extractant selection which can easily be transferred to other extraction tasks and the results of the performed experiments will be presented.

Centrifugal partitioning chromatography - multistage aqueous two phase extraction of biopharmaceutical products

Christopher Ladd Effio, Stefan A. Oelmeier, Jürgen Hubbuch

Karlsruhe Institute of Technology, Institute of Process Engineering in Life Sciences, Section IV: Biomolecular Separation Engineering, Karlsruhe, Germany

Aqueous Two Phase Extraction (ATPE) is gaining increasing importance as alternative, cost-efficient downstream process step for biological products like proteins, antibodies, viruses and cells. Aqueous two phase systems (ATPS) are most often composed of a polymer and salt in aqueous solution providing mild conditions for biomolecules. Separation from contaminants like host cell proteins (HCP), nucleic acids, cells and cell debris is achieved by differences in partitioning behaviour. Hence, ATPE is a promising method for capturing biopharmaceutical products from complex feedstocks like cell culture broths or cell lysates. While capacity and yield are only limited by the product solubility, the separation efficiency depends on physicochemical properties of contaminants and predominantly on the type of operation. Batch ATPE is a suitable method for the initial capture step in a downstream process, but provides low separation efficiency due to mass transfer limitations. A promising technique for multistage and large scale extraction is centrifugal partitioning chromatography (CPC). CPC is a liquid-liquid chromatography method: one phase of an ATPS is retained by a centrifugal field while the other phase is used as mobile phase. The separation mechanism is based on different migration velocities of molecules due to their difference in partitioning over the two immiscible liquid phases. In general the separation efficiency in CPC depends on three parameter groups: sample properties, system characteristics and operation settings.

The present work focuses on the evaluation of CPC as alternative purification step for proteins. Besides the separation of model proteins, the purification of industrial feedstocks was investigated. Case studies on monoclonal antibodies expressed in mammalian cells and virus-like particles (VLPs) derived from insect cells are presented. VLPs are composed of multiple copies of recombinantly expressed viral structural proteins which assemble into particles almost indistinguishable from the original virus. VLPs carry no genetic information and are therefore gaining increasing importance in vaccine technology, gene therapy and diagnostics.

For mammalian and insect cell feedstocks a solubility-guided process development approach was conducted by microscale extraction on a robotic liquid handling station. Studies were performed in 96 well plates with a sample consumption of less than 10 mg protein per plate and experimental times of only three hours per screening. ATPS screenings with different polymers, salts, tie-line lengths and pH values enabled the selection of adequate systems for the scale-up from 650 μ L batch systems to a 500 mL CPC column. Results demonstrate the high potential of CPC for the purification of biopharmaceutical products pointing out chances and limitations of the technique.

Multistage Monoclonal Antibody Purification by Aqueous Two-Phase Extraction - Experiment and Modeling

Jan Mündges, Jessica Zierow, Tim Zeiner

TU Dortmund, Laboratory of Fluid Separations, 44227 Dortmund, Germany

Monoclonal Antibodies (mAbs) are biologically active proteins produced by plasma cells in response to the presence of foreign substances. During the past years, the application of mAbs for therapeutic treatment of several diseases like cancer, asthma or autoimmune diseases has been increasing causing a high mAb demand. Through an intensified research on the field of upstream-processing, the mAb concentration in the fermentation broth has significantly been increased. Since purification of mAbs is a challenging step in the manufacturing process accounting for a major part of the total production costs, growing interest exists in finding alternative downstream-processing methods.

Aqueous two-phase systems (ATPS) are a promising option for the improvement of mAb purification. By mixing two different phase forming components, e.g. two hydrophilic polymers or a hydrophilic polymer and a salt in water at high concentration, two liquid phases can form. Purification of mAb is achieved because of a different partitioning of target component and impurities between both phases. Especially for sensitive products ATPS are a promising alternative as they offer mild separation conditions at high, continuous capacity.

Purpose of this work is the investigation of mAb purification from cell supernatant (CS) by aqueous two-phase extraction (ATPE). An ATPS consisting of polyethylene glycol 2000 (PEG), phosphate salt and water is applied for investigation. From literature and prior experiments it is known, that additional sodium chloride (NaCl) significantly influences mAb partitioning and selectivity. Therefore, multistage ATPE experiments with and without additional NaCl were performed in a Mixer-Settler Unit (MSU). The influence of flow rate, stage number and phase ratio on mAb purity and yield will be presented. Multistage experimental results were used to validate a process model, which is based on single stage equilibrium experiments, to describe multistage ATPE of mAb from CS. The model for multistage extraction significantly reduces the experimental effort. Accordance of multistage MSU results and modeling data as well as its impact on the downstream process will be discussed.

Predicting Phase Behavior of Aqueous-Protein Solutions

Christoph Brandenbusch, Christian Kress and Gabriele Sadowski

*Technische Universität Dortmund, Biochemical and Chemical Engineering,
Laboratory of Thermodynamics, Emil-Figge-Str.70, 44227 Dortmund, Germany*

The development of industrial scale bioprocesses has come into high scientific and industrial interest over the last decades. Especially in the red and white biotechnology, process costs are often dominated by up to 80 % by the downstream processing. First investigated in 1896, aqueous two-phase systems (ATPS) were shown to have an enormous potential for the extraction of valuable biomolecules (e.g. monoclonal antibodies). In general, ATPS show a high biocompatibility and are cheap in comparison to chromatographic methods. The most common ATPS consist of a hydrophilic polymer and a salt serving as phase-forming components. The distribution of the target protein within these systems can either be influenced by the choice of the phase forming components, or by a choice of an additional displacement salt. The latter is investigated within this work. The displacement salt influences both the solubility and the distribution of the protein between the two phases. Thus, knowledge of the influence of the different salts potentially useful to enhance the distribution coefficient is necessary.

One promising and fast measure accounting for complex interactions of biological macromolecules is the second osmotic virial coefficient (B_{22}) characterizing the interactions between the biological macromolecules in solution and the cross virial coefficient (B_{23}) characterizing interactions of the biological macromolecules with the salts / impurities. It combines the different influence factors such as pH, temperature, solvent, salt and salt concentration within one measure.

B_{22} as well as B_{23} data was measured for different proteins and salts in aqueous solution. The results were then used to characterize the distribution behavior of the target protein in the ATPS dependent on the displacement salt. The results point to the fact, that based on B_{22} and B_{23} the suitability of a salt as displacer for proteins in aqueous two-phase systems can be estimated. Furthermore the influence of the displacer on the solubility of the protein can be judged qualitatively serving as an ideal first measure in the development of aqueous two-phase extraction systems.

The results will help to improve the development and optimization of ATPS used for efficient separation of processes.

Ionic Liquid-based Three Phase Partitioning for protein recovery

*Enrique Alvarez-Guerra^{*1}, Angel Irabien²*

Summary

Downstream processing usually represents between 50 and 80% of the total production costs of proteins, since conventional methods to purify proteins (e.g. chromatography) are time and cost consuming, so they constitute the major bottleneck of the technical and economic viability of valorization processes. The aim of this work is the development of an alternative technique to recover proteins called Ionic Liquid-based Three Phase Partitioning (ILTPP). This technique uses Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) that lead to results that are characteristic of Three Phase Partitioning (TPP), since it promotes the accumulation of the target solute at the interface between the two liquid phases: ionic liquid-rich and salt-rich phases. ILTPP is applied to the recovery of lactoferrin (LF), a bovine whey protein that stands out due to its important nutraceutical properties.

The systems based on 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmimTfO) and dihydrogenophosphate-based salt are identified as the most suitable to perform ILTPP. Other ionic liquid/salt systems do not form two liquid phases or a coherent protein layer, or they may suffer from a lack of stability. In these BmimTfO-based systems, between 83 and 98% of the LF is accumulated at the liquid-liquid interface. LF recovery is higher at moderate acidic pH (3.1-4.0) and relatively low protein contents in the system. Depending on the pH, the LF selectivity with respect to BSA (another whey protein) varies between 3 and 1, so ILTPP can be used to recover more specifically an individual protein or a group of them. Furthermore, the ILTPP process can be carried out without net reagent consumption if the salt-rich phase is concentrated by means of vacuum evaporation, which enhances the economic and environmental profiles of the technique.

This work concludes that ILTPP can be seen as a promising technique to recover proteins such as LF from waste streams or complex media. It has been demonstrated that ILTPP combines the advantages of both ILATPS and TPP but, in contrast, it overcomes the main drawbacks associated with these methods: the difficulties to recover the target solute from the ionic liquid-rich phase and the use of volatile organic solvents (t-butanol), respectively.

Introduction

Proteins of interest are usually produced in highly complex media, so their separation and recovery implies complicated downstream processes, which may represent between 50 and 80% of the total production cost of proteins [1]. Therefore, separation and purification of proteins becomes a bottleneck in biotechnology, since conventional protein purification methods are time and cost consuming [2]. Liquid-liquid extraction techniques based on the use of ionic liquids show a great potential for the mentioned purpose, because the advantages related to extraction and ionic liquids are combined, overcoming the drawbacks associated with conventional volatile organic solvents [3]. Among the different available techniques, Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) are considered the common alternative to extracting biomolecules [4].

^{*1} Corresponding Author, Dpto. de Ingenierías Química y Biomolecular, Universidad de Cantabria, Santander, Spain; e-mail: alvarezge@unican.es

² Dpto. de Ingenierías Química y Biomolecular, Universidad de Cantabria, Santander, Spain

ILATPS are usually constituted by hydrophilic ionic liquids and inorganic salts that promote the formation of two aqueous phases: an ionic liquid-rich and a salt-rich phases. These systems provide several advantages, such as biocompatibility, high capacity and yield, low viscosity, little emulsion formation or quick phase separation [5]. Therefore, many different types of biomolecules have been extracted by means of ILATPS [6]: proteins, amino acids, pharmaceuticals, alkaloids... Nevertheless, despite their relevance for the process development, the recovery of the extracted solutes and the ionic liquid recyclability is not addressed in most of the literature concerning extraction with ionic liquids [7].

For this reason, a new technique called Ionic Liquid-based Three Phase Partitioning (ILTPP) is proposed. It uses the same ionic liquid/salt systems as ILATPS to achieve results that are characteristics of Three Phase Partitioning (TPP) [7]. TPP is a simple, efficient technique which can recover proteins at the liquid-liquid interface between the two phases formed by the salt (generally ammonium sulfate) and the organic solvent (generally t-butanol) added to the protein solution [8]. As a result, ILTPP combines the advantages of both ILATPS and ILTPP. On the one hand, the accumulation of the protein of interest at the interface makes its recovery easier, so the back extraction step is not required and the process is simplified, avoiding the main disadvantage related to the use of ILATPS. On the other hand, ILTPP does not require any volatile organic solvent such as t-butanol because ionic liquid are used instead.

The aim of the present work is the development of the ILTPP technique so that a suitable ionic liquid/salt system is identified to perform the process. ILTPP is applied to recover lactoferrin (LF), a bovine whey protein that presents important nutraceutical properties and nowadays is obtained at industrial scale by means of cation-exchange chromatography [9, 10]. The recovery of Bovine Serum Albumin, BSA (another whey protein) is also assessed so that values of ideal selectivities can be reported. Furthermore, the recyclability of the ionic liquid is studied and alternatives to reduce the amount of ionic liquid that cannot be reused are developed, since that has a great influence on the economic and environmental profile of the ILTPP process.

Methodology

The partition of proteins among the different phases of the ILTPP systems is carried out following the experimental procedure shown in Figure 1 [7]. As can be seen, once the desired amounts of each reagent are added to the centrifuge tubes, they are mixed at 30 rpm during 30 min in a horizontal rotating shaker. Then, centrifugation at 4000 rpm during 5 min is used to enhance phase separation and, after 90 min in when tubes are allowed to set in a thermostatic bath, the protein content in each phase is determined by means of Bradford method [11].

Regarding the studies about the ionic liquid recyclability, the composition of fluid phases was determined according to the experimental procedure reported by Neves et al. [12].

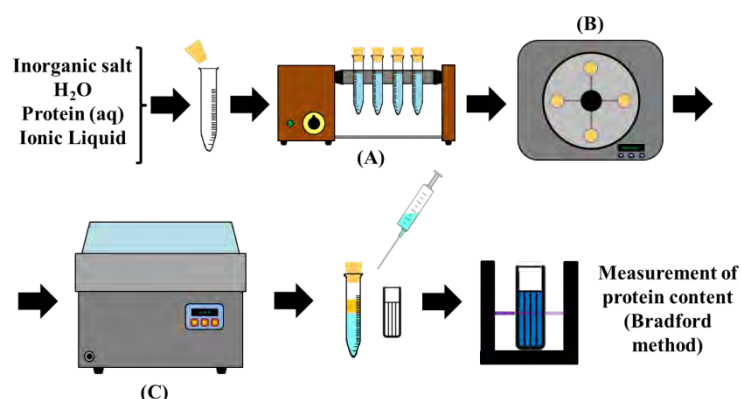


Fig. 1-Experimental procedure to study the protein distribution in the ILTPP systems [7]. (A) Horizontal rotating shaker. (B) Centrifuge. (C) Thermostatic bath.

Results and discussion

Selection of the ILTPP system

The ionic liquid/salt systems used in ILTPP must fulfill several characteristics so that this technique can be developed. In this way, these systems must form two liquid phases in which all the added salt is dissolved and induce the formation of a coherent, dense protein layer at the interface. Moreover, the ionic liquid should be stable in contact with water. Table 1 shows the assessment of several ILTPP systems according to the previous criteria [13].

Table 1-Main characteristics of several ionic liquid (IL)/salt systems used to perform ILTPP. Notation: green (the system fulfills this characteristic), red (the system does not fulfill this characteristic).

IL/salt system	System composition		Main characteristics				
	[IL] (w/w%)	[Salt] (w/w%)	Complete salt dissolution	Two liquid phases	Protein layer at the L-L interface	Dense/consistent protein layer	IL stability
BmimBF ₄ /NaH ₂ PO ₄	20.0	22.0	Green	Green	Green	Green	Red
Bmimdca/NaH ₂ PO ₄	20.0	22.0	Green	Green	Red	Red	Green
BmimTfO/NaH ₂ PO ₄	20.0	22.0	Green	Green	Green	Red	Green
	23.3	26.3	Green	Green	Green	Green	Green
	26.5	30.5	Red	Green	Green	Green	Green
BmimOAc/NaH ₂ PO ₄	20.0	22.0	Green	Red	Red	Red	Green
	26.5	30.5	Red	Green	Red	Red	Green
BmimBF ₄ /(NH ₄) ₂ SO ₄	20.0	22.0	Green	Green	Red	Red	Red
BmimTfO/(NH ₄) ₂ SO ₄	23.3	26.3	Green	Green	Green	Red	Green

As can be seen, systems based on BmimBF₄ suffer from a lack of stability when they are in contact with water, because they can be hydrolyzed. When Bmimdca or BmimOAc are selected as the ionic liquid of the system, the protein layer at the

interface cannot be formed and most of the protein is extracted into the ionic liquid-rich phase, which is not the aim of ILTPP. Therefore, the system constituted by intermediate concentrations of BmimTfO and NaH_2PO_4 is identified as the most suitable to carry out the process, since they fulfill all the ILTPP requirements.

Performance of the ILTPP technique with BmimTfO/ NaH_2PO_4 -based systems.

The recovery of LF and BSA at the liquid-liquid interface of BmimTfO/ NaH_2PO_4 systems is studied at several pH, remaining constant the ionic strength due to the inorganic salt. Table 2 reports the fraction of each protein recovered at the interface, as well as the LF/BSA selectivity, $S_{\text{LF/BSA}}$ [13].

Table 2-Influence of the pH on the protein recovery at the liquid-liquid interface and LF selectivity with respect to BSA, $S_{\text{LF/BSA}}$.

pH	[BmimTfO] (w/w%)	[NaH_2PO_4] (w/w%)	% recovered at L-L interface		$S_{\text{LF/BSA}}$
			LF	BSA	
3.1	22.7	27.9	98.1 ± 1.1	32.3 ± 4.5	3.04 ± 0.46
4.0	23.3	26.3	98.3 ± 1.7	56.6 ± 7.0	1.74 ± 0.24
5.5	24.6	22.0	82.9 ± 2.5	54.8 ± 4.4	1.51 ± 0.17

The fraction of LF recovered is clearly higher than the fraction of BSA: whereas between 83 and 98% of the LF is accumulated at the interface, this range decreases to 32-57% for the BSA. Both proteins exhibit different trend with the pH, whereas the lowest recovery of LF is obtained at pH=5.5, this lowest value for BSA occurs at pH=3.1. Therefore, the selectivity of the process is maximum at this latter pH ($S_{\text{LF/BSA}}=3$). With respect to the protein fraction that remains in the liquid phases, most of LF is present at the salt-rich phase under all the experimental conditions studied. In contrast, only at pH=5.5 the rest of BSA is contained in this salt-rich phase, since 46% and 66% of this protein is present in the ionic liquid-rich phase at pH=4.0 and 3.1, respectively. This different behavior of LF and BSA is attributed to their different isoelectric points (IEP): whereas LF (IEP: 8-9) is positively charged at the studied pH, BSA (IEP: 4.7-4.9) has a negative net charge at pH=5.5 and positive charge at pH=3.1 and 4.0.

Table 3-Influence of the protein concentration on the protein recovery at the liquid-liquid interface and LF selectivity with respect to BSA, $S_{\text{LF/BSA}}$.

Protein concentration (10^4 w/w)	% recovered at L-L interface		$S_{\text{LF/BSA}}$
	LF	BSA	
0.4	93.5 ± 5.0	88.3 ± 6.2	1.06 ± 0.13
0.8	90.7 ± 3.6	83.2 ± 2.1	1.09 ± 0.07
1.2	87.6 ± 3.0	76.4 ± 0.3	1.15 ± 0.04
1.6	82.9 ± 2.5	54.8 ± 4.4	1.51 ± 0.17

Nevertheless, despite the higher LF recovery and selectivity achieved at pH=3.1, recovered proteins could not be completely redissolved in water at more acidic conditions, so the performance of ILTPP at moderate pH such as 5.5 could be more interesting for the preservation of the protein properties. For this reason, the influence of the protein concentration is carried out at pH=5.5 (Table 3). It is concluded that the

lower the protein concentration, the higher the protein recovery. This trend is more important in the case of BSA, which is the cause that $S_{LF/BSA}$ decreases to almost 1 at relatively low protein concentrations. These conditions make it possible to recover different types of proteins (such as LF and BSA) simultaneously at the interface.

Ionic liquid recyclability

Figure 2 shows the diagrams of the ILTPP process when different alternatives are considered to recycle the ionic liquid. The fraction of ionic liquid that cannot be recycled with each recovery alternative for different LF concentrations in the feed stream, $[LF]_F$, is reported in Figure 3 [14].

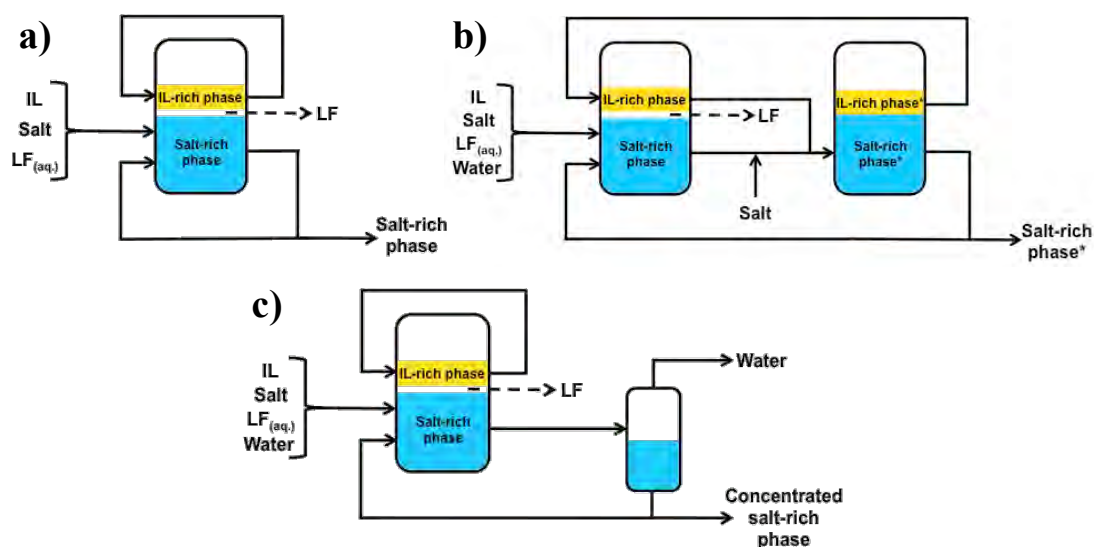


Fig. 2-Schematic diagrams of the ILTPP process when: a) no additional steps to recover the ionic liquid are considered; b) extra salt is added to the system to enhance the ionic liquid recovery; c) evaporation is used to enhance the ionic liquid recovery.

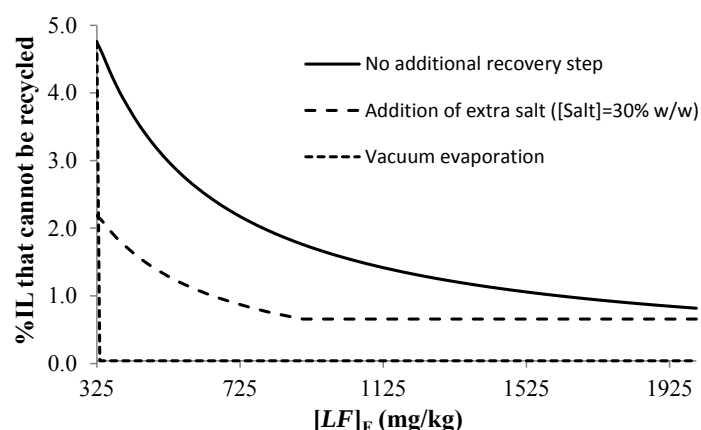


Fig. 3-Percentage of ionic liquid that cannot be recycled with each recovery alternative.

The evaporation of part of the water content in the salt-rich phase makes it possible to recycle all the ionic liquid (and salt), with the exception of a very narrow range of values of $[LF]_F$ at low concentrations. In contrast, when no additional recovery steps are used, between 0.8 and 4.7% of the ionic liquid is lost. The higher the LF concentration in the feed stream ($[LF]_F$), the lower the ionic liquid that cannot be

reused, because a higher fraction of the salt-rich phase can be recycled (a lower amount of feed stream is required to reach the desired protein concentration in the system). The addition of salt to the system reduces the ionic liquid concentration in the salt-rich phase, which enhances the ionic liquid recyclability. However, the effectiveness is notable only at low protein concentrations, because at high values of $[LF]_F$, the amount of salt-rich phase that can be recycled remains constant since, otherwise, the salt concentration in the system will increase.

Conclusions

In this work, Ionic Liquid-based Three Phase Partitioning (ILTPP) is presented as a promising technique to recover proteins at the liquid-liquid interface combining the advantages associated with Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) and Three Phase Partitioning (TPP). In contrast, ILTPP does not require any back extraction steps or the use of conventional organic solvents. The BmimTfO/NaH₂PO₄ system is identified as the most suitable to carry out ILTPP, because it fulfills all the characteristics required by this technique. This system leads to relatively high lactoferrin recoveries (83-98%) and selectivities respect to bovine serum albumin vary between 1 and 3. Therefore, depending on the experimental conditions, and especially on the pH, ILTPP can recover specific proteins such as lactoferrin or groups of proteins. In addition, when vacuum evaporation is used to recycle the ionic liquid and salt, this process can be performed without any consumption of reagents, which improves the economic and environmental profiles of this technique.

Acknowledgements

Authors acknowledge the collaboration of Prof. JAP Coutinho and Dr. SPM Ventura (Universidade de Aveiro, Portugal) in the work about the ionic liquid recyclability. The authors would like to thank the financial support of the Spanish Ministry of Economy and Competitiveness through the project EUI2008-03857 and The Tatua Co-operative Dairy Company Limited for providing the lactoferrin used in experiments.

References

- [1] Y Pei, J Wang, K Wu, X Xuan, X Lu, *Sep. Purif. Technol.*, 2009, 64, 288.
- [2] Q Zeng, Y Wang, N Li, X Huang, X Ding, X Lin, S Huang, X Liu, *Talanta*, 2013, 116, 409.
- [3] FJ Deive, A Rodríguez, LPN Rebelo, IM Marrucho, *Sep. Purif. Technol.*, 2012, 97, 205.
- [4] E Alvarez-Guerra, A Irabien, *Sep. Purif. Technol.*, 2012, 98, 432.
- [5] C Wu, J Wang, H Wang, Y Pei, Z Li, *J. Chromatogr. A*, 2011, 1218, 8587.
- [6] MG Freire, AFM Cláudio, JMM Araújo, JAP Coutinho, IM Marrucho, JNC Lopes, LPN Rebelo, *Chem. Soc. Rev.*, 2012, 41, 4966.
- [7] E Alvarez-Guerra, A Irabien, *Sep. Sci. Technol.*, 2014 (in press, DOI: 10.1080/01496395.2013.878722).
- [8] E Çalci, T Demir, E Biçak, S Önal, *Sep. Purif. Technol.*, 2009, 70, 123.
- [9] H Wakabayashi, K Yamauchi, M Takase, *Int. Dairy J.*, 2006, 16, 1241.
- [10] N Ndiaye, Y Pouliot, L Saucier, L Beaulieu, L Bazinet, *Sep. Purif. Technol.*, 2010, 74, 93.
- [11] MM Bradford, *Anal. Biochem.*, 1976, 72, 248.
- [12] CMSS Neves, MG Freire, JAP Coutinho, *RSC Adv.*, 2012, 2, 10882.
- [13] E Alvarez-Guerra, A Irabien, *J. Chem. Technol. Biotechnol.* (under review).
- [14] E Alvarez-Guerra, SPM Ventura, JAP Coutinho, A Irabien, *Fluid Phase Equilib.* (accepted).

Scalable Technology for the Extraction of Pharmaceuticals (STEP): outcomes from a 3 year high value manufacturing research programme

*Svetlana Ignatova¹, Peter Hewitson¹, Chris Thickitt², Nathalie Douillet², David Johns², Keith Freebairn², Philip Wood³, Guy Harris³, David Rooke³, Roland Brown⁴
and Ian A. Sutherland¹*

¹*Brunel Institute for Bioengineering, Brunel University, Uxbridge, UB8 3PH, UK*

²*GlaxoSmithKline, Pharmaceuticals R&D Facility, Gunnels Wood Road,
Stevenage SG1 2NY, UK*

³*Dynamic Extractions Ltd, Plymouth Road, Slough SL1 4LP, UK*

⁴*Pfizer Ltd, Ramsgate Road, Sandwich, Kent, CT13 9NJ, UK*

ABSTRACT

The manufacture of high value pharmaceutical products, whether from natural products, fermentation processes or chemical/biochemical synthesis, involves multiple, down stream processing steps (often using generic equipment common to various pharmaceutical industries) before a pure product is obtained. The plant required is highly capital intensive and process development is a complex and time consuming activity. Waste and its disposal are economically and environmentally challenging issues. We will be reporting on the outcome of a 3 year £1.5m Technology Strategy Board (TSB) funded research programme developing a small footprint, versatile, counter current extraction purification technology and methodology which can be operated at a range of scales in both batch and continuous modes and that can be inserted into existing process plant and systems. The product is always maintained in an easily managed liquid stream which is able to cope with crude extracts and particles without any pre-conditioning, reducing the number of processing steps and leading to highly efficient, environmentally friendly production processes with no expensive solid support materials and easily recycled liquids. Our consortium, integrates technology providers (Dynamic Extractions) and the scientific development team (Brunel) with end user needs (GSK & Pfizer), addressing major production challenges aimed at providing flexible, low capital platform technology driving substantial cost efficiency in both drug development and drug manufacturing processes. Advances in process automation, method development, continuous processing and throughput will be presented with scale up examples taken from the 85% success rate with end user applications.

Green Solvents for Natural Products Extraction

Farid Chemat, Maryline Abert Vian

Université d'Avignon et des Pays du Vaucluse, INRA, UMR 408, Green Extraction Center
F-84000 Avignon, France.

farid.chemat@univ-avignon.fr

Nowadays, we cannot find a production process in the perfume, cosmetic, pharmaceutical, food, bio fuel, or fine chemicals industries which do not use **solvent extraction processes**, such as: maceration, percolation, steam or hydro-distillation, decoction, infusion, and Soxhlet extraction. In the food industry, besides the well established huge extraction processes of sugar beet and sugar cane, and the preparation of decaffeinated tea and coffee, many formulations have been developed by adding plant extracts and nutraceuticals concentrates. Bioactive compounds or their precursors (antibiotics, chemo-preventive agents, alkaloids, *etc.*) are extracted by the pharmaceutical industry, either with conventional methods or modern technologies. Recent trends in extraction techniques have largely focused on finding solutions that minimize the use of solvents or to find alternatives for petroleum solvents. This, of course, must be achieved while also enabling process intensification and a cost-effective production of high quality extracts.

For example in the perfume industry, extraction of natural products was considered “clean” when compared with heavy chemical industries, but researchers and professional specialists found that its environmental impact is far greater than first appeared. The overall environmental impact of an industrial extraction cycle is not easily to estimate; however it is known that it requires at least the 50% of the energy of the whole industrial process. In spite of the high energy consumption and the large amount of solvents, often the yield is indicated in decimals. For example, a single milliliter of rose absolute (used in famous perfumes) that weighs less than 1 gram requires more than 1 kg of fresh roses as raw material (which became a chemical waste) but also a large quantity of solvents (*n*-hexane, alcohol), energy (fossil) and water as cooling and cleaning agent (waste water).

The lecture, which the reader has in hand, is an attempt to advance the ethics and practical objectives of “Green Solvents for Natural Products Extraction”. The purpose of this lecture is to address the needs and challenges in a single resource that provides practical information on the use of a wide variety of alternative solvents for extraction strategies in laboratory and industrial natural product extraction. This lecture is not intended to provide a comprehensive review of the topic of green solvents, but rather to be a first step toward a future cooperation in a new extraction of natural products built to improve both the fundamental and green parameters of the techniques and to increase the amount of extracts obtained from renewable resources with the minimum consumption of energy and alternative solvents, and the maximum safety for operators and the environment.

Process for uranium recovery from mixed sulfate/ chloride media

James Quinn, Australian Nuclear Science & Technology Organisation (ANSTO), New Illawarra rd, NSW, Sydney, Australia; Karin Soldenhoff, ANSTO, Sydney, Australia;

Sulfuric acid leaching, followed by solvent extraction with tertiary amines, is well established technology for uranium recovery. In many locations, good quality water is in short supply and the use of sea water or saline bore water could provide an attractive option. However, the presence of chloride above 3 g/L has a negative impact on uranium loading, thus ruling out the use of water with high salinity

The aim of this work was to assess alternative mixed organophosphorous and tertiary amine reagents and propose a process to allow for uranium recovery from liquors containing 20 g/L chloride, with performance comparable with current technology. In particular, the objectives set out for this research were:

- Ensure high uranium loading in the solvent in the presence of chloride;
- Prevent co-extraction of ferric ion; and
- Maximise stripping performance.

In this paper, we report on solvent extraction studies using Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) with and without Alamine 336, and compare its performance with DEHPA (di-2-ethylhexyl phosphoric acid) / Alamine 336 reagent mixtures.

Results showed that, with Cyanex 272, uranium was extracted by a cation exchange mechanism, with very high distribution coefficients measured at pH 1. Extraction of iron (III) was much weaker ($\beta_{U/Fe}=129$), and was consistent with cation exchange of $FeOH^{2+}$. Addition of Alamine 336 resulted in antagonism for iron (III) extraction, shifting the $pH_{0.5}$ from 1.54 to 1.85. Conversely, synergism was observed in the extraction of uranium, which resulted in an increase in the concentration of sulfuric acid required for stripping. McCabe Thiele analysis of extraction and stripping isotherms showed that 9.2 g/L uranium could be loaded on the solvent using 0.1 M Cyanex 272 at pH 1.75, and stripping, using 4 M H_2SO_4 , produced a solution containing 45 g/L uranium.

Compared with DEHPA/Alamine 336 mixed reagent, Cyanex 272 on its own was found to be a better option for extraction of uranium in the presence of high

concentrations of both iron (III) and chloride. The suggested process allows for the use of sea water or saline bore water for leaching.

Enhanced extraction of uranium from phosphoric acid with synergistic solvent mixture of DNPPA and bidentate octyl (phenyl) CMPO

D.K.Singh, S. Mondal, M.Anitha, J.N.Sharma and H.Singh

Materials Group, BARC, Mumbai-400085, India

Email: dksingh@barc.gov.in

Abstract

Fertilizer grade phosphoric acid is an important sustainable secondary source of uranium. Depleted source of primary ore bodies coupled with expanding nuclear power program has rekindled the interest in recovery of uranium from phosphoric acid. Solvent extraction technology using organophosphorus class extractants such as D2EHPA (di-2ethyl hexyl phosphoric acid), TOPO (tri-*n*-octyl phosphine oxide), DNPPA (di-nonyl phenyl phosphoric acid), TBP (tri-*n*-butyl phosphate), alkyl pyrophosphates etc have been demonstrated successfully to recover uranium from this source. All these processes have their own merits and demerits and search for a suitable extractant still draws considerable attention from the researchers throughout the world. In the present paper we report a novel synergistic combination of DNPPA and bidentate *n*-octyl (phenyl)-*N,N*-di-isobutyl carbamoyl methyl phosphine oxide (CMPO) which significantly enhances the extraction efficiency of uranium from phosphoric acid medium when compared to monodentate extractants such as TOPO. The effect of varying concentrations of phosphoric acid, DNPPA and CMPO on the extraction of uranium were determined. A mole ratio of DNPPA/CMPO of 2 has been found to be suitable for extraction of uranium. Effect of diverse cations including iron, rare earths etc on the extraction of uranium has also been investigated. The extraction reaction was exothermic in nature. Amongst various stripping reagent, 50% phosphorus acid was found to be efficient for quantitative (>90%) to bring back uranium values into aqueous phase. Direct precipitation of yellow cake ($\text{UO}_4 \cdot x\text{H}_2\text{O}$) from the resulting phosphorus acid solution was difficult, while from sodium carbonate solution it was easy and effective. A five stage counter current extraction at an appropriate O/A was found to be optimum for >95% uranium extraction from both weak and strong phosphoric acids. Feasibility of using this novel synergistic mixture for the recovery of uranium from phosphoric acid medium has been discussed.

Revisited physicochemistry of uranium (VI) extraction from wet phosphoric acid by D2EHPA-TOPO

Denis Beltrami ^{1,2}, Gerard Cote ¹, Hamid Mokhtari ², Bruno Courtaud ²,

Alexandre Chagnes¹

¹ ENSCP - Chimie ParisTech, Laboratoire d'Electrochimie, Chimie aux Interfaces et Modélisation pour l'Energie (LECIME, UR CNRS 7575), Paris, France

² AREVA Mines, Service d'Etudes de Procédés et Analyses (SEPA), Bessines-sur-Gartempe, France.

Since 1952, many researches were focused on the recovery of uranium from wet phosphoric acid (WPA) since this unconventional resource was economically attractive as a large part of the capital expenditure and the operational expenditure of mining, ore preparation and leaching are covered by the phosphate industries.

Recently, these resources have been brought to the fore again. After a brief introduction of the different processes developed in the past as well as their drawbacks, this paper will present the last researches regarding the physicochemistry involved in the recovery of uranium from WPA by the synergistic system used in the Oak Ridge process, i.e. Bis(2-ethyl-hexyl)phosphoric acid (D2EHPA)-tri-n-octylphosphine oxide (TOPO).

In peculiar, a physicochemical model for the calculation of the distribution coefficients of uranium (VI) between concentrated phosphoric acid and D2EHPA-TOPO diluted in Isane IP 185 as a function of TOPO and D2EHPA concentrations will be presented. The validity of this model was confirmed by fitting successfully the experimental extraction coefficients of uranium (VI) as a function of the composition of another synergistic system containing bis(1,3-dibutoxypropan-2-yl) phosphoric acid (BiDiBOPP) and di-n-hexyl-methoxyoctyl-phosphine oxide (di-n-HMOPO). Speciation in organic phase deduced from this model was confirmed by Time-Resolved Laser-Induced Fluorescence spectroscopy (TRLFS) and DFT calculations. It appears that TOPO and D2EHPA are associated in Isane IP 185 (an aliphatic diluent) as $(HL)_2TOPO$, $(HL)_5TOPO$, $(HL)_2(TOPO)_2$ whereas uranyl exists in organic phase as $UO_2(HL_2)_2$, $UO_2(HL_2)_2TOPO$, and UO_2L_2TOPO where L is the deprotonated form of D2EHPA (HL) and TOPO is located in the coordination shell of uranyl.

Comprehension of synergistic mechanisms for uranium extraction from phosphoric ores

O.Pecheur, CEA, DEN/DRCP/SCPS/LILA, 30207 Bagnols/Cèze, France

D.Guillaumont, CEA, DEN/DRCP/SCPS/LILA, 30207 Bagnols/Cèze, France

S.Dourdain, UMR 5257, ICSM, CEA/CNRS/universités, 30207 Bagnols/Cèze, France

F.Testard, CEA, DSM/IRAMIS/SCM/LIONS, 91191 Gif-sur-Yvette, France

Phosphate rocks, used to produce fertilizers for agriculture, are considered as an unconventional resource of uranium. They are known to contain uranium in a low but significant amount. The estimated concentration of uranium in phosphate rocks ranges from 70 to 200 ppm and often attains 800 ppm. This could yield to 9 to 22 million tons of uranium reserves ^[1].

In order to recover uranium from phosphates ores, a process based on liquid-liquid extraction was designed in the 1960's ^[2]: an organic phase containing selective ligands for uranium is contacted to an aqueous phase resulting of the acidic treatment of phosphate rocks.

The two ligands used in this process, HDEHP (bis(2-ethylhexyl) hydrogen phosphate) and TOPO (tri-n-octylphosphine oxide), extract uranium synergistically : the uranium extraction coefficient is greater for the combination of the two molecules than for the individual ones. The main advantages of this process are its good selectivity for uranium and its chemical stability. But it has got also two drawbacks:

- The uranium extraction coefficient is too low to allow a one-step extraction cycle
- There is formation of iron precipitates during the stripping of uranium which damages the purity of the extracted uranium

To optimize the process, new extractant systems have to be designed but the synergistic mechanisms are still not completely understood. The current literature concerning the extraction mechanisms of synergistic systems is still rather incomplete, so it's necessary to improve the comprehension of the phenomenon happening in the extraction middle.

In this work, the synergistic mechanisms are investigated with two different approaches:

- The molecular approach: during the liquid-liquid extraction, the ligands form complexes with uranium in the organic phase. The aim of the molecular approach is to investigate the interaction of uranium with the ligands and the interactions between the ligands at the molecular scale. These interactions have been investigated through spectroscopic and theoretical studies. The theoretical part consists in modeling the complexes and the experimental part consists in acquiring data to probe the structure of the complexes.
- The supramolecular approach: the species formed by HDEHP, TOPO and the cations are considered as small aggregates with particular properties: CAC (Critical Aggregation Concentration), aggregation number, diameter of the aggregate. These properties have been investigated with neutron (SANS) and X-ray scattering (SAXS) and related to the extractant properties. The aim of the supramolecular approach is to investigate the effect of aggregation on synergism.

The comprehension of these mechanisms is expected to support the optimization of uranium extraction.

[1] <http://www.world-nuclear.org>.

[2] F.J.Hurst et al., Ind. and Eng. Chem. Process Design and Dev., 1972, Vol. 11(1), p. 122-128.

New Process for the Selective Extraction of Uranium from Phosphoric Ores

*Bernier G.*¹, Miguiditchian M.¹, Pacary V.¹, Bertrand M.¹, Camès B.¹,
Hérès X.¹, Mokhtari H.².*

Summary

In the fertilizer and food industries, commercially available phosphoric acid, obtained by action of sulphuric acid on calcium phosphate rocks (wet process phosphoric acid – WPA), contains low concentration of uranium (30 to 300 ppm of U_3O_8) with high concentrations of iron (several g/L). Liquid-liquid extraction processes have been developed during the seventies in order to recover uranium as a by-product of industrial phosphoric acid. The production stopped in the late 90s due to the decline in the price of uranium. Moreover the worldwide uranium resources associated with phosphorite deposits constitutes an important secondary source of uranium for nuclear applications. Further studies are in progress at CEA with AREVA since 2009 to propose a new extracting molecule improving extraction performances of uranium and greater selectivity versus other cationic impurities including iron, the main impurity. Parametric experiments in batch conditions led to select and optimize a new design of bitopic extracting molecule which shows a high extraction of uranium(VI) with a very high selectivity towards Fe(III): extraction and stripping isotherms to determine the stoichiometry of the complexes. A model was developed and implemented in the CEA PAREX simulation code to simulate the operations of solvent extraction in continuous laboratory contactors. A process flowsheet was proposed for the selective extraction of uranium from phosphoric acid solution and implemented successfully, on the laboratory platform PROUST at CEA Marcoule with a genuine solution of an industrial phosphoric acid. This process was further implemented on industrial solutions in the AREVA Mines facilities.

1 - Introduction

In the fertilizer and food industries, commercially available phosphoric acid, obtained by action of sulphuric acid on calcium phosphate (wet process phosphoric acid – WPA, 30% wt. P_2O_5), contains low concentration of uranium (30 to 300 ppm of U_3O_8) with high concentrations of iron and aluminium (ranging from 2 to 6 g/L) as well as other impurities such as molybdenum, vanadium or titanium. The recovery of uranium will allow to decontaminate the phosphoric acid and in the same time valorize uranium for the nuclear industry¹. Indeed, the worldwide uranium resources associated with natural phosphate rocks are estimated at approximately 4 Mt which constitutes an important secondary source for uranium production².

Separation of uranium from phosphoric acid has been a worldwide area of intense research. Several processes have been investigated to recover uranium from WPA. Solvent extraction is the most used method and various organic extractants have been developed ($D_2EHPA/TOPO$ ³, $URPHOS$ ^{4 5}, $OPAP$ ⁶, $OPPA$ ⁷, $URPHOS$ bis^{8 9}) to selectively extract uranium and purify it from other elements present in phosphoric acid to respect ASTM C 967 08 specifications. Separation of uranium from iron is the most difficult as iron is from ten to thirty times more concentrated than uranium in industrial phosphoric acids and can lead to the formation of cruds during the stripping

1

* G. Bernier, CEA, Nuclear Energy Division, RadioChemistry & Processes Department, F-30207 Bagnols sur Cèze, France; Tel. : +33 4 66 79 16 05; fax: + 33 4 66 79 65 67 E-mail address : gilles.bernier@cea.fr

2

AREVA BU Mines/SEPA – 2 Route de Lavaugrasse – 87250 Bessines sur Gartempe, France

step of the process. The Fe/U massic ratio must be lower than 0.15% in the purified uranium to fulfill the ASTM criteria.

Recently, bifunctional extracting molecules which combine both cationic exchanger and neutral donor functions on the same molecule have been designed by the CEA and a patent has been filed by AREVA and CEA¹⁰. Several new amidophosphonic ligands were synthesized and tested for the selective separation of uranium from phosphoric acid¹¹. After screening, DEHCNPB or butyl-N,N-bis(EthylHexyl)-carbamoylnonyl phosphonate (Figure 1) appears to be the best candidate to extract uranium from 5M H₃PO₄ solutions with very high selectivity towards Fe(III) and other cationic impurities ($SF_{U/Fe} \approx 2800$)¹².

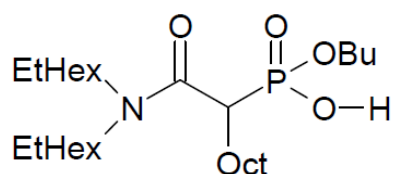


Figure 1: Structure of DEHCNPB

This paper presents the experimental work done to develop a full liquid-liquid extraction process with this molecule and to elaborate a phenomenological model from parametric laboratory studies. This model was then implemented in the CEA PAREX code in order to design a flowsheet, which was tested on the PROUST platform in Marcoule to demonstrate the scientific feasibility of the selective extraction of uranium from an industrial phosphoric acid solution.

2 – Laboratory parametric studies

2 –1 Preparation of solutions and distribution ratio measurements

DEHCNPB ligand was synthesised by Pharmasynthese according to the previous published synthesis¹². Organic solution is prepared by dilution of the extractant at 0.1 M in n-dodecane and the accurate concentration was titrated by sodium hydroxide. The addition of a phase modifier is not necessary with this extractant.

Synthetic aqueous solutions of phosphoric acid were prepared by mixing concentrated solutions of phosphoric acid, uranium and iron phosphates. Uranium and iron distribution ratios were measured in batch conditions to evaluate the efficiency of U and Fe extraction and the U/Fe selectivity. In order to improve the detection limits of iron in organic phase, aqueous solutions were spiked with ⁵⁹Fe and iron distribution ratios were determined by gamma spectrometry. Equal volumes of aqueous and organic solutions were vigorously shaken to obtain a good emulsion, during thirty minutes for equilibrium distribution measurements. The concentrations of uranium and iron in aqueous phase, before and after contact, were measured by Inductively Coupled Plasma with atomic emission spectroscopy (ICP-AES). The cation concentrations in the organic phase were also determined by ICP-AES after two successive stripping with ammonium oxalate and 0.5 M ammonium carbonate.

2 –3 Equilibrium studies

The influence of the concentration of DEHCNPB on uranium and iron extraction as well as the impact of uranium loading were studied in order to characterize the stoichiometry of the complexes formed in organic phase and to model the extraction equilibriums.

2 –3 –1 Influence of the DEHCNPB concentration on uranium extraction

The distribution coefficient of uranium(VI), D_U , was measured at 5M H₃PO₄ at different concentrations of DEHCNPB varying from 0.01 to 0.1 mol/L. The plot of $\log D_U$ versus $\log [DEHCNPB]_{free}$ is linear with a slope of 2 which confirms that UO_2^{2+}

is extracted by two molecules of DEHCNPB corresponding to the release of 2 protons in aqueous phase.

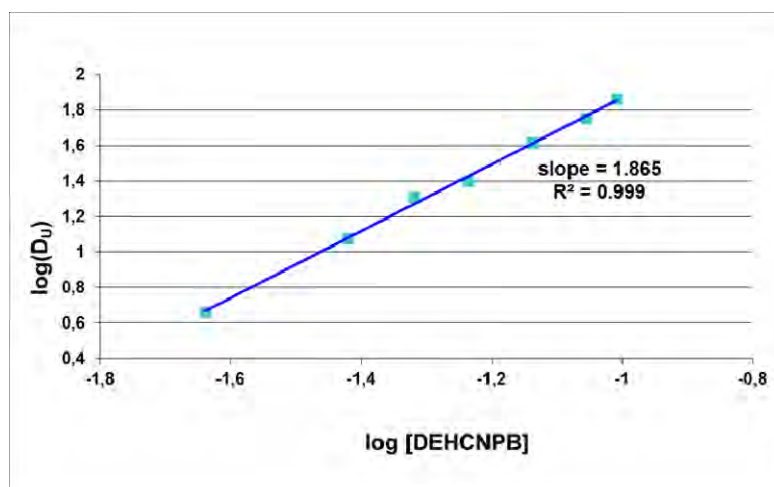


Figure 2: Influence of the initial concentration of DEHCNPB on D_U at 5 M H_3PO_4 at 23°C

2–3–2 Influence of the DEHCNPB concentration on iron extraction

The distribution coefficient of iron(III) (spiked with ^{59}Fe), D_{Fe} , was measured at 5 M H_3PO_4 at different concentrations of DEHCNPB varying from 0.01 to 0.1 mole/L. The plot of $\log D_{Fe}$ versus $\log [DEHCNPB]_{free}$ is linear with a slope of 1.6. The extraction of Fe(III) by 1 and 2 molecules of DEHCNPB was thus assumed in organic phase.

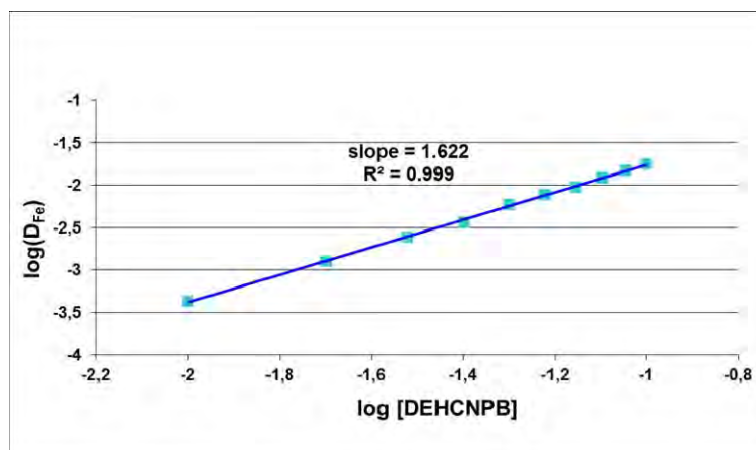


Figure 3: Influence of the initial concentration of DEHCNPB on D_{Fe} at 5 M H_3PO_4 at 23°C

2–3–3 Influence of uranium loading

0.1M DEHCNPB solutions were contacted with increasing concentrations of uranium at 5 M H_3PO_4 . It was possible to load up to 5.5 g/L of uranium in organic phase with 0.1M of extractant diluted in n-dodecane without forming any third phase. The molar DEHCNPB/U ratio at saturation seems to show that 4 or 5 molecules of extractant are needed to extract U(VI) which indicates that 2 dimers of DEHCNPB would coordinate uranium in the complex. However, this hypothesis will have to be confirmed by further SAXS, SANS or NMR measurements.

2–3–4 Test with a genuine industrial phosphoric acid solution

The performances of extraction were evaluated with a genuine solution of industrial phosphoric acid whose initial composition is given in Table 1.

The results are very close to those obtained with synthetic solutions and confirm the great selectivity of DEHCNPB for uranium. Among all the other cations present in the genuine solution, only molybdenum is slightly extracted ($D_{Mo} = 0.15$) but the selectivity remains large enough ($SF_{U/Mo} > 600$).

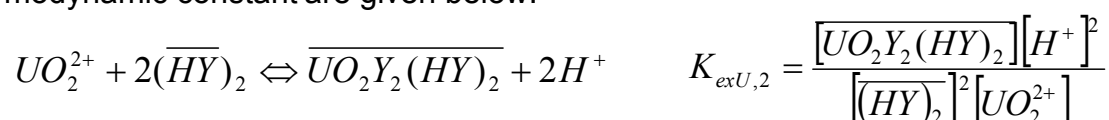
Elements	U	Fe	Mo	Cr	Zn	Cd	Al	V	Ti	Zr
Conc. (mg/L)	155	2470	6	276	393	19	1880	264	55	44
D_M	>100	0.02	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 1: Initial composition of an industrial phosphoric acid solution and distributions ratios measured with 0.1M DEHCNPB at 23°C

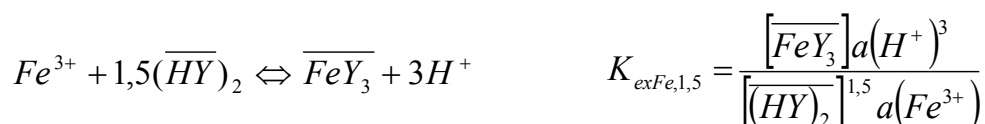
3 – Modelling of the extraction with DEHCNPB

Extraction mechanisms have been proposed based on the experimental data acquired with this new solvent. The goal of the modelling is to determine the thermodynamic constants associated with the different steps of the process: extraction, iron scrubbing and uranium stripping.

A cationic exchange between uranium and DEHCNPB, named HY, is considered in its proton-dimer form. The global form of this equilibrium and the associated thermodynamic constant are given below:



In aqueous phase, environment effects are almost constants and as phosphoric acid is poorly dissociated, the activity coefficients were not considered to take into account deviations from ideality. The proposed mechanism for the extraction of iron is also a cationic exchange mechanism. The global form of this equilibrium and the associated thermodynamic constant are given below:



The experimental study of the influence of the DEHCNPB concentration on Fe(III) distribution ratios shows a slope of 1.6. It was thus proposed that a dimer and a monomer would bind iron in the organic complex. Several extraction equilibrium were proposed and their constants were optimized by minimizing the differences between experimental and calculated organic concentrations after application of the mass action law. Mass balances were resolved in both phases in order to determine the free concentrations according to the optimization procedure computed in the Scilab calculation software. The aim of this algorithm is to minimize the root mean square deviation between calculated and experimental distribution ratios.

The comparison between experimental and calculated data for the isotherm of uranium extraction is represented in Figure 4.

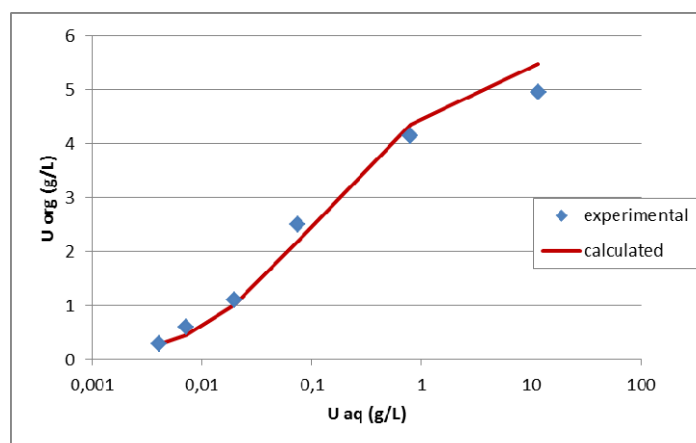


Figure 4: Comparison of experimental and calculated isotherm of extraction of U with 0.1 M DEHCNPB/TPH and 5 M H_3PO_4 at 25°C

4 – Flowsheet design and counter-current test

The model was implemented into the PAREX¹³ simulation code to calculate a flowsheet in order to perform a counter current laboratory run, depicted in Figure 5:

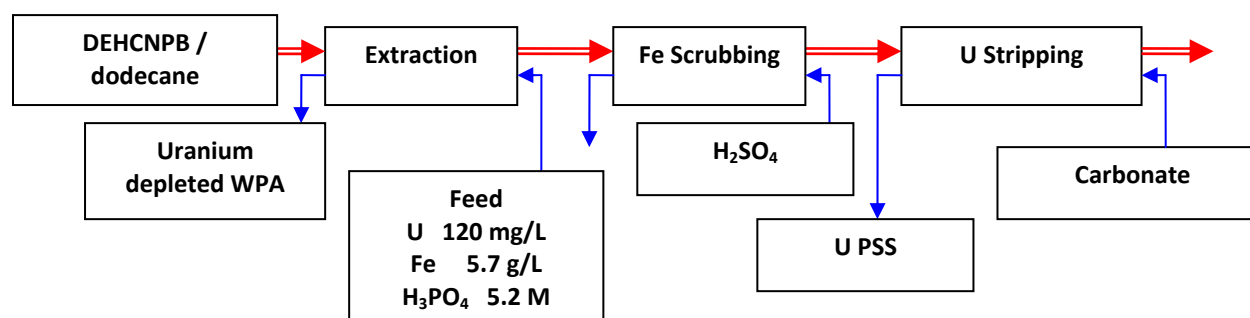


Figure 5: Flowsheet tested for the extraction of uranium by a genuine phosphoric acid on the PROUST platform

This flowsheet was tested on the PROUST platform in Marcoule. Liquid-liquid contacting equipment were Poly(methyl methacrylate) (PMMA) lab-scale mixer settler, heated at 35°C for the extraction step and at 45°C for the iron scrubbing and the uranium stripping steps. Perforated stainless steel blades were used for mixing.

The test was very successful as more than 91% of uranium was recovered, concentrated from 0.12 to 5.6 g/L and very well decontaminated from iron and other impurities. The proportion of iron in the uranium output was found to be lower than 0.043% that meets the American Society for Testing and Materials (ASTM) specification ($Fe/U < 0.15\%$). Furthermore, no cruds were observed in the stripping section and the hydrodynamic behaviour was good throughout the test.

Concentrations profiles were measured in aqueous and organic phases at the end of the test and were compared to the values calculated with the PAREX code. Figure 6 shows the good agreement between experimental and calculated profiles of uranium which validate the extraction model developed in this study.

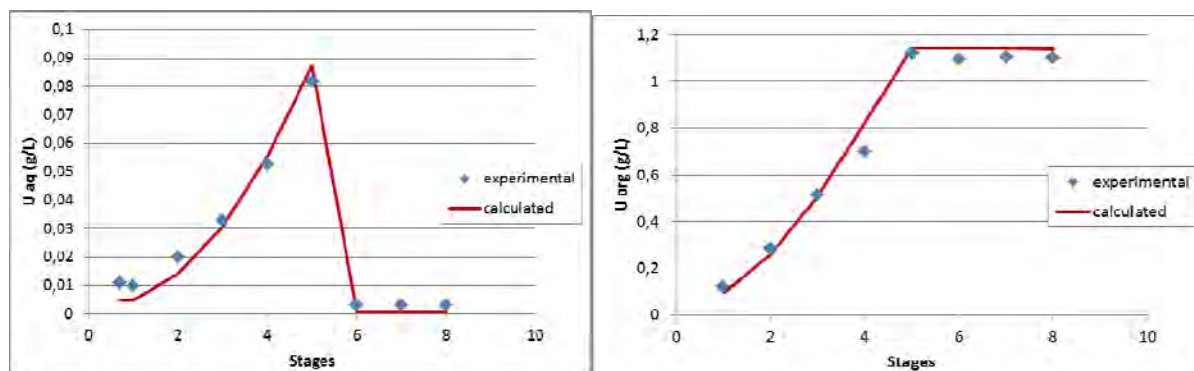


Figure 6: Comparison of experimental and calculated uranium aqueous (left) and organic (right) profiles after the counter-current test with an industrial phosphoric acid

5 – Conclusions

The amidophosphonate DEHCNPB molecule is very selective for the extraction of uranium from phosphoric acid even in presence of high concentrations of iron (3 to 5 g/L) in the genuine phosphoric acid solution. Parametric studies of the impact of the concentrations of extractant and uranium were used to characterize the stoichiometry of the extracted complex in the organic phase and to propose extraction mechanisms. From these experimental results, a model was developed and implemented in the PAREX code in order to calculate a flowsheet. This process flowsheet was implemented in the PROUST platform in G1 facility during 2012, to treat an industrial phosphoric acid solution in laboratory-scale mixer-settlers. The performances of the run are very promising as most of the uranium was recovered with less than 0.043% of iron in the uranium output. Mass balances determined during the test showed that stationary point was achieved. The experimental and calculated profiles of uranium and iron were in good agreement which validates the extraction model. Experiments are now in progress to optimize this flowsheet in order to develop a more compact and efficient process for uranium recovery from phosphoric acid.

References

1. P. Michel, Les Tech. Ind. Min. – Hydrometallurgie Vol. 2, décembre 2006
2. S. Gabriel, A. Baschwitz, G. Mathonniere, T. Elouet, F. Fizaine, Annals of Nuclear Energy 2013, 58, 213-220
3. F. J. Hurst, D.J. Course, U. S. Patent 3 711 591, Janvier 1973
4. F. Hurst, K. Brown, D. Crouse, Ind. Eng. Chem. Process Des. Dev., 1972, 11, 122-128
5. COGEMA APC, French Patent 77-20552, Juillet 1977
6. F. J. Hurst, D.J. Crouse, Ind. Eng. Chem. Process Des. Dev., 1974, 13, 286-291
7. W.L. Mc-Cready, J.A. Wethington, F.J. Hurst, Nucl. Technol., 1981, 53, 344-353
8. G. Lyaudet, P. Du Penhoat, A. Textoris, Ind. Minerale Mines Carrieres Tech., 1989, 71, 168
9. A. Textoris, G. Lyaudet, A. Bathelier, US Patent 5,017,344 (1991)
10. G. Arrachart, N. Aychet, G. Bernier, F. Burdet, A. Leydier, M. Miguiditchian, S. Pellet-Rostaing, G. Plancque, R. Turgis, E. Zekri, (CEA/ICSM) Patent WO 2013/167516 A1 (AREVA Mines)
11. R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguiditchian, S. Pellet-Rostaing, Solv. Ext. And Ion Exch, 2014, accepted
12. R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguiditchian, S. Pellet-Rostaing, 214, submitted
13. C. Sorel, M. Montuir, C. Balaguer, P. Baron, B. Dinh, X. Heres, V. Pacary, H. Roussel, Proceedings of the ISEC 2011 conference, Santiago, Chile, 3-6, 2011

Solvent Extraction versus Nano-Filtration for Upgrading Uranium and Recovery of Acid from an Ion Exchange Eluate

*S.J. Archer^{*1}, V. Coetzee², E.L. Forner², N. Morgan², M.H. Kotze³*

Summary

Recovery of uranium from most acidic and alkali leach solutions or slurries can be achieved via ion exchange (IX), solvent extraction (SX), direct precipitation or a combination of the aforementioned methods. This study considers a particular case, namely, the Mkuju River Project (MRP), where Resin-in-Pulp (RIP) technology is employed to recover uranium from acidic leached slurry with preg-robbing characteristics. Loaded resin is eluted by means of a fluidised bed ion exchange circuit using one molar sulphuric acid. The eluate generated typically contains 5 g/L - 9 g/L U_3O_8 and 70 g/L - 85 g/L sulphuric acid with minimal impurities. This allows for the production of an on-spec uranium peroxide precipitate by means of direct precipitation, without the need for SX or other purification methods. One disadvantage of the process is that the free acid in the eluate has to be neutralised prior to precipitation resulting in a significant operational expenditure in terms of unrecovered acid as well as neutralising reagent requirements.

Two technologies are presented as possible methods for the recovery of free acid, namely, SX and nano-filtration (NF) as well as a combination of the two. A high level trade-off study is presented in which cost differentials are used to evaluate different flow sheet options for acid recovery in order to establish the most economical option in terms of both operating expenditure (OPEX) and capital expenditure (CAPEX). A stochastic approach is also used to quantify the uncertainty in expected operating and capital expenditure ranges. This has been done by utilizing Monte Carlo simulations. A probability distribution has been applied to the key input variables to be used in the simulation in order to describe the inherent uncertainty associated with them.

Introduction

Recovery of uranium from most acidic and alkali leach solutions or slurries can be done via ion exchange (IX), solvent extraction (SX), direct precipitation or a combination of the aforementioned methods. This study considers a particular case, namely, the Mkuju River Project (MRP), where Resin-in-Pulp (RIP) technology is employed to recover uranium from acidic leached slurry with preg-robbing characteristics. Loaded resin is eluted by means of a fluidised bed ion exchange circuit using one molar sulphuric acid. The eluate generated typically contains 5 g/L - 9 g/L U_3O_8 and 70 g/L - 85 g/L sulphuric acid with minimal impurities. This allows for the production of an on-spec uranium peroxide precipitate by means of direct precipitation, without the need for SX or other purification methods. The disadvantage of the process is that the free acid in the eluate has to be neutralised prior to precipitation, resulting in a significant operational expenditure in terms of unrecovered acid as well as neutralising reagent requirements.

Two technologies are presented as possible methods for the recovery of free acid from the eluate, namely, SX and nano-filtration (NF), which can be configured to provide three alternative flow sheets.

¹ *Corresponding Author, DRA Mineral Projects (Pty) Ltd, South Africa, Sidney.Archer@DRAGlobal.com

² DRA Mineral Projects (Pty) Ltd, South Africa

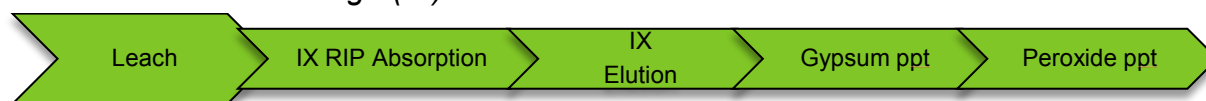
³ LANXESS (Pty) Ltd, South Africa

The annual production of ~6.7m pounds per annum U_3O_8 is kept constant for the various options and the differentials in terms of OPEX and CAPEX are evaluated utilising a Monte Carlo simulation in which a probability distribution is applied to key system variables to describe the inherent uncertainties.

Description of flow sheet options

The three flow sheet options, including the base case flow sheet, share the Mkuju River Project (MRP) front-end processing steps of leaching, RIP ion exchange absorption and elution as well as the back-end processing steps of gypsum precipitation and uranium peroxide precipitation.

Base Case: Ion Exchange (IX)



The processing route for MRP is based on an atmospheric acid leach and allows the use of proven process technologies due to the unique ore mineralogy which contains minimal impurities. As a result, the uranium peroxide final product specifications could be achieved without the inclusion of a SX or other purification unit operations. Employing a RIP carousel circuit post leach, particularly for the MRP, offers CAPEX, OPEX and revenue benefits in comparison to alternative processing options. RIP eliminates the need for costly solid-liquid separation and clarification (Soldenhoff *et al.*, 2012) and it improves the overall uranium recovery due to the presence of “preg-robbing” clay minerals. Loaded resin from RIP is eluted with 1M H_2SO_4 to produce an eluate containing 5 g/L to 9 g/L U_3O_8 and 70 g/L to 85 g/L H_2SO_4 . The average pilot plant eluate composition is presented in Table 1.

Table 1: Average elemental concentrations (mg/L) in Mkuju River Project IX eluate.

Average elemental concentrations in mg/L										
Element	Al	Ca	Fe	K	Mg	Mn	P	S	Si	U_3O_8
Concentration	8	20	39	4	3	1	66	23 934	44	9 871

Burnt lime is used to raise the pH of the eluate to reduce the sulphur content by means of gypsum precipitation. During this unit operation ferric is co-precipitated primarily as a phosphate. The residual phosphate precipitates contain a small amount of uranium. The resultant precipitate is filtered and recycled back to leach to recover co-precipitated uranium. The filtrate proceeds to peroxide precipitation which, in itself, is selective for precipitating uranium at a relatively low pH. However, careful consideration in the design is required to remove entrained solution from the peroxide precipitate in order for the final product to meet converter specifications.

Option 1 – IX-Nano-filtration (NF)



To recover the majority of free acid in the eluate and limit the amount of burnt lime required for the Base Case flow sheet, it is proposed to employ NF. This was evaluated at ANSTO in an extensive pilot trial using commercially available NF membranes to treat an eluate with a composition as presented in Table 1. Calcium and silica are the two species that were of concern since they would be upgraded to levels that could possibly result in fouling of the membrane via polymerisation and precipitation. This, however, was not encountered as the silica and calcium in the eluate were at low enough tenors. The low silica tenor in the eluate primarily resulted from the mild leach conditions. Furthermore, dissolved silica in the pregnant leach solution (PLS) did not contaminate the resin during loading and thus minimal quantities reported to the eluate.

An acid recovery to permeate of greater than 80%, with less than 5% U_3O_8 misplacement was achieved. This would allow for the permeate to be recycled either to elution or leach, depending on the build-up of impurities, particularly phosphates. Both routes allow for a reduced overall acid consumption for the facility and hence a reduction in the burnt lime consumption for neutralisation. A conservative acid recovery range of 75% - 85% was applied for evaluation purposes during this study.

The brine, comprising a uranium rich solution, first needs to be diluted to eluate U_3O_8 tenors thereby limiting uranium losses during gypsum precipitation. These losses result from localised precipitation and entrainment during solid-liquid separation.

Option 2 – IX-Solvent Extraction (SX)



Option 2 follows the same front-end processing steps as discussed for the base case, however, the eluate is sent to SX where uranium is extracted using 6% (v/v) Alamine®336. There are numerous mechanisms which allow for the stripping of uranium-loaded Alamine®336; however ~4.5M H_2SO_4 strip liquor (SL) has been shown to produce concentrations of loaded strip liquor (LSL) containing 75 g/L to 80 g/L U_3O_8 with a residual acid concentration of ~4.1M H_2SO_4 (Kotze *et al.*, 2012). Thus the free acid in the raffinate can be recycled either to elution, or leach depending on impurity build-up. The quantity of acid required for stripping is less than the acid in the raffinate or IX eluate, thus reducing the overall acid requirement. This method also allows for the selective removal of phosphate and ferric species from a uranium containing solution, thereby improving the final product purity. It also allows for selective peroxide precipitation to be employed post free acid neutralisation.

However, the LSL would require dilution to prevent uranium losses (as discussed in Option 1) from occurring during gypsum precipitation.

Option 3 – IX-SX-NF



Option 3 combines solvent extraction of the IX eluate with a strong acid strip on the loaded solvent, followed by NF to recover the free acid in the LSL (Van Tonder *et al.*, 2012). However, the LSL needs to be diluted before being fed to NF in order to prevent osmotic pressure build-up which limits acid recovery. The LSL is diluted from ~75 g/L U_3O_8 to ~9 g/L and, in doing so, the acid tenor also decreases from ~400 g/L to ~40 g/L. The NF permeate can be recycled; with a portion sent to SX strip liquor make-up and the residual solution recycled to the leach. This study considers a conservative recovery of acid from the LSL, via NF, ranging from 75% to 85% including a U_3O_8 misplacement to the permeate of 5%.

Once again, as discussed in Options 1 and 2, the brine generated needs to be diluted to eluate tenors in order to prevent uranium losses during gypsum precipitation.

The main design parameters for each flow sheet are summarised in Table 2. It should be noted that both the upfront circuit (Leach to IX) as well as the downstream circuits (gypsum precipitation to final product handling) are identical for all flow sheet options and are not considered as differentials. This assumption holds true for the gypsum precipitation reactors, however, the solid-liquid separation requirements would differ due to the quantity of gypsum formed for each flow sheet option but this is assumed to be insignificant.

Table 2: Key differential design parameters for four uranium purification flowsheet options

Process Design Parameter	Value	Applicable Flowsheet Option
Solvent Extraction		
Solvent tertiary amine content	6 wt%Alamine®336	IX-SX & IX-SX-NF
SX Loaded strip liquor U_3O_8 tenor	80 g/L	IX-SX & IX-SX-NF
SX Loaded strip liquor H_2SO_4 tenor	400 g/L	IX-SX & IX-SX-NF
Nano Filtration		
NF Feed U_3O_8 concentration	5 g/L - 9 g/L	IX-NF & IX-SX-NF
NF Feed H_2SO_4 concentration	45 g/L	IX-SX-NF
NF Brine U_3O_8 concentration	40 g/L	IX-NF & IX-SX-NF
NF permeate U_3O_8 mass split	5 wt%	IX-NF & IX-SX-NF
NF Acid recovery	75 wt% to 85 wt%	IX-NF & IX-SX-NF

Techno-financial evaluation

Overall basis of comparison

IX elution circuit is selected as the base case against which all the cost differentials are calculated. Analysis is done on a bare-bones basis, in real terms and excludes the effects of taxes, interest, financing terms or any cost escalation. The costs shown are not to be regarded as definitive, but rather differential costs relative to the base-case option. Any costs considered to be common between the various options have been excluded from the analysis. The technical basis for comparison of the system economics is provided in Table 3.

Table 3: Basis of comparison for all flowsheet options

Process design parameter	Value
U ₃ O ₈ production	6.7Mlb/a - 7Mlb/a U ₃ O ₈
Head grade	464 ppm
Operating hours per annum	7884 h

CAPEX basis of comparison

The main CAPEX considerations include:

- Differences in the major mechanical equipment;
- A typical design criteria for each flow sheet in support of mass balancing and equipment sizing;
- Mechanical equipment costs were determined from recently executed studies as well as DRA's internal database;
- Internal DRA factors were applied for civils, structural (supply and erection), platework (supply and erection), mechanical erection, piping (supply and installation), electrical, control and instrumentation (supply and installation), transport, project services and P&G's.

OPEX basis

The major OPEX considerations include:

- Reagent costs estimated from DRA's recently updated (2013) reagent supply database;
- Reagent consumptions were determined using high level mass balances and based on testwork outcomes;
- Power, labour and general maintenance costs were found to have a negligible effect on the differential OPEX.

Financial Analysis

The CAPEX and OPEX cost estimates are summarised in the bar charts shown Figure 1. The bars show the estimated costs for the 90% confidence range, as well as the maximum and minimum ranges expected. OPEX estimates shown are annual expected costs.

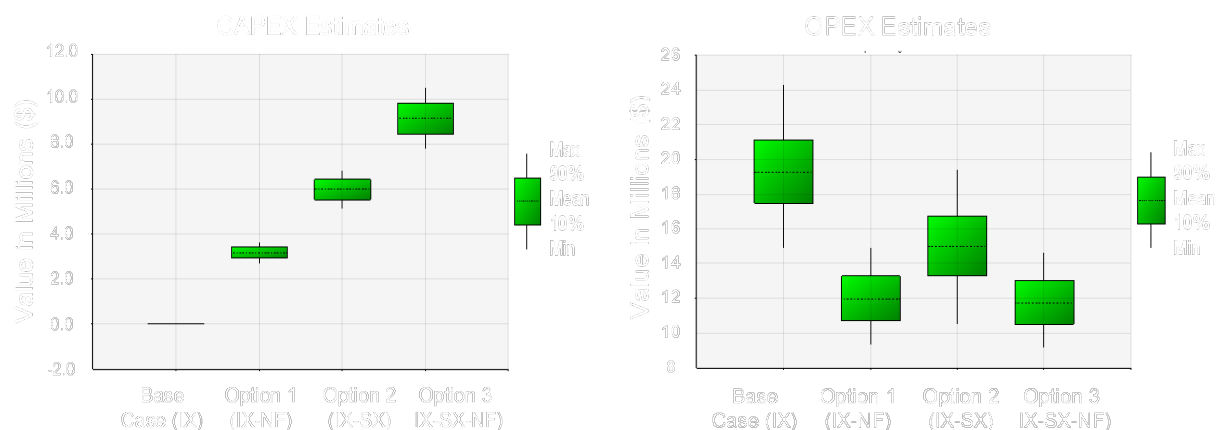


Figure 1: CAPEX & OPEX cost estimates

The OPEX estimates are based on upside and downside regarding both reagent consumption and supply cost: 1.) Acid supply costs (excl. transport) are based on US\$100/t, with an upside of US\$80/t and downside of US\$130/t (based on feedback from numerous reputable reagent suppliers); 2.) Lime cost is based on a range from US\$300 to US\$450/t, which is the range obtained from reputable reagent suppliers in the area.

Based on the expected ranges/uncertainties assigned to key reagent consumption and supply rates, the scatter plot (CAPEX vs OPEX) for the various options, shown in Figure 2a, summarises the uncertainty scatters. The box-plot graph shown in Figure 2b shows the differential Net Present Cost for each option relative to the base case.

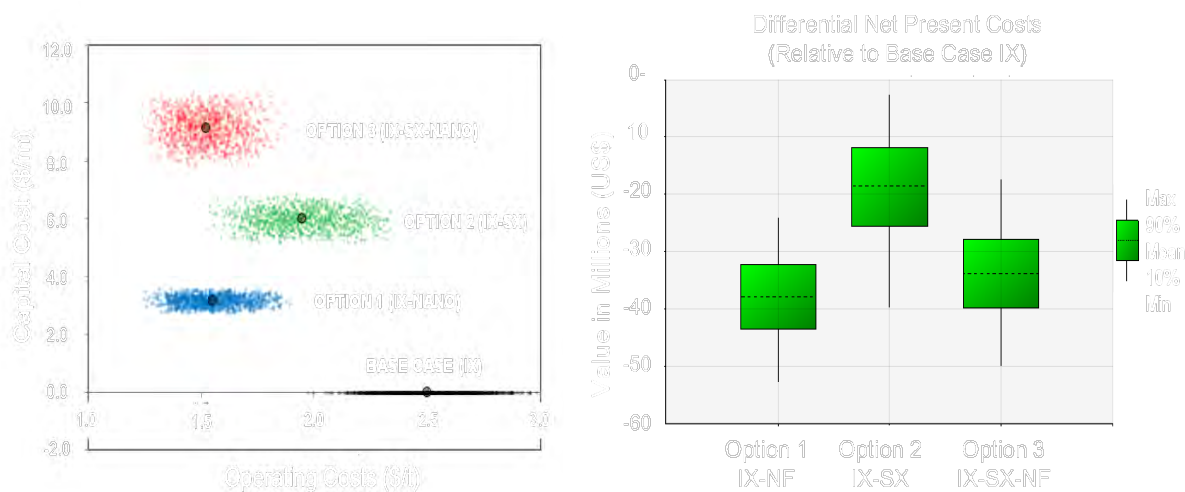


Figure 2: a) Scatter plot of uncertainties in CAPEX vs OPEX b) Differential Net Present Costs relative to Base Case

Figure 2 shows that all options relative to the base case will return improved cash flows over a 10 year life of mine, despite the higher capital expenditure required. The options that consider the use of Nano technology, namely Option 1 (IX-NF) and Option 3 (IX-SX-NF) provide the highest cost savings over life of mine. The expected life of mine economic benefit is calculated to be between \$20m and \$50m. Option 2 (IX-SX) is expected to provide some cost benefit when compared with the base case

IX option, mainly because of reduced lime consumption. There is, however, a moderate likelihood of breaking even with the IX base case option, in terms of life of mine cost savings.

Sensitivity analysis

A tornado chart, indicating the major uncertainty contributors, for Option 1 (IX-NF) relative to the base case (IX) is shown in Figure 3.

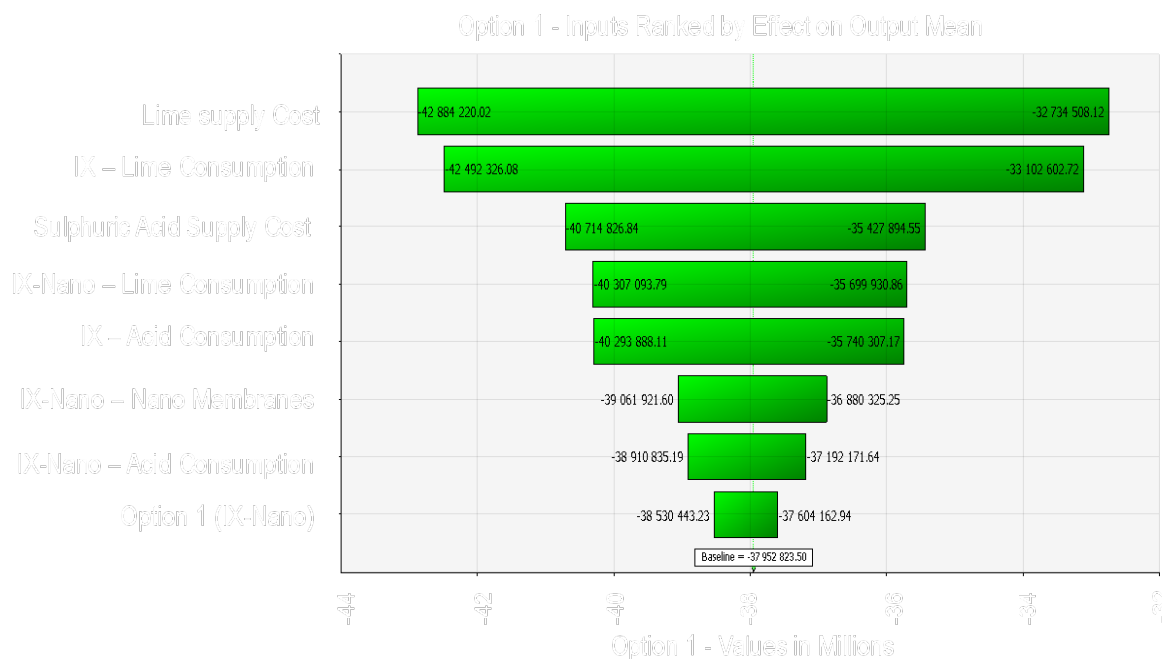


Figure 3: Tornado chart for best OPEX case (Option 1 IX-NF) vs worst OPEX case (Base Case IX)

The greatest uncertainty lies in the consumption and supply cost of lime. Even at the extremities of the lime supply cost estimate i.e. US\$300/t and US\$450/t, the use of NF on its own is still expected to return economic benefits to the project.

Conclusions

A stochastic approach has been used to quantify the differential in operating expenditure and revenue between SX and NF. The aim of this study was to minimise OPEX in terms of the key system parameters, namely acid consumption and lime consumption. Together with a basic high level evaluation of the CAPEX requirements for SX and NF; a comparison of the economics revealed that a flow sheet consisting of RIP IX followed by NF is optimum where ore mineralogy similar to that of the Mkuju River Project is present. Ore mineralogy plays a key part in the process route selection and understanding of metallurgical behaviour. However, if there are significant quantities of impurities present, such as silica, then SX should be included before the NF unit operation, for optimal acid and uranium recovery.

Acknowledgements

Thank you to Uranium One for allowing us to present this paper and to Mr. A Manis of ANSTO for the comprehensive and professional research and development of the NF technology for the Mkuju River Project.

References

1. Kotze, M.H., du Preez, A.C. & Mokwana, C. Comparison of reagents for stripping Uranium – loaded Alamine®336, *ALTA 2012 Uranium Conference – SX/IX*
2. Soldenhoff, K., Safinski, T., Manh Tran, T., & Archer, S.J. Impact of Silica on the Adsorption and Elution of Uranium, *IEX 2012, The International Ion Exchange Conference*.
3. van Tonder, D. & Edwards, C. Strong acid versus ammonia strip in Uranium SX circuits, *ALTA 2012 Uranium Conference – SX/IX*.

Novel Solvent Extraction Process for the Recovery of Gold from Chloride Media

*Neil Davidson^{*i}, Ben Eadeⁱⁱ, Richard A. Grant*

A novel extractant system for gold (Au) from chloride media has been developed using 80 % v/v Texanol in Shellsol D70. Using this system it is possible to extract Au, Fe and Te from a feed containing platinum group metals (PGM). Any co-extracted PGM and base metals (BM) can be scrubbed or stripped from the loaded organic if necessary before quantitatively stripping the Au with water. In contrast to the current commercial systems (methyl isobutyl ketone (MIBK) and dibutyl carbitol) this system allows the full benefits of a fast and continuous solvent extraction system to be realised using a low cost organic with a high flash point and resulting in a high purity Au strip solution which can be processed as required. A degradation study was also performed on the extractant system to determine its stability under the proposed conditions. This showed that Texanol degraded, probably via ester hydrolysis, resulting in a drop in extractant concentration as successive cycles were completed. This was accompanied by a drop in the distribution coefficients for all metals across all stages which would reduce the extraction efficiencies of the target metals.

Introduction

Traditionally, Au is extracted from chloride media using extractants such as MIBK,¹ or dibutyl carbitol.^{2,3} Both extractants have a high affinity for Au, thus the Au cannot be stripped from the organic phase and instead must be reduced out. This tends to be a slow process so some of the benefits of a quick and continuous solvent extraction plant are lost by carrying out batch reductions on the loaded organic.⁴ In addition to this there are environmental, health and safety (EHS) and operational challenges with using these organics due to low flash points and the loss of organic during the process. There is an attractive opportunity to develop a new solvent extraction system for Au using a safe, cheap extractant, where all the stages can be performed in conventional mixer settlers.

Other solvent extraction systems for Au have been developed using alcohols, where it is possible to strip the Au from the organic phase with water.⁵ However these systems are unable to efficiently extract other base metals impurities (Fe and Te) commonly found in these liquors. Mixed extractant systems involving an alcohol and a di-ester claim to be able to extract Au, Fe and Te which can then be stripped into water,⁶ but there is no published data on the lifetime of such a system.

For a commercial process the distribution coefficients of all elements present in the feed need to be considered over all of the solvent extraction stages (extraction, scrub and strip). The lifetime of an extractant also needs to be considered in conjunction with the cost of the extractant to ensure that the process is economically viable.

Methodology

Feed Preparation

For the initial screening experiment and the development of the strip conditions the feed was prepared by adding a solution of TeO₂ in 6 M HCl to a real refining liquor resulting in a feed containing Pt (100000 mg L⁻¹), Pd (50000 mg L⁻¹), Rh (11000 mg L⁻¹), Ru (6000 mg L⁻¹), Ir (4500 mg L⁻¹), Au (3300 mg L⁻¹), Fe (300 mg L⁻¹), Te (100 mg L⁻¹) in [H⁺] = 6.0 M.

For the lifetime experiment a solution containing HAuCl₄, H₂IrCl₆, PdCl₂, H₂PtCl₆, RhCl₃, RuCl₃, FeCl₃, TeO₂ in 6 M HCl was refluxed for 16 hrs and then adjusted such that the resulting synthetic feed contained: Pt (100000 mg L⁻¹), Pd (40000 mg L⁻¹),

^{*i} Corresponding Author, Johnson Matthey Technology Centre, Sonning Common, United Kingdom

ⁱⁱ Johnson Matthey Technology Centre, Sonning Common, United Kingdom

Rh (10000 mg L⁻¹), Ru (10000 mg L⁻¹), Ir (5000 mg L⁻¹), Au (3000 mg L⁻¹), Fe (1000 mg L⁻¹), Te (170 mg L⁻¹) in [H⁺] = 6.0 M.

Solvent Extraction Experiments

80 % v/v Texanol in Shellsol D70 was contacted for 2 minutes at a phase ratio of organic : aqueous (O:A) = 1:1 with the required feed solution. The raffinate was separated and re-contacted three more times with portions of fresh organic.

The first loaded organic was contacted for 2 minutes at a phase ratio of O:A = 2:1 with a scrub solution of 6 M HCl. The scrub was repeated with fresh 6 M HCl.

The base metals were stripped from the scrubbed organic by contacting the organic for 2 minutes with 1–2 M HCl at a phase ratio of O:A = 1:1 (during development of strip conditions) or O:A = 2:1 (during organic lifetime investigation).

The gold was stripped from the organic by contacting the organic for 2 minutes with water at a phase ratio of O:A = 1:1. The organic was separated and re-contacted twice more with water.

Analysis of Samples

Aqueous samples were analysed by ICP-OES and organic concentrations were determined by calculating the difference between the initial and the equilibrium concentration in the aqueous phase after the aqueous concentrations had been normalized on Rh to account for volume changes in the aqueous phase during extraction. ICP-OES analysis was also carried out on the final stripped or scrubbed organic to allow more accurate calculations of the organic concentrations in the strip stages.

Organic samples taken during the investigation into the organic lifetime were analysed by GC-FID.

The solubility of Texanol was measured by back extracting a saturated solution of Texanol in 6 M HCl using toluene and analyzing the toluene phase by GC along with suitable standards of Texanol in toluene.

Results and Discussion

Novel Extractant System

An extractant system comprising of 80 % v/v Texanol in Shellsol D70 was screened by carrying out 4 extractions (O:A = 1:1) and 2 scrubs with 6 M HCl (O:A = 2:1). Table 1 shows the distribution coefficients for the PGM, Au, Fe and Te along with the overall extraction efficiency after 4 stages.

	Feed mg L ⁻¹	1st Raffinate mg L ⁻¹	D	2nd Raffinate mg L ⁻¹	D	3rd Raffinate mg L ⁻¹	D	4th Raffinate mg L ⁻¹	D	Overall % Extraction
Pt	97991	96485	0.04	92483	0.05	93327	0.04	90822	0.04	16.6
Pd	47611	47661	0.03	46291	0.04	47214	0.03	46244	0.04	12.6
Rh	10724	11037	0.00	11147	0.00	11721	0.00	11917	0.00	0.0
Ru	6106	6242	0.004	6372	-	6541	-	6645	-	2.1
Ir	4506	4276	0.07	4095	0.05	3933	0.09	3774	0.06	24.6
Au	3242	6	526.3	0	-	0	-	0	-	100.0
Fe	274	2	113.4	0	-	0	-	0	-	100.0
Te	104	31	2.5	8	2.7	3	1.6	1	2.8	99.3

Table 1: Extraction distribution coefficients for 80 % v/v Texanol in Shellsol solvent extraction system

Near complete extraction of Au, Fe and Te was achieved with limited extraction of PGM. It is possible to scrub the co-extracted PGM out of the loaded organic, as

shown in Table 2, resulting in a scrubbed organic containing Au, Fe and Te, with Pt (5 mg L^{-1}) the only impurity measurable by ICP-OES. The scrubbing distribution coefficients for Te were only just above one, which resulted in over 50 % of the Te being scrubbed out. On a counter current solvent extraction plant this could cause a buildup of Te as the scrub liquor would be combined with the feed prior to extraction.

	1 st Loaded Organic mg L ⁻¹	1st Scrub mg L ⁻¹	D	2nd Scrub mg L ⁻¹	D	Scrubbed Organic mg L ⁻¹	Overall % Scrubbed
Pt	3832	7323	0.02	331	0.02	5	99.9
Pd	1193	2336	0.01	54	-	-2	100.1
Rh	-1	0	-	-1	-	-1	-
Ru	23	42	-	3	-	0	100.8
Ir	283	529	0.03	35	0.01	0	99.8
Au	3150	8	372	9	344	3141	0.3
Fe	270	6	44.1	7	37.8	263	2.4
Te	77	43	1.3	34	1.1	38	50.3

Table 2: Scrub distribution coefficients for 80 % v/v Texanol in Shellsol solvent extraction system

These distribution coefficients suggest that this system would be well suited for the selective removal of Au, Fe and Te from PGM refining liquors.

Development of Base Metal Strip

There would be a financial benefit if it were possible to produce a Au strip liquor with low levels of impurities in it. The literature on existing dibutyl carbitol systems suggests that the base metals can be scrubbed from dibutyl carbitol using weak acid (1–2 M HCl).^{2,4} Therefore stripping trials were carried out on the scrubbed organic using strip acid ranging from 1 M HCl to 2 M HCl. The distribution coefficients for this low acid base metal (BM) strip stage are shown in Table 3.

	1 M HCl Strip		1.5 M HCl Strip		2 M HCl Strip	
	D	% Stripped	D	% Stripped	D	% Stripped
Au	9.7	9.3	17.3	5.5	27.5	3.5
Fe	0.0004	100.0	0.0004	100.0	0.0031	99.4
Te	-	100.0	-	100.0	-	100.0

Table 3: Variation in distribution coefficient with base metal strip acidity

All of the low acid strips were successful in completely stripping Te from the organic. The strip efficiency decreased for both Au and Fe with increasing acidity meaning that it is not possible to strip all of the Fe without stripping some Au. Although a pure Au strip liquor would be financially beneficial in a precious metals refinery it is likely to be more costly to recover large amounts of Au from this low acid stream. It is also likely that a small amount of Fe could be successfully rejected during a Au precipitation. The optimization of this strip acidity would depend heavily on the particular circumstances of an individual refinery, but for the purposes of the further investigations it was assumed that a 2 M HCl strip with a phase ratio of O:A = 2:1 would be optimal in order to minimize the loss of Au to the BM strip.

The organics resulting from the low acid BM strips were stripped with water and the distribution coefficients measured. The Au distribution coefficients ranged from 0.2 to 0.1 meaning that complete stripping of the Au (>99 %) was possible in 3 strip stages (O:A = 1:1).

Degradation Study

The screening experiments showed that 80 % v/v Texanol in Shellsol D70 was a very promising novel extractant for Au, Fe and Te from a liquor containing PGM. Therefore a degradation study was conducted to determine how the extractant system would perform over multiple cycles, similar to what it would be required to do in an industrial process.

10 solvent extraction cycles were conducted, each comprising of one extraction (O:A = 1:1), two scrubs with 6 M HCl (O:A = 2:1), one BM strip with 2 M HCl (O:A = 2:1) and three Au strips with water (O:A = 1:1). The distribution coefficients were monitored across all stages over the 10 cycles. ICP-OES analysis of the final stripped organic at the end of each cycle confirmed that no metal remained in the organic at the end of each cycle.

For all elements and in all stages the distribution coefficients dropped as the number of completed cycles increased. This is highlighted by the Fe and Te distribution coefficients during the 1st extraction and 1st scrub stages (Figure 1) and the Au distribution coefficients in the BM strip stage (Figure 2).

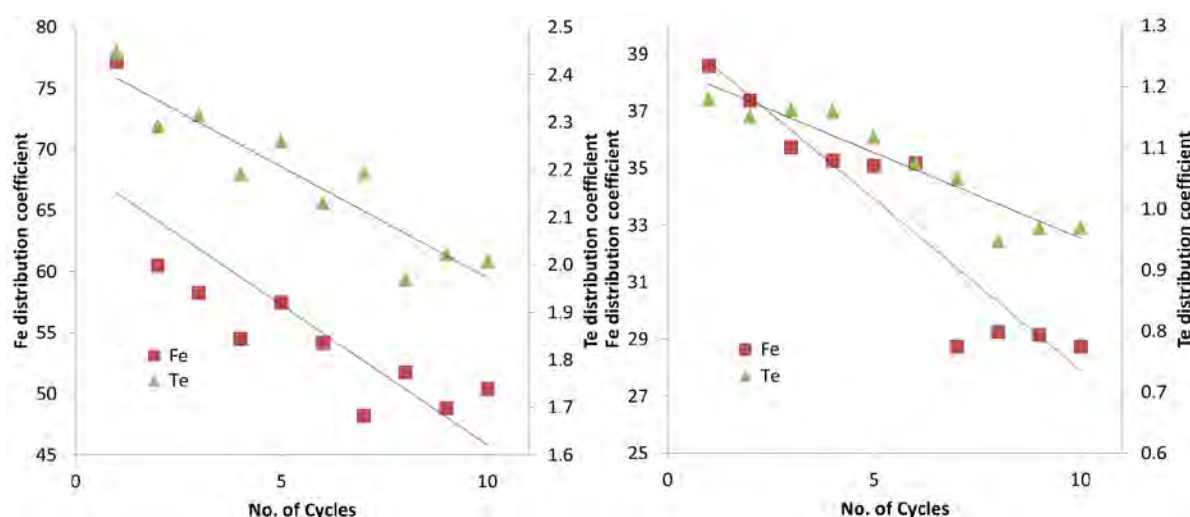


Figure 1: Change in Fe and Te distribution coefficients for the 1st extraction (left) and 1st scrub (right) during the degradation study

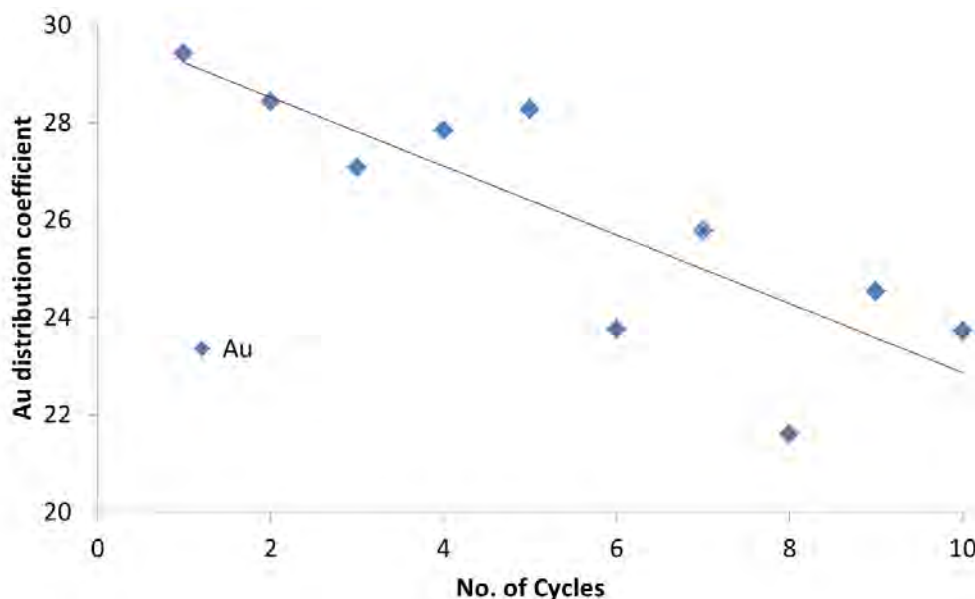


Figure 2: Change in Au distribution coefficient for the base metal strip during the degradation study

The universal drop in distribution coefficients means that as the organic aged on a solvent extraction plant the extraction efficiencies for Au, Fe and Te would drop. In particular the amount of Te that is scrubbed out of the loaded organic would rapidly increase, and be recycled into the feed, until unacceptable amounts of Te broke through into the raffinate. The reduction in the Au distribution coefficient in the BM strip would lead to larger amounts of Au deporting to this stream, from where it would have to be recovered.

The composition of the organic phase at the end of each cycle was monitored by GC-FID and the Texanol concentration calculated using the initial organic as a standard. The only major impurity present in the samples was identified, with the aid of GC-MS, as TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) and its concentration calculated relative to a TXIB standard. The composition of the starting organic was measure as 79.6 % v/v Texanol and 0.4 % v/v TXIB. Hexadecane (1 % v/v) was added to the starting organic as an internal standard. After normalizing the GC peak areas on the internal standard, the relative change in amounts of these extractant species in the organic phase is shown in Figure 3.

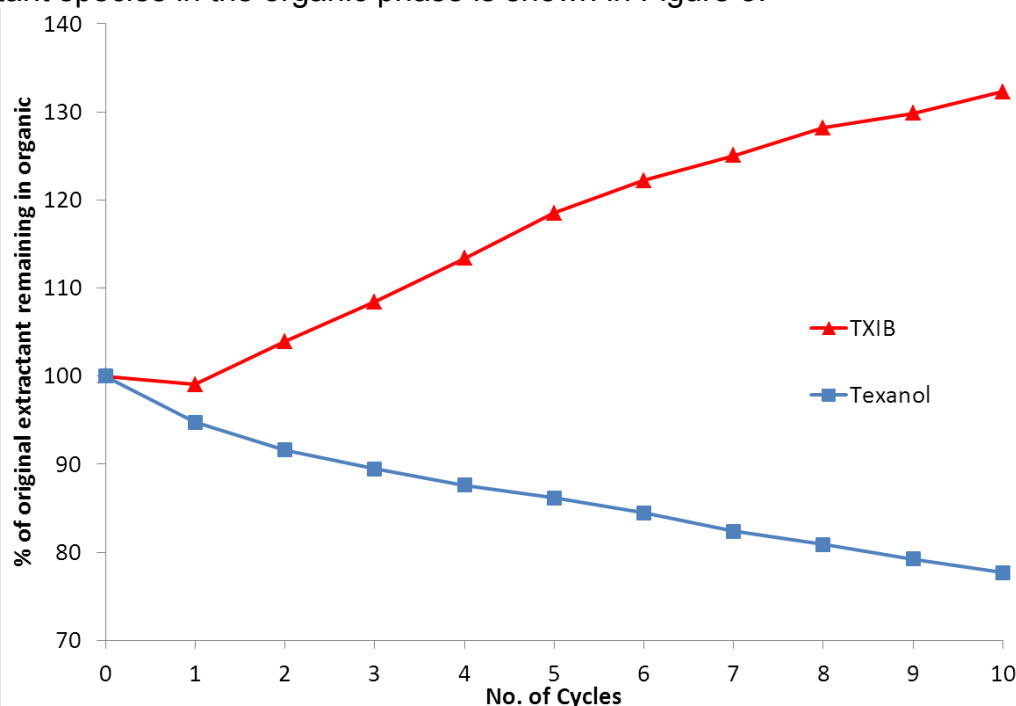
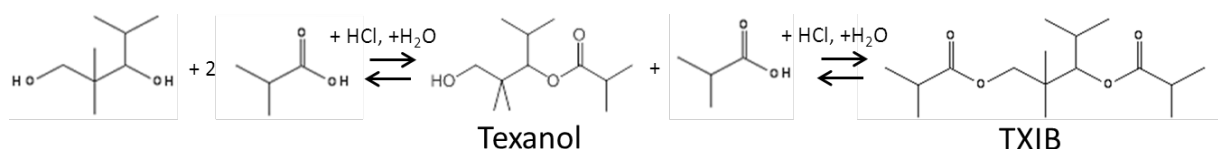


Figure 3: Relative change in the mass of extractant species in the organic during the degradation test

The mass of Texanol in the organic dropped by 22 % over the 10 cycles which was accompanied by a drop in the volume of the organic of 19 %, as highlighted by the internal standard. This resulted in an overall decrease in extractant concentration which would explain the decrease in distribution coefficients. This loss of extractant could either be due to solubility losses to the aqueous phases or organic degradation. The solubility losses for Texanol are likely to be small due to its low solubility in 6 M HCl (0.38 % v/v) and water (< 0.1 % v/v).⁷ Based on these values the drop in Texanol concentration due to solubility losses would be expected to be below 1 % per cycle. The results show a loss of over 2 % per cycle suggesting that some organic degradation must also be occurring. The increase in absolute mass of TXIB in the organic phase suggests a possible degradation mechanism. Texanol and TXIB share a similar organic backbone and the conversion of Texanol to TXIB could take place via the mechanism suggested in Scheme 1.



Scheme 1: Possible degradation mechanism for Texanol

In the 6 M HCl environment, necessary to extract the target metals, the esterification and hydrolysis reactions shown in Scheme 1 could take place freely. As the only components that were detected in the organic phase were Texanol and TXIB it is likely that all the other possible organic degradation products have a high solubility in the aqueous phase and deported to the raffinate, scrubs and strips.

Conclusions

Upon first examination 80 % v/v Texanol in Shellsol D70 appeared to be a very attractive and cheap extractant which could be used to remove Au, Fe and Te from PGM refining liquors. Using a low acid strip it was possible to selectively strip Fe and Te from the loaded organic allowing the Au to be stripped with water to produce a high purity strip liquor.

However, upon conducting a degradation study on the novel extractant system it was shown that Texanol degrades rapidly, probably *via* ester hydrolysis, in the highly acidic conditions. The majority of the degradation products appear to deport to the aqueous phase resulting in a steady drop in extractant concentration in the organic phase over time. If this extractant system were to be used industrially the composition of the organic phase would have to be constantly adjusted to maintain the extractant concentration. The organic degradation products would also have to be removed from the aqueous streams to avoid contamination of downstream processes. Both of these considerations would add to the operating cost of this process meaning that it is unlikely to be economically viable when compared to MIBK or dibutyl carbitol.

Acknowledgements

The authors would like to thank Anglo American Platinum Limited and Johnson Matthey for their financial support of this project and for permission to publish.

References

- [1] F.K. Crundwell, M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*, Elsevier, 2011, p.498-499
- [2] J.E. Barnes, J.D. Edwards, *Solvent Extraction at Inco's Acton Precious Metal Refinery*, *Chemistry and Industry*, 6 Mar. 1982, p. 151-155
- [3] D.F.C. Morris, M. Ali Khan, *Application of Solvent Extraction to the Refining of Precious Metals – III – Purification of Gold*, *Talanta*, 1986, 15, 1301-1305
- [4] B.F. Rimmer, *Refining of gold from precious metal concentrates by liquid-liquid extraction*, *Chemistry and Industry*, 19 Jan. 1974, p. 63-66
- [5] R.A. Grant, V.A. Drake, *The Application of Solvent Extraction to the Refining of Gold*, *International Solvent Extraction Conference*, Cape Town, South Africa, 2002, p.940-945
- [6] E. Paatero, M. Haapalainen, 2011, *Method For Recovering Gold By Solvent Extraction*, World Patent 2011/154603
- [7] Eastman Texanol brochure, http://www.eastman.com/Literature_Center/M/M329.pdf

Metal separation by solvent extraction with CYANEX 471X

Jiaxu Yang*¹, Christian Ekberg¹, Teodora Retegan¹

Summary

Triisobutyl phosphine sulfide (CYANEX 471X) is a solvating extractant primarily used for the recovery of silver and separation of palladium from platinum. However, since extensive studies have been done on the extraction of mono- and divalent metal ions, it could also be of interest to study the extraction of metals from the acidic leach solution of E-waste by CYANEX 471X. In this work, CYANEX 471X was investigated for the purpose of recovering Li(I) from spent vehicle batteries and removal of Ag(I) and Hg(II) from waste flat panel displays. Extraction of metal ions at different initial acid concentration, extractant concentration and mixing time was investigated. Mercury and Silver was selectively extracted from 1 HNO₃ and 1 M HCl containing high concentration of different metal ions with 0.1 – 0.5 M Cyanex 471X in kerosene. Quantitative extraction of mercury could be achieved at extractant concentration of 0.5 M.

¹ Industrial Materials Recycling & Nuclear Chemistry ,Department of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden

Introduction

As modern electronic equipment becomes more and more sophisticated, the number of different types of materials involved in their constructions has also increased. Some of these materials contain rare and valuable metals, while others are harmful to the environment. For example, in a laptop computer, indium is used in the transparent electrode in the display, Rare Earth Elements (REEs) can be found in various parts such as backlight and loudspeakers. Other than that, mercury can also be found in liquid crystal displays (LCDs) which uses Cold Cathode Florescent Lamps (CCFLs) as backlight. Even though trend has shown that CCFLs are being phased out of LCD-TVs and monitors, there can still be a significant amount of mercury to be found in discarded older LCDs and florescent lamps. Due to relatively low concentrations of metals such as indium in E-waste, one of the methods to recycle precious metals from E-waste has been acid leaching followed by solvent extraction [1]. It has been shown that triisobutyl phosphine sulfide (TIBPS or Cyanex 471X) is able to selectively extract many weak Lewis acids such as Ag(I) [2]- [3], Pd(II) [4], Au(III) [5] and Hg(II) [6] [7] from various acidic media. This makes Cyanex 471X potentially useful for removing harmful metal ions from acidic solutions containing many different metal ions.

In the present work, the extraction of metal ions from 1 HNO₃ and 1 M HCl by Cyanex 471X diluted in kerosene was studied. Aqueous phase used in this study FPD waste leachate, which contains various metals such as Cu, Fe and Zn. The effect of mixing time, acid concentration and temperature on the distribution ratios of different metals, Hg(II) in particular, was studied. The purpose was to investigate the possibility of using Cyanex 471X to separate Hg(II) from the leachate solution of Flat Panel Displays waste before further treatment to recover other valuable metals.

Methodology

In all the experiments performed, the aqueous phase was obtained by leaching of mechanically crushed FPD waste at a solid to liquid ratio of 0.1 g/ml in either 1 M HCl (37% puriss, Sigma-Aldrich) or 1 M HNO₃ (64-66% puriss, Sigma-Aldrich). Measured values of Initial metal concentrations in the aqueous phase is presented in Table 1. The values presented in the table have a measurement uncertainty of 5%. Mercury concentration in the acid leachate was spiked by the addition of HgCl₂ and Hg(NO₃) dissolved in 1 M HCl and 1 M HNO₃, respectively.

Table 1: metal concentrations in the aqueous phase (μM)

	1 M HCl	1 M HNO ₃
Ag	120	5
Co	110	56
Cr	1200	220
Cu	2800	1300
Eu	270	180
Fe	99000	42000
Gd	670	440
Hg	760	780
In	500	340

Li	1100	1500
Mn	10000	2200
Mo	85	48
Nd	190	120
Ni	2600	750
Sn	1100	76
Y	11000	7400
Zn	1300	8600

The organic phase consisted of Cyanex 471X (Cytec) dissolved in kerosene (Solvent-70, Statoil). Concentration of the extractant was 0.1 M, unless otherwise stated. Equal volumes (1 ml) of both phases were mixed in 3.5 ml glass vials under mechanical shaking at 1500 rpm (IKA VIBRAX VXR). For kinetics study, mixing time varied between 5 min and 60 min, for other studies mixing time of 40 minutes was used. Extraction temperature was varied between 293K and 333K in the temperature study, in other experiments temperature was kept at 293±1K.

Metal concentrations in the aqueous phase before and after extraction were determined using Inductively Coupled Plasma with Optical Emission Spectrometer (ICP-OES, Thermo iCAP-6000). The metal content was quantified by calibrating with external standards. Distribution ratios were calculated by mass balance in the aqueous phase.

Results & Discussion

Most of the distribution ratios presented in the figures have uncertainties between 15% and 20%. The uncertainties were calculated as relative standard deviations of triplet samplings.

Extraction kinetics

The results in Figure 1 shows the extraction kinetics of Cyanex 471X. At extractant concentration of 0.1 M, silver and mercury was the only metal ions extracted from both nitrate and chloride media. From the figure, it can be seen that even though 40 minutes were needed for extraction to reach equilibrium, short contact times such as 5 minutes was still enough to achieve distribution ratios which were approximately the same as the equilibrium values.

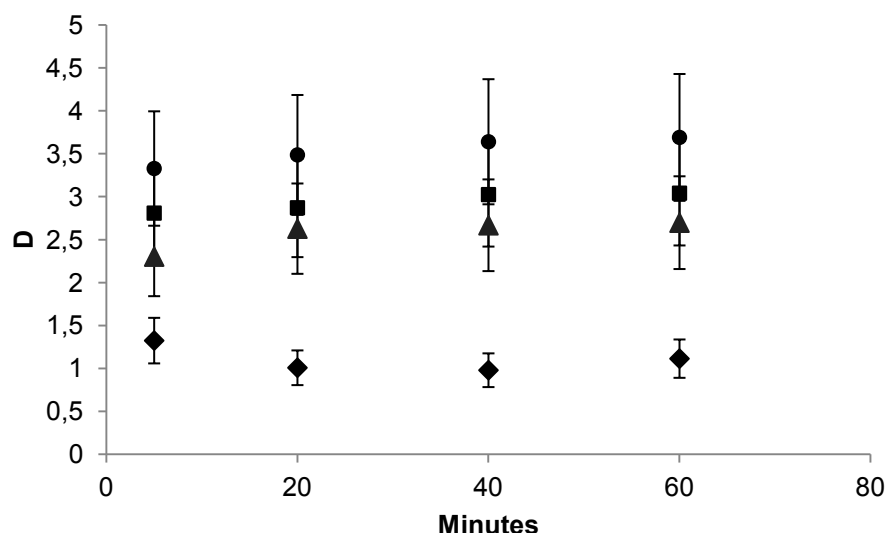


Figure 1: the effect of mixing time on the distribution ratios of (♦) Ag(I) in 1 M HNO₃ (●) Hg(II) in 1 M HCl (■) Ag(I) in 1 M HCl (▲) Hg(II) in 1 M HNO₃.

Effect of extractant concentration on metal extraction

In Figure 2, the effect of extractant concentration on the distribution ratio of Hg(II) in nitrate and chloride media is shown.

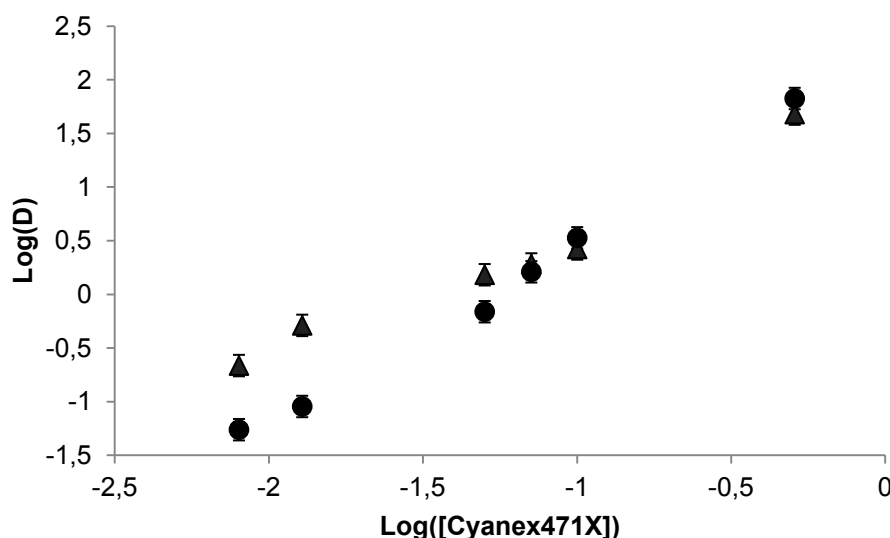


Figure 2: the effect of Cyanex 471X concentration on the distribution ratios of (●) Hg(II) in 1 M HCl (▲) Hg(II) in 1 M HNO₃.

In addition to the increase in the distribution ratios of Hg(II) and Ag(I) with extractant concentration, it was also noticed that at small amount (0.2) of other metal ions such as copper and tin were also extracted at extractant concentration of 0.5 or greater. By linear regression, the slope of Hg(II) extraction in chloride media was approximately 2, and in nitrate media it was 1.2. This indicates that the stoichiometry between mercury and Cyanex 471X is 1:2 in HCl, and 1:1 in HNO₃. The result obtained from this work for chloride media was lower than it was previously reported

[6]. This could be due to the presence of large amounts of other metal ions in the aqueous phase, which forms soluble chloride complex.

Effect of acid concentration on metal extraction

The effect of HNO_3 and HCl concentration on the extraction of mercury can be seen in Figure 3. 1 M HClO_4 was used to keep the ionic strength constant.

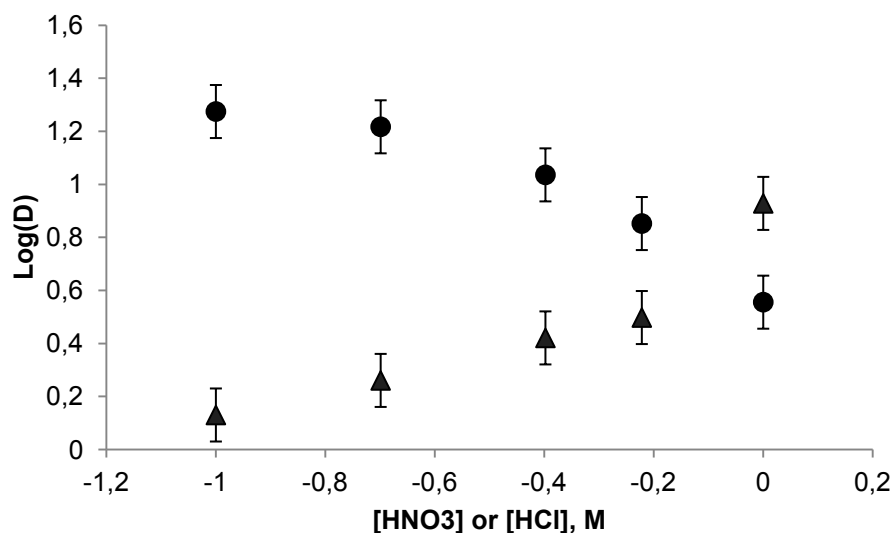


Figure 3: the effect of nitric and hydrochloric acid concentration on the distribution ratios of (●) Hg(II) in 1 M HCl (▲) Hg(II) in 1 M HNO_3 .

The distribution ratio of Hg(II) increases with decreasing $[\text{Cl}^-]$ between 1 M and 0.1 M. This is due to the stability constant of HgCl_4^{2-} ($K_4 \approx 10$) and HgCl_3^- ($K_4 \approx 9.1$) being higher than unity [8]. Thus at chloride concentration of 1 M, the molar fraction of non-extractable anionic mercury complex in aqueous phase is much higher than HgCl_2 . However, for nitrate media the trend is the opposite, the distribution ratio of Hg(II) increased with nitrate concentration. This indicates that the concentration of extractable $\text{Hg(NO}_3)_2$ complex increases from 0.1 M to 1 M HNO_3 .

Effect of temperature on metal extraction

From results in Figure 2, possible extraction reactions for Hg(II) are presented in Equation (1) and (2), from which the equilibrium constant K_{ex} was calculated.

(1)

(2)

Between 293K and 333K Figure 4 shows the effect of temperature on the K_{ex} of mercury extraction. The values of ΔH° of extraction were calculated from the gradient of the fitted line. For 1 M HCl it was -45 ± 9 kJ/mol and -20 ± 6 kJ/mol for 1 M HNO_3 . The extraction of Hg(II) from both aqueous media are exothermic processes, thus the distribution ratio of Hg(II) is inversely proportional to temperature. Since the entropy change is also negative, the extraction of Hg(II) is enthalpy-driven reactions within the temperature range studied.

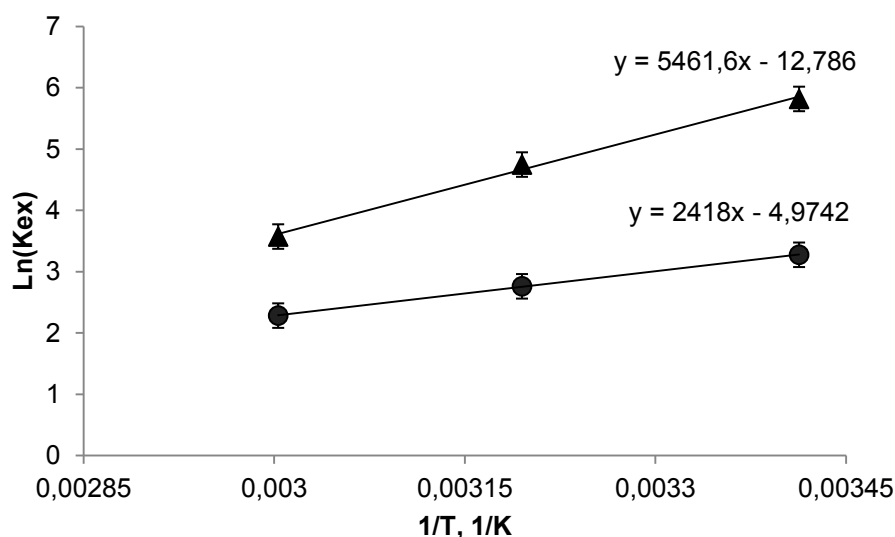


Figure 4: the effect of extraction temperature on the distribution ratios of Hg(II) in 1 M HCl (▲) Hg(II) in 1 M HNO_3 .

Conclusion

In the present study, the effect of several factors on the extraction of metals with Cyanex 471X diluted in kerosene were studied. Extraction kinetics showed that a mixing time of approximately 40 minutes were needed for the distribution ratio of Hg(II) to reach equilibrium. By varying extractant concentration, it was found that the stoichiometry for Hg(II) extraction was 1:2 in chloride media and 1:1 in nitrate media. Distribution ratios for Hg(II) were found to decrease with increasing HCl concentration from 0.1 M to 1 M, due to the formation of anionic mercury chlorides at higher chloride concentrations. Temperature studies showed that mercury extraction was higher at room temperature than 60°C. Due to having good selectivity for Hg(II), and relatively fast extraction kinetics, Cyanex 471X at a concentration between 0.1 M and 0.5 M can be used for removing mercury from the leachate of FPD waste.

Acknowledgement

The authors would like to thank Recyval-Nano, an EU FP7 project (no. 310312) for providing financial support.

References

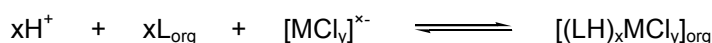
- [1] S. Virolainen, D. Ibane and E. Paatero, "Recovery of Indium from Indium-Tin-Oxide by Solvent Extraction," *Hydrometallurgy*, vol. 107, no. 1-2, pp. 56-61, 2011.
- [2] Z. Hubicki and H. Hubicka, "Studies of extractive removal of silver (I) from nitrate solutions by Cyanex 471X," *Hydrometallurgy*, vol. 37, no. 2, pp. 207-219, 1995.
- [3] W. R. A. Rickelton, "Selective recovery of silver by solvent extraction with triisobutylphosphine sulfide.," *Minerals and Metallurgical Processing*, vol. 4, no. 1, pp. 7-10, 1987.
- [4] I. Ahmed, A. Nayl and J. Daoud, "Extraction of palladium from nitrate solution by CYANEX 471X," *International Journal of Mineral Processing*, vol. 101, no. 1-4, pp. 89-93, 2011.
- [5] S. Martínez, P. Navarro, A. Sastre and F. Alguacil, "The solvent extraction system Au(III) — HCl-Cyanex 471X," *Hydrometallurgy*, vol. 43, no. 1-3, pp. 1-12, 1996.
- [6] T. Francis, T. P. Rao and M. Reddy, "Cyanex 471X as extractant for the recovery of Hg(II) from industrial wastes," *Hydrometallurgy*, vol. 57, no. 3, pp. 263-268, 2000.
- [7] R. Singh and S. Tandon, "Extraction and separation of mercury(II) using triisobutyl phosphine sulfide (TIBPS/Cyanex) as an extractant and its application to industrial effluent," *Talanta*, vol. 44, no. 5, pp. 843-848, 1997.
- [8] N. Rice and M. SmithJ, *Appl. Chem. Biotechnol.*, vol. 25, p. 376, 1975.

Outer-Sphere Coordination Chemistry: Use of Amido-Ammonium Ligands as Selective Extractants for Precious Metals

*Robert C. Luckay^{*1}, George Murray², Peter A. Tasker², Jennifer R. Turkington² and A. Matthew Wilson²*

Summary

Hydrochloric acid is used as a leaching agent in the extractive metallurgy of many precious metals, forming chloridometalates in the process. Separation and concentration by solvent extraction using anion exchange reagents is facilitated by recognition of the outer coordination spheres and formation of neutral anion-ligand packages and an understanding of the nature of hydrogen-bonding interactions to chloridometalates is very important in designing new selective extractants. Three amido functionalised pro-ligands L¹-L³ have been synthesized containing the sequence of atoms R₂N-CH₂-NH-CO-R, which upon protonation forms a six membered "proton-chelate" with a hydrogen bond between the tertiary ammonium N-H⁺ group and the amido oxygen. The monocationic ligands, LH⁺, extract the precious metalate from acidic solutions containing high concentrations of chloride ions as in:



Plots of metalate uptake vs [L]:[MCl_y]^{x-} at low pH and high [Cl⁻] concentration indicate that one, two or three LH⁺ ligands are needed to balance the charge on the chloridometalate and form neutral complexes. [AuCl₄]⁻ was most readily extracted, followed by [PtCl₆]²⁻ and [IrCl₆]³⁻, as expected from the Hofmeister bias. A reversal of the Hofmeister bias was shown by L² with respect to [AuCl₄]⁻ and [PtCl₆]²⁻. It was found that with decreased [Cl⁻] concentration, there is improved extraction of the precious metalate but the work confirms that the amidoamine extractants L¹-L³ show high selectivity for precious chloridometalates over chloride anions.

Introduction

The digital revolution has increased the need for precious metals due to their specific properties in varied fields. This increased demand is driving the development of separation technologies, e.g. solvent extraction (SX), for their efficient extraction and recycling.¹ The main steps of a hydrometallurgical solvent extraction flowsheet are typically leaching, extraction, stripping and reduction.^{2,3}

Gold remains a standard for measuring the strength of global markets and also finds many high-tech applications. Ores are usually processed by the well-established cyanidation process, but the less used Minataur process leaches gold using hydrochloric acid and nitric acid to obtain tetrachloroauric acid, HAuCl₄, which is concentrated and separated by solvent extraction and the gold precipitated using a reducing agent such as SO₂.^{4,5} Dibutyl carbitol (DBC) was initially used as an extractant, but stripping requires direct precipitation of gold from the organic phase, resulting in high organic losses.⁴ In South Africa, one of the precious metal refineries recovers gold first by SX, the liquor is then processed and palladium recovered by

¹*Department of Chemistry & Polymer Science, Stellenbosch University, Private Bag X1, Matieland, Stellenbosch, 7602, South Africa

² EastCHEM School of Chemistry, University of Edinburgh, Edinburgh, EH3 9JJ, UK

SX, then follows platinum by SX. Ruthenium and osmium are removed by distillation, iridium is recovered by SX and finally rhodium is recovered by IX.³

For the metals involved in this paper, the extraction of their chloridometalates is represented by equation 1.



The Hofmeister bias has its origins in protein chemistry and originally defined the extent to which soluble anions salt out proteins.⁶ Applying the bias to our extraction hierarchy means that low charged chloridometalates such as $[\text{AuCl}_4]^-$ are extracted most readily and other metalates are extracted in order of increasing charge. The aim of the current work is to design and test new extractants for the recovery of chloridometalates such as $[\text{AuCl}_4]^-$, $[\text{PtCl}_6]^{2-}$ and $[\text{IrCl}_6]^{3-}$ and to see whether the Hofmeister bias is followed with this series of metalates.

Experimental

Reagents, solvents and ICP-OES standards were acquired from Sigma-Aldrich, Alfa Aesar, Fisher or Acros and used without further purification. Distilled water was obtained from a Milli-Q purification system. ^1H and ^{13}C NMR spectra were collected on a Bruker AVA 400 NMR spectrometer. Mass spectrometry was performed on a VG Autospec instrument using ionization techniques including ESI and EI. Elemental analyses were obtained from London Metropolitan University. ICP-OES data were gathered on a Perkin Elmer Optima 5300DV and were manipulated using Winlab32 and Microsoft Excel. Ligands $\text{L}^1 - \text{L}^3$ were synthesized as described in the literature⁷.

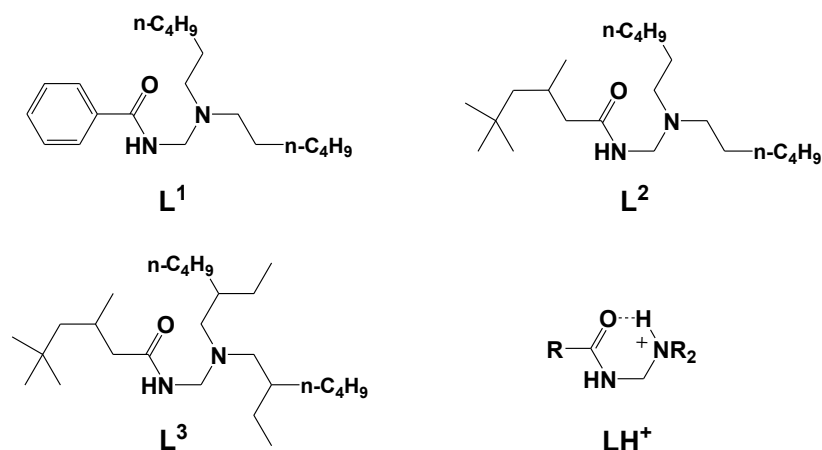


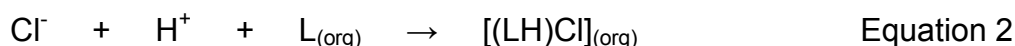
Figure 1. Pro-ligands L which have been synthesized for the present study and the “proton chelate” structure formed by LH^+ .

For the solvent extraction, volumetric measurements were made using calibrated auto-pipettes. Extractant solutions (ca. 0.1 mol dm^{-3}) were prepared in toluene. Solutions were diluted with toluene to adjust reagent: metal chloride ratio in individual extractions. Metal chloride solutions (ca. 0.01 mol dm^{-3}) were prepared in 6 M HCl. Aqueous and organic phases were contacted in sealed vials and stirred at 1000 r.p.m. for 24 h. Aliquots (0.5 ml) from each phase was diluted to 10 ml using 2-

methoxy-1-propanol. Multiple metal standards were made up to 10 ml from 1000 mg/L analytical standards.

Results and Discussion

Metal SX processes usually consist of several extract and strip stages and can involve different types of reactions. The relevant reaction for extraction in this work involves the formation of a neutral assembly under acidic conditions as shown in equation 1.⁷ This is not the only reaction that can take place; ligands can also form ion pairs with chloride ions from the hydrochloric acid (equation 2).⁷



Whilst extractant design can give high selectivity for chloridometalate over chloride, given the very high chloride concentrations in the feed solution, it is likely that some reagent will always be used inefficiently by associating with chloride. Extractant selectivity (in single metal streams) is proportional to K_M / K_{Cl} where K_M and K_{Cl} are the equilibrium constants of the chloridometalate and chloride transport. Increasing extractant concentration, $[\text{L}]$, drives both equilibria (equation 1 and 2) to the right, improving metal recovery. The strength of an extractant can be assessed by determining how much is required to transport a given percentage of the chloridometalate into the organic phase. This is dependent on the complex stability, extractant hydrophobicity and selectivity over chloride. To evaluate the performance of extractants, a solution of MCl_y^{x-} in HCl was contacted with solutions of various extractant concentration, providing a plot of percentage of metalate uptake versus $[\text{L}]:[\text{MCl}_y]^{x-}$. This indicates the concentration of extractant needed to achieve extraction of individual metals at low pH and high $[\text{Cl}^-]$ concentration. The plot has relevance to industrial procedures for recovery of precious metals. Due to the value of the metals and the cost downstream processing, using high reagent concentration is acceptable. Metal uptakes by a given extractant are plotted versus $[\text{L}]:[\text{MCl}_y]^{x-}$ for the chloridometalates of interest, indicating the order of preference in which metals are extracted and whether they follow the Hofmeister bias.

Extraction by L¹

Extractant L¹ has a central nitrogen atom with a benzamido arm and two hexyl chains to enhance solubility in hydrocarbons. The central nitrogen is easily protonated, forming a 6-membered “proton chelate” (Figure 1). The extraction of $[\text{AuCl}_4]^-$, $[\text{PtCl}_6]^{2-}$ and $[\text{IrCl}_6]^{3-}$ is detailed in Figure 2. The metals were extracted in individual experiments as opposed to mixed-metal extraction tests. Loading levels follow the Hofmeister bias. At concentration ratio 1:1, approximately 70% of $[\text{AuCl}_4]^-$ is extracted and at 2:1 all the metalate is transferred to the organic phase. This indicates that formation of a gold-containing complex is favoured over a chloride-ligand complex. The soft N-H/C-H donor set of L¹H⁺ binds more effectively with the large, charge diffuse, chloridoaurate rather than the small, hard, chloride ion.

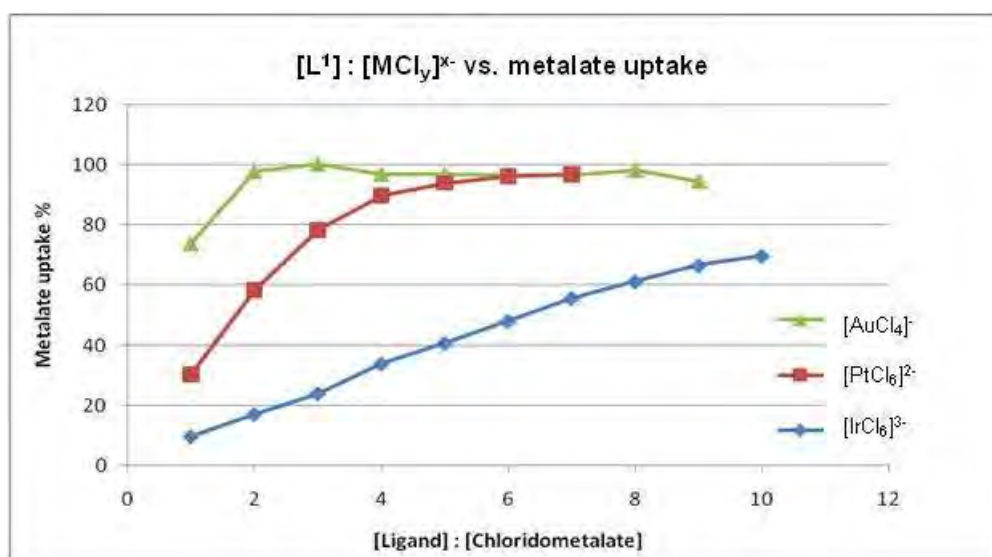


Figure 2. Metalate uptake by L^1 versus the ratio of ligand:chloridometalate.

The chloridoplatinate is more weakly extracted at low ligand concentrations and only when the ligand:Pt reaches 5:1 is almost all of the platinum extracted. The higher hydration energy of chloridoplatinate makes outer-sphere coordination more difficult.

The $[\text{IrCl}_6]^{3-}$ ion fails to exceed 70% extraction even with a ten-fold excess of L^1 . Chloridoiridate has an even higher hydration energy making it very reluctant to replace its solvation shell with ligands.

Extraction by L^2

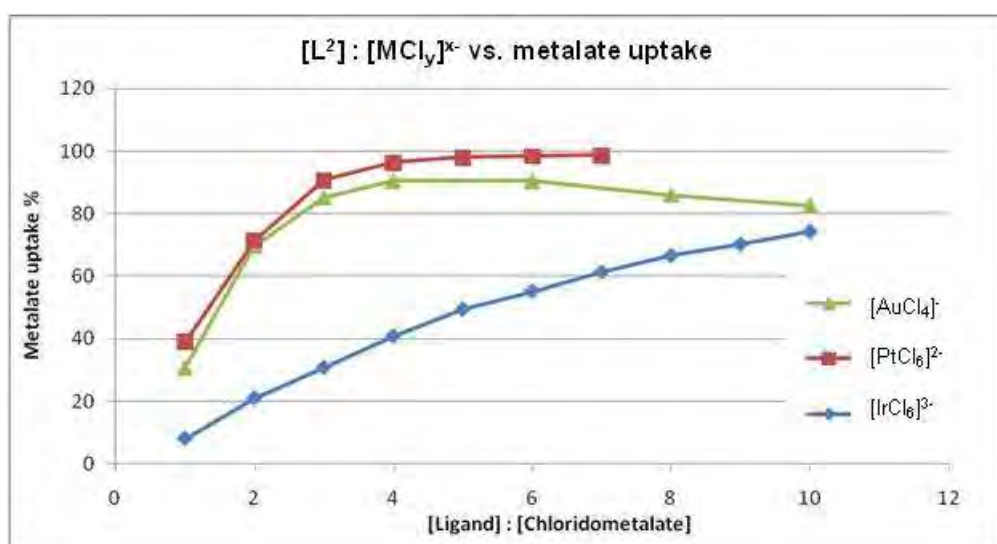


Figure 3. Metalate uptake by L^2 versus the ratio of ligand:chloridometalate.

Extractant L^2 has a similar structure to L^1 but with the phenyl group replaced by a 3,5,5-trimethylhexyl unit which is substantially more lipophilic but may provide steric hindrance to complex formation as a result of its β -branching (see Figure 1)

Complexes are likely to contain similar hydrogen-bonded structures to those proposed for L^1 . The extraction of $[AuCl_4]^-$, $[PtCl_6]^{2-}$ and $[IrCl_6]^{3-}$ is detailed in Figure 3.

L^2 extracts the precious chloridometalates in an “anti-Hofmeister” order with $[PtCl_6]^{2-}$ and $[AuCl_4]^-$ being extracted approximately equally strongly. This deviation from the Hofmeister bias might result from the bulk of the 3,5,5-trimethylhexanamide arm and some incompatibility with the square planar gold $[AuCl_4]^-$ anion. The extraction of $[PtCl_6]^{2-}$ is slightly more efficient than with L^1 , whilst the loading profiles (Figures 2 and 3) for $[IrCl_6]^{3-}$ are very similar.

Extraction by L^3

L^3 has a similar structure to L^2 , differing only in having two 2-ethylhexyl substituents in the tertiary amine unit. Such 2-ethylhexyl groups are commonly used to impart hydrocarbon solubility in metal solvent extractants. The uptake of $[AuCl_4]^-$, $[PtCl_6]^{2-}$ and $[IrCl_6]^{3-}$ is detailed in Figure 4.

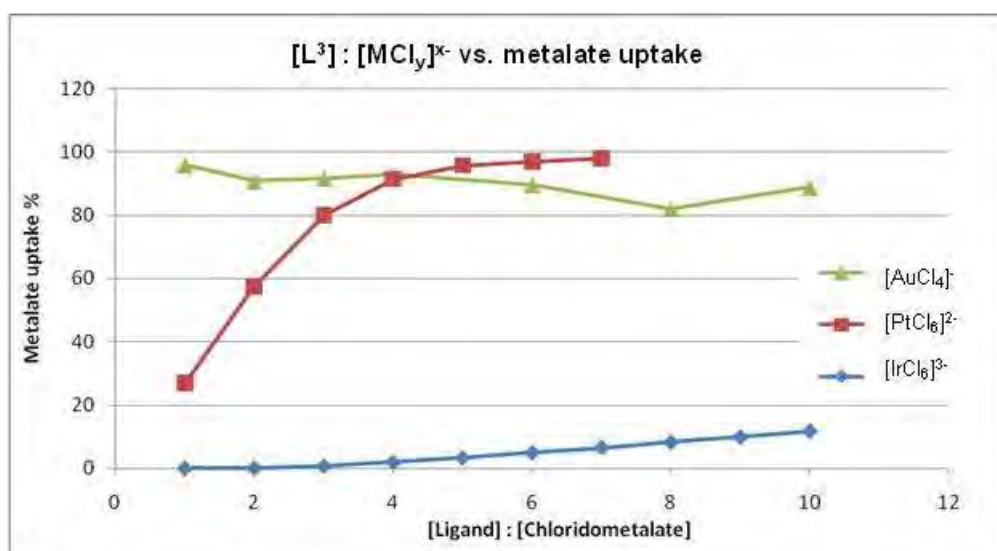


Figure 4. Metalate uptake by L^3 versus the ratio of ligand:chloridometalate.

Reagent L^3 extracts the precious metals in the expected Hofmeister⁶ order. Chloridoaurate is almost quantitatively extracted at a ratio of 1:1, ligand to metalate, indicating excellent selectivity for $AuCl_4^-$ over Cl^- . It also shows a markedly better performance than L^2 , which might be attributed to it having two 2-ethylhexyl substituents that may provide a more favourable hydrophobic coverage of the anion in the 1:1 assembly $[(L^3H)AuCl_4]$. The extraction of chloridoplatinate is unremarkable, being comparable with L^1 and L^2 described above, and chloridoiridate is very poorly extracted, even at very high ligand concentration. The very weak uptake of the latter by L^3 might be a consequence of the increased bulk of the extractant making it more difficult to accommodate three ligands around the trianion, $[IrCl_6]^{3-}$, to generate neutral, organic soluble species.

Conclusions

The extractants L^1 and L^3 follow the Hofmeister bias when loading Au(III), Pt(IV) and Ir(III) from 6 molar HCl solutions, with metal uptakes following the order $[\text{AuCl}_4]^- > [\text{PtCl}_6]^{2-} > [\text{IrCl}_6]^{3-}$ which would be expected from the higher hydration energies of the more highly charged anions. In contrast, L^2 shows a slight preference for uptake of $[\text{PtCl}_6]^{2-}$ over $[\text{AuCl}_4]^-$ and it is important for reagent development to define the origins of this “anti-Hofmeister” behavior.

All three reagents exhibit selectivity of extraction of chloridometalate over chloride and the origins of this are likely to be in the structures of the monocationic ligands, LH^+ , which can provide an array of hydrogen bond donors in an anion receptor site that suits the “softer” (charge diffuse) chloridometalate better than the “hard” chloride ion. Pre-organisation of these binding sites results from the presence of a “proton chelate” formed by hydrogen bonding between the ammonium NH and the amido oxygen atom as demonstrated in comparable complexes with the chloridometalates of base metals.⁷

The strongest extractant for $[\text{AuCl}_4]^-$ is L^3 which gives almost quantitative uptake when a stoichiometric amount is present. All three reagents are efficient extractants for Pt(IV), with L^3 being the strongest, giving ca. 90% uptake when a 50% molar excess is used. All are weak Ir(III)-extractants with L^3 , being particularly so, ensuring that a very efficient Au(III)/Ir(III) separation could be achieved.

Acknowledgments

RCL thanks Oppenheimer Memorial Trust and Anglo Platinum for financial assistance as well as UoE for hosting him during his sabbatical.

References

1. Turkington, J. R.; Bailey, P. J.; Love, J. B.; Wilson, A. M.; Tasker, P. A., *Chemical Communications* 2013, 49 (19), 1891-1899.
2. Habashi, F., *Handbook of extractive metallurgy*. Wiley-VCH: Weinheim ; Chichester, 1997.
3. P. A. Tasker, P. G. Plieger and L. C. West, in *Comprehensive Coordination Chemistry II*, ed. M. D. Ward, Elsevier Ltd, Oxford, 2004, 9, pp. 759-808.
4. Syed, S., *Hydrometallurgy*, 2012, 115–116 (0), 30-51.
5. Sole, K. C.; Feather, A. M.; Cole, P. M.; *Hydrometallurgy*, 2005, 78, 52-78.
6. Hofmeister, F., *Arch Exp Pathol Pharmacol*, 1888, 24, 247-260; Moyer, B. A.; Bonnesen, P.V.; Custelcean, R.; Delmau, L. H.; Hay, B. P.; *Kem. Ind.*, 2005, 54, 65-87.
7. Turkington, J. R.; Cocalia, V.; Kendall, K.; Morrison, C. A.; Richardson, P.; Sassi, T.; Tasker, P. A.; Bailey, P. J.; Sole, K. C., *Inorganic Chemistry* 2012, 51 (23), 12805-12819.

Recycling of Co^{2+} , Cu^{2+} and Li^+ from Li-ion battery scrap

H. Noll, M. Fritz, M. Siebenhofer, Graz University of Technology, Institute of Chemical Engineering and Environmental Technology, Inffeldgasse 25C, 8010 Graz

In the last years the usage of Lithium Ion Batteries (LIB) has notably increased. LIB are used as power sources in cell phones, laptops, video cameras etc. LiCoO_2 has been a basic cathode material. For adjusting stability and conductivity several elements such as Ni, Mn may be admixed to the spinells. About 25% of the global Co production is meanwhile needed for LIB production. In the mean LIB-cathodes may contain 3% Li, 23% Co, 12% Cu, 2% Fe, 13% Al, 1.5% Ni and Mn-traces. As a consequence the demand for recycling processes for the valuable constituents of spent Lithium ion batteries, such as Cobalt, Copper, Nickel, Lithium etc. is highly desirable. The element mixture of spent LIBs recommends recycling by I,I-extraction.

After dismantling of the battery body the reaction potential, caused by short circuiting of the residual charge and the electrolyte, has to be neutralized. In lab scale this first step may be managed by wet crushing.

Battery scrap from Lithium Ion Batteries is then treated by acid or alkaline leaching to get the target constituents dissolved. From comparison of different leaching strategies dual step acidic leaching with sulfuric acid in a first step, followed by oxidizing leaching with hydrogen peroxide has evolved as highly efficient process. Leaching solutions typically contain Co^{2+} , Al^{3+} , Cu^{2+} , Li^+ and Fe^{3+} ions. The crude leaching liquor is then prepared for isolation of the target constituents. In a first step the trivalent ions Fe^{3+} and Al^{3+} can be removed by precipitation with LiOH leaving Cobalt, Copper and Lithium in the filtrate phase after separation of hydroxide precipitates by filtration. Precipitation with LiOH is not a must but recommended to avoid formation of mixtures of alkaline metal ions in the leach liquor.

In a next step different recycling routes for separation of constituents by I,I-extraction of constituents from the refined leach liquor may be designed.

Separation of Cobalt, Copper, and Lithium with combinations of the ion exchangers DEHPA, LIX 84 and Cyanex 272 was investigated in order to evaluate whether selective separation of the constituents Cobalt, Copper and from Li^+ by solvent extraction is feasible. While selectivity of Co^{2+} and Cu^{2+} over Li^+ is limited when the reactive solvent DEHPA is used, Cyanex 272 is a highly selective extractant, leaving Li^+ in the raffinate phase. After reextraction Cu^{2+} is then selectively separated from Co^{2+} with LIX 84.

I,I-extraction as well as liquid membrane permeation may be applied. Latter process has been validated in bench scale too. Microporous Polyethylene flat sheet bodies with a thickness of 2 mm, a pore size distribution of 7-12 μm and a porosity of 0.36 were contacted with the corresponding solvent mixtures to provide rigid membranes for mass transfer. The experiments were conducted in a lab scale unit, providing two compartments for the aqueous donor and acceptor solutions, separated by the solvent laden porous membrane. Cobalt and Copper were separated with either DEHPA or Cyanex 272, leaving Li^+ finally in the raffinate phase for further processing. Cobalt and Copper were then separated with a membrane prepared with LIX 84. In principle the process has proven feasible for application in the recycling of valuable constituents from Li-ion batteries.

LiSXTM: A Breakthrough in Lithium Production

*Jonathan Lipp^{*1}*

The traditional technology for producing lithium from South America's Salar calls for huge arrays of solar evaporation ponds. These ponds consume vast areas and the process itself has a residence time of ca. 18 month, as about 90% of the solution needs to evaporate. Up to recently no alternative was available for this technology. A new solvent extraction technology was developed to facilitate faster and economic lithium production. Results indicate a distribution coefficient up to 30, and selectivity greater than 1,000 towards Na extraction. The loaded solvent is stripped using a strong mineral acid, and the product solution is the lithium derivative of that stripping acid. Utilization of this new LiSXTM technology results in reducing the area needed for a commercial plant as well as reduces the residence time. In addition applying different stripping acids can diversify the product line of such facility.

Introduction

Production of lithium has recently gained a lot of interest due to its crucial role in alternative energy sources. Current technology for lithium production relays on massive liquid evaporation. In the salt flats (Salars) of South America this is performed in a huge array of solar evaporation ponds, while in other places process energy is exploited for that purpose. While the later process is quite costly, the former is lengthy and may take up to 18 month of residence time [1], and is very susceptible to weather conditions. These limitation combined with relatively low lithium recovery are the main driving force in the pursuit of a new technology.

Liquid-liquid solvent extraction (SX) processes can overcome the obstacle of low recovery and high energy demand. Additionally, SX would facilitate reduction in both footprint and residence time. Therefore, in the past couple of decades, a lot of effort has been aimed at developing such a sustainable SX process [2]. Numerous extractants ranging from alcohols through crown ethers to ferric chloride have been studied. Nevertheless, the objective of a full running process remained elusive until recently. New development has finally overcome the hindrance related to this process and introduced a comprehensive SX process for the recovery and production of lithium (LiSXTM). This paper aims at elucidating this process.

Experimental

Materials

All chemical used in the reported work (reagent grade) were used as received. Both aqueous and organic solutions used were synthesized. The proprietary solvent had a maximum lithium capacity of 1.75 g/L.

^{*1} Tenova Bateman Technologies, Yokneam, Israel

Phase contact and analysis

All phase contacts were carried out in a separation funnel by 3 minutes of manual shaking at ambient temperature. The phases were allowed to separate and samples were subsequently taken for chemical analysis. Analyses of Li, all the other metals and SO_4^{2-} were performed using ICP or Atomic Absorption (AA), while titration was used for Cl^- determination. As a rule, High concentrations of a metal interfere with the determination of other metals that are present in very low concentrations. We therefore used standard solutions that contained a background of the ion present in high concentration in order to determine the ions present in low concentrations. For example, in the case of low lithium concentrations in the presence of high sodium concentrations analyses were performed by using standard solutions of Li containing similar Na concentrations to the concentrations in the diluted samples. In a similar way, low concentrations of other elements were quantified. The lowest concentration that can be determined in this manner is 3 mg/L. It should be noted that the analytical accuracy of his method is $\pm 10\%$. Organic solutions were stripped quantitatively using nitric acid solutions and the resulting aqueous solutions were analyzed. The concentrations in the organic solutions were calculated using the phase ratio in the stripping.

pH Optimization & Extraction Equilibrium

pH optimization was performed for the extraction stage using an aqueous solution containing 0.23 g/L. This solution was contacted using phase ratio of O:A=1 with the proprietary solvent. Different amounts of NaOH were introduced to the mixture in order to achieve pH variation. Extraction equilibrium was performed by contacting the proprietary solvent with an aqueous solution containing 0.75 g/L lithium at constant pH, using various O:A phase ratios.

Extraction Stage

Three aqueous solutions were synthesized representing – Salar solution (stream 1); spent solution from carbonization plant (stream 2); and low lithium concentration waste solution (stream 3). Table 1 displays the chemical composition of those streams. The O:A ratio, was calculated using $\text{O:A} = C_{\text{Lif}}/1.75$, where C_{Lif} is the lithium concentration in the feed solution measured in g/L. Hence, O:A=0.41, O:A=1.2 and O:A=0.13 were used for extracting lithium from streams 1, 2 and 3 respectively. This stage was performed in both single contact and cross current modes. Using the former loaded solvent (LS) was produced while the latter was used to evaluate the

expected lithium concentration in the raffinate. In the cross current mode the raffinate from was introduced to another batch of the fresh solvent.

Table 1 – Aqueous Feed Stream composition the LiSXTM process

Element	Li	Na	K	SO ₄	B	Cl	S.G.
Units	mg/L	g/L	g/L	mg/L	mg/L	g/L	
Stream 1	720	115	20	100	500	205	1.25
Stream 2	2100	120	25	275	1000	215	1.21
Stream 3	230	8	1	6500	20	10	1.03

Phase separation and mass transfer tests for this stage were performed by stirring stream 1 and a barren solvent at O:A=0.41 in a beaker with a mechanical agitator (6-blade turbine – 46mm diameter and 7mm width - rotating at about 1300-1450 rpm). Both organic continuous (OC) and aqueous continuous (AC) dispersions have been evaluated. Phase separation times were measured after allowing the phases to separate, until a very thin layer of <~1 mm of bubbles/emulsion was left. At that point samples were removed for analysis to evaluate the mass transfer rate.

Scrubbing Stage

A sufficient amount of LS was prepared and scrubbed in order to remove co-extracted impurities and produce the purified solvent (PS). This stage was tested in two deferent routes using diluted sulfuric acid (1%) – PS1; and hydrochloric acid (0.7%) – PS2. Several scrubbing stages were where the solvent was introduced to fresh batches of scrub solution in each stage. The last couple of stages were carried out using distilled water. All tests were done using O:A=10.

Stripping Stage

PS1 was stripped using 24% sulfuric acid solution while PS2 was stripped using 32% hydrochloric acid. The phase ratio was determined by $O:A = [H^+]/[Li]_{org}$, where $[H^+]$ is the molar concentration of hydronium ion in the acid solution (assuming full dissociation), and $[Li]_{org}$ is the molar concentration of lithium in the PS.

Result and discusion

pH Optimization & Extraction Equilibrium

Initial tests were aimed at evaluation of the pH at which the extraction process should be performed. The experimental data were plotted on Figure 1a, and fitted with a trend line. These results indicate that the extraction process should be performed at

pH12, and thus this was the chosen pH value for the extraction experiments. Additionally, it is evident from this figure that at for the stripping stage pH7 would be low enough to ensure complete removal of the lithium from the organic phase. Figure 1b displays the equilibrium data for the extraction process at pH12, as it is combined with the operating lines for stream 1 (green) and stream 3 (red). McCabe–Thiele evaluation of the required number of stages indicated that three theoretical stages will be required for extracting the lithium from stream 3 (indicated by the dashed black line). It can be evaluated from this figure that two theoretical stages will suffice for streams 1 and 2.

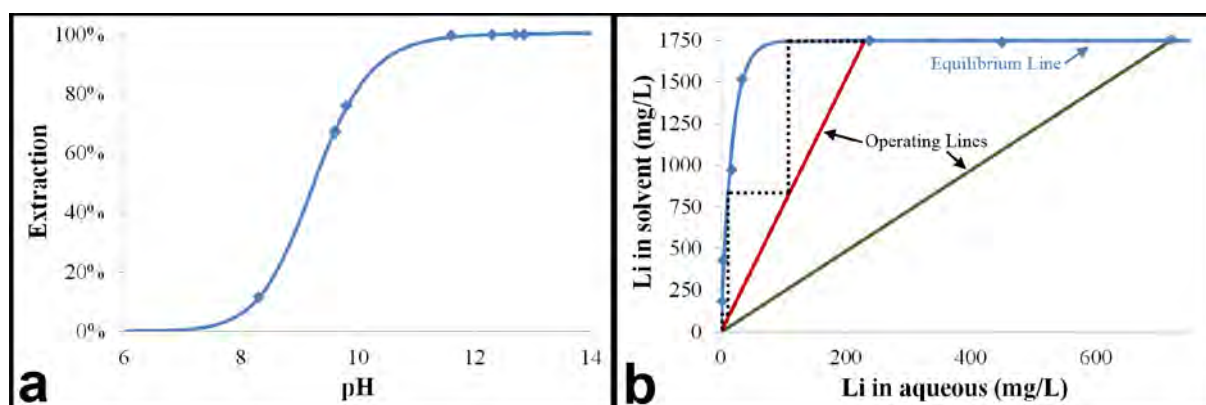


Figure 1 Lithium extraction – (a) Maximum Extraction vs. pH; (b) Extraction Isotherm at pH=12

Extraction Stage

The extraction stage, as discussed above, was performed in both single contact and cross current modes. The single contact resulted in loaded solvent and raffinate, while the cross current yielded the final raffinate. Table 2 displays these results, which indicate a lithium distribution coefficient of 10-30, accompanied by selectivity of lithium over sodium in the range of 1000-6600. These results give clear evidence that the proprietary solvent used is most suitable for lithium extraction. The resulting loaded solvents have very similar chemical compositions, and are not affected not from the original lithium concentration, not from the impurities level and not from the dominant anion in the feed solution. Notwithstanding that stream 2 resulted in a slightly more contaminated LS. Therefore this was the LS used to study downstream processes. Residual lithium concentration evaluation, seen in the final raffinate composition, displayed lithium levels below detection limit for all three streams. This accumulates to a lithium recovery rate of practically 100%.

Table 2 – Extraction tests results

	Element	Li	Na	K
	Units	mg/L	mg/L	mg/L
Stream 1	LS	1760	320	15
	Raffinate	100	120000	19000

	Final Raffinate	<3	119500	19500
Stream 2	LS	1750	375	20
	Raffinate	150	121000	25500
	Final Raffinate	<3	121000	23000
Stream 3	LS	1500	240	3>
	Raffinate	50	8400	1050
	Final Raffinate	<3	9000	975

Further evaluation of the extraction process included the examination of the mass transfer and phase separation. The results of these tests are presented in Table 3, and indicate rapid mass transfer. Additionally, phase separation time gives clear preference to aqueous continuous dispersion, where AC operation reduces the phase separation time by roughly an order of magnitude.

Table 3 – Phase Separation and Mass Transfer results

Mixing time (sec)	Phase Separation Time (min)		Li mg/L (Aq)	
	AC	OC	AC	OC
20	2.5	38	100	100
40	5.25	49	100	105
60	6.2	>60	105	100
120	6.2	>60	105	100
180	7	>60	100	105

Scrubbing Stage

The scrubbing tests, as discussed above, were performed in two different batches using either HCl or H₂SO₄. The results of these are given in Table 4. It is evident that each scrubbing stage further eliminates the co-extracted impurities, and elevates the lithium purity in the solvent. In the reported experiments 4 stages sufficed to reduce all impurities level in the solvent below the analytical detection limit and produce the purified solvents. In addition no difference was observed between the two acids, indicating the indifference of this process to the prevailing anion. Some lithium is co-scrubbed by this process, but as in a continuous process this stream is recycled back into the feed, and thus these concentrations does not impact the overall recovery.

Table 4 - Scrubbing Test Results

Stage No.	Scrubbing with HCl						Scrubbing with H ₂ SO ₄					
	mg/L in Solvent			mg/L in Aq. Phase			mg/L in Solvent			mg/L in Aq. Phase		
	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K
0	1750	375	20	-	-	-	1750	375	20	-	-	-
1	1750	72	4	280	4010	190	1720	70	<3	240	3050	325
2	1710	15	<3	240	840	35	1705	15	<3	120	870	37
3	1690	<3	<3	170	130	7	1700	7	<3	80	150	6
4	1705	<3	<3	130	50	<3	1695	<3	<3	50	35	<3

Stripping Stage

The purified solvent moved on to be stripped. As can be seen in Table 5, this process yielded highly pure (>99.9%), saturated lithium product solution. Similarly to the scrubbing stage the type of the acid did not influence the process. However, as the various lithium salts have different solubility, the anion will determine the lithium concentration in the product. This observation, give clear evidence of the LiSXTM ability to produce various lithium salts, were a production facility could easily diversify is product line.

Table 5 – Phase Separation and Mass Transfer results

Element	Li	Na	K	SO ₄	B	Cl	pH
Units	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Strip by HCl	68.2	<3	<3	<3	<3	355000	4.6
Strip by H ₂ SO ₄	41	12	<3	297000	<3	<3	5

Conclusions

LiSXTM, a new solvent extraction method for production and recovering lithium has been presented. Tests were performed on solution with lithium concentration span of 230-2100 mg/L. The extraction process used a proprietary solvent that strongly favors lithium over other alkali ion, with a distribution coefficient as high as 30, and with selectivity over sodium which is greater than 1000. Residual lithium raffinate concentration was below detection limit indicating 100% recovery. These results were independent of the lithium and impurity concentrations as well as of the prevailing anion. Mass transfer is quite rapid while the phase separation time indicates that the extraction should be executed using AC dispersion. Scrubbing process facilitated impurity elimination from the loaded solvent and the production of PS. The PS was stripped using strong acids, and resulted with purified saturated lithium solution. This process was not influenced from the type of the acid, indicating that any strong mineral acid could be used. This introduces a high degree of freedom for the lithium producers on two accounts: as lithium salts can be directly produced without going through lithium carbonate; and as any acid can be used a production facility can easily diversify its product line. These advantages combined with the standard characterization of SX processes i.e., low residence time, small factory footprint, independence of weather, and low energy consumption give clear indication for the attractiveness of LiSXTM to become the new generation of lithium production processes.

References

1. Ober, J. A. (2002). *Lithium*. Retrieved from U.S. Geological Survey Minerals Yearbook website:
<http://minerals.usgs.gov/minerals/pubs/commodity/lithium/lithmyb02.pdf>
2. Garrett, D. E. (2004). *Handbook of lithium and natural calcium chloride their deposits, processing, uses and properties* (1st ed.). Great Britain: Elsevier.

Modular Mixer-Settler Technology for Medium Scale Satellite Mining Operations

*Matinheikki Juri^{*1}, Saario Rami², Fredriksson Henri²*

Summary

Current trends in mining industry have created a need for fast track projects that are typically implemented in remote locations. In response to this need, Outotec has developed a prefabricated and transportable modular solvent extraction plant. This paper evaluates its suitability for short-term mining operation use, and compares it to conventional technology. Results indicate that modular solvent extraction design has significant benefits compared to conventional design and has potential for more efficient solvent extraction in metals extraction.

Introduction

Solvent extraction, using mixer-settlers, is a well proven technology which has been used in extractive metallurgy since the 1950s (for a review see (Schlesinger et al. 2011)). Declining ore grades and more complex ores has meant that the energy required for each extracted metal tonne and the associated greenhouse gases are increasing (Norgate & Jahanshahi 2010). This in turn has increased interest in metal extraction from smaller, higher grade mineral deposits in remote areas and old mine dumps and tailings requiring remote operation solutions. Additionally, health and safety issues are a major priority in mining industry. (Antonijević et al. 2008, Fisher & Schnittger 2012, McNab & Garcia-Vasquez 2011) Due to these facts, life cycle of new plants can be relatively short, from 5 up to 10 years Therefore, low capital investment and low operational costs together with fast and safe installation & operation are fundamental requirements for solvent extraction plants of today.

Outotec developed its proprietary Vertical Smooth Flow (VSF[®]) solvent extraction technology in the 1970's and today more than 30% of SX copper and approximately 20% of SX Cobalt is produced using VSF[®] technology. Technology has formed basis for current SX-plant design is widely distinguished (Bacon & Mihaylov 2002). In 2013 Outotec introduced a new modular VSF[®]X mixer-settler design that allows flexibility for the construction of settlers with different capacities using the same standard modules. Settler modules are factory fabricated and easily transportable modules that can be quickly installed at site. Furthermore, these modules can be dismantled and relocated to another site, thus providing the benefit of significant residual value. (Saario et al. 2013)

This paper evaluates the potential advantages of the modular technology for medium scale plant. Comparison between conventional and modular technology is conducted in four different assessment categories: implementation, cost efficiency, operation & maintenance and sustainability.

^{*1} Corresponding Author, Outotec (Finland) Oy, Puolikkotie 10, 02230 Espoo, Finland, juri.matinheikki@outotec.com

² Outotec (Finland) Oy, Puolikkotie 10, 02230 Espoo, Finland

Background

New generation modular mixer-settlers were introduced at the Copper 2013 conference. The benefits of large scale modular plant were discussed by Saario et al. (Saario et al. 2013). The general features of modular mixer-settlers are introduced briefly.

Modular Mixer-Settlers

The modular settler design is based on separately transportable ISO-standard container sized settler modules. These are manufactured and transported via a predefined and proven supply chain. This supply philosophy allows flexibility for SX-plants to be custom designed using standard modules and allows faster and more economical project implementation.

The container sized units include inlet & outlet launder units and coalescing section units equipped with Dispersion Depletor Gate (DDG) fences. Multiple units can be connected to construct an optimally sized solution, whether small, medium or large scale. A transportable settler unit for a medium scale operation is shown in Figure 1.

Procurement & Manufacturing

The materials used for the settler modules are primarily carbon steel for the frame and fibre reinforced plastic (FRP) for components that are in touch with the SX process solutions. Manufacturing is performed in a factory environment using standardized working methods, ensuring high quality and controlled production schedule. The finished modules can be transported rapidly to the project site, where they can be easily stored as stacked for minimized footprint until the installation starts.

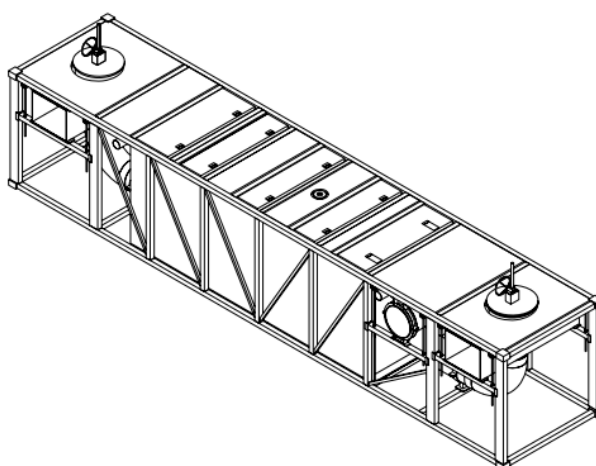


Figure 1- Modular settler unit (dimensions: 12192 x 2438 x 2438 mm)

Installation

Settler modules are installed on a pre-constructed concrete foundation slab and support pillars by a mobile crane. Installation of the modules is designed to be simple

and quick and the construction is elevated to minimise excavation work. The settler design ensures that the weight of each module is less than 10 metric tonnes and this allows installation with a single standard crane (e.g. 50 tonne mobile crane). The on-site lamination work is minimized since all lamination joints are predefined and the work procedures are standardized. The reduced number of installation personnel and the standardized working procedures allow for easier supervision on-site and an improved work safety environment.

Operation & Maintenance

A significant benefit of the modular design is that maintenance can be performed on a single settler module without shutting down or by-passing the whole settler. The elevated structure makes early leak detection possible before serious problems occur. The settler structure is completely enclosed for operator safety and so that emissions to atmosphere are minimised. Settlers can be accessed through water-locked and lockable hatches for operation and maintenance.

Relocation & Disposal

The settler modules can be dismantled with non-destructive methods and moved to another location for re-use, offering a sustainable end-of-life solution. In case the re-use option is not appropriate, the majority of the materials used are recyclable, providing additional end-of-life possibilities.

Material & Methods

The benefits of modular designed plant for short-term mining operation use are evaluated through a *Total Cost of Ownership* (TCO) concept. TCO is principally designed to be used as a purchasing tool or philosophy which aims to understand the total life cycle costs of a procured good or service. TCO can be a complex analysis requiring a relatively large amount of data. In this study the *value-based approach* is used, that combines cost data with qualitative performance data. (Ellram 1995) The method assigns numerical values for qualitative features and this approach is justified since most of the evaluated features are qualitative by their very nature. It should be noted that the evaluations and calculations were made by Outotec's in-house industry experts.

The value-based evaluation is divided into four main categories: *cost efficiency*, *operations & maintenance*, *sustainability* and *implementation*. Each of these categories is divided to various subcategories.

The cost efficiency category evaluates and compares pure costs of each solution. It consists of two different subcategories: *capital expenditures* (CAPEX) and *operational expenditures* (OPEX). Increasing CAPEX and OPEX have a significant impact on the feasibility of mining projects due to progressively shorter plant life times; therefore it is critical to control capital expenditures rigidly (Hopwood 2012).

The operation and maintenance category does not directly assess the operational costs since they are evaluated in the OPEX subcategory above, but it focuses on more technical aspects of both solutions. This category is divided into two subcategories. *Maintenance* subcategory evaluates the total maintainability of the plant and focuses on possible features which may improve or decline the maintainability. *Availability* is important factor in metal extraction and mining. Thus, this subcategory assesses features which affect plant availability.

Sustainability is seen as important for modern mining industry in order to receive legitimacy and social license to operate (Mudd 2010). This category is divided into four subcategories: *material selection*, *safety*, *plant closure* and *relocation*. The material selection subcategory evaluates eco-friendliness of used materials. The safety subcategory focuses on safety of installation and operation. The plant closure subcategory is an important sustainability factor evaluating how simple, predesigned and ecological the plant closure procedure is. In short term remote mines the relocation possibility is a major feature and should be evaluated in terms of its general existence and simplicity.

The implementation subcategory focuses on various aspects affecting the project implementation and building of the SX plant. The *Engineering* phase is an important phase in each project and its punctuality and duration has significant effect on the following phases. *Logistics* is an important factor in short life cycle satellite projects which can be situated in remote and inaccessible locations. *Installation* in these locations may also be difficult due to harsh environment and scarce resources, such as water, energy and skilled labor.

The importance of the different subcategories was evaluated and a weighting was given for each subcategory. In total 100 points were divided between 11 subcategories. The performance of both modular and conventional solutions in each subcategory was evaluated on a scale of 1 to 5 (1=poor, 2=fair, 3=good, 4=very good, 5=excellent). Total points were calculated by multiplying points from each subcategory by its weighting and summing the weighted points of every subcategory.

Results

Results of the value-based comparison between modular and conventional SX-plants, conducted according to method described above, are presented in Table 1. A short description and justification for each used value is included for each subcategory. The comparison indicates that modular plant technology has superior performance in every category. The percentage difference in total points is 51% in benefit of modular plant. The average difference in each sub-category is 53%. Further detail is presented in Table 1. Although results are based on value-based evaluation, they indicate that modular plant possesses significant potential for short term satellite plant usage.

Table 1- Value-based comparison of modular and conventional SX-plants

Evaluation categories	Weight	Modular Plant			Conventional Plant			Comparison	
		Points (scale 1-5)	Weighted points	Brief Description	Points (scale 1-5)	Weighted points	Brief Description	Difference	Percentage Difference
Cost Efficiency	30								
Capital expenditures	15	4	60	Faster implementation, earlier positive cash flow, lower installation cost, residual value after plant closure due to reusable modules	3	45	Known technology, but CAPEX overruns in several recent projects, emphasis on site installation, vulnerable to cost and schedule overruns	15	29 %
Operational expenditures	15	4	60	Lower entrainment, lower organic consumption, preventive maintenance, shorter shutdowns	3	45	Higher entrainment levels → high organic consumption, crud formation, longer plant shutdowns	15	29 %
Operation & Maintenance	20								
Maintenance	5	5	25	Preventive maintenance due to sectioned settler (closing down one section), better crud control due to early and controlled maintenance	2	10	Known technology, emphasis on reactive maintenance requiring plant shutdown, difficult maintenance operations, low/no design for maintenance mentality, crud problem	15	86 %
Availability	15	4	60	High availability due to preventive maintenance, no unexpected maintenance shutdowns	2	30	Plant shutdowns decrease availability, unpredictable shutdowns may occur	30	67 %
Sustainability	30								
Material selections	5	4	20	Maximized use of recyclable materials	3	15	High portion of concrete structures	5	29 %
Safety	10	4	40	Enclosed settler, low VOC emissions due to hermetic settler and water-locks, lockable hatches, minimized lamination during installation	3	30	Moderate safety, currently most of settlers are closed, sampling & maintenance not optimized for safety, high portion of lamination work	10	29 %
Plant closure	5	4	20	Easy dismantling of settlers, recyclable materials, transportable modules	3	15	Plant closure is complicated, destructive methods required, low recyclability	5	29 %
Relocation	10	4	40	Non-destructive dismantling procedures, transportation, settler reinstallation possibility, residual value	1	10	No relocation possibility without destructive dismantling	30	120 %
Implementation	20								
Engineering	5	4	20	Shortened engineering time due to productized solution	3	15	Conventional and known technologies, but solution varies from project to project	5	29 %
Logistics	5	5	25	Settler modules are transportable as freight containers, some packing required (auxiliary equipment)	3	15	Partly modular settler components require packing to containers, reverse logistics of empty containers	10	50 %
Installation	10	4	40	Shortened installation, less manhours required at site due to prefabrication, standard installation methods, reduced amount of lamination work	2	20	Complicated and time consuming installation procedures, lots of site lamination, longer total installation time, high number of workers	20	67 %
TOTAL	100	46	410		28	250		160	48 %

Scale: 1-5 (1=poor, 2=fair, 3=good, 4=very good, 5=excellent performance)

Conclusions

This comparison study reveals that highly modularized plant design bring major benefits when mining operations are located in remote locations and expected plant lifetime is relatively short. Considerable CAPEX and OPEX savings are possible when using modular design, even in medium or small scale operations. Transportability and quick plant erection are key factors for feasible plants, especially where demanding installation conditions exist.

The modular solvent extraction technology minimizes environmental impact and improves operator safety. The ability to relocate the plant is a significant advantage and could revolutionize use of solvent extraction in metal extraction and form new industry standards. Together these aspects will provide sustainable technological solution for metals solvent extraction in medium scale remote operations.

References

- ANTONIJEVIĆ, M, DIMITRIJEVIĆ, M, STEVANOVIĆ, Z, SERBULA, S and BOGDANOVIC, G, 2008. Investigation of the possibility of copper recovery from the flotation tailings by acid leaching. *Journal of Hazardous Materials*, vol. 158, no. 1, pp. 23-34.
- BACON, G and MIHAYLOV, I, 2002. Solvent extraction as an enabling technology in the nickel industry. *Journal of the South African Institute of Mining and Metallurgy*, vol. 102, no. 8, pp. 435-443.
- ELLRAM, L M, 1995. Total cost of ownership: an analysis approach for purchasing. *International Journal of Physical Distribution & Logistics Management*, vol. 25, no. 8, pp. 4-23.
- FISHER, B S and SCHNITTGER, S., 2012. *Autonomous and Remote Operation Technologies in the Mining Industry*. Kingston, Australia: BAEconomics Pty Ltd.
- HOPWOOD, P., 2012. *Tracking the trends 2013 - The top 10 issues mining companies may face in the coming year*. Canada: Deloitte [viewed 10.3.2014]. Available from: http://www.deloitte.com/view/en_CA/ca/industries/energyandresources/mining/tracking-the-trends-2013/index.htm.
- MCNAB, K and GARCIA-VASQUEZ, M., 2011. *Autonomous and remote operation technologies in Australian mining*. Brisbane: Prepared for CSIRO Minerals Down Under Flagship, Minerals Futures Cluster Collaboration, by the Centre for Social Responsibility in Mining, Sustainable Minerals Institute, The University of Queensland.
- MUDD, G M, 2010. The environmental sustainability of mining in Australia: key mega-trends and looming constraints. *Resources Policy*, vol. 35, no. 2, pp. 98-115.
- NORGATE, T and JAHANSHAHI, S, 2010. Low grade ores—Smelt, leach or concentrate?. *Minerals Engineering*, vol. 23, no. 2, pp. 65-73.
- SAARIO, R, FREDRIKSSON, H, VAARNO, J and MATINHEIKKI, J. 2013. CAPEX Comparison between Conventional and Modular Type of Mixer-settlers and Plants *Copper 2013 International Conference* The Chilean Institute of Mining Engineers (IIMCH). Santiago. pp.149-161.
- SCHLESINGER, M, KING, M, SOLE, K and DAVENPORT, W., 2011. *Extractive metallurgy of copper*. 5th ed. Amsterdam: Elsevier.

Combined sedimentation and mass-transfer experiments with a concentration gradient in the continuous phase

E. Cvetkovic¹, A. Pfennig¹

¹*Institute of Chemical Engineering and Environmental Technology (CEET), Graz
University of Technology, Graz, Austria*

Modern design methods for liquid-liquid extraction use a combination of lab-scale experiments and simulation tools, reducing time and costs compared to the conventional approach of scaling-up pilot-plant experiments. At CEET the simulation tool ReDrop is used to model extraction columns on the basis of single-drop measurements, which give information about the specific system properties.

In the past mainly two types of single-drop cells have been used to characterize the material system: Sedimentation cells and mass-transfer cells. Sedimentation cells are used to measure the sedimentation velocity of single drops, which varies significantly with drop diameter and system properties. In mass-transfer cells the mass-transfer rate is measured at different drop sizes and residence times. Since drops are small compared to the cell volume, the concentration of the continuous phase in the mass-transfer cell remains constant, whereas in extraction columns a concentration gradient can be found in both phases over the equipment height. Hence, in single-drop cells mass transfer is fast at the beginning and then decreases rapidly, while in extraction columns the mass-transfer rate does not change in this extent over time. Furthermore, past measurements have shown that sedimentation and mass transfer cannot be seen independently. The measurements showed that generally the sedimentation velocity is reduced with increasing mass transfer.

Therefore, mass transfer and sedimentation have been measured simultaneously to show their interdependency and in a second step, mass transfer and sedimentation were measured in a cell with a concentration profile in the continuous phase. The influence of various parameters was determined: drop size, residence time, concentration level, concentration difference between the phases and mass-transfer direction. By using model-based experimental analysis (MEXA), the number of experiments could be reduced significantly, while the information retrieved could be maximized at the same time. The obtained experimental results were compared to conventional single-drop experiments and were used to optimize and link the sedimentation and mass-transfer models in ReDrop.

Predictions of droplet diameter, dispersed phase holdup and axial diffusion for a rotating disc contactor

Hang Chen, Ze Sun, Guimin Lu, Xingfu Song, Jianguo Yu**

Coupled CFD-PBM simulation was validated to be effective for the simulation of a pilot-scale rotating disc contactor. The predicted droplet diameter and dispersed phase holdup are presented. The results show that the droplet diameter decreases with the increasing agitation rate, while the holdup has the inverse variation trend. The species transport equation was also solved for the simulation of residence time distributions. Based on the axial mixing model, a multi-parameter optimization process was applied to calculate the Peclet number in the column. The agreement between the simulated and fitted residence time distributions illustrates the method is feasible for the estimation of axial diffusion.

1. Introduction

Liquid-liquid extraction is widely used in chemical, biochemical and environmental industries. It has a long history. However, the state of the art for the layout of an extraction column still have some issues to be solved.

The HTU-NTU concept is a traditional method for the design of extraction columns. Nevertheless, expensive experiments are always necessary to estimate the stage efficiency. On the other hand, the back- and forward- mixing models are too simple for the complicated hydrodynamic description. Hence, the CFD (Computational Fluid Dynamics) is proposed for a highly efficient design. Fei et al¹ and Drumm et al² studied the single- and two- phase velocity fields of RDCs (rotating disc contactor) respectively. The experimental validation demonstrated that the CFD is an useful tool for the column design. However, the hydrodynamics in the extraction column also involves droplets coalescence and breakage, which have significant effects on interfacial area. Therefore, only the CFD simulation is insufficient. To this end, PBM (Population Balance Model) was proposed and coupled with the CFD further.³ The development of PBM for extractors mainly attributes to the research group of Prof. Bart. Simon et al^{4,5} estimated the coalescence and breakage models for a RDC. Attarakih et al⁶ solved the population balance equations for the interacting hydrodynamics and mass transfer in liquid-liquid extraction columns. Drumm et al⁷ and Hlawitschka et al⁸ successfully coupled the CFD and PBM for different columns. There is no doubt that the CFD-PBM approach is a highly efficient design method.

According to the two-film theory, the parameters of droplet diameter, dispersed phase holdup and axial diffusion coefficient have significant effects on the mass transfer. In this study, the predictions of these three most important parameters by the CFD-PBM simulation are presented.

2. Mathematical models

* To whom correspondence should be addressed. Telephone: 86-21-64252826. Fax: 86-21-64250981. E-mail: Ze Sun: zsun@ecust.edu.cn; Jianguo Yu: jgyu@ecust.edu.cn. National Engineering Research Center for Integrated Utilization of Salt Lake Resource, East China University of Science and Technology, Shanghai 200237, People's Republic of China

2.1 CFD model

The physical model of a pilot-scale RDC was established in Fluent 14.0. The column diameter, stator opening diameter, rotor diameter and shaft diameter are 150 mm, 105 mm, 90 mm and 54 mm respectively. A 30 mm compartment height and 1 mm internals thickness were employed. The Eulerian approach and realizable k- ϵ model were used for multi-phase flow and turbulence simulations respectively. Only the drag force was included for the interphase interaction and it was calculated with the Schiller-Naumann model.

2.2 PBM model

The PBM simulation was established based on the conservation equation of a number density function. Birth and death terms in the conservation equation are critical. Drumm et al⁷ found that the original model of Luo and Svedesen overestimated the coalescence rate and suggested a constant decrease of an empirical factor 10 in the coalescence terms. This modified model was applied here.

2.3 Species transport model

For the calculation of axial diffusion coefficient, the following species transport equation without mass transfer was solved based on the CFD model.

$$\frac{\partial}{\partial t}(\rho \alpha_k Y_i) + \nabla \cdot (\rho \alpha_k \vec{u}_k Y_i) = 0$$

For a pulse input, the tracer mass fraction Y_i was specified as one in a small area at the beginning. Afterwards, the concentration of the tracer was recorded at a point under the specified area to get a residence time distribution curve.

The axial diffusion in the RDC was expressed with the dimensionless Pe (vl/D_{ea}), where v , l and D_{ea} are the characteristic velocity, length and axial diffusion coefficient. To calculate Pe , the analytical solution of the axial diffusion model shown as follows was employed for fitting. τ is the mean residence time. A multi-parameter optimization process was applied to estimate the Pe .

$$\bar{Y}_i = \left(\frac{Pe\tau^3}{4\pi t^3} \right)^{0.5} \exp \left(-\frac{Pe\tau}{4\pi t} \left(1 - \frac{t}{\tau} \right)^2 \right)$$

2.4 Numerical scheme

The mesh size is 0.5 mm for the RDC. Pressure and velocity boundaries were defined at the top and bottom of the column respectively. The rotor was set as a moving wall, while other walls were kept stationary. All of the walls were defined as no slip boundary. The method of QMOM was used to solve the PBM model. The governing equations were discretized by the QUICK scheme. The SIMPLE algorithm was employed for the pressure-velocity coupling.

3. Results and discussion

3.1 Model validation

First of all, the simulated flow field of the RDC is shown in Figure 1. The continuous phase and dispersed phase flow rates are 200 L/h and 100L/h respectively, and the stirrer revolution is 150 rpm. There are distinctive vortices between the internals. Although the continuous phase flows from top to bottom, it flows inversely near the disc tips due to the high throughput of the dispersed phase. To validate the physical model, the predicted velocities were compared with the referenced PIV (Particle Image Velocimetry) data² in Figure 2. The agreement between the simulation and PIV experiment indicates that the physical model is reasonable and available.

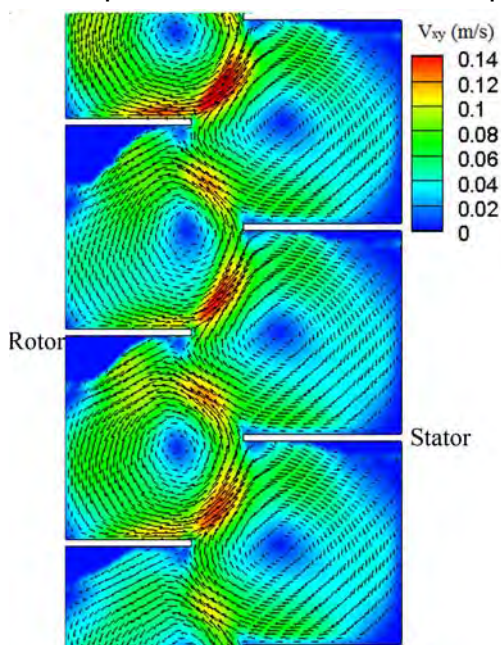


Figure 1. Simulated continuous phase flow field of the RDC

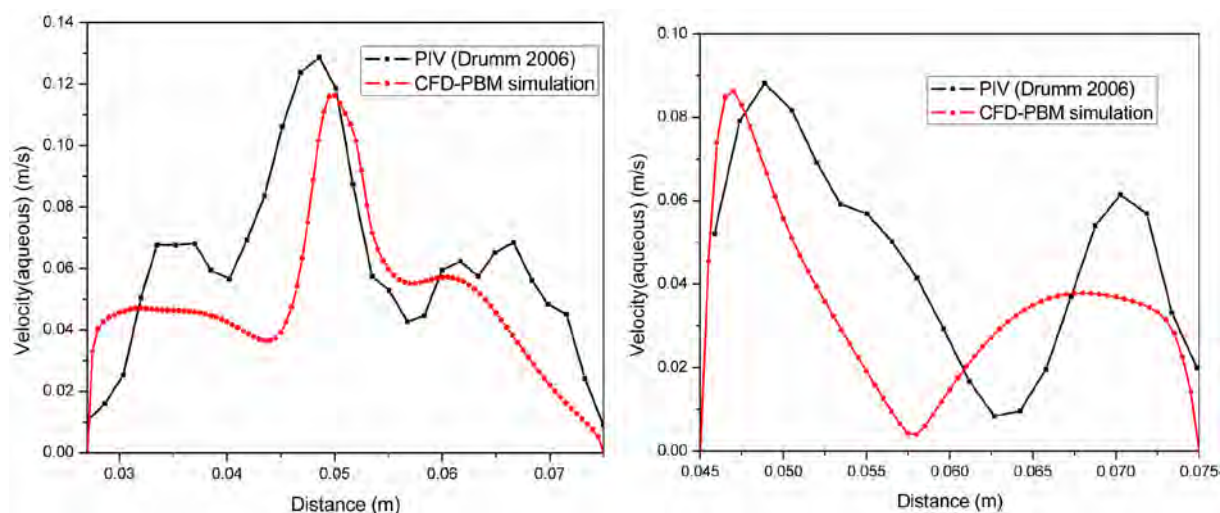


Figure 2. Comparison of simulated velocities with experimental data, left: at half compartment height above the stirrer, right: at rotor level

3.2 Droplet diameter prediction

The droplet diameter was successfully evaluated by the CFD-PBM simulation. Figure 3 displays the estimated droplet size distributions at different agitation rates, while the continuous phase and dispersed phase flow rates are 200 L/h and 160L/h. It is obvious that the droplet diameter decreases with the increasing agitation rate. This is true. Because the increase of turbulence dissipation rate resulting from the rising agitation rate leads to the growth of droplet breakage. Compared to the empirical correlation, the droplet diameter evaluation at different agitation rates has the averaged deviation of 23.8%.

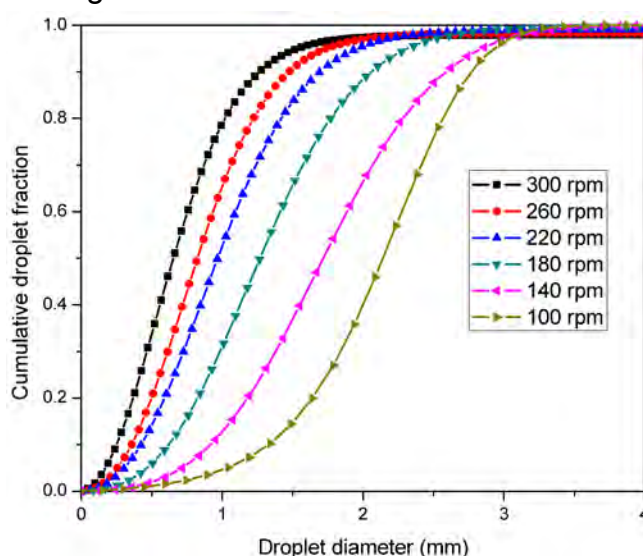


Figure 3. Simulated droplet size distributions at different agitation rates

3.3 Dispersed phase holdup prediction

Dispersed phase holdup has a significant effect on the interfacial area. The holdup contours at the agitation rates of 150 rpm and 300 rpm are presented in Figure 4. It can be seen that the dispersed phase is mainly accumulated under the internals. The interesting thing is that the holdup under the discs increases drastically when the revolution changes from 150 rpm to 300 rpm. The reason is that the centrifugal force is relatively stronger when the agitation rate increases. Then the light dispersed phase concentrates more in the centre of the column due to the centrifugal effect.

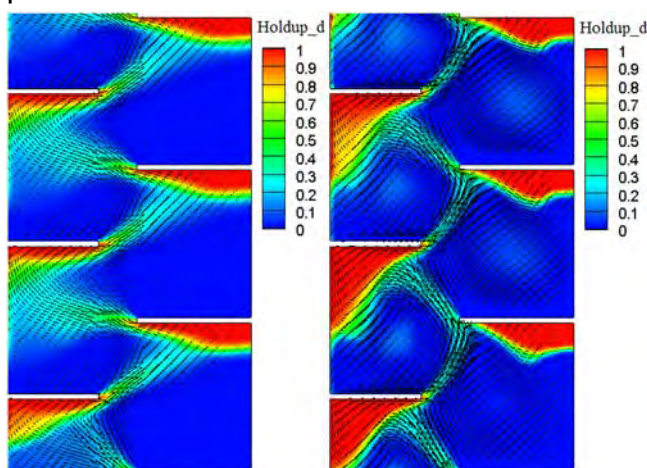


Figure 4. Dispersed phase velocity vectors and holdup contours, left: 150 rpm, right: 300 rpm

3.4 Axial diffusion prediction

Axial diffusion is always disadvantageous for the extraction operation. Because it reduces the mass transfer driving force. The residence time distributions at different agitation rates were simulated by solving the species transport equation. The analytical solution of the axial diffusion model was employed to fit the distribution curves. Figure 5 indicates that the results of the fitting agree well with the simulated residence time distributions. Hence, the method of multi-parameter optimization for the calculation of Pe is suitable. According to the calculated Pe , the axial diffusion increases with the rising agitation rate.

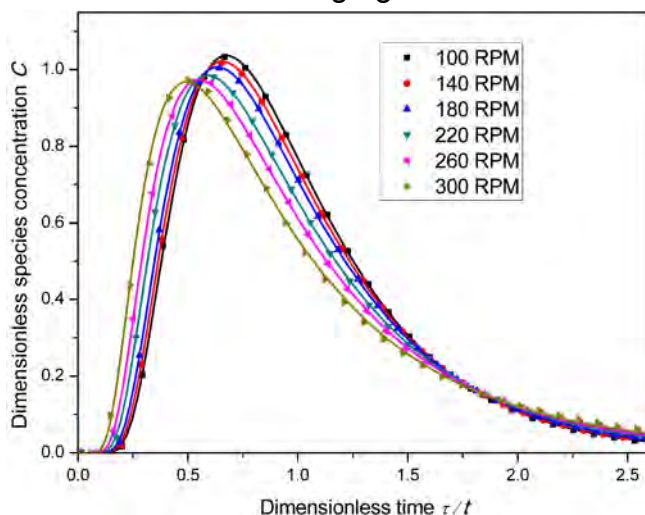


Figure 5. Simulated and fitted residence time distributions at different agitations rates

4. Conclusion

A CFD-PBM simulation was carried out in Fluent 14.0. The physical model was validated by the flow field comparison with referenced PIV data. The CFD-PBM approach successfully predicted the critical parameters of droplet diameter, dispersed phase holdup and axial diffusion. The results show that the droplet diameter decreases with the rising agitation rate. Because the rising agitation rate causes the growth of droplets breakage rate. In contrast, the variation of the holdup has the inverse trend due to the intensified centrifugal effect. A multi-parameter optimization process based on the axial diffusion mode is suitable to estimate the Pe . It is also demonstrated that the agitation rate has an important effect on the axial diffusion.

Acknowledgement

We acknowledge the financial support provided by the National Natural Science Foundation of China (Grant 21206038), the Specialized Research Fund for the Doctoral Program of Higher Education (New Teachers) (Grant 20120074120014).

References

- [1] Fei, W. Y., Wang, Y. D., Wan, Y. K. Physical modelling and numerical simulation of velocity fields in rotating disc contactor via CFD simulation and LDV measurement. *Chem. Eng. J.* 2000, 78, 131-139.
- [2] Drumm, C., Bart, H.-J. Hydrodynamics in a RDC extractor: single and two-phase PIV measurements and CFD simulations. *Chem. Eng. Technol.* 2006, 29(11): 1297-1302.
- [3] Bart, H.-J. Extraction columns in hydrometallurgy. *Hydrometallurgy.* 2005, 78: 21-29.
- [4] Simon, M., Bart, H.-J. Experimental studies of coalescence in liquid-liquid systems. *Chem. Eng. Technol.* 2002, 25, 481-484.
- [5] Simon, M., Schmidt, S. A., Bart, H.-J. The droplet population balance model – estimation of breakage and coalescence. *Chem. Eng. Technol.* 2003, 26, 745-750.
- [6] Attarakih, M. M., Bart, H.-J., Faqir, N. M. Numerical solution of the bivariate population balance equation for the interacting hydrodynamics and mass transfer in liquid-liquid extraction columns. *Chem. Eng. Sci.* 2006, 61, 113-123.
- [7] Drumm, C., Attarakih, M., Bart, H.-J. Coupling of CFD with DPBM for an RDC extractor. *Chem. Eng. Sci.* 2009, 64(4): 721-732.
- [8] Hlawitschka, M. W., Jaradat, M., Chen, F., et al. A CFD-Population Balance Model for the Simulation of Kühni Extraction Column. *Computer-Aided Chem. Eng.* 2011, 29, 66-70.

Ionic influence on coalescence and repulsion behavior in liquid-liquid dispersions

Felix Gebauer, Hans-Jörg Bart, Chair of Separation Science and Technology,
TU Kaiserslautern, <http://www.uni-kl.de/tvt/>

Jörn Villwock, Johannes Kamp, Matthias Kraume, Chair of Chemical & Process
Engineering, TU Berlin, <http://www.verfahrenstechnik.tu-berlin.de>

In spite of extensive studies of coalescence events in liquid-liquid dispersions these are still not fully understood. Most of the numerical simulations of solvent extraction processes use population balance equation (PBE) modelling techniques. Coalescence terms in PBE do not consider ionic effects, on this account they use fitting parameters. In this study a combination of different measurement techniques is used to get a more detailed appreciation about coalescence effects. For the validation of the testing system in reference to the coalescence tendency a shaking apparatus is used. The characteristic settling time of different testing systems is used for the validation (Figure 1). A closer look on coalescence effects allows a high-speed experimental imaging study. This consists in binary droplet collisions between a free rising and fixed droplet. The comparability of the results is achieved by using an EFCE test system. They can be used for a further development of PBE coalescence kernels in order to reduce the dependency on pilot scale experiments for calibration.

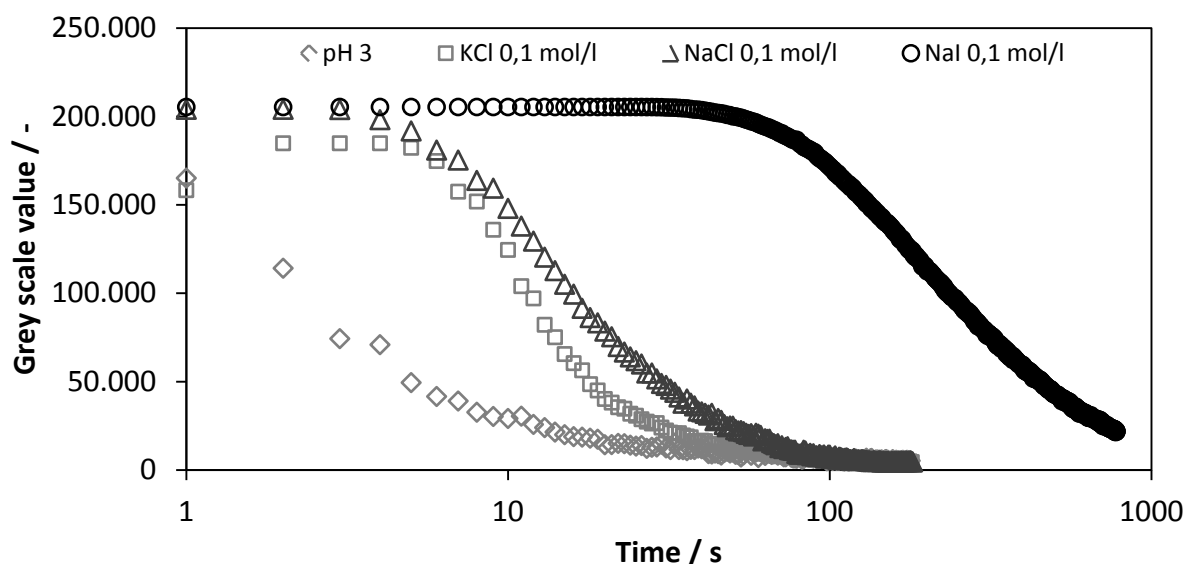


Fig. 1: Comparison of coalescence tendency in toluene/water systems with different ion species

Acknowledgements

The authors gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft DFG (German Research Foundation) for this work (Coalescence efficiency in binary systems, BA 1569/55-1)

Influence of ion species and ionic strength on the dynamic coalescence of single drops

J. Villwock, J. Kamp, M. Kraume, Chair of Chemical and Process Engineering, TU Berlin, Germany

F. Gebauer, H.-J. Bart, Chair of Separation Science and Technology, TU Kaiserslautern, Germany

In many industrial processes, dispersions of two immiscible liquids play an important role. The drop size distribution (DSD), which is the result of drop breakage and coalescence, determines the process efficiency. Up to now, no reliable prediction of the DSD with existing literature models is possible. In particular, the influence of ions on the coalescence process (e.g. coalescence rate and time) is insufficiently described. Hence, the overall aim is to gain a fundamental understanding of the electrostatic interactions in terms of ion species and concentration and the implementation into existing models.

Therefore, serial examinations were carried out in a fully automated test cell with a high speed camera (see Fig. 1). For the image analysis, Matlab® is used. With this setup, it is possible to test one parameter combination (e.g. $\bar{r}$, ion concentration; at least 100 single experiments) in approx. one hour. The experiments are conducted with the EFCE standard test system toluene/water. The addition of NaCl (pH 7) and NaOH (pH 13) with concentrations from 10^{-3} to 10^{-1} mol/L show a strong decline of the coalescence efficiency compared to the salt-free system. On the basis of the Hofmeister series and the HSAB theory, different ion species (mono- and multivalent, hard and soft) with varying concentrations are investigated. Simultaneous settling tests are carried out and correlated with the single drop experiments.

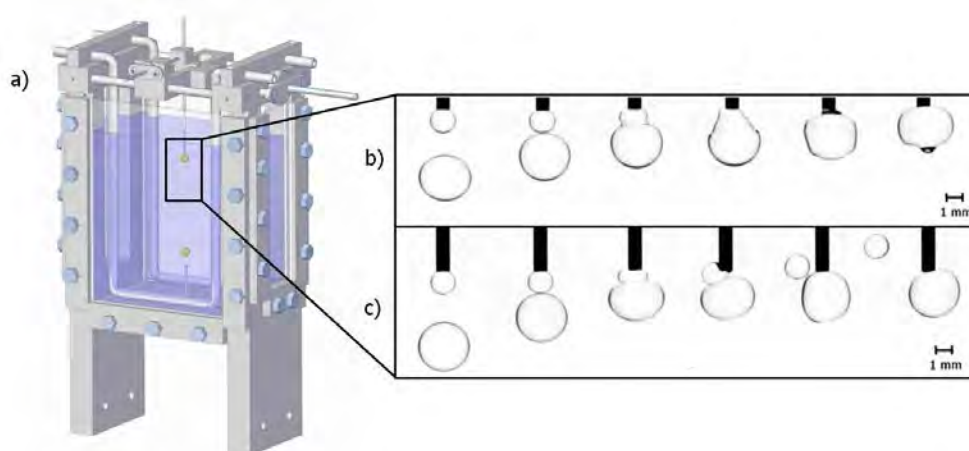


Fig. 1: Fully automated test cell for serial examinations of droplet coalescence (a) and sample image sequences for coalescence (b) and repulsion (c)

The authors gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft DFG (German Research Foundation) for this work (Project no. KR 1639/19-1).

Impact of drop size and relative velocity on coalescence in liquid/liquid dispersions

Johannes Kamp, Jörn Villwock, Matthias Kraume

Chair of Chemical & Process Engineering, Technische Universität Berlin, Germany

Dispersions of two immiscible liquids are an integral part of several unit operations, in particular in extraction processes. The drop size distribution (DSD), which is the result of the competing phenomena of drop breakage and coalescence, determines a decisive part of the overall process efficiency. Existing models for the coalescence rate include the physical phase properties, but also hydrodynamic characteristics like energy dissipation rate and relative velocity. However, these influencing parameters (especially the drop size and energy dissipation rate) are implemented in existent models with different proportionalities and in some cases even contradictorily. An experimental validation requires a reduction of influencing factors, therefore it is necessary to reduce the problem to the fundamental behaviour of single droplet coalescence and quantify the impact of the parameters separately.

In this work the coalescence process, which quantifies if two droplets coalesce or repel each other after collision, is investigated in detail. Therefore, a novel developed test cell is used where a rising drop collides with a pendant one recorded by a high speed camera (see fig. 1). The drop generation, detachment, collision and the triggered recording of the process is fully automated. This allows carrying out serial examinations of droplet collisions under different system conditions (varying e.g. drop sizes and relative velocity). Analysing the recorded images of the coalescence process, important quantities like coalescence probability, contact and coalescence time, relative velocity, momentum and deformation are evaluated. Conducting these experiments, the EFCE recommended model system toluene / water is used. In this presentation the influence of the drop size and the relative velocity will be discussed and compared to models in literature.

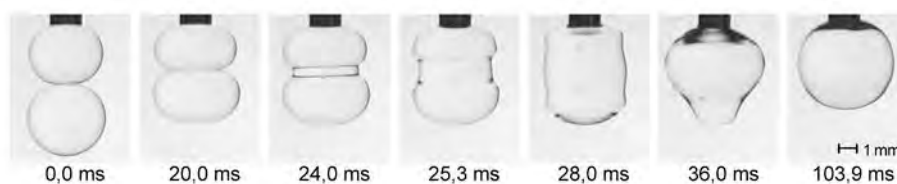


Fig. 1: Coalescence of two droplets

Partially founded by DFG project "Coalescence efficiency in binary systems".

Kinetics of Liquid/Liquid Extraction of Europium(III) Cation by Two Malonic Diamides

*J.P. Simonin^{*1}, L. Perrigaud¹, K. Perrigaud¹, and T.H. Vu¹.*

In connection with the DIAMEX separation process, the kinetics of extraction of Eu(III) ion by two diamides, DMDBTDMA and DMDOHEMA, were studied using the rotating membrane cell technique. The kinetics with DMDBTDMA from a nitric acid solution were found to be very fast, in keeping with a previous work using the Nitsch cell, and in disagreement with another work using a Lewis-type cell. A simple model for turbulent transport in the latter cell is proposed to interpret this result. The extraction kinetics with DMDOHEMA were found to be slower than with DMDBTDMA at 22°C. The activation energy of the interfacial reaction was deduced from experiments at 11°C, 22°C and 33°C. The activation energy of the distribution ratio is shown to have a particular effect on that of the overall kinetic rate constant in the general case.

Introduction

Malonic acid diamides have been selected as a class of extractants for the DIAMEX process, which consists of the selective co-extraction of minor actinides (Am and Cm) and fission lanthanides in the reprocessing of nuclear spent fuel. Two diamides have been studied in particular^[1]: the N,N'-dimethyl-N,N'-dibutyl-tetradecyl malonic diamide (DMDBTDMA), and the N,N'-dimethyl-N,N'-dioctyl-2-(2-hexyloxy-ethyl) malonic diamide (DMDOHEMA).

The kinetics of transfer by these solvents is an important parameter for the design of industrial extractors, but they have not been studied extensively in the literature.^[2-6] In refs. [2-4] the kinetics were studied using a Lewis-type cell, however characterized by poorly defined hydrodynamics and often misleading kinetic regime.^[7,8] In contrast, the cell used by Weigl et al.^[5] is much more reliable. The workers using the Lewis-type cell for the extraction of Eu(III) by DMDBTDMA concluded that the transfer was controlled by a slow interfacial chemical reaction.^[3,4] On the other hand, the use of the Nitsch cell pointed to a diffusion controlled process.^[5] It was therefore desirable to further study this system with the use of a different technique in order to resolve this issue.

In this work, the rotating membrane cell (RMC) technique is employed for this purpose, and a model is proposed for the estimation of diffusive transport in a Lewis-type cell as used in refs. [2-4]. Moreover, the extraction kinetics of Eu(III) by DMDOHEMA are studied using the RMC at different temperatures. The activation energies of the various relevant parameters involved in the overall extraction process are measured and their influence is discussed.

MODEL FOR DIFFUSIVE TRANSPORT IN A LEWIS-TYPE CELL

A Lewis-type cell consists of two immiscible liquid phases in contact that are stirred independently by stirring bars or propellers. These stirrers produce a turbulent hydrodynamic flow in the cell, which results in hydrodynamic boundary layers, and

* Corresponding Author, Laboratoire PHENIX (UMR CNRS 8234), Université P.M. Curie, Paris, France, jpsimonin@gmail.com

¹ Laboratoire PHENIX (UMR CNRS 8234), Université P.M. Curie, Paris, France.

diffusion layers for the extracted solute, in the vicinity of the interface. The thickness of these layers may be assessed using the classic theory of turbulence, as presented in the book by Levich.^[9]

Agitation produces turbulence eddies of various scales in the cell. Let V_0 be the characteristic velocity of the largest scale eddies in one of the phases. The order of magnitude of the hydrodynamic boundary layer thickness is then given by (Eq. (4.16) of ref. [9]),

$$\delta_H \approx \frac{\nu}{V_0} \quad (1)$$

in which ν is the kinematic viscosity of the liquid. This thickness corresponds to the distance from the interface at which the Reynolds number of the flow near the interface ($Re = V\delta / \nu$, with V the average velocity of the fluid at a distance δ from the interface) is approximately equal to unity. Eq. (1) expresses the thickness of the 'viscous sublayer'.^[9]

According to the Landau and Levich hypothesis of gradual damping of turbulence in the viscous sublayer, the thickness of the diffusion layer is approximately given by Eq. (25.18) of ref. [9], from which one gets the kinetic rate constant for diffusion in a given phase is,^[7,8] $k_D = D / \delta_D$, as

$$k_D = \alpha^{-1} V_0 Sc^{-3/4} \quad (2)$$

with Sc the dimensionless Schmidt number ($Sc \equiv \nu/D$), D the solute diffusion coefficient, and α a parameter of the order of unity.

For an extraction experiment, the total resistance to transfer due to diffusive transport is,^[7,8]

$$R_D \equiv \frac{1}{k_D^{extr}} = \frac{1}{k_D^{aq}} + \frac{1}{K k_D^{org}} \quad (3)$$

in which K is the distribution ratio ($= C_{org}/C_{aq}$), *aq* stands for aqueous phase, *org* for organic phase, and *extr* for extraction.

THE RMC TECHNIQUE

A sketch of the technique is shown in Figure 1.

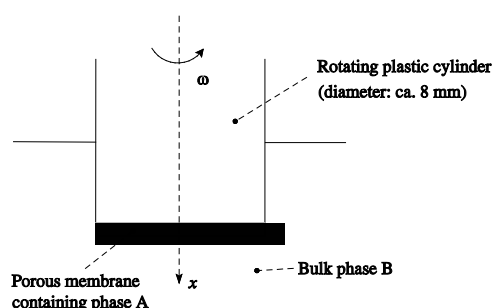


Figure 1. Sketch of the RMC technique.

The cell consists of a thin membrane glued on the base of a cylinder made of perspex. The membrane is a hydrophilic HVLP Durapore filter (Millipore™, thickness $\approx 120 \mu\text{m}$, diameter of ca. 8 mm). It is impregnated with the aqueous phase in the

present work. This phase, denoted by A, is spiked with the radioactive tracer to be extracted. The cell is mounted on a rotating-electrode spindle that can be rotated at a definite speed. Initially, it is set into rotation at a known speed and it is immersed into the outer phase B.

The main feature of the RMC is that transport is controlled in both phases. In phase A, transport in the pores of the membrane is purely diffusive. In phase B, rotating-disc hydrodynamics is promoted, as described by the theory of Levich.^[9] The proportion of matter extracted during an interval of time t reads,^[10-12]

$$P(t) = 1 - \exp(-t/\tau) \quad (4)$$

where the time τ is is given by

$$\tau = \tau_A + \tau_\chi + \tau_B \quad \text{with} \quad \tau_\chi = \frac{L}{k_f}, \quad \tau_A = \frac{L^2}{3D_m}, \quad \tau_B = \frac{\sigma L \delta_B}{K D_B} \quad (5)$$

in which k_f is the forward kinetic rate constant (from A to B), L is the membrane thickness, D_m ($= D_A/f$, with f the tortuosity) and D_B are the solute diffusion coefficients in the membrane and in B, respectively, σ is the membrane porosity, δ_B is the diffusion layer thickness in phase B (given by the Levich equation^[9]) and K is the distribution ratio ($K = k_f / k_r$, with k_r the reverse rate constant for the B-to-A reaction).

Activation energy

The activation energy of the global kinetic rate constant k may be calculated from the equation $E_k = -\frac{\partial \ln k}{\partial (1/T)} = k \frac{\partial k^{-1}}{\partial (1/T)}$. Thus, if every activated quantity, $X = D_{aq}, D_{org}, v_{org}$ and K , is written as $X = X_0 \exp[-E_X/R(1/T - 1/T_0)]$ with T_0 the reference temperature at which $X = X_0$, then one finds that for the RMC,

$$E_k = \frac{\tau_A}{\tau} E_{Daq} + \frac{\tau_f}{\tau} E_{kf} + \frac{\tau_B}{\tau} \left(\frac{2}{3} E_{Dorg} - \frac{1}{6} E_{vorg} + E_K \right) \quad (6)$$

in which all contributions are expected to be positive, except for E_K which can be positive or negative. In the general case of techniques with stirred phases^[7,8],

$$E_k = \frac{k_A^{-1}}{k^{-1}} \left[\frac{\partial \ln k_A^{-1}}{\partial (1/T)} \right] + \frac{k_f^{-1}}{k^{-1}} [E_{kf}] + \frac{(K k_B)^{-1}}{k^{-1}} \left[E_K + \frac{\partial \ln k_B^{-1}}{\partial (1/T)} \right] \quad (7)$$

Since the efficiency of stirring is expected to increase with temperature, the terms $\partial \ln k_A^{-1} / \partial (1/T)$ and $\partial \ln k_B^{-1} / \partial (1/T)$ are positive. E_k is the average of three contributions (in brackets) weighed by positive factors ($k_A^{-1} / k^{-1}, \dots$) smaller than unity and whose sum is equal to one.

RESULTS AND DISCUSSION

Experiments with DMDBTDMA.

The extraction kinetics of Eu(III) from a 2 M HNO₃ aqueous solution into an organic

solution of 0.5 M DMBTDMA in TPH were studied using the RMC technique at 600 rpm and 22°C, as in previous studies.^[4,5] The result is shown in Figure 2.

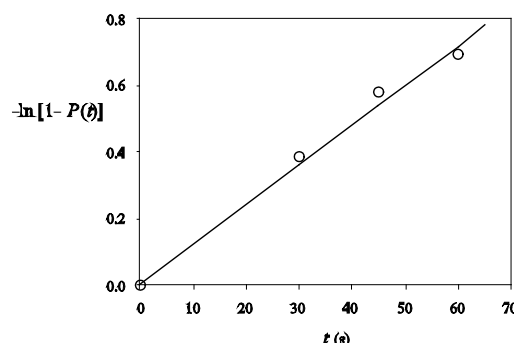


Figure 2. Extraction kinetics by DMBTDMA: (O) experimental results, solid line = diffusive limit

The extraction process is fast, with an extraction rate of ca. 50 % after 1 min. The main result observed in Figure 2 is that the extraction is controlled by diffusion because the experimental points are located on the line corresponding to the diffusive limit, which is not a fit of the experimental points and involves no adjustable parameter. The present result is therefore in agreement with the observation made in ref. [5], and in contradiction with the result of ref. [4] which reported a slow interfacial reaction, with a kinetic rate constant $k_f \sim 7 \times 10^{-5} \text{ cm s}^{-1}$.

The model proposed above to describe the diffusive contribution to mass transfer in a Lewis-type cell was applied to the system of ref. [4]. The velocity of the eddies, V_0 , was of the order of a few cm s^{-1} when the rotation speed of the stirring bars was typically 200 rpm. Taking $\alpha=1$, $V_0^{\text{aq}}=4 \text{ cm s}^{-1}$, $V_0^{\text{org}}=2 \text{ cm s}^{-1}$ (as observed by the author of this study), it is found from Eq. (2) that: $k_D^{\text{aq}} \approx 3.34 \times 10^{-2} \text{ cm s}^{-1}$, $K k_D^{\text{org}} \approx 8.8 \times 10^{-5} \text{ cm s}^{-1}$. Thus Eq. (3) entails that $k_D^{\text{extr}} \approx K k_D^{\text{org}} \approx 8.8 \times 10^{-5} \text{ cm s}^{-1}$ because the main resistance then originates from the convective transport in organic phase. This result for k_D^{extr} is in good agreement with the observed value, $k_f \sim 7 \times 10^{-5} \text{ cm s}^{-1}$, which is likely partly fortuitous. Nevertheless, the accord of k_D^{extr} with the value of k_f of ref. [4] suggests that mass transfer was controlled by diffusive transport, not by the interfacial chemical reaction, in this experiment.

Experiments with DMDOHEMA

The kinetics of extraction of Eu(III) from (pre-equilibrated) 3M nitric acid solutions were investigated using the RMC technique at 11°C, 22°C and 33°C, into organic solutions of 0.65 M DMDOHEMA in TPH. These concentrations are typical of the envisaged DIAMEX process at industrial scale.

The extraction kinetic rate constants were deduced from experimental data obtained for $P(t)$. The results at the three temperatures studied are shown in Figure 3 and the values found for k_f from a fit of τ and using Eqs. (4) and (5) are given in Table 1. It is seen that the extraction rate constant increases significantly with T . The extraction process with DMDOHEMA is slower than with DMBTDMA at 22°C, but it also becomes diffusion controlled at 33°C as shown in Figure 3, with the experimental points close to the diffusive limit (dashed line).

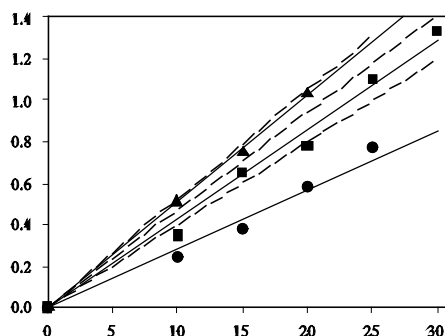


Figure 3. Experimental results for $-\ln[1-P(t)]$ at various temperatures: (●) 11°C, (■) 22°C, (▲) 33°C. Solid lines (bottom line=11°C, top=33°C): results of fits using Eq. (4-5); Dashed lines: diffusive limits (bottom line=11°C, top=33°C).

Table 1: Values of the distribution ratio, and of the extraction kinetic rate constant for the 3M HNO_3 /0.65 M DMDOHEMA system at the 3 temperatures studied in this work.

t (°C)	K	k_f ($10^{-3} \text{ cm s}^{-1}$)
11	5.45	1.20
22	3.12	5.58
33	1.65	20.9

The activation energy, E_{kf} , for the rate constant k_f was determined. The values of $\ln[k_f(T)/k_f(T_0)]$ with $T_0=295.15 \text{ K}$ ($=22^\circ\text{C}$), are plotted in Figure 4 together with the similar plots for the parameters D_{aq} , D_{org} , v_{org} and K . From these plots one gets $E_{kf} \approx 94.0 \text{ kJ mol}^{-1}$, $E_{Daq} \approx 19.5 \text{ kJ mol}^{-1}$, $E_{Dorg} \approx 25.3 \text{ kJ mol}^{-1}$, $E_{vorg} \approx -18.3 \text{ kJ mol}^{-1}$, $E_K \approx -39.2 \text{ kJ mol}^{-1}$, respectively. The activation energies of the diffusion coefficients are both of the order of 20 kJ mol^{-1} , as for small ions like Na^+ and Cl^- in water between 0 and 50°C (results not shown).

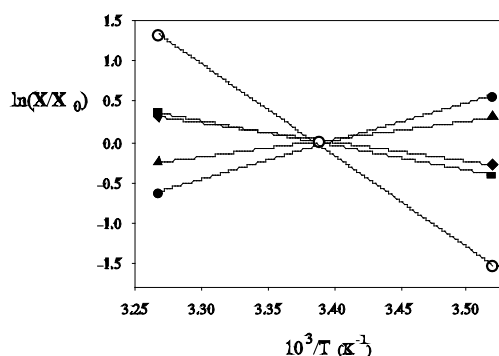


Figure 4. Plot of $\ln(X(T)/X(T_0))$ vs. $10^3/T$ for $X = k_f$ (○), D_{aq} (◆), D_{org} (■), v_{org} (▲), K (●).

A particular feature is that the distribution ratio K decreases with temperature, thus making the associated activation energy *negative*. The numerical value of E_K found from the results for these activation energies and Eq. (6) is $E_K \approx 17.6 \text{ kJ mol}^{-1}$. This is a rather low value, typical of a diffusion controlled process, which is nearly the case here at 22°C (see Figure 3). It is observed in Eq. (6) that the contribution from E_K

more than compensates the contribution from E_{kf} ($-8.85 \text{ kJ mol}^{-1}$ and $+8.65 \text{ kJ mol}^{-1}$, respectively).

The general case may also be discussed on the basis of Eq. (7). The latter relation shows that the activation energy for the apparent rate constant k can be low not only in the case of diffusion controlled processes or interfacial chemical reactions of low activation energy.^[7,8] It can also be low if K is not large, so that the last term in Eq. (7) contributes significantly, and if the activation energy of K is sufficiently negative and large in absolute value. In such a case, the activation energy E_k may erroneously point to a diffusion controlled process. In the extreme case, E_k could even become negative if K decreases rapidly with temperature and if the process is controlled by transport in phase B.

This discussion brings further support to the contention that the raw value of the activation energy of the global kinetic rate constant is not a reliable indicator of the extraction regime.

CONCLUSION

The extraction kinetics of europium(III) cation by DMDBDMA at 22°C seems to be very fast, controlled by diffusion. The slow interfacial reaction kinetics reported in the literature using a Lewis-type cell may have been caused by the effect of a remaining diffusion layer in the organic phase. The kinetics of extraction by DMDOHEMA is found to be slower than by DMDBDMA at 22°C, but it accelerates rapidly with temperature and becomes fast at 33°C.

When the distribution ratio decreases with temperature, this can lower the activation energy of the global rate constant by bringing a negative contribution.

References

1. Baron, P.; Hérès, X.; Lecomte, M.; Masson, M. *Proc. Global 2001*, Paris, France, September 9-13.
2. Toulemonde, V. PhD thesis, Université Paris 6, 1995.
3. Dal Don, M. PhD thesis, Université Paris 11, 1997.
4. Charbonnel, M.C.; Dal Don, M.; Berthon, C.; Presson, M.T.; Madic, C.; Moulin, C., *Proceedings of ISEC'99*, Barcelona, Spain, 1999, Elsevier: Amsterdam, 2000, pp. 1333-1338.
5. Weigl, M.; Geist, A.; Gompfer, K.; Kim, J.I., *Solvent Extr. Ion Exch.* **2001**, *19*, 215-229.
6. Bosland, L., PhD thesis, Université Paris 6, 2005.
7. Durand-Vidal, S.; Simonin, J.P.; Turq, P. *Electrolytes at Interfaces*, Kluwer: Dordrecht, 2000.
8. Danesi, P. R., Chapter 5, Solvent Extraction Kinetics, in *Solvent Extraction Principles and Practice*, Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G.R. Eds.; Marcel Dekker: New York, 2004, pp. 203-251.
9. Levich, V. G. *Physicochemical Hydrodynamics*, Prentice Hall: Englewood Cliffs, 1962.
10. Lewis, F.; Harwood, L.M.; Hudson, M.J.; Drew, M.G.B.; Desreux, J.F.; Vidick, G.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.H.; Simonin, J.P. *J. Am. Chem. Soc.* **2011**, *133*, 13093–13102.
11. Simonin, J. P.; Weill, J., *Solv. Extr. Ion Exch.* **1998**, *16*, 1493–1514.
12. Simonin, J. P.; Hendrawan, H., *J. Phys. Chem. B* **2000**, *104*, 7163-7170.

Palladium-malonamides: molecular aspects of L/L extraction

*R. Poirot¹, D. Bourgeois¹, D. Meyer^{*1}*

Liquid-liquid extraction of palladium(II) from nitric media was carried out using *N,N'*-dimethyl,*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA) in *n*-heptane. To this purpose, various experimental parameters such as reaction time, extractant concentration, pH and nitrate concentration were investigated in detail. Focus was set on the molecular level and understanding of the key physicochemical parameters necessary for an effective separation. Mechanistic studies involved complete analysis of the organic phases, including chemical speciation at the molecular level (coordination chemistry with NMR, IR, XRD and XPS), and supramolecular ordering characterization (with SAXS, DLS and NMR) enables deep knowledge of this system. Pd(II) complexes were identified and characterized. Emphasis was set on the study of the apparent discrepancy between molecular complexes (1:1 Pd:malonamide) and macroscopic behavior (slope 2 for malonamide).

Introduction

Palladium (Pd) is a member of platinum group metals (PGM), and as such its recovery has become of increasing interest last years. World production of Pd was ca. 200 tons in 2012 and has been remaining stable for several years.^[1] This metal of high value has good catalytic properties and good corrosion resistance. It is used in new technologies, especially in the production of catalytic converters (67%). Already 26% of the palladium demand is provided from recycling, mostly from used autocatalysts.^[2] More generally, the amount of palladium that can be recovered from the so-called secondary resources, *ie* recycling of catalytic converters and electronic scrap, is very important.^[3] Exploitation of new recycling sources is a challenge for future supply of this rare metal.^[4]

Liquid-liquid (L/L) extraction has proven to be a very effective method for the separation and selective isolation of PGM metals.^[5] A large number of specific extractants have been discovered by the PGM refineries in the 1970s and are still used today. Thus, for palladium, the two families of extractants mainly used are dialkylsulfides (dihexylsulfide, DHS, and dioctylsulfide, DOS) and hydroxyoximes (aliphatic or aromatic), which are soft bases in HSAB model.^[6] Most studies in Pd L/L extraction are dedicated to hydrochloric media, as crude ore treatment relies on a treatment with hydrochloric acid.

On the other hand, to our knowledge, only few studies deal with the recovery of Pd from nitric effluents: Such media are not so often envisioned, but may become of increasing interest with the need for recycling of electric and electronic devices, where Pd is present. As classical extractants used for Pd extraction are expected to be rapidly oxidized in nitric media, new systems have to be designed.^[7] Pd is found as one of the most abundant transition metals among the fission products in nuclear spent fuel, and its separation and recovery from high level liquid waste (HLLW) nitric

¹ ICSM, UMR 5257 CEA/CNRS/UM2/ENSCM, Site de Marcoule Bât. 426, BP 17171, 30207 Bagnols/Cèze cedex, France

solutions was considered. Although the presence of (minor) radioactive Pd isotopes hampers the use of such a Pd source,^[8] and that all studies were designed in the frame of HLLW treatment, useful information regarding the L/L extraction of Pd from nitric media can be found in these studies.^[9] Various systems were evaluated, and shown to suffer from different problems such as: slow kinetics, poor distribution coefficient, poor solubility and poor stability.^[10] *N,N'*-tetrasubstituted malonamides were developed in the frame of nuclear industry.^[11] Their efficiency for multivalent cation extraction and their stability in nitric media was demonstrated. Also, *N,N'*-diphenyltetradecyl malonamide (DPHTDMA) was demonstrated to be a suitable extractant for the recovery of Pd(II) from hydrochloric media, albeit with the use of Sn(II) as a labilizing agent.^[12] Thus malonamides appear as good candidates towards Pd extraction, and the aim of this work is to investigate the behavior of palladium during extraction with malonamides, and principally with *N,N'*-dimethyl,*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA, Figure 1, CAS: 107513-23-5) in nitric media. Within this framework, our purpose is to study liquid/liquid (L/L) extraction towards Pd recovery in nitric media, and especially to focus on the molecular level and understand the key physicochemical parameters necessary for an effective separation

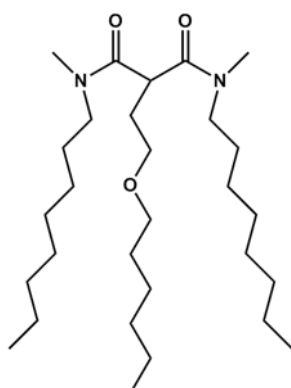


Figure 1. DMDOHEMA

Extraction mechanism

The behavior of palladium has been studied in details regarding influence of each parameter on its extraction. Influence of nitrate and DMDOHEMA concentrations have been given particular attention to determine the mechanism which palladium is extracted. The stoichiometry in extraction mechanism is usually determined with the slope analysis method. As can be seen in Figure 2 and Figure 3, those results suggest that species bearing 1:2 metal:extractant stoichiometries are involved in the extraction mechanism. This can be summarized by the following equilibrium:

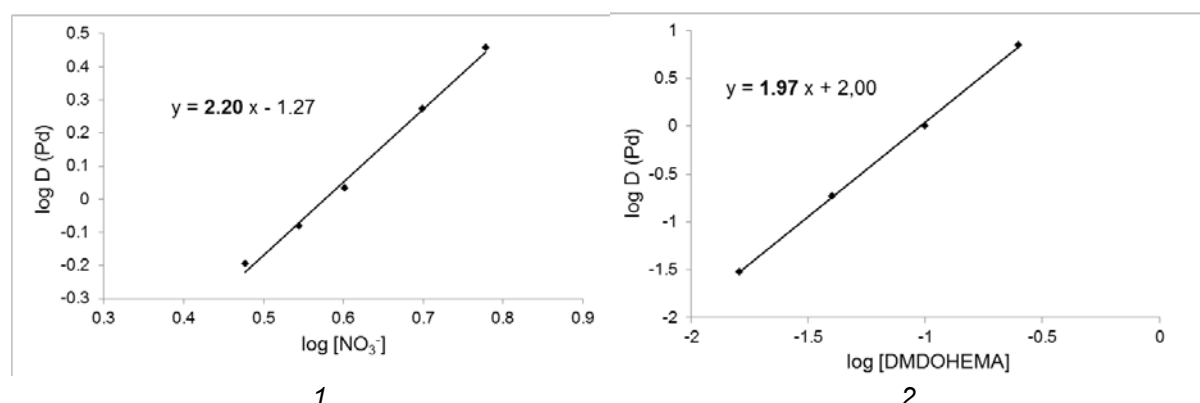


Figure 2. Effect of $[\text{NO}_3^-]$ on the extraction of Pd(II).

Figure 3. Effect of $[\text{DMDOHEMA}]$ on the extraction of Pd(II).

Saturation of organic phase – solid phase appearance

In order to determine the loading capacity of DMDOHEMA for palladium(II), adequate experiments were carried out using concentration in DMDOHEMA and HNO_3 known to extract greatly palladium (respectively 0.6M and 3M). Aqueous phases loaded with an increasing amount of Pd, comprised between 250 and 4000ppm were used (2.8×10^{-3} to 3.8×10^{-2} M respectively). At those concentrations, more than 95% of Pd is extracted for low initial concentrations. As reported on Figure 4, there is a maximum load in Pd in the organic phase reached at concentrations higher than 2000 ppm (19mM). This saturation was physically noticeable with appearance of a third phase observed at the interface. This phase appears as a solid wax, and was deeply analyzed. This phase was observed in several conditions, its appearance depends on $[\text{DMDOHEMA}]$, $[\text{NO}_3^-]$ and on the solvent used.

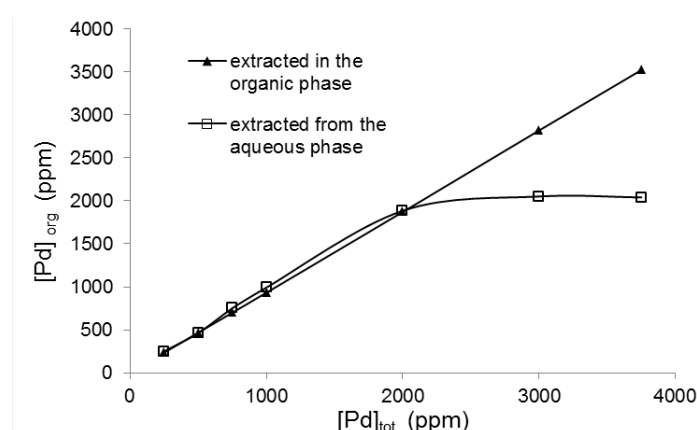


Figure 4. Effect of Pd concentration on extraction.

Solid phase analyzes

Solids were analyzed by several methods (IR, XPS, NMR), and it is proved they have the same composition. First, the IR analysis depicted in Figure 5 indicates a coordinated carbonyl moiety of DMDOHEMA in this precipitate.

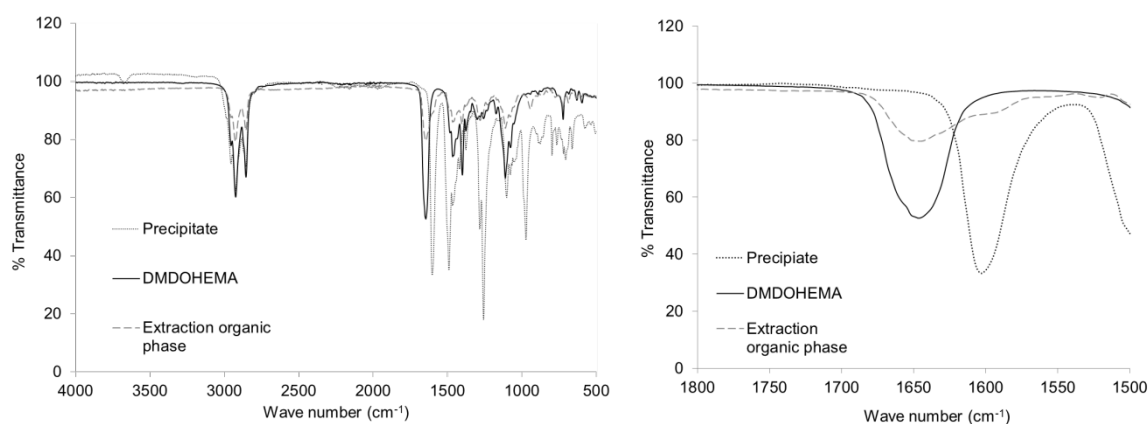


Figure 5. IR analysis of precipitate.

As Pd(II) reduction can occur in aqueous media, solid was analyzed with X-ray Photoelectron Spectrometry (XPS). This method enables to determine the oxidation degree and the chemical environment of transition metals after analysis of absorption of X-ray photons of different energies. It also enables semi-quantitative elementary chemical analysis. The results obtained indicate ratio between Pd and N atoms attributed to DMDOHEMA is close to a 1:1 Pd:DMDOHEMA ratio. Thus, this shows a deficiency in DMDOHEMA ligand in comparison with the expected $\text{Pd}(\text{DMDOHEMA})_2(\text{NO}_3)_2$ complex anticipated from slope analysis. The number of coordinated DMDOHEMA in the precipitates seems to differ from the complex found in organic phases.

Thanks to NMR, stoichiometry between Pd and DMDOHEMA in the precipitates was determined after comparison with complexes prepared after dissolution solid $\text{Pd}(\text{NO}_3)_2 \cdot x(\text{H}_2\text{O})$ into DMDOHEMA solutions in toluene (Figure 6). The N-methyl signals are very similar to those obtained with the precipitate. Addition of excess of DMDOHEMA allowed us to confirm a 1:1 Pd:DMDOHEMA composition for the precipitates obtained during L/L extraction experiments.

X-Ray Diffraction Monocrystal

This method enables to perfectly know the first coordination sphere of a metal. In our case, it is of prime interest to understand how DMDOHEMA coordinate palladium. However, monocrystal of DMDOHEMA has never been done this day: Its long hydrocarbonated chains prevent a great crystallization. For this reason we synthesized a new malonamide which is able to crystallize easier. XRD structure of this malonamide with palladium prove once again that the coordination of palladium with malonamides occurs in a 1:1 ratio (Figure 7).

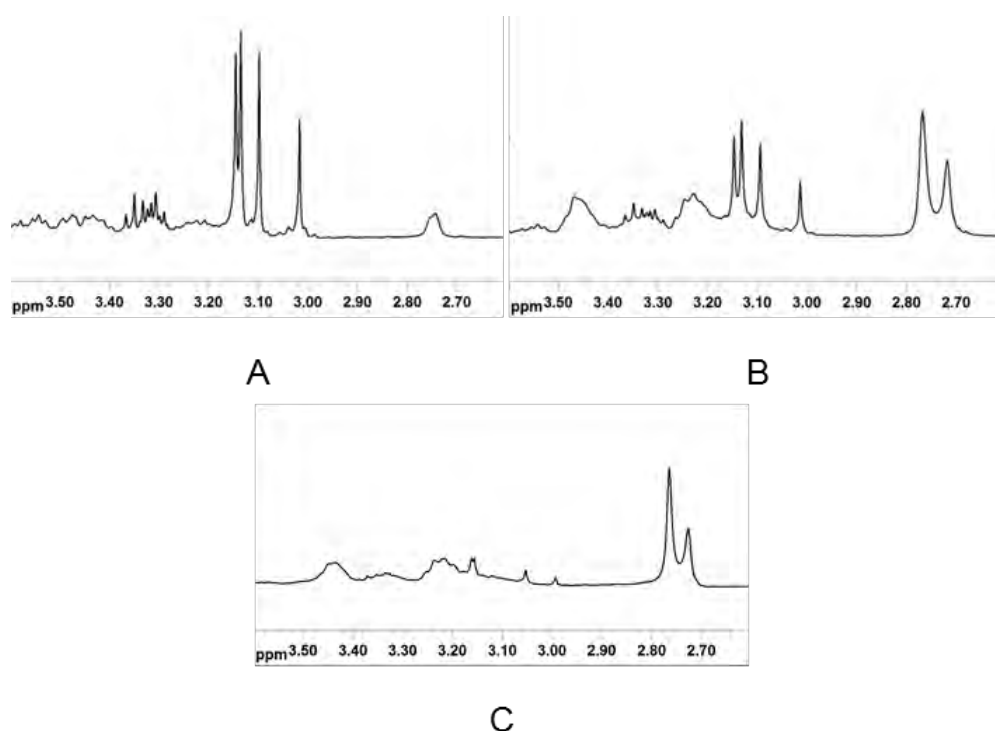


Figure 6. Synthetic organic phases with different Pd: DMDOHEMA ratios. A: 1:1, B: 1:2, C: 1:5.

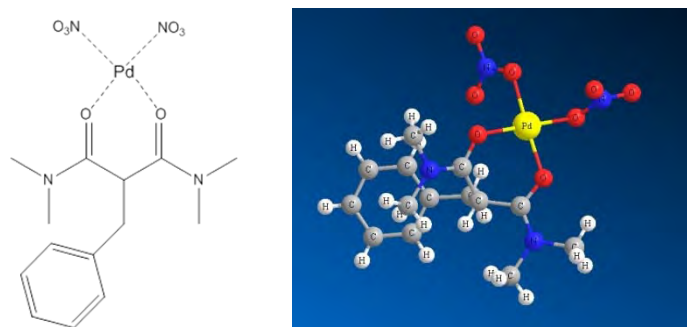


Figure 7. XRD of a complex Pd-malonamide

Supramolecular aspects

A difference in stoichiometry between the extraction system indicating a ratio 1:2 and the results obtained in different analyzes of organic phases (NMR), precipitates (XPS, NMR) and crystal structure showing all a ratio 1:1. This difference can be explained by the fact that palladium coordinates a DMDOHEMA and 2 nitrates to form a neutral species in the first sphere which will combine with a second malonamide to create a macromolecular species more soluble in lipophilic phase (Figure 8). In order to highlight the function of this second malonamide, SAXS, DLS and NMR analyzes on organic phases were performed.

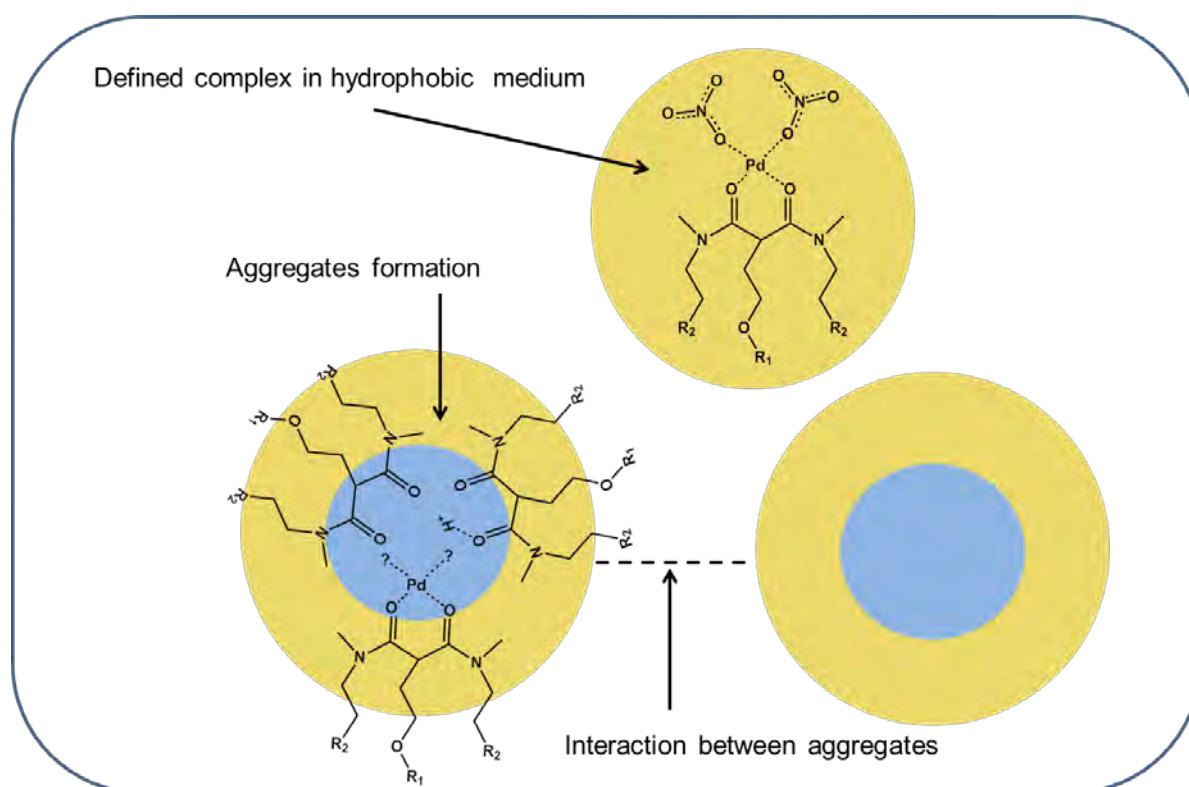


Figure 8. palladium-DMDOHEMA in lipophilic medium

References

- ¹ USGS, *Minerals Yearbook, Platinum Group Metals*, **2012**.
- ² Cowley A. *Platinum 2013 Interim Review*, Johnson Matthey, **2013**, available at <http://www.platinum.matthey.com/publications/pgm-market-reviews/market-review-archive/platinum-2013-interim-review>.
- ³ Schluep, M.; Hagelueken, C.; Kuehr, R.; Magalini, F.; Maurer, C.; Meskers, C.; Mueller, E.; Wang, F. UNEP. Recycling - From E-Waste to Resources, in *Sustainable Innovation and Technology Transfer Industrial Sector Studies*, **2009**, available at http://www.unep.org/PDF/PressReleases/E-Waste_publication_screen_FINALVERSION-sml.pdf.
- ⁴ Tsydenova, O.; Bengtsson, *Waste Management*, **2011**, 31, 45–58.
- ⁵ M. Cox, Solvent Extraction in Hydrometallurgy, In *Principles and practices of solvent extraction, Revised and Expanded*, Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G.R. Eds, Marcel Dekker, New York, **2004**, 455-505.
- ⁶ Albazi, S.J.; Freiser, H.; *Solvent Extr. Ion Exch.*, **1987**, 5, 265-275.
- ⁷ Mohan Raj, M.; Dharmaraja, A.; Panchanatheswaran, K.; Venkatesan, K.A.; Srinivasan, T.G.; Vasudeva Rao, P.R.; *Hydrometallurgy*, **2006**, 84, 118-124.
- ⁸ Kolarik, Z.; Renard, E.V.; *Platinum Metals Review*, **2005**, 49, 79–90.
- ⁹ Kolarik, Z.; Renard, E.V.; *Platinum Metals Review*, **2003**, 47, 74-87.
- Ruhela, R.; Sharma, J. N.; Tomar, B. S.; Panja, S.; Tripathi, S.C.; Hubli, R.C.; Suri, A.K.; *Radiochimica Acta*, **2010**, 98, 209-214.
- Dakshinamoorthy, A.; Dharmi, P.S.; Naik, P.W.; Dudwadkar, N.L.; Munshi, S.K.; Dey, P.K.; Venugopal, V.; *Desalination*, **2008**, 232, 26-36.
- ¹⁰ Al-Bazi, S.J.; Freiser, H.; *Solv. Extr. Ion Exch.*, **1987**, 5, 265-275.
- Shukla, J.P.; Singh, R.K.; Sawant, S.R.; Varadarajan, N.; *Anal. Chim. Acta*, **1993**, 276, 181-187.
- Rizvi, G.H.; Mathur, J.N.; Murali, M.S.; Iyer, R.H.; *Sep. Sci. Tech.*, **1996**, 31, 1805-1816.
- Mezhov, E.A.; Druzhenkov, V.V.; Sirotinin, A.N.; *Radiochemistry*, **2002**, 44, 146-150.
- ¹¹ Cuillerdier, C.; Hoel, P.; Musikas, C.; Nigond; *L. Eur. Pat. Appl.* EP 505277 A1, 23 September 1992.
- Manchanda, V.K.; Pathak, P.N.; *Sep. Purif. Technol.*, **2004**, 35, 85–103.
- ¹² Malik, P.; Paiva, A.P.; *Solv. Extr. Ion Exch.*, **2010**, 28, 49-72.

Selective Extraction of Copper(II) from Ammonia Solution

Karolina Wieszczycka, Marta Krupa, Aleksandra Wojciechowska, Andrzej Olszanowski,

*Poznan University of Technology, Institute of Chemical Technology and Engineering,
Pl. Marii Skłodowskiej-Curie 2, 60-965 Poznan, Poland*

Summary

In the present study, the solvent extraction and separation of copper(II) ions from ammonium sulphate/ammonia solution containing also zinc(II), cobalt(II) and nickel(II) ions by oxime of 1-(2-pyridyl)tridecan-1-one has been investigated. The studies focused on evaluating the influence of several experimental parameters, such as pH, metals ions concentrations and type of diluents on the selective recovery of copper(II) ions from ammonium sulphate/ammonia solutions.

Introduction

Due to its benefits over other reagents, ammonia has proven to be a widely used extractant in hydrometallurgical processes[1,2]. Application of ammonia as a leaching agent in the recovery of copper from low-grade ores and concentrates has been broadly investigated because of its many advantages, e.g. the process is non-corrosive, ammonia could be recycled and Fe, Al and other impurities are insoluble in that system. Moreover, this leaching system allows for a more selective extraction of the valuable metals, such as copper, nickel and cobalt.

Over the last few years the extraction of metal ions from chloride, ammonia, sulphate and chloride/sulphate aqueous solutions by hydrophobic pyridylketoximes has been widely investigated. The studies have mainly focused on extraction of copper(II) zinc(II), iron(III), nickel(II) and cadmium(II) ions and oxime of 1-(2-pyridyl)tridecan-1-one was proposed as the most effective metal extractant [3-9]. However, problems relating to the separation of copper from multielemental ammonia solutions have not yet been studied.

In the present study, the solvent extraction and separation of copper(II) ions from ammonium sulphate/ammonia solution containing also zinc(II), cobalt(II) and nickel(II) ions by oxime of 1-(2-pyridyl)tridecan-1-one has been investigated. The influence of pH of the aqueous phase and copper(II) ion concentration on the extraction were also studied. The stoichiometry of the extracted species in the organic phase has been predicted from the slope analysis and conformed by the results of ammonia content in the organic phase.

Experimental

Reagents

All reagents used in this study were of reagent grade. Toluene (POCH, Poland) and decan-1-ol (Merck, Germany) were used as components of the organic phase. The

aqueous feed solutions were prepared by dissolving the appropriate amounts of $\text{CuSO}_4 \times 5 \text{ H}_2\text{O}$ (Aldrich, Germany) and $(\text{NH}_4)_2\text{SO}_4$ (Merck, Germany) in the de-ionised water. Oxime of 1-(2-pyridyl)tridecan-1-one (Fig. 1) was synthesised by treating 2-pyridyl cyanide with dodecylmagnesium bromide in diethyl ether as a diluent and next, the synthesised ketone was treated with hydroxylamine hydrochloride in the presence of sodium carbonate [3]. ^1H NMR (CDCl_3) δ in ppm: 9.13 (s); 8.64 (s); 7.81 (d); 7.66 (t); 7.26 (d); 2.97 (t); 1.56(q); 1.29-1.24 (m); 0.87 (t). ^{13}C NMR (CDCl_3) δ in ppm: 160.6; 154.0; 148.9; 138.6; 123.6; 120.9; 31.9; 29.9; 29.8; 29.7; 29.6; 29.4; 29.3; 29.1; 26.3; 24.7; 22.7; 14.1.

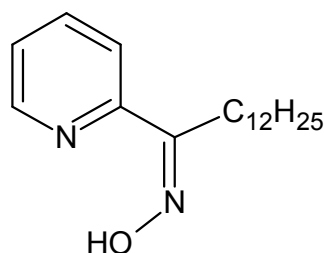


Fig. 1. Structure of 1-(2-pyridyl)tridecan-1-one oxime

Extraction studies

The basic studies were carried out at a constant copper(II) concentration equal to 1 g/L and at constant concentration of ammonium sulphate – 25 g/L. The pH of the aqueous solution was adjusted (713 pH Meter, Metrohm) to a desired value by adding concentrated or 2% solutions of ammonia. The concentrations of the oxime in the organic phase were changing from 0.02 to 0.1 mol/L. Extraction and stripping were carried out in a test tube using equal volumes (5 mL) of both phases (O/W; 1:1). The two phases were shaken for 15 minutes at room temperature (23-25 °C) using Bio-mix BWR 04. The selectivity study was carried out using an aqueous feed solutions containing 1 g/L of sulphate salts of copper(II), cobalt(II), nickel(II) and zinc(II) in ultrapure water at the constant concentration of ammonia sulphate (25 g/L) and at constant pH of 9. Before and after the extraction and stripping processes, the metals' concentrations in the aqueous phase were analysed with atomic absorption spectrometry (HITACHI Z-8200 Polarised Zeeman).

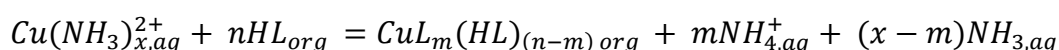
The concentration of the metal ions in the organic phase was calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction. The distribution coefficient (D) was taken as the ratio of the copper(II) concentrations in the organic phase to the concentration in the aqueous phase after reaching equilibrium. The separation factor $\beta_{\text{Cu(II)}/\text{M(II)}}$ was taken as the ratio of the copper(II) distribution coefficient to the zinc(II), nickel(II) or cobalt(II) distribution coefficient.

Results and discussion

Basic extraction studies

Hydrophobic 2-pyridylketoxime can react with divalent metals causing solvating complexes or a stable chelate, however in the case of copper(II) ions, independently from the aqueous feed composition, only a chelate has been observed.

The ammonia sulphate solutions containing copper ions are very specific, especially if pH of the aqueous solutions is higher than 7. Then under these conditions a free ammonia as well as copper-ammine complexes will be formed in the aqueous phase and the extraction of copper(II) with 2-pyridylketoxime can be described by the equation:



with equilibrium constant

$$K_{ex} = \frac{[CuL_m(HL)_{(n-m)}][NH_4^+]^m [NH_3]^{(x-m)}}{[Cu(NH_3)_x^{2+}][HL]^n}$$

and distribution ratio, which can be expressed as:

$$\log D = \log K_{ex} + n \log [HL] - m \log [NH_4^+] - (x-m) \log [NH_3]$$

Effect of pH on the extraction of copper(II) ions from ammonia sulphate/ammonium solution was studied in the range of pH 6 -11. The obtained results have shown that the metal was extracted in 100% and the extraction did not depend on the pH of the aqueous phase (Fig. 2). Moreover, the equilibrium pH was slightly higher than the initial pH ($\Delta pH = 0.46-0.5$) and that could wrongly suggest the coordination through solvating mechanism.

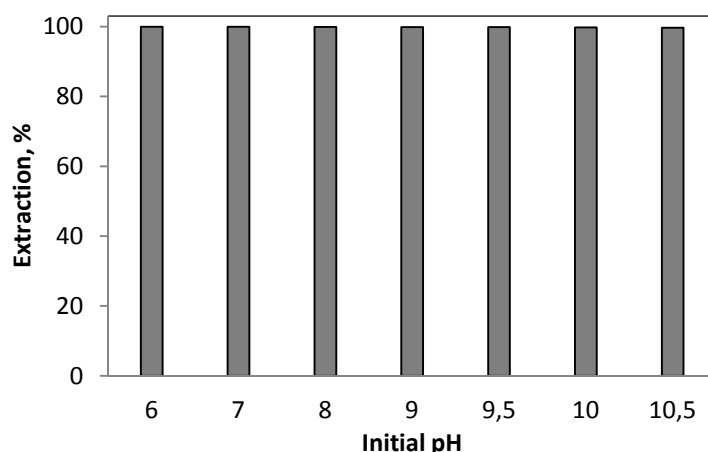


Fig. 2. Effect of pH on copper(II) extraction from ammonium sulphate/ammonia solution with 1-(2-pyridyl)tridecan-1-one oxime.

The effect of contact time on extraction indicated that the copper recovery with the hydrophobic pyridineketoxime was very fast and just after one minute of shaking the process can reach equilibrium.

The extraction isotherm for copper(II) ions was obtained by contacting the metal aqueous solution with 0.1 mol/L of 1-(2-pyridyl)tridecan-1-one oxime at 1:1 phase ratio and at the pH of the aqueous phase equal to 9. The study indicated that for the copper(II) ions' concentrations varying from 0.1 to 2.5 g/L the percentage of extraction was equal to 100%, however, further increase of the metal concentration decreased the extraction efficiency and finally the loading capacity values reached 3.3 g/L.

Effect of ligand concentration was studied using an aqueous feed solution containing 1 g/L of copper(II) ions, 25 g/L ammonium sulphate and pH of the solutions was 7 or 9. From these results the linear increase of copper(II) ions extraction with the increasing oxime concentration was observed. Furthermore, the logarithm variation of the copper distribution coefficient and the initial oxime concentration gave the straight lines with slopes, which values depended on the pH of the aqueous feed solutions. In case of the results obtained for solutions with pH of 7, the slope pointed the coordination of metal ions by two molecules of the oxime, but the studies carried out at pH of 9 indicated the presence of the complex, in which one molecule of the metal was coordinated by three molecules of the oxime (Fig. 3).

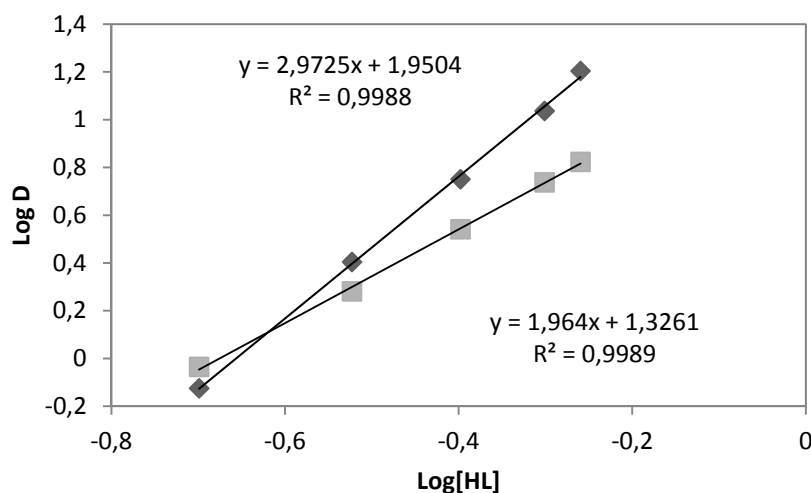


Fig.3. Logarithmic relation between copper(II) distribution coefficient and 1-(2-pyridyl)tridecan-1-one oxime concentration ($[Cu^{2+}] = 1\text{ g/L}$; $[HL] = 0.01 - 0.1\text{ mol/L}$; $[(NH_4)_2SO_4] = 25\text{ g/L}$; pH = 7(■) and 9(◆).

Oxime of 1-(2-pyridyl)tridecan-1-one formed very stable copper(II) complexes and the metal from the loaded organic phase was stripped only by mixing with an aqueous solution containing oxalate ions.

Separation studies

Oxime of 1-(2-pyridyl)tridecan-1-one is dissolves well in the aromatic as well as aliphatic diluents, however, the use of toluene as a diluent enabled to lower the transport of a co-extracted ammonia. Moreover, the studies indicated that the use of decan-1-ol as a modifying agent into the organic phase (toluene:decan-1-ol volume ratio 9:1) reduced the nickel(II) ions extraction to 0.05%.

Extraction studies of the individual metal solutions containing 1 g/L nickel(II), cobalt(II) or zinc(II) ions indicated that only cobalt(II) ions were transported into the organic phase and the extraction was no lower than 80%. It suggested that the selective extraction of copper(II) from ammonium sulphate/ammonia solutions could be impossible, however, the extraction of individual compounds from multimetal solutions containing 1 g/L of copper(II), nickel(II), cobalt(II) and zinc(II) ions unequivocally demonstrated that nickel(II) and zinc(II) ions remained in the aqueous phase during the extraction and cobalt(II) ions were extracted in only 6.9%. This may suggest that the 2-pyridylketoxime can form more stable complexes with copper(II) ions rather than with cobalt(II), moreover, a further increase of copper(II) ions concentration confirmed such theory and just 2 g/L concentration of copper(II) ions reduced the cobalt(II) extraction to 0.3%. Unfortunately, the increase of copper(II) ions extraction negatively influenced the copper(II) separation over zinc(II) and nickel(II) ions, however the transport of these metals was not higher than 1-3%.

Based on the data pertaining to the extraction behaviour of these metals, the 0.1 M 1-(2-pyridyl)tridecan-1-one oxime was contacted with synthetic solutions containing: 7 g/L copper(II), 0.28 mg/L cobalt(II), 0.49 mg/L nickel(II) and 0.58 g/L zinc(II) ions at pH = 9 [10]. The obtained results confirmed that the 2-pyridylketoxime can efficiently extract of copper(II) ions from the ammonia solutions and the selectivity of the process is very high. ($\beta_{\text{Cu/Zn}} = 1.5 \times 10^7$, $\beta_{\text{Cu/Ni}} = 1.7 \times 10^6$ and $\beta_{\text{Cu/Co}} = 1.8 \times 10^6$).

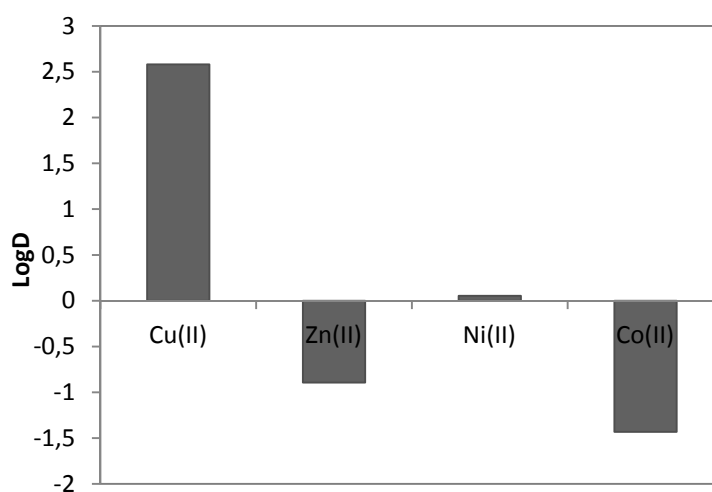


Fig. 4. Extraction of metals from synthetic solutions containing 7 g/L copper(II), 0.28 mg/L cobalt(II), 0.49 mg/L nickel(II) and 0.58 g/L zinc(II) ions.

Conclusions

The basic extraction studies indicated that oxime of 1-(2-pyridyl)tridecan-1-one can effectively extract of copper(II) ions from ammonium sulphate/ammonia solutions and the process depended on the extractant and the metal ions concentration. pH of the aqueous phase did not influence the efficient of the extraction but it influenced on the copper-oxime complex structure. The selectivity studies of the copper(II) ions recovery from multimetal ammonium sulphate/ammonia solution using hydrophobic 2-pyridineketoxime indicated that only cobalt(II) ions could be co-extracted with copper into the organic phase, however, the increase of copper(II) ions concentration to 2 g/L reduced the cobalt(II) extraction to 0.3%. The increase of copper(II) ions extraction negatively influenced the copper(II) separation over zinc(II) and nickel(II) ions, but the transport of these metals was inconsiderable.

Acknowledgements

This research was supported with 32-374/14 DS-PB grant.

Reference

1. K.H. Park, D. Mohapatra, B.R. Reddy and C.W. Nam. A study on the oxidative ammonia/ammonium sulphate leaching of a complex matte. *Hydrometallurgy* 86, 164-171 (2007)
2. T. Çalbana, S.Çolaka, M. Yeşilyurta, Optimization of leaching of copper from oxidized copper ore in $\text{NH}_3\text{-(NH}_4)_2\text{SO}_4$ medium, *Chem. Eng. Com.* 192 (11), 1515-1524 (2005)
3. K. Klonowska – Wieszczycka, A. Olszanowski, A. Parus B. Zydorczak, Removal of copper(II) from chloride solutions using hydrophobic pyridyl ketone oximes, *Solvent Extr. Ion Exch.* 27 (1), 50-62 (2009)
4. A. Parus, K. Wieszczycka, A. Olszanowski, Solvent extraction of iron(III) from chloride solutions in the presence of copper(II) and zinc(II) using hydrophobic pyridyl ketoximes, *Sep. Sci. Technol.* 46(1) 87-93 (2011)
5. A. Parus, K. Wieszczycka, A. Olszanowski, Cadmium(II) extraction from chloride solutions by hydrophobic pyridyl ketoximes, *Hydrometallurgy* 105, 284–289 (2011)
6. K. Wieszczycka, M. Kaczerewska, M. Krupa, A. Parus, A. Olszanowski, Solvent extraction of copper(II) from ammonium chloride and hydrochloric acid solutions with hydrophobic pyridineketoximes *Sep. Purif. Technol.* 95, 157-164 (2012)
7. A. Parus, K. Wieszczycka, A. Olszanowski, Solvent extraction of zinc(II) ions from chloride solutions by hydrophobic alkyl-pyridyl ketoximes, *Sep. Sci. Technol.* 48(2), 319-327 (2012)
8. K. Wieszczycka, M. Krupa, A. Olszanowski, Extraction of copper(II) with hydrophobic pyridyl ketoximes from chloride and sulphate solutions, *Sep. Sci. Technol.* 47(9), 1278-1284 (2012)
9. K. Wieszczycka, M. Krupa, A. Wojciechowska, A. Olszanowski, Recovery of nickel(II) ions from sulphate/chloride solutions using hydrophobic pyridylketoximes, *Solvent Extr. Ion Exch.* (2014) DOI:10.1080/07366299.2013.850334
10. K. Ochrowicz, M. Jeziorek, K. Wejman, Copper(II) extraction from ammonia leach solution, *Physicochem. Probl. Miner. Process.* 50(1), 327–335 (2014)

and Inst. of Physical and Theoretical Chemistry, University of Regensburg

Absolute Solubility of Artemisinin

$\Delta G_{\text{fus}} = 11.39 \text{ kJ/mol}$

Solvent	Experiment ($\log S$)	COSMO-RS ($\log S$)	COSMO-QS ($\log S$)
Carbon tetrachloride	-3.1	-3.1	-3.1
Hexane	-3.1	-3.1	-3.1
Chloroform	-1.1	-1.1	-1.1
Toluene	-1.2	-2.1	-1.2
Propylene carbonate	-2.8	-2.8	-2.8
Dimethylacetamide	-2.8	-2.1	-2.8
Acetone	-2.1	-2.1	-2.1
Ethyl acetate	-1.2	-2.1	-1.2
DMF	-1.2	-2.1	-1.2
DMSO	-2.8	-2.1	-2.8
Acetonitrile	-3.1	-3.1	-1.2
Water at 25°C	-5.8	-5.8	-5.8
Ethanol	-3.1	-3.1	-3.1
Isopropanol	-2.8	-2.8	-2.8
n-Butanol	-2.8	-2.8	-2.8
Isooctane	-2.8	-2.8	-2.8
Ethoxyethane	-2.8	-2.8	-2.8
Methylcel	-2.8	-2.8	-2.8

- 378

Influences of interfacial phenomena on transport processes in micellar liquid/liquid systems

N. Paul (n.paul@mailbox.tu-berlin.de), S.-J. Kim, M. Kraume

Chair of Chemical and Process Engineering, Ackerstraße 71-76, 13355 Berlin, Germany

Micellar liquid/liquid systems are innovative solvent systems which can be applied to increase the reaction rates of multiphase systems. Furthermore, these systems fulfill many principles of the “green chemistry” e.g. using water as a solvent. In micellar systems surfactants adsorb at the liquid/liquid interfaces where these molecules influence the occurring transport processes. This reduction of the transport processes is referred to two mechanisms. Due to the adsorption at the interface an additional mass transfer resistance is created. Furthermore, the fluid dynamics will change. Quantifying the influences of surfactants on the mass transfer is the goal of this work. Therefore, the mass transfer is observed at the smallest transfer unit: at single droplets.

For the experimental investigations different systems were observed: water was always used as the continuous phase and various long chain alcohols were applied as dispersed phases. An azo dye (Pyridine-2-methylaniline) was used as transferred component and as an example of a non-ionic surfactant Triton X-100 was chosen. The liquid/liquid mass transfer and the fluid dynamics were measured during a single drop rise in special test cells. Furthermore, many experiments to quantify the occurring interfacial phenomena were carried out (e.g. colloidal probe atomic force microscope measurements, oscillating drop measurements etc.).

With an increase of surfactant concentration a reduction of the liquid/liquid mass transfer was observed, which is referred to the mechanisms above. But in micellar systems (for high surfactant concentrations) these mechanisms need to be extended. The phase behaviour at the interface changed and a microemulsion layer is created at the liquid/liquid interface, which is responsible for an additional mass transfer resistance. Without the consideration of this microemulsion layer the mass transfer is overestimated. To understand and to be able to predict the formation of microemulsion layers at the liquid/liquid interface the experiments were carried in various test systems.

Electrostatically Induced Droplet Agitation in Solvent Extraction

*Simon Assmann, Department of Metallurgical and Minerals Engineering,
WA School of Mines, Curtin University, Kalgoorlie, Australia;*

*Don Ibane, Department of Metallurgical and Minerals Engineering, WA
School of Mines, Curtin University, Kalgoorlie, Australia;*

*Christopher McRae, Department of Chemistry and Biomolecular
Sciences, Macquarie University, Sydney, Australia*

Abstract

It is inherent in mechanically agitated solvent extraction (SX) contactors that the droplet motion decreases as the droplet size decreases, leading to poor mass transfer. This is one of the main disadvantages of the conventional SX technology. In theory, this can be surmounted by the use of electrostatic agitation. Accordingly, electrostatic fields can be used to make droplets of feed solutions oscillate and zigzag as they fall through the organic phase by gravity, but little data is available to support this. The present study investigated how the properties of electrostatic fields influence droplet oscillation and zigzagging using a high-speed imaging system.

The results show that alternating current (AC) fields induce both droplet zigzagging and droplet oscillation, but the dominant form of agitation is dependent on the charge-to-mass ratio of droplets. High charge-to-mass ratio results in interfacial polarisation of droplets, leading to increases in their horizontal velocity and hence, their zigzagging. Conversely, low charge-to-mass ratio results in orientational polarisation of droplets, favouring their oscillation. The shift from zigzagging to oscillation is dependent on the relative amounts of interfacial and orientational polarisation that a droplet exhibits.

These findings are particularly useful in the design of electrostatically agitated contactors in solvent extraction.

Introduction

It is well known that decreasing the droplet size leads to decreases in droplet motion in mechanically agitated solvent extraction (SX) contactors (Ritcey 2006). This is undesirable in SX applications as the rate of mass transfer approaches that of diffusion alone (Nagata & Yamaguchi 1960).

Electrostatic solvent extraction (ESX) is a modification of SX that uses electrostatic fields, rather than mechanical agitation, to achieve mixing of the immiscible phases. ESX is based on the principle that when a conductive liquid that is suspended in a relatively non-conductive liquid is subjected to a strong electrostatic field, it disperses into smaller so-called daughter droplets (Taylor 1964). An electrostatic field can also be used to induce agitation of these daughter droplets in a way that cannot be achieved using mechanical agitation.

Two main forms of electrostatically induced droplet agitation have been reported: zigzagging and oscillation. Droplet zigzagging refers to an alternating horizontal movement of a droplet that occurs in addition to its vertical movement owing to

gravity. In the presence of AC electrostatic fields, zigzagging droplets periodically change direction in response to the alternating polarity of the electrodes (Reeves et al. 1999, Steffens 2011). Droplet oscillation is the periodic elongation and contraction of a spherical droplet about its horizontal axis. Although droplets can exhibit natural oscillation in the absence of a field, AC fields appear to induce forced droplet oscillation (Collard 2011, Steffens 2011). Previous investigators have reported that zigzagging and oscillation somehow are dependent on experimental variables such as the field strength and frequency, droplet charge, and the physical properties of the solutions among others. It is, however, unclear under what conditions these two motions, which constitute electrostatic agitation, occur, and whether they can be controlled as this would be useful in the development of ESX applications.

The electrostatic forces applied to droplets causes them to polarise, and two mechanisms of polarisation that are applicable to liquid-liquid systems have been proposed. Interfacial polarisation is the interaction between electric charge that accumulates on the interface of droplets and the external field, while orientational polarisation is the alignment of dissolved polar species, such as water molecules, in response to the field (Pohl 1973). The former occurs because electric charges migrate through a liquid with non-zero conductivity toward a discontinuity of electrical properties such as a liquid-liquid interface (Melcher & Taylor 1969).

The present study was aimed to investigate the effect of electrostatic fields on droplet agitation as a step toward the development of an application of ESX in the separation of cobalt and nickel from pregnant liquor solutions of lateritic nickel ores.

Materials and Methods

Reagents and Test Solutions

The follow reagents were used in this experimental work: ShellSol®2046 (Industrial, Shell), Cyanex®272 (Industrial, Cytec Australia), acetic acid (AR, Chem-Supply), sodium hydroxide (AR, Chem-Supply), cobalt sulphate heptahydrate (AR, Chem-Supply), sodium sulphate (AR, BDH). All reagents were used as supplied.

The test solutions consisted of a cobalt sulphate (0.3 g/L Co) and sodium sulphate (0.2 mol/L) solution in an acetic acid/acetate buffer at a pH of 5.5 as the aqueous phase, and Cyanex 272 (10% v/v) in ShellSol 2046 as the organic phase.

Experimental Set-up

The experimental set-up consisted of a glass droplet column equipped with a state of the art high-speed imaging system. Droplets were released from a flat-tipped stainless steel needle (35 mm length, 0.6 mm Ø) that was shielded by an earthed metal cylinder. The electrostatic field, generated using an AC power supply (California Instruments, 801RP), was applied between two parallel-plate electrodes

that were constructed from ethylene tetrafluoroethylene (ETFE)-coated stainless steel.

The high-speed imaging system (Oxford Lasers VisiSizer D30V, IMG0021), consisting of a laser and a high-speed camera that were placed on either side of the droplet column, was used to observe the behaviour of droplets and to measure the diameter and velocity of droplets in the presence of electrostatic fields. The laser provided backlighting illumination, and the high-speed camera captured images at a rate of 500 frames/second. A diagram of the experimental set-up is shown in Figure 1.

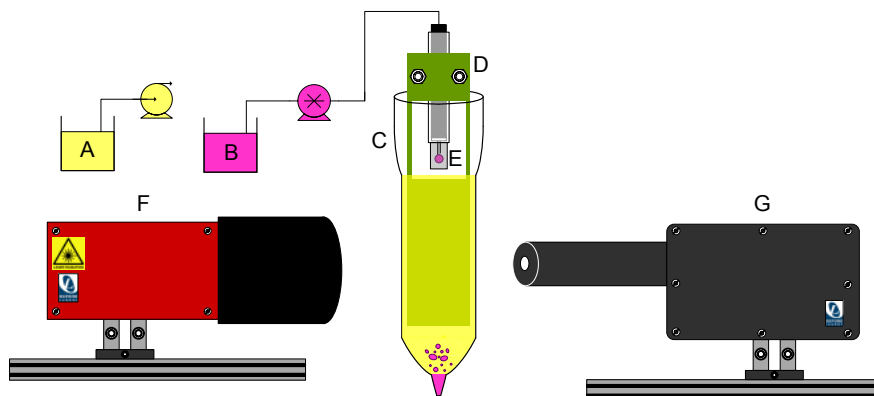


Figure 1 Droplet column experimental set-up (A - organic phase, B - aqueous phase, C - droplet column, D - parallel-plate electrodes, E - shielded feed needle, F - laser, G - high-speed camera)

Experimental Procedures

The droplet column was filled with the organic phase, the power supply was turned on, and the desired voltage (2.50 – 3.50 kV/cm) and frequency (20 – 60 Hz) was selected. Single droplets of the aqueous phase were then released into the column, which then dispersed to form daughter droplets as they reached the influence of the electrostatic field. The laser and high-speed camera were placed half-way down the column to facilitate investigation of the agitation of the daughter droplets.

Experimental data was processed using the software that was supplied with the high-speed imaging system (Photron FastCam Viewer, VisiSize v6.206). An average of approximately 40,000 droplets was measured within an experimental run, and ten runs were carried out for each set of experimental conditions.

Results and Discussion

Effect on Droplet Zigzagging

The effect of electrostatic fields on droplet zigzagging was investigated by measuring the horizontal component of the velocity of the droplets as they fell through the column in a zigzagging fashion. Increases in the frequency of the applied field resulted in linear decreases in the average horizontal velocity of the droplets regardless of their size and a narrower range of horizontal velocities (Figure 2). This

may be attributed to the corresponding decreases in the time available for droplets to gain horizontal velocity towards an electrode before being forced to change direction in response to the alternating AC field.

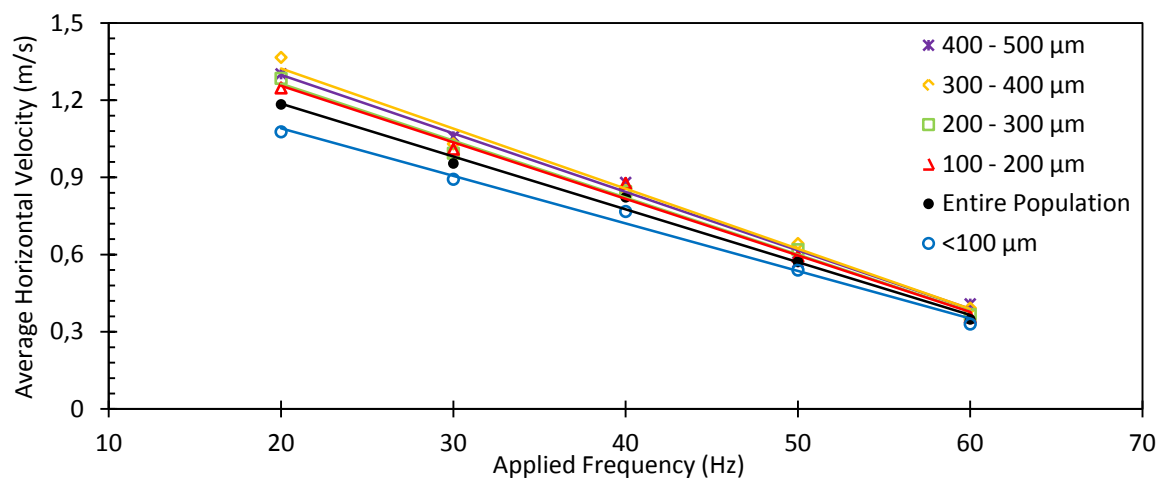


Figure 2 Effect of the frequency of AC fields (3.50 kV/cm) on the average horizontal velocity of droplets in various size fractions

Increases in the mean field strength, which refers to the applied voltage divided by the distance between the two electrodes, resulted in linear increases in the average horizontal velocity of the whole range of droplet sizes (Figure 3). This may be attributed to the increases in the strength of the electrostatic force that is imparted onto the droplets.

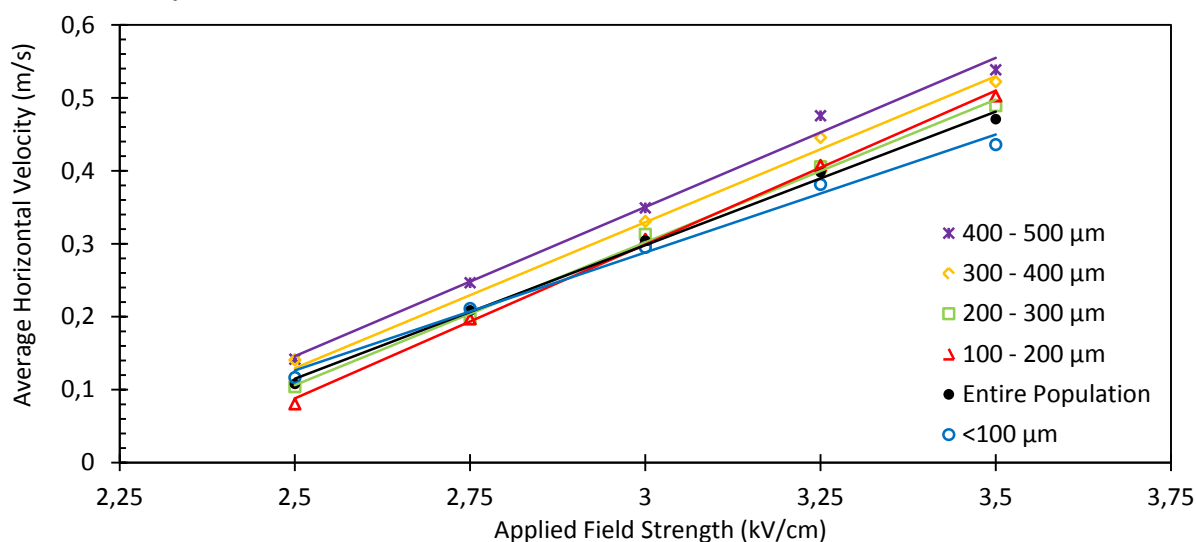


Figure 3 Effect of the field strength of AC fields (50 Hz) on the average horizontal velocity of droplets in various size fractions

It was evident that not all droplets zigzag but a far greater proportion of small droplets did zigzag compared with large droplets. It is also evident that the zigzagging was directly linked to the changing polarity of the electrodes indicating a much stronger attraction of the droplet to one of the electrodes. This suggested that zigzagging droplets have higher charge-to-mass ratio than those that were not, which is understandable given that smaller droplets can more easily acquire sufficient

electrical charge to attain a high charge-to-mass ratio. This acquisition of charge and the resulting bulk movement of a droplet towards an electrode indicate the predominance of interfacial polarisation under these conditions.

Effect on Droplet Oscillation

All field strengths and frequencies of the AC fields used in this investigation induced droplet oscillation and the frequency of the oscillation was observed to synchronise with the frequency of the applied field. For example, a recording of a droplet oscillation at a camera frame rate of 500 frames/second showed that a droplet required 5 frames to complete a full oscillation in the presence of an AC field with a frequency of 50 Hz. Clearly, the pulsing electrostatic force of the applied field was inducing the droplet oscillation.

Increases in the frequency of the applied field led to decreases in the amplitude of elongation of the oscillating droplets. Figure 4 shows a typical droplet dispersion induced by AC fields (3.5 kV/cm) at a peak in the voltage cycle. Clearly, droplets in the presence of low frequency (20 Hz) exhibited significantly greater elongation than those in the presence of high frequency (60 Hz). It is also evident that some elongated droplets formed conical ends at low frequency, whereas all elongated droplets retained rounded ends at high frequency. These observations may be attributed to the decreases in the time that an electrostatic force is exerted onto droplets as the frequency of the applied field increases. That is, as the frequency increases, the droplets have less time to respond to the electrostatic force before its polarity changes as the field cycles.

It is also evident in Figure 4 that not all droplets oscillate but the proportion of those that do and the amplitude of their elongation were significantly greater for large droplets. Given that increases in the droplet size lead to increases in the number of dissolved polar species, this behavior may be attributed to orientational polarisation suggesting that this polarisation dominates as the size of the droplets increase.

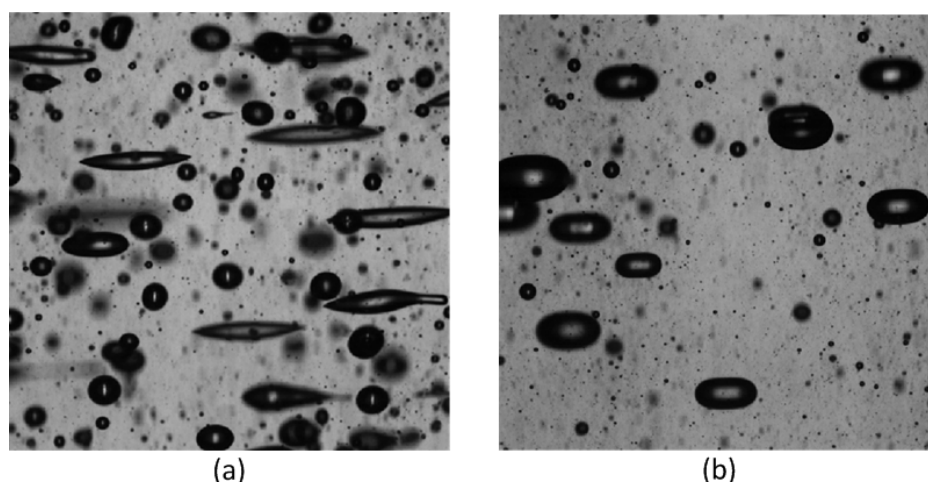


Figure 4 Oscillation induced by AC fields (3.5 kV/cm) at a peak in the voltage cycle with a frequency of (a) 20 Hz, and (b) 60 Hz

A further evidence of the importance of a droplet's charge-to-mass ratio may be observed in Figure 5. This series of photographs shows that two droplets with approximately the same spherical diameter exhibit significantly different amplitudes of elongation. This is not an isolated case. Given that both droplets have approximately the same number of polar species and thus, should exhibit comparable orientational polarisation, the larger amplitude of elongation indicated the co-existence of interfacial polarisation resulting in a stronger net electrostatic force.

Clearly, for a given droplet dispersion, AC fields induce both interfacial and orientation polarisation resulting in droplet zigzagging and droplet oscillation respectively. The former predominates with small droplets while the latter predominates with large droplets. Both can be optimised by optimising the field strength and frequency of the applied field.

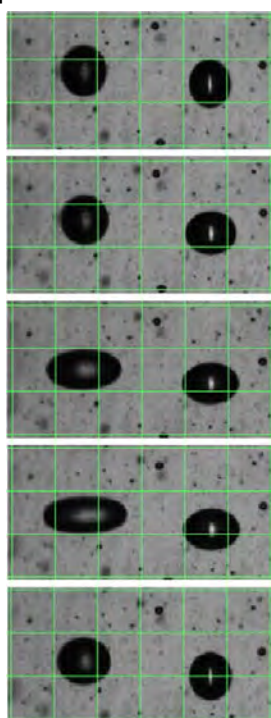


Figure 5 Two droplets with similar diameters exhibit different amplitudes of elongation when oscillating in the presence of an AC field (3.5 kV/cm, 60 Hz) (grid = 500 μm)

Conclusions

The application of AC electrostatic fields induces both droplet zigzagging and droplet oscillation. The dominant form of agitation is dependent on the dominant mechanism of polarisation, which is in turn dependent on the charge-to-mass ratio of the droplets. High charge-to-mass ratio results in interfacial polarisation of droplets, favouring zigzagging. On the other hand, low charge-to-mass ratio results in orientational polarisation of droplets, favouring oscillation. The shift from zigzagging to oscillation is dependent on the relative amounts of interfacial and orientational polarisation that a droplet exhibits.

Acknowledgements

The authors would like to thank the Australian Postgraduate Award, the Minerals & Energy Research Institute of Western Australia (MERIWA) and the Parker CRC for Hydrometallurgy for the PhD scholarships of Simon Assmann, Shell Chemicals (Peter Haig) for supplying the ShellSol 2046, and Cytec Australia (Shane Wiggett) for supplying the Cyanex 272.

References

Collard, JM 2011, 'Separation and purification of dissolved metals using electrostatic pseudo liquid membrane (ESPLIM)', PhD thesis, Curtin University of Technology, Kalgoorlie.

Melcher, JR & Taylor GI 1969, 'Electrohydrodynamics: A review of the role of interfacial shear stresses', *Annual Review of Fluid Mechanics*, vol. 1, pp. 111-146.

Nagata, S & Yamaguchi, I 1960, 'Mass transfer and chemical reaction in liquid-liquid agitation systems', *Memoirs of the Faculty of Engineering, Kyoto University*, vol. 22, pp. 249-276.

Pohl, HA 1973, 'Nonuniform field effects: Dielectrophoresis', in Moore AD (ed.), *Electrostatics and its Applications*, John Wiley & Sons, New York, pp. 336-362.

Ritcey, GM 2006, *Solvent Extraction. Principles and Applications to Process Metallurgy*, vol. 1, 2nd edn, G.M. Ritcey & Associates Incorporated, Ottawa.

Reeves, MJ, Bailey, AG, Howard, AG, & Broan, CJ 1999, 'Factors influencing operational efficiency of an electrostatic solvent extraction system', *Institute of Physics Conference Series*, no. 163, pp. 257-260.

Steffens, MJ 2011, 'Development of an electrostatically assisted solvent extraction column', PhD thesis, Curtin University of Technology, Kalgoorlie.

Taylor, G 1964, 'Disintegration of water drops in an electric field', *Proceedings of the Royal Society of London*, vol. A280, pp. 383-397.

Preparation of the novel ionic liquids functionalized resins with tunable structure for metal ions separation

Hongmin Cui^{1,2}, Ji Chen^{1,*}, Yu Liu¹

¹ State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. Email:

Jchen@ciac.ac.cn; Tel/Fax: 86-43185262646

² Graduate School of the Chinese Academy of Sciences, Beijing 100049

Separation and recovery of valuable metal ions, such as, rare earths (REs), and heavy metals, Cr(IV), dilute solutions has received increasing attention in view of resource sustainable development and environmental improvement. For this reason, varied supported ionic liquids (SILs) including P-SILs, SM-SILs and M-SILs have been investigated in our laboratory for the last ten years[1]. To further enhance the interaction between the extractant and the support, the novel ionic liquids functionalized resins by incorporating Aliquat 336 or P204, Cyanex 272 as cations or anions into chitosan and poly(styrene-divinylbenzen) backbones are prepared through non-covalent interactions, the structures were shown in Fig.1. [A336][CMCTS] has showed satisfied adsorption ability towards Pb(II) and Yttrium(III). [2,3]

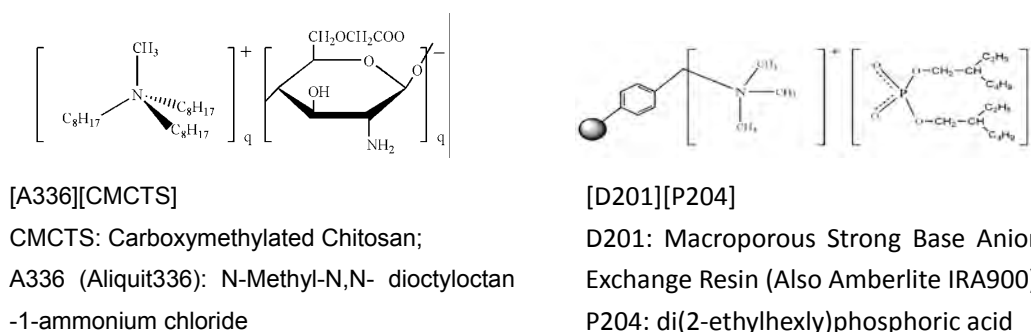


Fig.1 Chemical structure of [A336][CMCTS] and [D201][P204]

The immobilization of the ligands P204 by acid-base interaction with polymer matrix produced an interaction, which was stronger than the usual physical adsorption of the extractants onto the inert polymeric support. Furthermore, the prepared resins could be adjusted through a judicious choice of cationic and anionic components. The adsorption behaviors of REs(III) were also investigated in chloride solutions by the as-prepared resins. It was found that the adsorption mechanism could be explained as the formation of metal complexes between RE(III) and the P=O from P204. The results presented here should pave the way for the use of the novel resins for the recovery of RE(III) from ore processing.

Reference:

[1] L. Zhu, J. Chen *Sci. China Chem.* **2012**, 55(8), 1479-1487; [2] H. Cui, J. Chen et al, *Chem. Eng. J.* **2013**, 232, 372-379.[3] H. Cui, J. Chen *Chin. J. Anal. Chem.*, in press.

Optimizing Plant-Material Extraction Processes

Jan Bernd Bol, Andreas Pfennig, Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria

The extraction of plant materials is a subfield of solid-liquid extraction dealing with the task of obtaining substances from herbal materials. The design of industrial processes for the extraction of these natural products has been based mostly on empirical methods so far. Due to the complexity and diversity of plant material the extraction process is influenced by many factors such as the extractor type, solvents and pre-treatment methods like milling. Additionally variations of a specified plant material with respect to origin and harvesting season have to be considered for adjusting the optimal process conditions.

The particle size of the plant material has a strong influence on the space-time-yield. Due to the reduced diffusion path in smaller particles the equilibrium concentration will be reached within shorter time, even at constant diffusion coefficients. Since milling processes usually result in a distributed particle size, this distribution has to be taken into account when modeling the extraction process.

By varying the solvent or the milling intensity the space-time-yield or the selectivity of the extraction can be improved. While the process cost might increase the revenue for the product might increase as well. Here the overall process cost have to be considered in order to find the most economic variant and process conditions.

To deal with this optimization problem Model Based Experimental Analysis (MEXA) is used. MEXA is a tool for optimal experimental design. Provided that at least a minimum number of experiments – mostly only two or three – have been performed based on available models validated in this project MEXA can be used to fit the parameters and optimize experimental conditions for all successive experiments such, that the information per experiment is maximized. Thus, the number of necessary experiments is significantly reduced without losing accuracy in order to find the most economic process. In the presentation it will be shown how particle-size distributions and cost functions are used in the standardized procedure for the design of optimized plant-material extraction.

Solvent extraction optimization of added value components from oats: scale up perspective

Orozco-Mena R. O., Ortega-Rivas E., Pérez-Vega S. B.*
School of Chemical Science, Autonomous University of Chihuahua, Circuit 1,
New University Campus, CP 31125 Chihuahua, Mexico
e-mail: sama_1218@hotmail.com

Summary

The study covers the feasibility for obtaining added value components from oats by solvent extraction. Design of experiments was developed in order to evaluate factors such as time, temperature, particle size, and solvent in the extraction process. A factorial design of 1 block and two levels with 32 runs were developed. The results were analyzed by ANOVA, having as response variables Total Polyphenols Content (TPC) and Oxygen radical absorbance capacity (ORAC). Total polyphenols were determined by Folin-Ciocalteu method and ORAC capacity by a fluorescence method. As a result from the ANOVA the factors that had significant influence in the TPC response variable were particle size and solvent polarity, while the interactions that also were significant were particle size-solvent, solvent-temperature, size-temperature-time, and solvent-temperature-time. Regarding ORAC capacity response the significant factors were time, particle size, and solvent, while the most significant interactions were time-solvent, temperature-time, and solvent-temperature-time. ANOVA analysis was developed with a significance level of 95%. The results show that the higher values of TPC was 1.6 mg GAE/g and ORAC values of 32 mmol TE/g, this while using a solvent of higher polarity such as water, smaller particle size (0.5 mm), temperature of 30°C, and extraction time of 60 minutes. As a result, variables such as solvent and solid size seem to have more influence in the extraction process than temperature and time. Solubility curves were developed for 4 different solvents to evaluate behavior of TPC, ORAC and yield extraction at 8 different mass/volume ratios. The results demonstrated that greater mass/volume ratio led to extraction enhancement. Highest TPC measurements were achieved with isopropyl alcohol (7.99 mg GAE/g). Best ORAC values were obtained with Ethylene glycol (42 µmol TE/g), and the best yield extraction was reached with ethanol (0.18 g_{extract}/g_{oat}). Simulation process was developed to study the cost feasibility for future process implementation. The results showed that extraction with isopropyl alcohol was the most profitable option to scale-up the process due its low cost and the ease to recover.

INTRODUCTION

In 2010 in the state of Chihuahua 65,296.20 tons of oat were harvested which has an estimated value of production of \$ 170,753,100, MXP making the state the largest producer of oat nationwide¹. Therefore oatmeal is one of the main agricultural products harvested within the state⁷, not only by the quantity harvested but also by the characteristics of oat grains. Because oats have a high content of unsaturated fatty acids, it contains various antioxidant compounds that protect grains from lipid oxidation. Oxidation gives lipid food undesirable characteristics such as taste and smell of rancidity, discoloration and decreased nutritional value. The substances in oats with antioxidant activity include tocopherols and several esters of long hydroxycinnamates chain¹. Antioxidants are molecules that have the ability to avoid or prevent oxidation with other molecules^{2,3,4}. Due to the complexity of isolating the phenolic compounds, it is convenient to evaluate the antioxidant capacity of the whole extract so beneficial health effects are due to the cooperative action of all phenolic species⁵. Oxygen Radical Absorption Capacity technique (ORAC) has frequently been used to determine the total antioxidant capacity (TAC)

because the human body conditions are simulated (pH 7.4 and a temperature of 37 ° C). Obtaining antioxidant compounds from grains is by solvent extraction. The antioxidant activity of the extract is directly related to the characteristics of the solvent and the phenolic compounds. This project aims to use and extend new methodologies for the search and evaluation of solvents that help meet the needs of the process, but also make the process sustainable. This research focuses, through analysis and experimentation methodologies, to extend key information for the early stages of process development by identification and evaluation of solvents for extraction of value added compounds in oats.

Materials and methods

Extractions and factorial analysis

Oats were obtained from a local food distribution center for cattle, which has no knowledge of the harvest conditions. Ground oats were screened using sieves opening size of 0.074, 0.125, 0.207, 0.5, 1.0, 1.8 and 2 cm. Two factorial designs were performed. Process variables were solvent, extraction time, temperature and particle size of the solid. The extractions were performed at a solid/liquid ratio of 1:5 (5 g oat/20 ml solvent). The extractions were done in Erlenmeyer flasks of 250 ml, which were placed in a shaker–incubator equipment. Stirring velocity was kept constant (150 rpm). Temperature and extraction time were set according to each experiment.

The values used in the analysis of the first factorial were determined based on the literature^{3,6,7,8,9,10}. Particle size (0.5 and 2 mm), solvent [water and isopropyl alcohol (IPA)], extraction time (20 and 60 min) and extraction temperature (30 to 50 °C) were chosen. The variables used for the second factorial were determined based on the results of the first experimental section; particle size (0.075 to 0.5 mm), solvent [ethylene glycol (MEG) and ethanol EtOH] time (20 and 60 min) and extraction temperature (30 to 50 °C). Upon completion of the factorial analyses, optimization of extraction parameters were made.

The results were analyzed by ANOVA (significance of 95%) by means of significance of process variables. Total Phenolic Content (TPC) and ORAC value were selected as response variables for optimization.

TPC determination

Phenolic content in the extracts was determined according to Folin Ciocalteu's technique¹¹. The procedure is briefly described. 40 µL of the standard solutions or extracts were placed in test tubes with 3 mL of distilled water. Subsequently, 200 µL of Folin Ciocalteu's reagent (yellowing) were added and allowed to stand for 10 minutes. Then, 600 µL of 20% Na₂CO₃ solution was added (blue coloring). Solutions were incubated in a water bath at 40 °C for 15 minutes (bath Isotemp 210). Finally, sample reading is performed in a spectrophotometer (Helyos Gamma, Thermo Electron Corporation) at a wavelength of 755 nm. Calibration curve ($R^2 \leq 0.98$) of gallic acid standard was used to calculate the total phenols

content (TPC) of extracts. Results were expressed as gallic acid equivalents per unit mass (mg GAE/g).

Antioxidant activity assay

ORAC technique consists in measuring the degradation of a fluorescent molecule (fluorescein) due to the addition of azo compounds (AAPH) and the delay of this reaction due to antioxidants' protection¹². Microplate reader (Varioskan Flash, Thermo Electron, Corp.) was used to measure fluorescence decay against time. 40 μ L of each extract or standard were placed in a well of a 96-well microplate with 200 μ L of a 140 nM fluorescein solution. Microplate was incubated at 37 °C for 20 min. After incubation, 35 μ L of 0.32 M AAPH solution were added. All solutions were made in a phosphate buffer solution of 75 mM and pH 7.4. Fluorescence readings were made (λ_{ex} = 485 nm and λ_{em} = 535 nm) every 4 minutes for two hours. All standards and samples were run in triplicate. Antioxidant capacity is represented by the area under the fluorescence decay curve (AUC). Trolox solutions (4, 8, 16, 32 and 64 μ M) were used as standards to compare their AUC values with those of extracts. Results were expressed as micromoles of Trolox equivalents per unit mass (μ mole TE/g).

Solubility curves

Solubility curves were used to analyze the behavior of the extraction systems at different solid/solvent ratios. Curves were performed using the 4 solvents used before in the factorial designs [ethylene glycol (MEG) and ethanol EtOH, water and isopropyl alcohol (IPA)]. The parameters evaluated were: ORAC, TPC and extraction yield ($g_{\text{extract}}/g_{\text{oat}}$). Extractions were performed with the following solid/solvent ratios: 1:2.5, 1:5, 1:7.5, 1:10, 1:12.5, 1:15, 1:17.5 and 1:20.

Process simulation

To make the simulation process Aspen Batch Process Developer (Version 7.3) software was used. The software was fed with data obtained at laboratory scale (solvents, composition of oat, equipment and operating conditions, extraction yields, etc.). The simulation scale up was performed based on the capacity of a extractor (1300 L) and three different levels of the mass/volume ratios were tested (results from solubility curves). The ratios for the 4 solvents used were: 1:2.5, 1:10 and 1:20.

RESULTS AND DISCUSSION

Factorial analysis

For the first factorial, temperature and time had no significant effect on TPC and ORAC responses. However, it was found that the particle size and the kind of solvent do had significant effects (Figure 1 AB). The results indicated that, in the second factorial, the only factor that showed a significant effect on responses was the type of solvent (Figure CD). Unlike the first factorial design, in the second one particle size did no longer represent a significant effect on the responses. This is

important because it indicates that the smaller particle size would represent a positive effect on the extraction. However, sizes below 0.5 mm will not represent further significant increase in responses, so the optimum particle size for extraction of antioxidant compounds is 0.5 mm. The maximum values of PFT and ORAC obtained were 2.1 mg GAE/g and 35 μ mole TE/g using MEG solvent, the smaller particle size (0.075 mm), 50 °C and 60 minutes of extraction time.

Solubility curves

The analysis of the solubility curves showed that responses of PFT, ORAC and extraction yield increased as the mass/volume ratio was increased. Higher PFT (7.99 mg GAE/g) was reached in the extractions performed with IPA at a ratio of 1:20. The greatest ORAC value (81.03 μ mole TE/g) was achieved in the extractions performed with MEG at a ratio of 1:20. The best extraction yield (0.18 g_{extract}/g_{oat}) was obtained with EtOH with 1:20 mass/volume ratio (Figure 1). In the factorials analyses, it was found that extracts made with MEG were those who had higher ORAC (second factorial analysis and solubility curves). However, data obtained in the solubility curves showed that EtOH extraction yields were the highest. Nevertheless, it is not possible to derive conclusions based on the information gathered so far. A deeper assessment on physicochemical properties of solvents and process simulation is needed for a different perspective to determine which solvent is best suited to scale the process of extracting antioxidant compounds from oats.

Process simulation

The total costs per kg of extract in the simulation campaign are shown in the 3D Figure. It was found that processes performed with water and MEG were more energy-consuming than those performed with EtOH and IPA. Extractions with water had higher costs generated at a campaign level (USD/kg) even when costs in batch analyses were the lowest (Figure 3A). This is because of the high latent heat of vaporization of water. Energetic consumption to heat and evaporate the solvent causes the process to generate higher operating costs (Figure 3B). In addition, savings generated due to the solvent recovery were minimal. The process that generated the lowest costs was carried out with IPA at a ratio of 1:2.5.

CONCLUSIONS

The most important variables for the extraction of antioxidant compounds of *Avena sativa* are particle size and the polarity of the solvent. The smaller the particle size (until a limit of 0.5 mm) and the greater the polarity of the solvent, the better the extraction will be favored. Further particle size reduction did no longer represent a significant effect. From simulation results, although water is a solvent of low cost and possess almost no risk of toxicity, energy expenditure required when using this solvent at industrial level is very high and, therefore, represents a major environmental impact and energy costs. It can be seen that it is possible to bring an industrial level extraction process using IPA solvent, with relatively low operating costs.

Figures

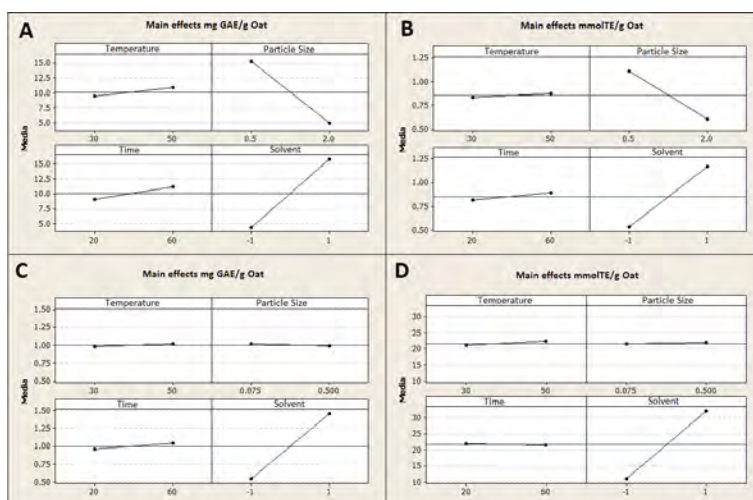


Figure 1. First factorial main effects plot on mg GAE/g (A) and $\mu\text{mol TE/g}$ (B). Second factorial main effects plot on mg GAE/g (C) and $\mu\text{mol TE/g}$ (D).

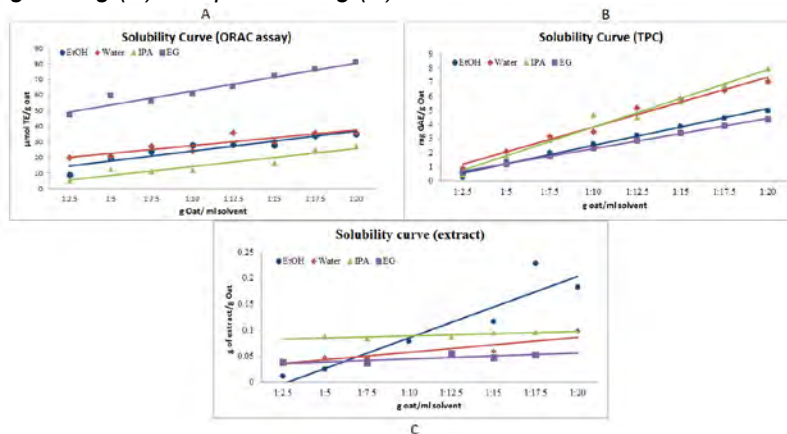


Figure 2. Solubility curves results; ORAC (A), TPC (B) and extraction yield (C).

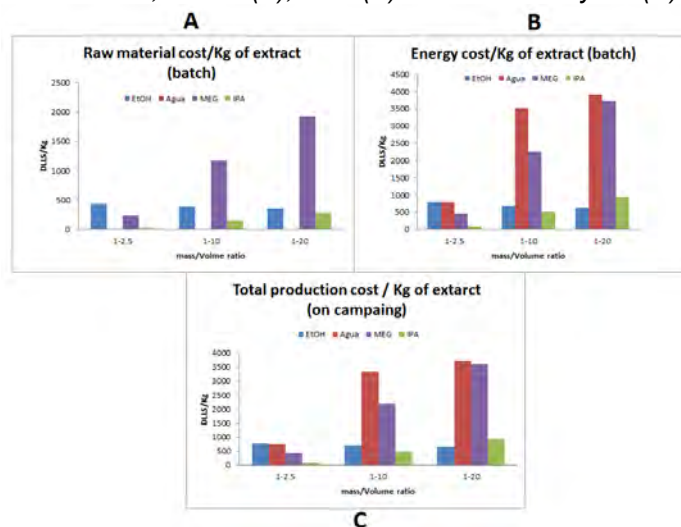


Figure 3. Cost of raw material per kilogram of extract (A), Total energy costs per kg of extract (B) and total production costs per kg of extract campaign (C).

REFERENCES

1. SIAP. 2013. *Cierre de la producción agrícola por cultivo* [Online]. Available: http://www.siap.gob.mx/index.php?option=com_wrapper&view=wrapper&Itemid=350#.UUyW1ZayXvI.email [Accessed 01 April 2013 2013].
2. BADARINATH, A., MALLIKARJUNA, K., CHETTY, C. M. S., RAMKANTH, S., RAJAN, T. V. S. & K.GNANAPRAKASH 2010. A Review on In-vitro Antioxidant Methods: Comparisons, Correlations and Considerations. *International Journal of PharmTech Research*, 2, 1276-1285.
3. EMMONS, L. & PETERSON, M. 1999. Antioxidant Activity and Phenolic Contents of Oat Groats and Hulls. *Cereal Chemistry*, 76, 902-906.
4. PETERSON, M. 2001. Oat Antioxidants. *Journal of Cereal Science*, 33, 115-129.
5. REŞAT, A., KUBILAY, G., BIRSEN, D., MUSTAFA, Ö., SALIHA, Ç., BURCU, B., IŞIL, B. & DILEK, Ö. 2007. Comparative Evaluation of Various Total Antioxidant Capacity Assays Applied to Phenolic Compounds with the CUPRAC Assay. *molecules*, 12, 1496-1547.
6. ZILIC, S., SUKALOVICB, V. H.-T., DODIGA, D., MAKSIMOVI, V., MAKSIMOVI, M. & BASI, Z. 2011. Antioxidant activity of small grain cereals caused by phenolics and lipid soluble antioxidants. *Journal of Cereal Science*, 54, 417-424.
7. HANDELMAN, G., CAO, G., WALTER, M., NIGHTINGALE, Z., PAUL, G., PRIOR, R. & BLUMBERG, J. 1999. Antioxidant Capacity of Oat (*Avena sativa* L.) Extracts. 1. Inhibition of Low-Density Lipoprotein Oxidation and Oxygen Radical Absorbance Capacity. *J. Agric. Food Chem*, 48, 4888-4893.
8. LEHTINEN, P. & LAAKSO, S. 1998. Effect of Extraction Conditions on the Recovery and Potency of Antioxidants in Oat Fiber. *J. Agric. Food Chem*, 46, 4842-4845.
9. BRYNGELSSON, S., DIMBERG, L. H. & ELDIN, A. K. 2002. Effects of Commercial Processing on Levels of Antioxidants in Oats (*Avena sativa* L.). *J. Agric. Food Chem*, 50, 1890-1896. CAO, G. & PRIOR, R. 1998. Comparison of different analytical methods for assessing total antioxidant capacity of human serum. *Clinical Chemistry*, 44, 1309-1315.
10. VERARDO, V., SEREA, C., SEGAL, R. & CABONI, M. F. 2011. Free and bound minor polar compounds in oats: Different extraction methods and analytical determinations. *Journal of Cereal Science*, 54, 211-217.
11. SINGLETON, V., R. R. O. & LAMUELA-RAVENTÓS, R. 1999. Analysis of Total Phenols and Other Oxidation Substrates and Antioxidants by Means of Folin-Ciocalteu Reagent. *METHODS IN ENZYMOLOGY*, 229, 152-178.
12. CAO, G., C.P. VERDON, WU, A., WANG, H. & PRIOR, R. 1995. Automated assay of Oxygen radical absorbance capacity with the COBAS FARA II. *Clinical Chemistry*, 6, 1738-1744.

Surfactant-based *in situ* Extraction of Microalgae Products

Racheva R.^{*1}, Kerner M.², Smirnova I.¹

The aim of this study is a surfactant screening for a potential surfactant-based *in situ* extraction process of microalgae cultures. Furthermore, the implementation of the surfactant-based extraction in a pilot plant for outdoor cultivation of microalgae designed. The main process requirements for a micellar *in situ* extraction system are biocompatibility of the surfactant with microalgae, stable phase separation behavior of the resulting two phase system, and favorable partitioning of the target substance between the micellar and the aqueous phase. The cloud point temperature, as well as the biocompatibility of Triton X-114, Tergitol 15-S-7, Ecosurf SA-7, Ecosurf EH-6, Triton DF-12, Triton DF-16, and Triton CF-32 with the microalgae *Scenedesmus obliquus* was investigated. Subsequently, the phase separation behavior of the different surfactant solutions was studied. Triton X-114 was determined as the most biocompatible surfactant. The rapid formation of stable interfacial border of the Triton X-114 extraction system assures an efficient separation process and substantial preconcentration of the target substances (palmitic acid produced by the microalgae) in the surfactant-rich phase. The partitioning behavior of palmitic acid was predicted using the model COSMO-RS. These results were compared to experimental data. Based on this data, *in situ* extraction of fatty acids from microalgae culture was designed and realized in a pilot plant. The results confirm that surfactant-based *in situ* extraction systems are a promising alternative to established solvent batch extraction from of dried algal biomass.

Introduction

The interest in microalgae products is constantly growing. Different species of microalgae are cultivated in order to produce valuable compounds like β -carotene (*Dunaliella salina*), astaxanthine (*Haematococcus pluvialis*), free fatty acids (*Chlorella vulgaris*) etc. [1]. State of the art of microalgae processing currently includes energy consuming cell harvesting, dewatering and classical extraction from the algae biomass, using organic solvents (mainly n-alkanes like hexane), supercritical carbon dioxide or ultrasonic-assisted extraction procedures [2,3]. Common among these techniques is that algae cells are disrupted and thus a time and cost consuming re-growing step of the algae biomass is needed. The *in situ* extraction is generally carried out in two-phase systems, where one phase is the microorganism containing culture medium and the other phase is an extractive agent (organic solvent or surfactant solution), which is biocompatible with the cultivated organism. In such systems target substances can be accumulated in the extract phase, simultaneously with the microorganisms' cultivation [4].

^{1*} Institute for Thermal Separation Processes, Hamburg University of Technology, Eißendorferstr. 38, 21073 Hamburg; E-mail: ralena.racheva@tuhh.de

² SSC Ltd. Beim alten Gaswerk 5, 22761 Hamburg

Non-ionic surfactant-water mixtures can be alternative extraction media for the *in situ* extraction of algae. The amphiphile molecules of non-ionic surfactants form dynamic aggregates (micelles) in aqueous solutions. Heating the micellar solution above the cloud point temperature (CPT) induces a split in two phases (a surfactant-rich phase and an aqueous phase) [5]. After phase separation of the cloud-point system, hydrophobic solutes (solubilized in the micelles) accumulate in the surfactant-rich phase. Some nonionic surfactants, e.g. Triton X-100 and Triton X-114 or Tergitol 15-S-7, show relatively low cloud point temperatures (65, 23, and 39°C). This allows the application of the corresponding cloud point system as a two phase extraction media for whole cell bioprocesses [6].

It is generally possible to use nonionic surfactant systems to extract hydrophobic substances (for instance fatty acids) from microalgae. It was shown that a mixture of the microalgae culture with the nonionic surfactant Triton X-114 form stable phases whereby the microalgae cells predominantly accumulate in the aqueous top-phase [7].

Experimental

Biocompatibility of microalgae with different surfactants was studied by determining the relative photosynthetic activity (RPA). The maximal photosynthetic yield of *S. obl.* in presence of surfactant was measured and then normalized to a surfactant free reference sample. Phase separation behavior of surfactant systems was studied. The solutions were heated with 1°C/min and their clouding temperature and subsequent phase formation was noted.

Concentrations of palmitic acid and Triton X-114 in the surfactant rich- and in the dilute phases were determined. Based on these data the partitioning coefficient of palmitic acid between both phases was calculated as a ratio of its mole fractions in each phase. Experimentally determined values were compared with values calculated using the model COSMO-RS according Mehling *et al.* [8].

For the implementation of the cloud point extraction of microalgae culture in pilot scale, the outdoor cultivation system, described by Hindersin *et al.* [9], was applied. Extraction was carried out in a bypass and was performed in a tempered water bath at 37°C.

Results and Discussion

The microalgae strain *Scenedesmus obliquus* (*S. obl.*), which was used in this study, does not tolerate temperatures above 40°C [9]. Hence primary criterion for the surfactant selection was the cloud point temperature (CPT) of the corresponding surfactant solution (Tab. 1).

Tab. 1: Applied surfactants with corresponding cloud point temperatures (CPT) and phase separation characteristics

Surfactant	CPT of 1 wt% aqueous solution [°C] ^(a)	CPT of 1 wt% aqueous solution [°C] ^(b)	Clouding	Stable interfacial border
Triton X-114	25	25,4±0,1	+	+
Tergitol 15-S-7	37	36,1±0,5	+	+
Ecosurf SA-7	37	41,0±0,2	+	-
Ecosurf EH-6	40	36,8±0,3	+	-
Triton DF-12	17	15,4±0,1	+	-
Triton DF-16	36		Proven toxic to <i>S. obl.</i>	
Triton CF-32	25		Proven toxic to <i>S. obl.</i>	

(a) Manufacturer data; (b) Experimentally determined [10]

Biocompatibility of surfactants

Besides the nonionic surfactants Triton X-114 and Tergitol 15-S-7, which have shown a high biocompatibility in former studies [7], nonionic surfactants from the Ecosurf series (Ecosurf SA-7, Ecosurf EA-6) as well as the low foaming surfactants Triton DF-12, Triton DF-16 and Triton CF-32 were investigated for their biocompatibility.

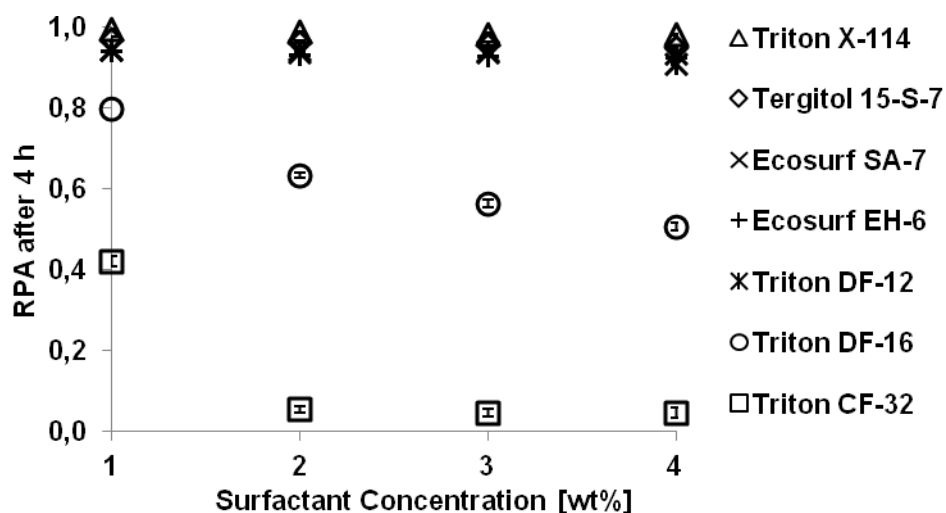


Fig. 1: Influence of surfactants on the RPA of microalgae *S.obl* after 4 hours contact as a function of the surfactant concentration [10]

The influence of the surfactants solutions with different concentrations (1, 2, 3, 4 and 5 wt%) on RPA of *S. obl.* was determined after contact period of 4 hours and illustrates the biocompatibility of the surfactants (Fig.1). RPA generally decreases with increasing surfactant concentration. On one hand, higher concentration of Triton X-114, Tergitol 15-S-7, Ecosurf SA-7, Ecosurf EH-6 and Triton DF-12 leads to slightly lower RPA values after 4h of exposure. On the other hand, Triton DF-16 and Triton CF-32 lead to significant cell vitality decrease even at 1 wt% surfactant concentration. The intolerable toxicity of Triton DF-16 and Triton CF-32 can be referred to their

higher hydrophobicity ($\log P_{o/w} = 4$ and $\log P_{o/w} = 4.3$, respectively) [11]. It can be concluded that Triton DF-16 and Triton CF-32, in the observed concentration interval, were not biocompatible with the investigated microalgae and thus not further studied.

Phase separation behavior of surfactant solutions

For the application of the *in situ* cloud point extraction, the exact CPTs as well as the stability of the two phase systems are important (Tab.1). The formation of a stable interfacial border between the two phases did not occur at all Ecosurf SA-7, Ecosurf EH-6 and Triton DF-12 solutions. These surfactants were therefore excluded from further studies.

The micellar system containing Tergitol 15-S-7 formed a clear interfacial phase boundary above a temperature of 45°C, which is not tolerable for *S. obl.* Therefore Tergitol 15-S-7 was not applicable for a CPE, under the tested setup. Only Triton X-114 demonstrated a stable and rapid phase separation characteristics at temperatures below 40°C. It can be concluded that Triton X-114 is the most appropriate surfactant for cloud-point extraction of microalgae products (fatty acids) among the tested surfactants.

Cloud Point Extraction of Fatty Acids

Palmitic acid is the most plentiful fatty acid in *S. obl.* cultures [1]. Experimental determined partitioning coefficients of palmitic acids (16:0) between the micellar- and the aqueous phase of the Triton X-114/water cloud point system were compared with the predicted values using the model COSMO-RS (Fig. 2).

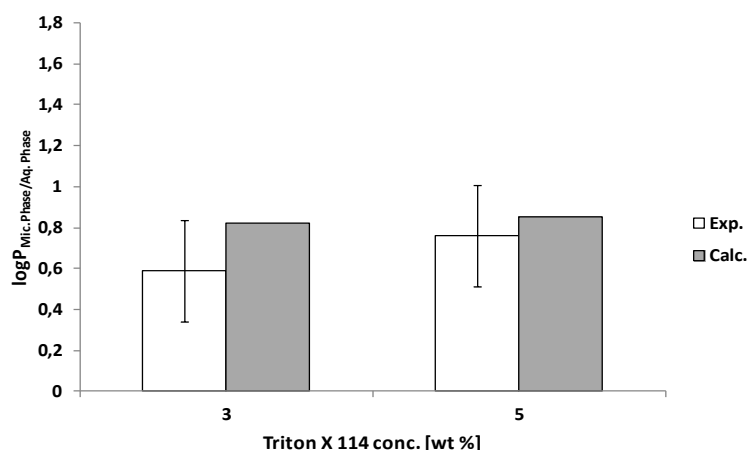


Fig. 2 Experimental and predicted partitioning coefficient of palmitic acid (16:0) between micellar- and aqueous phases [10]

Experimental determined palmitic acid distribution coefficients 16:0 (3 and 5wt% TX-114) differed slightly from the predicted values (Fig. 2). Positive $\log P_{\text{Mic. Phase/Aq. Phase}}$ values ensure favorable partitioning of palmitic acid in the surfactant rich phase.

Cloud Point Extraction in Pilot Scale

Lab-scale experiments showed the best results using a 3 % wt Triton X-114/ microalgae mixture and temperature induced phase separation at 37°C [10]. These parameters were applied for cloud point extraction at a pilot plant for outdoor cultivation of microalgae [9]. Extraction was carried out in a tempered water bath until stable phase separation was reached (Fig 3).

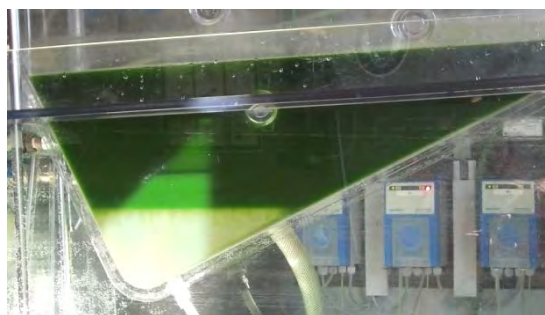


Fig. 3: Micellar system (microalgae culture + 3% wt Triton X-114) after being exposed to a 37°C water bath for 30 minutes, aqueous phase with microalgae (top) ,micellar phase (bottom) [10]

The interfacial boundary between the two phases was also stable in pilot scale. Hence, the important requirement to separate the micellar- from the aqueous phase (with the accumulated microalgae), in order to recycle the cells for further cultivation, was reached with the experimental setup.

Conclusion

In this work micellar *in situ* extraction of fatty acids from microalgae was investigated in lab- and pilot scale. The biocompatibility of seven nonionic surfactants (Triton X-114, Tergitol 15-S-7, Ecosurf SA-7, Ecosurf EH-6, Triton DF-12, Triton DF-16, and Triton CF-32) with the microalgae *Scenedesmus obliquus* was studied. Clouding temperature and phase separation stability of the seven surfactant aqueous solutions were also determined. These experiments showed that the nonionic surfactant Triton X-114 is the most suitable surfactant for an *in situ* extraction process of *S. obl.* microalgae cultures. Furthermore, the partitioning of a hydrophobic target substance (palmitic acid) was studied. Due to Triton X-114 high biocompatibility with *S. obl.*, combined with rapid formation of stable phase boundary and accumulation of palmitic acid in the micellar phase, it is suitable to develop an *in situ* extraction in larger scale. Finally, the extraction process with Triton X-114 was tested successfully in pilot scale. These results prove micellar extraction as applicable *in situ* separation process from microalgae cultures and suggest a feasible alternative for extraction with organic solvents or carbon dioxide from microalgae biomass.

References

1. Ördög, V., Stirk, W. A., Bálint, P., Lovász, C., Pulz, O., and Staden, J. *J Appl Phycol* 25, 1, 233–243.
2. Morweiser, M., Kruse, O., Hankamer, B., and Posten, C. *Appl Microbiol Biotechnol* 87, 4, 1291–1301.
3. Mercer, P. and Armenta, R. E. *Eur. J. Lipid Sci. Technol.* 113, 5, 539–547.
4. Kleinegris, D. M., Janssen, M., Brandenburg, W. A., and Wijffels, R. H. *Biotechnology Advances* 29, 5, 502–507.
5. Hinze, W. L. and Pramauro, E. *Critical Reviews in Analytical Chemistry* 24, 2, 133–177.
6. Ingram, T., Storm, S., Glembin, P., Bendt, S., Huber, D., Mehling, T., and Smirnova, I. *Chemie Ingenieur Technik*
7. Glembin, P., Kerner, M., and Smirnova, I. *Separation and Purification Technology* 103, 21–27.
8. Mehling, T., Ingram, T., and Smirnova, I. *Langmuir* 28, 1, 118–124.
9. Hindersin, S., Leupold, M., Kerner, M., and Hanelt, D. *Bioprocess Biosyst Eng* 36, 3, 345–355.
10. Glembin, P., Racheva, R., Kerner, M., and Smirnova, I. *Green Chemistry*, Submitted manuscript.
11. Mojaat, M., Foucault, A., Pruvost, J., and Legrand, J. *Journal of Biotechnology* 133, 4, 433–441.

Enhanced early stage solvent selection and evaluation in the extraction of peanut skin polyphenols

Medina–González S., Almeida–Trasviña H., Salmerón–Ochoa I, Pérez–Vega S.*
School of Chemical Science, Autonomous University of Chihuahua, Circuit 1,
New University Campus, CP 31125 Chihuahua, Mexico

Corresponding author:

* sama_1218@hotmail.com (Pérez–Vega)

Abstract

Solvent extraction giving emphasis to a sustainable process scale-up was investigated. Ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA), and water were evaluated by a response surface methodology (RSM) and process simulation with Aspen Batch Process Developer. From a lab scale, total phenolic content (TPC) and antioxidant capacity (ORAC) was evaluated. For scale-up, energy, HSE, costs, yield, and process mass intensity (PMI) were evaluated. EG showed the highest contents of TPC (>270 mg GAE/g skin) and ORAC (<3000 μ M Trolox/ g skin), whereas IPA showed the lowest (<145 mg GAE/g skin and <2000 μ M Trolox/ g skin). From a scale-up perspective, water and EG showed the best HSE performance. IPA and EtOH consumed less energy. MeOH, EtOH, and EG presented the smallest PMI scores. Solvent cost result an important factor affecting process cost. As a result, MeOH, EtOH, and IPA presented the best performance from a holistic perspective.

Practical applications

Solvent selection is a critical task during process development. Even more, the task is more complicated when extracting complex molecules such as polyphenols. Currently, there is a lack of friendly early stage tools and methodologies to improve solvent selection. Because of this, the methodology proposed during this research can be applied during development stages to obtain a more holistic view about the solvent selected: not only from typical view that only regards with yield or with solvents that have good Health, Safety, and Environment (HSE) characteristics, ignoring cost or scale-up issues. Chemical engineer can apply the methodology here proposed to evaluate the extraction of added value compounds such as polyphenols and make a more realistic selection and evaluation of solvents. This with the aim of implementing in the near future a sustainable process, considering that a processes that is not economically viable cannot be considered sustainable.

Key words: solvent extraction; solvent selection; early stage; sustainability; scale up.

Extraction of apigenin from dried parsley (*Petroselinum crispum* L.) powder by water, organic solvent and supercritical carbon dioxide

Yoshiaki Saotome^{*1} and Masanao Imai²

Summary

Apigenin is one of the anti-oxidative flavonoid that is contained especially in parsley. Apigenin was extracted by water, 1-butanol and solubility in supercritical carbon dioxide (SCCO₂). Solubility of apigenin was increased with increasing of temperature. Solubility of apigenin by 1-butanol was also increased, the maximum was appeared at 90°C as 1.62×10^{-6} [mol-apigenin / mol-butanol]. The molar solubility of apigenin in 1-butanol was superior 27-fold than that of water since its hydrophobic character. In contrast, SCCO₂ was remarkably increased with pressure. It was 4.24×10^{-7} [mol-apigenin / mol-SCCO₂] while pressure 20MPa and temperature 40°C that was 7.0-fold than that of water. The result indicated that SCCO₂ extraction is promising and alternative process for extracting apigenin from parsley.

1. Introduction

Apigenin (Fig.1) is one of bio-active ingredients found in many vegetables and herbs, especially in parsley (*Petroselinum crispum* L.). In natural resources, it was contained as a glycoside component Apiin (Fig.2). Apigenin is anticipated as an anti-inflammatory activity [3] and anti-cancer functions for human health [1,2].

Separation techniques of bio-functional component were investigated as solid-liquid extraction [4], high pressure solvent extraction [5] and super-critical extraction [6]. Especially, super-critical carbon dioxide was expected as a green solvent in bio-industry. Extraction of caffeine was successfully applied in food industry [7].

This paper demonstrated that extraction of apigenin using of super-critical carbon dioxide and solubility of apigenin was discussed based on solubility parameter of super-critical carbon dioxide.

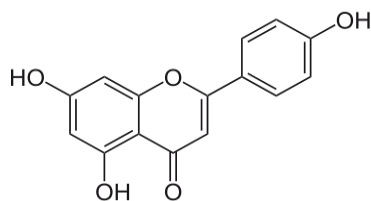


Fig.1 structure of apigenin and

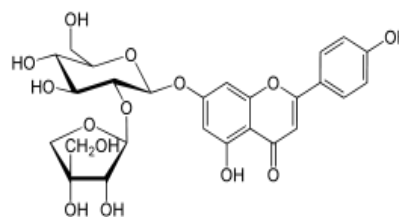


Fig.2 structure of apiin

^{*1} Yoshiaki Saotome, Graduate school of Bioresource, Nihon University E-mailaddress: bryo13013@g.nihon-u.ac.jp

² Masanao Imai, Nihon University E-mailaddress: xlt05104@nifty.ne.jp

2. Materials and Method

2.1 Plant bioresources of apigenin

Stalks of parsley (*Petroselinum crispum* L.) harvested from Chiba prefecture in Japan was employed as an experimental samples. They were washed and then dried at 343K for 240 min. Dried parsley was smashed to powder using the mill mixer (SUN mill mixer FM-50) and sieved in 150-250 μ m. The parsley powder was preserved in desiccator.

2.2 Chemicals

Apigenin was purchased from Sigma-Aldrich Ltd, product code A3145-5MG, Distilled water, 1-Butanol Acetonitrile were obtained from Wako Pure Chemical Ind. Co. Ltd. Phosphate buffer solution (pH2.5) was purchased from Nakalai Tesque Inc.

2.3 Extraction apigenin by water or organic solvent

Dried parsley powder (2.0g) was put a net bag made of cellulose and then introduced into bulk solvent (70mL) and then stirred magnetically. Temperature range was from 288 to 363K. Extraction time was 30 minutes throughout in this study. Suction filtration is done after centrifugation at 4500 min⁻¹ for 15 minutes. The transparent clear sample (1mL) was diluted to 10mL and then analyzed by HPLC.

2.4 Extraction by supercritical carbon dioxide

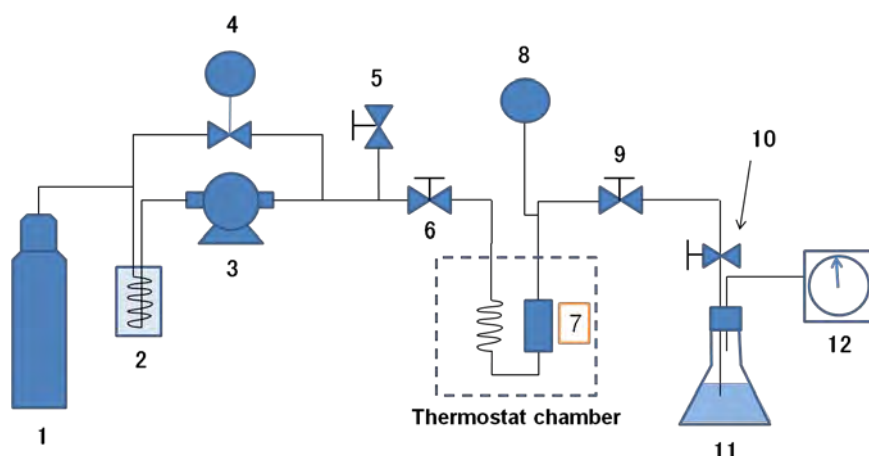


Fig.3 The diagram of SCCO₂ extractive process.

- | | | | |
|--------------------------|-------------------------|-----------------------|--------------------|
| (1) CO ₂ Tank | (4) Back pressure valve | (7) Extraction vessel | (10) Valve - 4 |
| (2) Chiller | (5) Valve - 1 | (8) Gauge | (11) Trap vessel |
| (3) CO ₂ pump | (6) Valve - 2 | (9) Valve - 3 | (12) Wet gas meter |

CO₂ gas was chilled by a chiller and pressurized by CO₂ pump. When pressure was attained at desired pressure, a valve – 2 was opened. SCCO₂ was introduced fully in extraction vessel. Extraction vessel was held for 30 minutes from valve – 2 were closed. SCCO₂ contained parsley components were introduced into a trap with opening of valve - 3, Valve - 4. Trap was analyzed by HPLC and quantity of blown CO₂ gas was measured by a wet gas meter.

2.5 HPLC analysis for apigenin

Chromatographic analysis was controlled by a ChromNAV (ver. 1.12A2), equipped with a manual sample injector (model 7725 RHEODYNE) and an intelligent UV/VIS Detector (JASCO UV-970). Wave length was set at 269 nm for Apigenin. The column was COSMOSIL cholesteryl packed column (4.6mm ID × 250mm). The mobile phase composed from solution A and B, whose volumetric ratio was 6:4. The solution A was composed with distilled water and phosphate buffer solution (pH2.5) (v:v 4:1). The solution B was acetonitrile. The flow rate was 1 mL min⁻¹.

2.6 Solubility parameter

Solubility parameter [8] is a major parameter to indicate hydrophobicity of solvent.

$$\delta = \sqrt{\left(\frac{\Delta H - RT}{V}\right)} \quad (1)$$

Where, ΔH is molar enthalpy of vaporization.

In this study, solubility parameter of SCCO₂ was calculated as followed [9].

$$\delta = 1.25 P_c^{1/2} \left(\frac{\rho_{rSCF}}{\rho_{rliq}} \right) \quad (2)$$

where δ is the solubility parameter of the gas in [cal/cm³]^{0.5}, P_c is critical pressure [atm], ρ_{rSCF} is reduced density, defined as ρ/ρ_c . ρ_c is the critical density, and ρ_{rliq} is the reduced density at normal boiling point. It was evaluated as 2.66. Where ρ is the density of carbon dioxide [g/cm³]. δ [cal/cm³]^{0.5} was recalculated to δ [J/cm³]^{0.5} In this study. (where 1 [cal/cm³]^{0.5} = 2.0455 [J]^{0.5})

The δ = [cal/cm³]^{0.5} was recalculated to δ [J/cm³]^{0.5} in this study. (Where, 1 [cal/cm³]^{0.5} = 2.0455 [J]^{0.5})

3. Results and Discussion

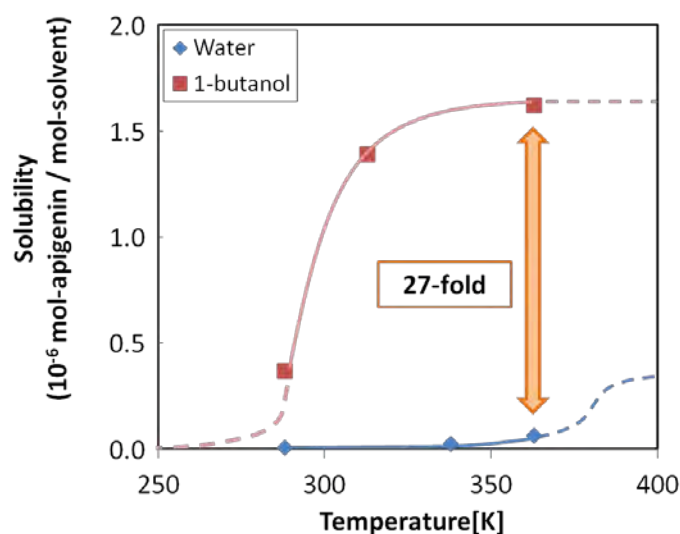


Fig.4 Solubility of apigenin in solvent on temperature

Solubility of apigenin by 1-butanol was remarkably increased and attained the maximum at 363K (90°C) as 1.62×10^{-6} [mol-apigenin / mol-butanol]. In contrast, solubility of apigenin by water was examined in ranging 288 ~ 363K. The maximum solubility was 6.10×10^{-8} [mol-apigenin / mol-water] at 363K. Solubility of apigenin by 1-butanol was superior 27-fold than that of water since its hydrophobic character.

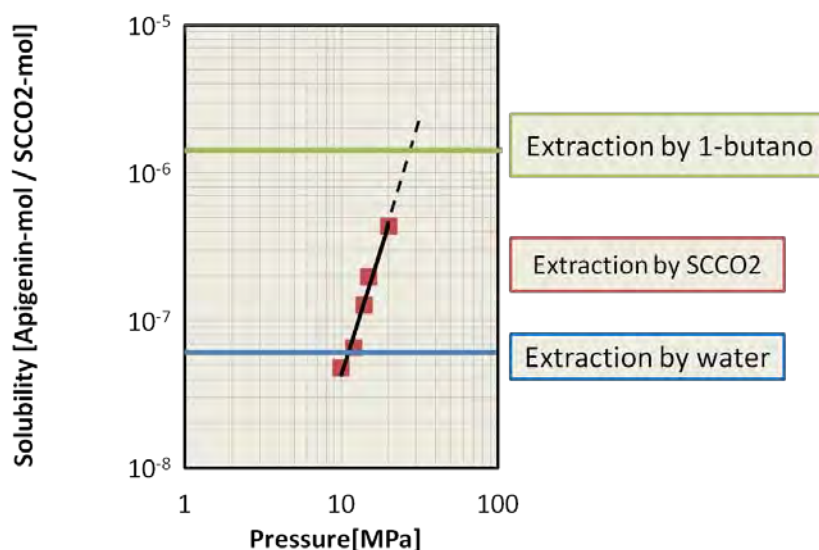


Fig.5 Solubility of apigenin in SCCO₂ on pressure 313K(40 °C)

Fig.5 Solubility of apigenin in SCCO₂ on pressure 313K(40°C)

The solubility in supercritical carbon dioxide (SCCO₂) was remarkably increased with pressure. It was 4.24×10^{-7} [mol-apigenin / mol-SCCO₂] while pressure 20MPa and temperature 313K. That was 7.0-fold than that of water. The solubility was strongly depended on pressure of SCCO₂.

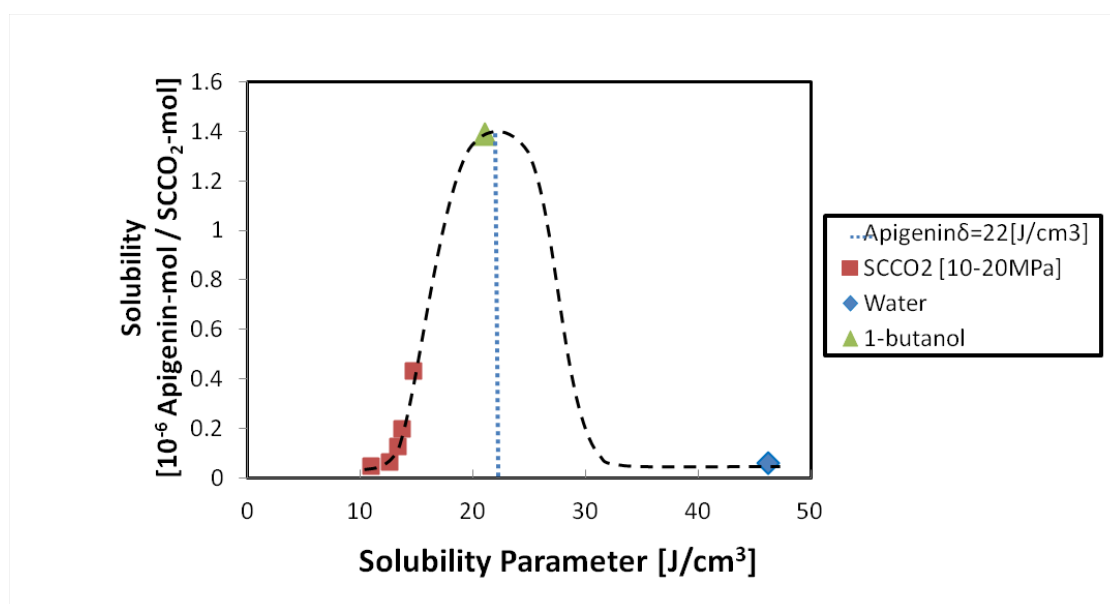


Fig.6 Solubility of Apigenin VS Solubility Parameter the data were obtained at 313K(40 °C)

Fig.6 depicts a correlation between solubility of apigenin and solubility parameter of SCCO₂ and solvents. Solubility parameter δ of apigenin, 1-butanol, and water was calculated by equation (1). ΔH was referred from [10]. The results were apigenin was 22.0[J/cm³], 1-butanol was 21.1[J/cm³] and water 46.2[J/cm³]. Solubility parameter of SCCO₂ was increased with increasing pressure because density was increased according to pressure. It approached to solubility parameter of apigenin. As presented by Fig.6 the solubility of apigenin was increased with increasing solubility parameter.

4. Conclusion

The solubility of apigenin in SCCO₂ was remarkably increased with increasing of pressure. The correlation between the solubility parameter of SCCO₂ and solvents (1-butanol and water) was demonstrated. The solubility was strongly depended on the solubility parameter. The bell-shaped curve was appeared and the maximum solubility was obtained at the solubility of 1-butanol. The solubility in supercritical carbon dioxide was well accorded with change of solubility parameter.

Reference

[1] Sanjeev Shukla and Sanjay Gupta,

Apigenin and Cancer Chemoprevention, Bioactive Foods in Promoting Health Fruits and Vegetables, Chapter 41, Pp 663–689 (2010)

[2] Megumi Funakoshi-Tago, Kei Nakamura, Kenji Tago, Tadahiko Mashino, Tadashi Kasahara, Anti-inflammatory activity of structurally related flavonoids, Apigenin, Luteolin and Fisetin International Immunopharmacology vol.11, Pp1150–1159 (2011)

- [3] Yasir Hasan Siddique *, Tanveer Beg, Mohammad Afzal, Antigenotoxic effect of apigenin against anti-cancerous drugs, *Toxicology in Vitro* vol.22, Pp625–631 (2008)
- [4] Devanand L Luthria, Sudarsan Mukhopadhyay and Albert L Kwansa, A systematic approach for extraction of phenolic compounds using parsley (*Petroselinum crispum*) flakes as a model, *Journal of the Science of Food and Agriculture* vol.86 Pp 1350–1358 (2006)
- [5] Devanand L. Luthria, Influence of experimental conditions on the extraction of phenolic compounds from parsley (*Petroselinum crispum*) flakes using a pressurized liquid extractor, *Food Chemistry* vol.107, Pp745–752 (2008)
- [6] Kashif Ghafoor, Fahad Y. AL-Juhaimi, Yong HeeChoi, Supercritical Fluid Extraction of Phenolic Compounds and Antioxidants from Grape(*Vitis labrusca* B.) Seeds, *Plant Foods Hum Nutr*, vol.67 Pp407-414 (2012)
- [7] Harro Lentz, Manfred Gehrig and Josef Schulmeyer, Dynamic solubility measurements of caffeine in carbon dioxide and in carbon dioxide saturates with water, *Physica* vol.139 & 140B, Pp70-72 (1986)
- [8] J.H. Hildebrand, R.L. Scott, *Solubility of Nonelectrolytes*, 3 ed. Reinhold, New York (1964)
- [9] J.C. Giddings, M.N. Myers, L. McLaren, R.A. Keller, High-pressure gas chromatography of nonvolatile species, *Science* vol.162, Pp67–73. (1968)
- [10] ChemSpider Search and share chemistry
- Apigenin
<http://www.chemspider.com/Chemical-Structure.4444100.html?rid=5de1add3-dd8c-4fb2-b626-bc259177b9a2> (14 March 2014)
- 1-butanol
<http://www.chemspider.com/Chemical-Structure.258.html?rid=60b0d71b-004f-44b3-97af-77ed9b42e710> (14 March 2014)
- Water
<http://www.chemspider.com/Chemical-Structure.937.html?rid=a254d47b-f53f-4c85-94ae-f5cde1659de3> (14 March 2014)

1D to 3D CFD extraction column design - state-of-the-art and future challenges

*M. W. Hlawitschka^{1,2}, H.-J. Bart^{*1,2}*

Summary

This paper gives a state of the art in modelling solvent extraction columns using 1-D and 3-D CFD approaches in comparison to pseudo-homogeneous dispersion or back-mixing models. Parameter evaluation is based on standardized lab-scale cells for the determination of droplet rise, breakage, coalescence and mass transfer followed by additional mini-plant experiments for validation. 1-D modelling can help for any new geometry in respect to droplet rise and axial dispersion and energy dissipation, whereas in non-axisymmetric stirrer geometry this is resolved by 3-D CFD modelling. The later can be further combined by droplet population balance modelling (DPBM) to increase the accuracy of the column simulations and to give information about the change of local droplet size distribution and thus mass transfer area. The computational costs can be reduced by OpenSource CFD Codes, when using flexible meshes. Combined simulations using a three way coupled CFD/DPBM/mass transfer solver allow a prediction of efficiency of columns of any geometry and size in an early design stage.

Keywords: CFD, DPBM, column simulation

Introduction

Solvent extraction columns are widely used in chemical, petrochemical, hydrometallurgical and nuclear processes. The main apparatus used for solvent extraction is still the mixer-settler (cascade) because of its reliability, flexibility and easy design. In addition, they can handle highly viscous liquids up to solid-liquid slurries and systems with low and high interfacial tension at any residence times. The main disadvantage is the footprint of the mixer-settler caused by the settling zone and high solvent inventory involved. In comparison to that, solvent extraction columns provide a high number of theoretical stages requiring only a small footprint at low capital costs and are attractive at a high throughput.

Despite its advantages, solvent extraction columns are still of minor application caused by the uncertainties during the layout of these columns. The uncertainties mainly arise from the complex interactions of the liquid phases as for example back- and forward mixing and the interaction of the dispersed phase itself which finally influences the droplet size distribution by coalescence and breakage. These phenomena finally have an impact on the operation limits (e.g. flooding) and the efficiency of the column. Hence, in the field of solvent extraction design, a scale up from mini-plant columns to industrial sized columns has become an important, but is still a critical step. As the diameter of the solvent extraction column increases, the

^{*1} Mark W. Hlawitschka, Chair of Separation Science and Technology, TU Kaiserslautern, Kaiserslautern, Germany, bart@mv.uni-kl.de

² Center for Computational and Mathematical Modelling (CM²), TU Kaiserslautern, Kaiserslautern, Germany

tendency for back mixing phenomena also increases, which results in lower column efficiency. Hence, the key point for scale-up is to obtain a deep understanding how the efficiency changes with increasing column diameter and to account this for the final industrial column design.

For an improved design of solvent extraction columns, standardized lab-scale cells were developed that allow a monitoring of the droplet (swarm) behavior. Mini-plant column experiments can resolve long term effects (enrichment of impurities, scaling, etc.) with a minimum of matter involved. The gap between mini-plant experiments and pilot-plant scale can be partially closed by coupled CFD/DPBM/mass transfer simulations to gain a traditional basis for conventional scale up.

1D DROPLET POPULATION BALANCE MODELLING

An enhancement of the axial dispersion or back-mixing models was achieved by taking into account the changes in droplet size along the column height by DPBM. A first formulation of the droplet population balance equation for a differential height, ∂z , was formulated by Casamatta [1] based on the droplet volume distribution:

$$\frac{\partial P(v)}{\partial t} + \frac{\partial [u_d P(v)]}{\partial z} = \frac{\partial}{\partial z} \left(D_d \frac{\partial P(v)}{\partial z} \right) + R(v) + \delta(z - z_d) u_{d,sup} f(v) \quad (\text{Eqn. 1})$$

The left hand side of the equation gives the transport of the population balance along the column height. On the right hand side, D_d is the dispersed phase axial dispersion coefficient, $f(v)$ is the volumetric inlet distribution and $R(v)$ describes the net droplet volume production due to breakage and coalescence per unit time. In addition, two similar equations, describing the solute balances of the dispersed and continuous phases can be obtained:

$$\begin{aligned} \frac{\partial P(c)}{\partial t} = \frac{\partial [u_d P(c)]}{\partial z} + \frac{\partial}{\partial z} \left(D_d \frac{\partial P(v)}{\partial z} \right) + R\{\bar{c}_y P(v)\} + \frac{S(v)}{v} k_c P(c_x - m\bar{c}_y) \\ + \delta(z - z_d) u_{d,sup} f(v) \delta(c_y - c_{in}) \end{aligned} \quad (\text{Eqn. 2})$$

$$\frac{\partial (1 - \Phi) c_x}{\partial t} = \frac{\partial [u_c (1 - \Phi)]}{\partial z} + \frac{\partial}{\partial z} \left[D_c \frac{\partial [(1 - \Phi) c_x]}{\partial z} \right] - \int_{v_{min}}^{v_{max}} \frac{S(v)}{v} k_c P(c_x - m\bar{c}_y) dv \quad (\text{Eqn. 3})$$

The mass transfer is described by the two film theory, where the average solute concentration of all droplets having volume in the range $(v, v + dv)$ at level z is given by $\bar{c}_y$. The overall mass transfer coefficient is defined by k_c , the solute concentration in the continuous phase is given by c_x and the distribution coefficient is m . In addition, the surface area of droplets of volume v are given by S . The source term accounting for coalescence and breakage accounts in this context the mass transfer. In the above given continuous phase solute balance, the axial dispersion is given by D_c . In addition the hold-up of dispersed phase is defined by:

$$\Phi = \int_{v_{min}}^{v_{max}} P(v) dv, \quad (\text{Eqn. 4})$$

Where v_{min} and v_{max} are the minimum and maximum droplet volumes. The above equations are written quite general allowing fast modifications of the investigated

geometry by exchanging the required correlations for breakage and coalescence, hereby also energy dissipation, droplet velocity, mass transfer correlations and axial dispersion, where the first ones can be determined in a good agreement using mini-plant experiments.

Using the DPBM, several graphical tools facilitate nowadays the setup of the simulation. Among them are ReDrop, developed at the RWTH Aachen [2,3,4,5], LLECMOD [6,7,8,7,8,9,10] and PPBLAB [11], developed at the TU Kaiserslautern. All the three tools include correlations for pulsed, packed and agitated columns.

3-D CFD MODELLING OF SOLVENT EXTRACTION COLUMNS

3-D CFD simulations have been used intensively in the field of chemical engineering and the number of publications is still increasing. The simulations allow a description of the hydrodynamics without any geometrical constraints, where the geometrical possibilities are mainly limited by computational resources and restricted the simulations at the beginning to pure hydrodynamics investigations. Hence, the investigations of stirred solvent extraction columns started in 1993 with a publication of Weiss & Bart [12] describing the simulation of a single segment of an RDC column with the CFD code Fire. Rieger et al. [13] simulated a DN150 RDC column at low hold-up and employed the Euler-Euler model to predict the two-phase flow structure. Yudong et al. [14] measured and simulated the profile in a two dimensional represented RDC column using the CFD code PHOENICS. A validation of the velocity field was performed with LDA-measurements at several points. Fei et al. [15] investigated the single phase flow in stirred solvent extraction columns. The residence time distribution was numerically and experimentally investigated by Modes & Bart [16] and recently by Gurker & Marr [17]. The two phase flow field was simulated You & Xiao [18]. Ghaniyari-Benis et al. [19] simulated an RDC column using the Euler-Euler approach. A first study using CFD simulations for the optimization of solvent extraction columns was done by Kolb [20] for a mini-plant Kühni column. An early extension of the two-phase flow accounting the droplet size distribution was reached by Vikhansky et al. [21]. Drumm [22] further extended the CFD DPBM research. Therefore, he implemented and applied several population balance models (QMOM, DQMOM, SQMOM) using the commercial CFD code FLUENT for the simulation of the droplet interactions in an RDC column. The concept of Kolb [20] and Drumm [22] was applied by Aksamija & Siebenhofer [23] for the optimization of an RDC column, where it could be shown that a stator less design could outperform the state-of-the-art design by 36% regarding the HTU value. A first combination using a commercial CFD/DPBM/mass transfer code for the investigation of solvent extraction columns was done by Hlawitschka & Bart [24] and Jildeh et al. [25]. A further improvement regarding the simulation setup, computational time and flexibility could be reached by the extension of an OpenSource CFD Code [26]. The mesh generation was replaced for Kühni and RDC columns by an automated mesh

generation allowing a flexible design of the internals which is shown in Fig. 1 for different baffle heights. It can be observed that the velocity inside a single compartment increases with increased baffle heights. Where only slight deviations of the axial dispersion coefficient of the continuous phase can be observed between 3.0 mm and 4.5 mm baffle height, the axial dispersion coefficient increases by 20 %, when the height is increased to 8.0 mm. Also the effect of different compartment heights can be studied using CFD simulations. In general, an increase of the axial dispersion coefficient can be observed at higher compartment heights and higher rotational speeds (Fig. 3), which also results from changes in the local flow structure resulting in larger dead zones underneath the stator plates. The axial dispersion coefficient, which is also required for the 1-D approach, can be obtained by an additional Euler-Lagrange simulation.

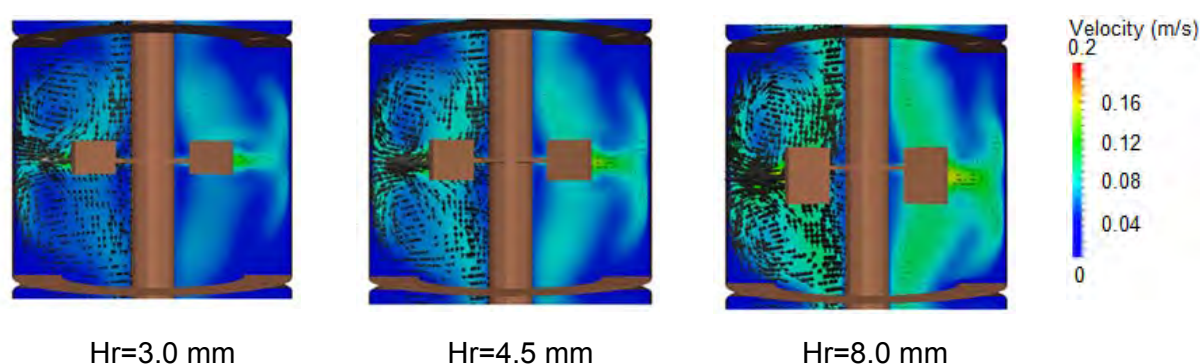


Fig. 1: Velocity field in a Kühni mini-plant column at different agitator design (baffle heights) at $6 \text{ m}^3/(\text{m}^2\text{h})$ and 200 rpm.

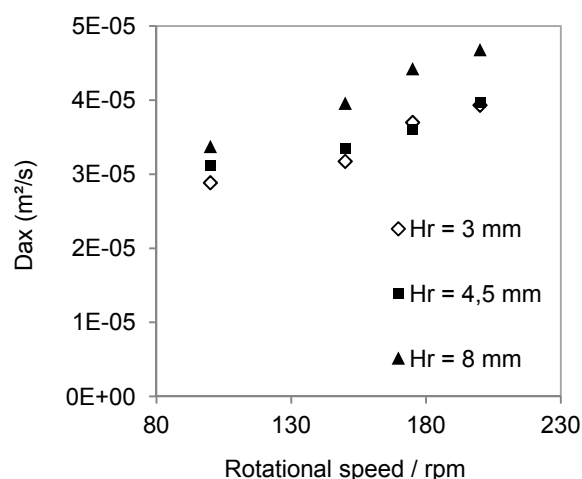


Fig. 2: Influence of the agitator baffle height at the axial dispersion coefficient ($6 \text{ m}^3/\text{m}^2\text{h}$).

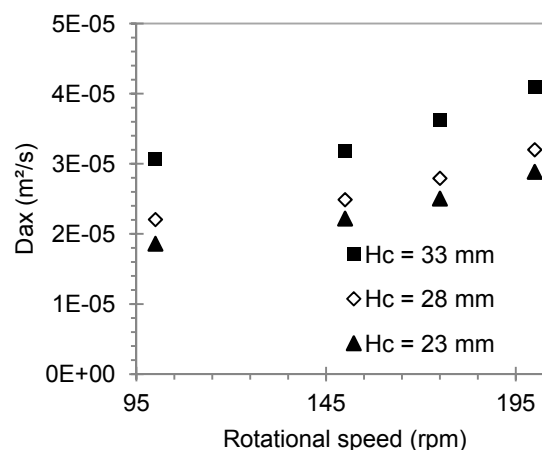


Fig. 3: Influence of the compartment height at the axial dispersion coefficient ($5 \text{ m}^3/\text{m}^2\text{h}$).

COMBINATION OF BOTH APPROACHES

Both approaches, the 1-D and 3-D, have advantages and disadvantages concerning the experimental effort, the accuracy and simulation times. The computational time for a mass transfer simulation heavily relies on the throughput. A 1-D simulation of

the final steady state of solvent extraction columns requires a simulation time of 5-7 times of the residence time of the liquids inside the column, whereas 3-D-CFD simulations are still limited on the simulation of time scales in the range of seconds and minutes due to the high computational load. As an example, the required time to reach steady state for a transient full mini-plant column (32 mm inner diameter, 1500 mm active height) simulation taking into account the mass transfer is approximated by one month on a modern cluster. The benefit is the full resolution of the local hydrodynamics, droplet size and mass transfer. The 1-D simulation instead, is able to simulate the transient behavior of the solute concentration within a few minutes including the simulation setup, but based on experimental derived correlations for droplet rise, axial dispersion and slowing factor. Therefore, a combination of 3-D CFD and 1-D CFD seems to be straight forward to reduce experimental effort for the 1D simulation and CPU time for mass transfer simulation. As a prove of concept, Fig. 4 shows the droplet size distribution obtained at the column top compared to experimental data and in Fig. 5, a high accuracy between the simulated concentration profile and the experimental data could be obtained.

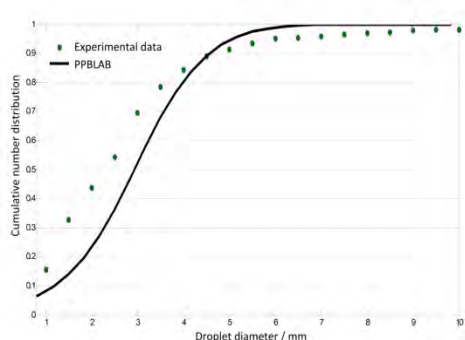


Fig. 4: Simulated droplet size using PPBLAB as compared to the measured outlet droplet size distribution at 150 rpm and a throughput of $18.7 \text{ m}^3\text{m}^{-2}\text{h}^{-1}$.³

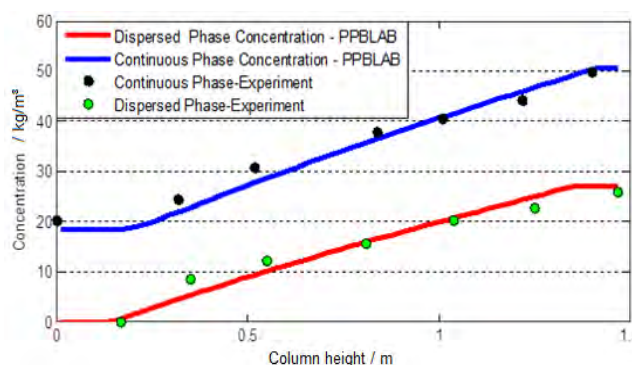


Fig.5: Comparison between the measured concentration profile and the PPBLAB simulation for 150 rpm and a throughput of $18.7 \text{ m}^3\text{m}^{-2}\text{h}^{-1}$.³

CONCLUSIONS

The experimental based design of solvent extraction columns can be supported by numerical modelling using 1-D and 3-D CFD approaches. The 1-D simulation of solvent extraction columns was facilitated by modern tools using graphical user interfaces. The tools allow a description of the hydrodynamics (e. g. holdup), solute concentration and droplet size at different boundary conditions within minutes based on literature based correlations. The further development of the 3-D simulation reduces the required number of experimental correlations, due to a direct description of the local hydrodynamics (flow field, energy dissipation) in any new geometry (changes in baffle height, etc.). A coupling of the 3-D CFD simulation with DPBM and mass transfer correlations allow the optimization of different column design and a

³ Simulation results obtained in cooperation with the University of Jordan, Department of Chemical Engineering, Amman-Jordan (Attarakih et al.)

prediction of column efficiency in an early design phase. A combination of both tools reduces the occurring disadvantages, regarding long computational time and lack of accuracy and may be regarded as a promising approach for future column design.

FUTURE CHALLENGES

Despite the promising results using DPBM for extraction column design and the prediction of mass transfer, the numerical codes still do not cover all the effects observed in solvent extraction columns. Among them are wetting properties, enrichment of impurities, crud formation and entrainment. The presented tools were mainly tested for standard test systems and common available column designs, which may not reflect the broad range of available column designs and system properties, such as viscosity, interfacial tension and mass transfer rates, occurring in industrial fields. Dynamic modelling of the columns using an integrated process has to be further investigated to identify cross effects. A main task should therefore be the extension of the models to account for reactive extraction, which is essential for efficient metals recovery in the future.

REFERENCES

1. G. Casamatta, PhD thesis, Institut National Polytechnique de Toulouse, Toulouse, 1981.
2. M. Kalem, F. Buchbender, A. Pfennig, *Chem. Eng. Res. Des.* 89, 1-9, 2011.
3. D. Adinata, J. M. Ayesterán, F. Buchbender, M. Kalem, N. Kopriwa, A. Pfennig, *Chem. Ing. Tech.* 83 (7), 1-14, 2011.
4. F. Buchbender, M. Schmidt, T. Steinmetz, A. Pfennig, *Chem. Ing. Tech.* 84 (4), 540-546, 2012.
5. F. Buchbender, Dissertation, RTWH Aachen, Aachen, Germany, 2013.
6. M. Attarakih, H.-J. Bart, N. Faqir, *Chem. Eng. Sci.* 61, 113-123, 2006.
7. M. M. Attarakih, H.-J. Bart, N. M. Faqir, *Chem. Eng. Process.* 45, 113-123, 2006.
8. M. M. Attarakih, H.-J. Bart, T. Steinmetz, M. Dietzen, N. M. Faqir, *Open Chem. Eng. J.* 2, 10-34, 2008.
9. M. Jaradat, M. Attarakih, H.-J. Bart, *Chem. Eng. J.* 165 (2), 379-387, 2010.
10. M. Jaradat, M. Attarakih, H.-J. Bart, *Chem. Eng. Res. Des.* 89, 2752-2760, 2011.
11. M. Attarakih, S. Al-Zyod, M. Abu-Khader and H.-J. Bart, *Procedia Eng.* 42, 1574-1591, 2012.
12. C. Weiss and H.-J. Bart, In D. H. Logsdail and M. J. Slater, *Solvent Extraction in the Process Industry*, London: Elsevier Applied Science, 1191-1197, 1993.
13. R. Rieger, C. Weiss, G. Wigley, H.-J. Bart, R. Marr, *Comput. Chem. Eng.* 20 (12), pp. 1467-75, 1996.
14. W. Yudong, F. Weiyang, D. Youyuan, W. Jiading, *Tsinghua Science and Technology* 1 (4), 323-326, 1996.
15. W. Y. Fei, Y. D. Wang, and Y. K. Wan, Y.K., *Chem. Eng. J.* 78 (2-3), 131-39, 2000.
16. G. Modes, H.-J. Bart, *Chem. Eng. Technol.* 24 (12), 1242-1245, 2001.
17. T. Gurker, T. and R. Marr, 2009. *Chem. Ing. Tech.* 81(8), 1090, 2009.
18. X. Y. You, X. Xiao, X., *Chem. Biochem. Eng. Q.* 19(1), 1-11, 2005.
19. S. Ghaniyari-Benis, N. Hedayat, A. Ziyari, M. Kazemzadeh, M. Shafiee, *Chem. Eng. Technol.* 32 (1), 93-102, 2009.
20. P. Kolb, Dissertation, TU Kaiserslautern, Kaiserslautern, Germany, 2005.
21. A. Vikhansky, M. Kraft, M. Simon, S. Schmidt, H.-J. Bart, *Technical Report 28 c4e-Preprint Series*, Cambridge, 2005.
22. C. Drumm, Dissertation, TU Kaiserslautern, Kaiserslautern, Germany, 2010.

23. E. Aksamija, M. Siebenhofer, *Chem. Ing. Techn.* 85 (9), 1388, 2013.
24. M. W. Hlawitschka, H.-J. Bart, *Comp. Aided Chem. Eng.*, 31, 920-924, 2012.
25. H. B. Jildeh, M. W. Hlawitschka, M. Attarakih, H.-J. Bart, *Procedia Engineering* 42, 1692-1710, 2012.
26. M. W. Hlawitschka, Dissertation, TU Kaiserslautern, Kaiserslautern, Germany, 2013.

Changing physical properties – A challenge for extraction equipment and processes

Dr.-Ing. Jörg Koch, Dr.-Ing. Juan Ramon Herguijuela

Sulzer Chemtech AG, Gewerbestr. 28, 4123 Allschwil, Switzerland

Countercurrent liquid-liquid-extraction columns are efficiently used to provide a high separation performance with a small foot print of the equipment. If the separation task needs a high mass transfer, the internal flow rates and the physical properties of both liquid phases can significantly change in the extraction process which often result in challenging hydrodynamic conditions. To compensate for these changes, the column internal geometry must be adapted over the column height. For an agitated column like the Kuhni column, this adaptation is done by modifying the free cross section of the partition plates and the diameter and type of agitators.

In some applications the change of physical properties is so strong (or heavy) that it can not be compensated for by changing the geometry of column internals only. If, for example, the density difference becomes very low the droplet velocity will be reduced and a long residence time for the phase separation is required; in extreme cases an extraction can no longer be operated at stable hydrodynamic conditions. An increased viscosity makes these conditions even worse. A mixer-settler offers the advantage of a longer residence time but only provides one equilibrium stage.

This paper presents case stories of different applications where the changing physical properties and a very high viscosity led to challenging operating conditions and how these were compensated by adapting the column internals. In one case the process had to be adapted by combining mixer-settlers with an extraction column to benefit from the longer residence time of mixer settlers and the high separation performance of columns. The process setup will be explained. The pilot plant will be described and first results of trial data will be shown. A process patent has been filed for this solution.

2-(Dibutylamino)ethanol as a switchable solvent for lipid extraction from *Desmodesmus* sp.

Ying Du,^{a,b,*} Khoa Van Tran,^b Boelo Schuur,^b Derk Willem Frederik Brilman^b

^a China University of Mining & Technology, School of Chemical Engineering and Technology, Xuzhou 221000, China

^b University of Twente, Sustainable Process Technology Group (SPT), Green Energy Initiative, Faculty of Science and Technology, PO Box 217, 7500 AE, Enschede, The Netherlands, +31-644421465, y.du@utwente.nl

Summary

Algae can be considered as an important sustainable feedstock for lipid extraction to produce food, cosmetics, pharmaceutical products and advanced biofuels. Next to the costs for cultivation, this route is especially hindered by the energy intensity of drying algae prior to extraction and solvent recovery afterwards. Therefore, the aim of this study is to extract lipids directly from wet algae slurries without the need for drying, and to recover the extracted oil and solvent subsequently by simple phase separation, using CO₂ as a trigger. In this work, 2-(dibutylamino)ethanol (DBAE) was selected for the extraction of lipids from wet algae slurries of the strain *Desmodesmus* sp. The ability of DBAE to extract lipids from *Desmodesmus* sp. and to change reversibly its miscibility with water under the introduction of CO₂ was measured.

1 Introduction

Fossil fuels have become an integral part of human daily life. It goes deeply in everyday life by means of transportation, electricity, etc. and accelerates technology development. However, this energy source has a limited supply and is anticipated to diminish in the next several decades. According to the British Petroleum statistics the reserves/production (R/P) ratio of the world's fossil oil is around 54 years [1].

Because of that, the last few decades have shown an explosion of research in the field of sustainable energy all over the world. In the research of Lam and Lee [2], it was predicted that in a near future, as an alternative renewable energy, biofuel will play a more crucial role in energy structure of the world. Algae can be considered as an important sustainable feedstock to produce food ingredients, cosmetics, pharmaceutical products and advanced biofuels. Next to the costs for cultivation, this route is especially hindered by the energy intensity of drying algae prior to lipid extraction and solvent recovery afterwards. Therefore, alternative methods that require less energy to extract lipids from algae are desired. The use of switchable solvents for oil extraction has recently been taken notice of and promising results have been published by some researchers [3-6]. In this paper, 2-

(dibutylamino)ethanol (DBAE) as a kind of switchable solvent has been investigated as solvent for lipid extraction from microalgae.

2 Materials

Algae of the strain *Desmodesmus* sp. used for this research were obtained from Ingrepro B.V. (The Netherlands), where they were grown in an open raceway system. The algae cells were broken by rotating a rubber cylinder containing 500 mL algae culture and triangular prism wear-resistant ceramic beads overnight. The water content in *Desmodesmus* sp. slurries was determined by weighing a sample before and after drying at 105 °C for 24 h.

The solvents and chemicals used in this study were as follows: 2-(dibutylamino)ethanol (99%, Sigma-Aldrich), Hexane ($\geq 95\%$, Sigma-Aldrich), Chloroform ($\geq 99.9\%$, Sigma-Aldrich), Methanol ($\geq 99.9\%$, Fluka).

3 Results and discussion

3.1 Oil extraction from algae

Lipid extraction employing Bligh and Dyer method was done duple according to the original Bligh and Dyer method [7], i.e. applying methanol : chloroform : water in the ratio 2:2:1.8. The extraction yield of B & D method ($7.17\% \pm 0.27\%$ yield) was taken as a reference of the total lipid amount in *Desmodesmus* sp. Before the DBAE extraction experiments, a preliminary test to find an appropriate CO₂ flow-rate and switching time was carried out. From this result, it was determined to use an atmospheric CO₂ flow at a rate of 0.4 LPM for all experiments.

3.1.1 Effect of mixing time at room temperature and high temperature

The effect of extraction time on the amount of extract was studied in detail in case of extraction using DBAE at room temperature and high temperature; the mentioned percentages are relative to the weight of the dry algae mass entered in the experiment. Experiments were carried out with a solvent to feed ratio of 0.5. In case of extraction at room temperature, Figure 1 shows a general tendency of increasing of lipid extraction yield. However, the difference between 12-minute extraction ($0.74\% \pm 0.20\%$ yield) and 5-hour extraction ($0.91\% \pm 0.18\%$ yield) is not that much. More importantly, this result was much smaller than the one from Bligh and Dyer method ($7.17\% \pm 0.27\%$ yield), making the application of DBAE at room temperature less interesting.

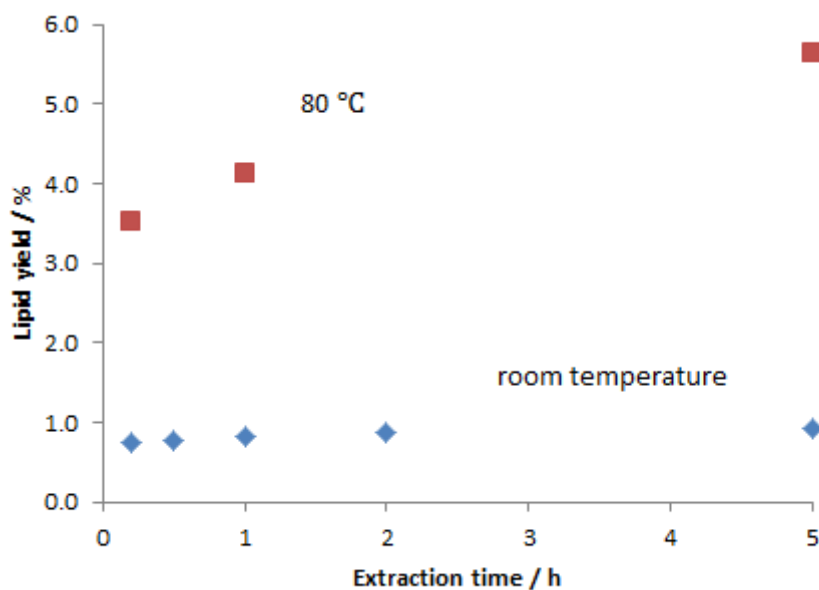


Figure 1. Effect of mixing time on lipid extraction from *Desmodemus* sp. using DBAE at room temperature and at 80°C

The extraction using DBAE at 80°C, with a solvent-to-feed ratio of 0.5, showed significant change compared to that at room temperature. In terms of mass extracted, the result was from 5 to 6 times higher than extraction at room temperature. The effect of mixing time was also remarkable in this case (see Figure 1). An increase in extraction time from 12 minutes to 5 hours observed a 60% improvement in the outcome, compared to almost no change when extracted at room temperature. These results suggested that mass transfer between the bulk medium and algae cell was the main limiting step in the extraction using DBAE.

3.1.2 Effect of solvent to feed ratio

Two solvent to feed ratios were investigated in this study. All experiments in this stage were performed under one hour of mixing time, at either room temperature or 80°. The results were shown in Table 1.

Table 1: Effect of solvent-to-feed ratio on extraction performance for one hour of extraction

	Extraction at room temperature		Extraction at 80°C	
	Solvent : feed = 0.3 (v/v)	Solvent : feed = 0.5 (v/v)	Solvent : feed = 0.3 (v/v)	Solvent : feed = 0.5 (v/v)
Lipid yield/%	1.09 ± 0.11	0.76 ± 0.3	1.87 ± 0.04	4.11 ± 0.14

From the results above, it can be said that changing solvent-to-feed ratio does have impact with the lipid extraction yield. In case of DBAE extraction at 80°C, when 66% more solvent was used for extraction, the lipid yield became more than twice higher. On the other hand, extraction using DBAE at room temperature showed a slightly

negative outcome when more solvent was used. This result in combination with the results in 3.1.1 brings us to the conclusion that at room temperature the limitation of high viscosity of DBAE has overwhelmed all other factors in terms of extraction yield.

3.2 Process prescription

The results in section 3.1 showed the possibility of using DBAE for lipid extraction from microalgae. In order to separate lipid from DBAE and recover the solvent, more experiments have been done to study the switchability of DBAE.

3.2.1 Switch from hydrophobic state to hydrophilic state

The experiment started with measuring the ability of DBAE to change its miscibility with water under the introduction of carbon dioxide. DBAE was considered switched when the amount of its organic phase stop decreasing. For comparison, two mixtures were made. One is DBAE and water in a ratio of 4:7, the other one is DBAE, water and sunflower oil in the ratio of 4:7:1. Time to fully switch was 60 min and 70 min respectively. The result showed that it took more time for the solvent to change their solubility but the impact was not drastic. It can be observed from Figure 2 that after introduction of CO₂ to the sample consisting of DBAE, water and sunflower oil, the height of the top layer decreased significantly. After measuring by FT-IR, it was confirmed that the separate top layer after CO₂ bubbling was essentially sunflower oil (see Figure 3).



Figure 2. Changes in miscibility before and after bubbling CO₂

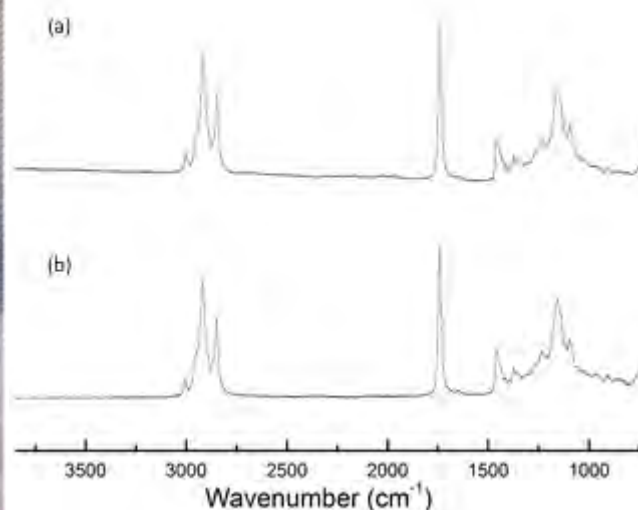


Figure 3. IR spectra of (a) sunflower oil and (b) top layer after bubbling CO₂

3.2.2 Switch from hydrophilic state to hydrophobic state

As a key property of switchable solvent in an extraction process, the possibility to recover the solvent after the extraction by switching it to a hydrophilic state, and then return it to the primary process after switching it back to hydrophobic state was studied. Back-switching was done by heating up to 80°C, both with and without the presence of a stripping gas such as N₂. The back-switching progress was considered

finished when further testing time only caused loss in total volume due to evaporative losses but no more increase in top (organic) phase volume.

For switching backward in the presence of sunflower oil, the mixture of water, solvent and oil was first contacted with carbon dioxide to separate oil from solvent. Solvent recovery was carried out after the removal of oil phase by respiration. Experimental results are illustrated in Table 2.

Table 2. Results of switching backward

Method	Solvent : water (mL : mL)	Heating time (min)	Top phase volume after switching (mL)	Recovery efficiency
80°C	4 : 7	10	3.0	75.0%
80°C + N ₂	4 : 7	10	3.5	87.5%

Experimental results showed that about 75% of DBAE can be recovered after 10 minutes at 80°C. During these 10 minutes, an intensive formation of bubbles was observed, indicating the reversal of the carbonate formation and promising a good switching back property in terms of recovery rate and recovery level. In another case, a combination of heating to 80°C and stripping with nitrogen was investigated. From the results in Table 2, it is obvious that nitrogen bubbling improved the progress of switching backward. This enhancement has been attributed to the ability of nitrogen to drag carbon dioxide together with it when moving out of the liquid phase and hence lowering the CO₂ equilibrium concentration in the solution. The FT-IR spectra of DBAE before switching and after switching back were compared in Figure 4. No extra peaks were observed in the recovered DBAE, suggesting a complete switching back with regard to purity of recovered solvent.

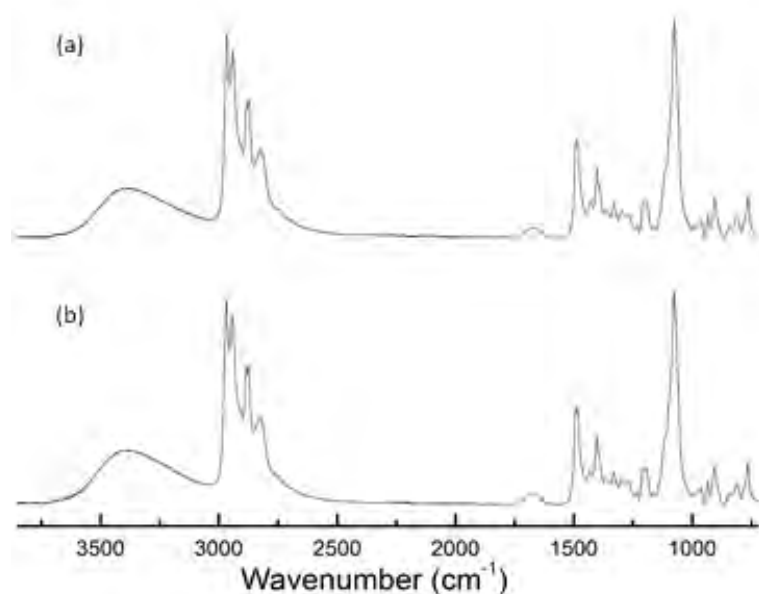


Figure 4. IR spectra of (a) DBAE after switching back and (b) DBAE before bubbling CO₂

4 Conclusions

In this work the DBAE has been proven to have good performance in both lipid extraction and switching property. Although the extraction using DBAE at room temperature was limited by its high viscosity, the extraction yield at 80°C was close to that of the Bligh and Dyer method. In further research, the extraction yield might be increased by optimizing extraction conditions. The best solvent recovery case was achieved by N₂ stripping at 80°C. However there was still 12.5% DBAE lost. This is subject of ongoing studies to reduce or recover these losses.

Reference

1. BP. *BP Statistical Review of World Energy June 2012*. 2012; Available from: http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2012.pdf.
2. Lam, M.K. and K.T. Lee, *Microalgae biofuels: A critical review of issues, problems and the way forward*. Biotechnology Advances, 2012. **30**(3): p. 673-690.
3. Samorì, C., et al., *Extraction of hydrocarbons from microalga Botryococcus braunii with switchable solvents*. Bioresource Technology, 2010. **101**(9): p. 3274-3279.
4. Du, Y., et al., *Secondary amines as switchable solvents for lipid extraction from non-broken microalgae*. Bioresource Technology, 2013. **149**(0): p. 253-260.
5. Samorì, C., et al., *Effective lipid extraction from algae cultures using switchable solvents*. Green Chemistry, 2013. **15**(2): p. 353-356.
6. Boyd, A.R., et al., *Switchable hydrophilicity solvents for lipid extraction from microalgae for biofuel production*. Bioresource Technology, 2012. **118**: p. 628-632.
7. Bligh, E.G. and W.J. Dyer, *A rapid method of total lipid extraction and purification*. Canadian journal of biochemistry and physiology, 1959. **37**(8): p. 911-917.

Microwave-assisted and Cloud Point Extraction and Separation of Active Ingredients from Natural Products

Fuli Deng, Xiangfeng Liang, Chao Hua, Huizhou Liu**

Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China

Cloud point extraction (CPE) based on micellar solubilization and unique phase separation behavior can be used for extraction and preconcentration solute with high extraction recovery through a simple operation. CPE is an environmentally friendly technology, which has been extensively applied for extraction of compounds in various matrices. Microwave-assisted extraction (MAE) is a technique that combines microwave heating and traditional solvent extraction. MAE has many advantages, such as higher extraction yield, shorter extraction time and less solvent, over conventional method of extraction of active ingredients from natural products. In this paper, MAE and CPE were applied for extraction and preconcentration of active ingredients from natural products.

Microwave-assisted micellar extraction and cloud point extraction was employed for extraction and determination mogroside V in *Siraitia grosvenorii*. Under optimal conditions, i.e. 5% GX-080 (w/v) and microwave-assisted extraction for 5 min at 96 °C, the microwave-assisted extraction yield of mogroside V reached 96.8% in a one-step extraction, which was higher than the efficiency of ultrasonic-assisted extraction. The cloud-point extraction yield was 80.7% while the preconcentration factor was about 10.8.

The combination of microwave-assisted micellar extraction and cloud-point extraction could be employed as a rapid and effective approach for extraction and separation of capsaicin and dihydrocapsaicin from peppers. Compared with soxhlet extraction, MAE yielded higher extraction efficiency, less solvent and shorter extraction time. Under optimal CPE conditions with non-ionic surfactant TX-100, i.e. addition of 0.1g/mL sodium chloride, equilibration time for 10 min at 70 °C, extraction efficiency of capsaicin and dihydrocapsaicin was 97.8% and 96.8%, respectively. The preconcentration factors were up to 12.

The combination of microwave-assisted extraction and cloud-point extraction was shown to be a green, rapid and effective method for extraction and preconcentration active ingredients from natural products.

Valorization of Hemp Wood to obtain high value bioproducts

S. Bassil¹, L. Candy¹, A. Thuret¹, A. Masseron², V. Simon¹, C. Raynaud¹

1. Laboratoire de Chimie Agro-Industrielle, UMR 1010 INRA/INP-ENSIACET, Toulouse, France.
2. Institut de Science des Matériaux de Mulhouse (IS2M), Equipe Matériaux à Porosité Contrôlée (MPC), ENSCMu, Mulhouse, France.

Biomass represents an important source for the production of multiple products including high-value chemicals. In this context, different lignocellulosic residues have been explored for extraction of aromatic monomers used for food, cosmetics and pharmaceutical applications.

Hemp (*Cannabis sativa* L.) is an annual herbaceous plant. Hemp fiber is used for paper and clothing. Hempseeds, an exceptionally rich source of the two fatty acids (w-6 and w-3) and of vitamins, are used in food, cosmetic and therapeutic industries [1, 2]. Hemp wood is a hemp coproduct that is rich in lignin and produced during hemp fiber extraction with a yield of 55%. The aim of this work is hemp wood valorization for extraction of aromatic monomers in particular ferulic acid and coumaric acid.

Characterization of hemp wood using Van Soest method provided a value of 91.2% in lignocellulosic materials (49.3% cellulose, 16.5% hemicelluloses and 25.4% lignin). Because ferulic acid and coumaric acid are covalently linked to lignin by ester or ether bonds, a sequential treatment involving mild alkaline hydrolysis followed by acid hydrolysis was carried out to determine the amount of these linkages in woody hemp. Predominant amount of coumaric acid (88.5%) is ester-linked to lignin whereas ferulic acid (66.7%) is predominantly ether-linked to lignin.

Microwave-assisted extraction and twin-screw extrusion extraction methods were compared to a number of lab-scale extraction methods including soaking treatment, soxhlet, and alkaline hydrolysis. Among classical cited methods and compared to flax shives which have similar amount of lignocellulosic materials, alkaline hydrolysis showed the highest yields of aromatic compounds (0.35mg/g of ferulic acid, 9 mg/g of coumaric acid) to (0.25mg/g of ferulic acid, 0.61mg/g of coumaric acid) for flax shives [3, 4].

The effects of experimental conditions, such as solvent (water and ethanol), extraction time, and liquid/solid ratio, on microwave-assisted extraction efficiency have been studied. Results were compared with those obtained by twin-screw extrusion. Twin-screw extrusion is a continuous system that allows to evaluate the thermo-mechanical effect on the extraction processes [5, 6]. The influence of pretreatment, screw profile, temperature, solvents on the extraction of phenolic compounds was investigated. A purification/concentration innovative process was developed for the post treatment of microwave-assisted extraction and twin-screw extrusion extracts. Batch adsorption experiments were conducted. Microporous solids were used. Zeolites were favorable adsorbents to isolate polyphenols.

MAE and twin-screw extrusion give promising results to obtain aromatic monomers of interest from hemp wood.

[1] Callaway, 2004, *Euphytica* 140, 65-72; [2] Anwar *et al.*, 2006, *J. Am. Oil. Chem. Soc.* 83, 323-329; [3] Anvar *et al.*, 2009, *Food chemistry* 115, 1542-1548; [4] Kim and Mazza, 2006, *J. Agric. Food Chem.* 54, 7575-7584; [5] Evon *et al.*, 2010, *Advanced Materials Research* 112, 63-72; [6] Ndiaye *et al.*, 1997, *Developments in thermochemical biomass conversion* 1, 756-764.

Salt influence on the partitioning of HMF in aqueous/organic systems

Sultan Mohammad, Christoph Held, Emrah Altuntepe, Gabriele Sadowski

*Technische Universität Dortmund; Laboratory of Thermodynamics, Dortmund,
Germany*

Abstract

Electrolytes influence many biological processes e.g., the production of organic molecules. In biological processes electrolytes might be present as part of a reaction, or electrolytes are added intentionally due to their impact on phase equilibria. Already small amounts of electrolytes can influence the separation performance of a unit operation. An example for a biological process in which electrolytes are used intentionally is the conversion of hexoses to the key chemical component 5-hydroxymethylfurfural (HMF). Extraction is the preferred unit operation for the separation of HMF from the reaction media. The separation strongly depends on the addition of salts, and the determination of the extraction performance requires the knowledge on the liquid-liquid phase equilibrium (LLE). LLEs are accessible via equilibrium measurements and via thermodynamic models.

The LLE of ternary systems containing HMF, water and an organic solvent (e.g. methyl isobutyl ketone (MIBK)) was measured in this work at atmospheric pressure and 298.15 K. The salt influence on the LLE of the system water/HMF/MIBK was measured for salt concentrations up to 3 moles per kg water. The salts under investigation were composed of the anions NO_3^- , PO_4^{3-} , Cl^- and of the alkali cations Li^+ , Na^+ and K^+ . Based on the LLE data, the distribution of HMF between the aqueous and the MIBK phase was calculated and expressed by the distribution coefficient K_{HMF} . It could be shown that K_{HMF} significantly depended on the kind and concentration of the salt. Some of the salts even caused increased K_{HMF} values at low salt concentrations and decreased values at higher salt concentrations.

Based on the experimental data, the electrolyte Perturbed-Chain SAFT (ePC-SAFT) model was applied to describe the salt influence on the LLE of the system HMF/water/organic solvent. Using pure-component parameters for water, organic solvent, HMF and for the ions obtained from independent experimental data, the LLE and the K_{HMF} values could be predicted as function of salt concentrations and HMF concentrations in good agreement with the experiments.

New dipicolinic acid derivatives for actinide-lanthanide separations

Kenneth L. Nash¹, Colt Heathman^{1,2}*

Summary

Soft donor complexing agents, whether lipophilic or water-miscible, have been central to the development of aqueous separations of trivalent actinides from fission product lanthanides for application in advanced nuclear fuel cycles. Various categories of aminopolycarboxylic acids have proven to be particularly useful in this application. The focus of this report is on improving the utility of 2,6-dicarboxypyridine (dipicolinic acid) for such applications through functionalization of dipicolinic acid at the 4-position on the ring. The purpose of the adjustment is to improve solubility and to adjust the H⁺ affinity of the cation receptor to enable its application in the acidic aqueous media that are preferred in nuclear fuel reprocessing.

Introduction

It was demonstrated by Seaborg and co-workers in the 1950s that the most expeditious approach to the group separation of trivalent actinides from lanthanides was through the introduction of more polarizable “soft” donors into the system.¹ In the 1990s, Choppin² established that mixed donor aminopolycarboxylates are about 8% more selective for actinides than lanthanides. Ogden³ has recently demonstrated an apparent 38% enhancement in actinide selectivity for reagents containing only N donor groups. In the N-donor-only correlation, the utility of the enhanced selectivity is compromised by comparatively weak bonding interactions overall. As a result, the search for suitable reagents for trivalent actinide/lanthanide separation reagents often focuses complexants based on mixed hard and soft donor complexing agents.

In a recent publication, Heathman⁴ has reported a stability constants describing Am³⁺ and Eu³⁺ interactions with 2,6-dicarboxypyridine (dipicolinic acid). Predictions based on these parameters establish that a potential Am³⁺ separation from Ln³⁺ might be developed based on this reagent. However, the limited solubility of dipicolinic acid in strongly acidic media was recognized as a significant impediment to exploiting this An/Ln selectivity, hence adjustment of the solubility became desirable.

In this report, the more subtle difference between aliphatic and aromatic (pyridine) donor atoms is explored in an investigation of the effectiveness of 2,6-dicarboxypyridine (dipicolinic acid) as a potential reagent for actinide/lanthanide separations applications. To overcome the inherent solubility limitations of dipicolinic acids, four new derivatives have been prepared and their f-element complexing ability characterized. These water-soluble derivatives exhibit a 15-160 fold increased

*¹ Washington State University, Department of Chemistry, P.O. Box 644630, Pullman, WA 99164-4630, USA knash@wsu.edu

² present address, Oak Ridge National Laboratory, Oak Ridge, TN, USA

solubility in acidic aqueous solutions (relative to dipicolinate), a wider range of acidities, and comparable effectiveness with regards to actinide-lanthanide selectivity. The trans-lanthanide pattern of complex stability indicates potential broad applicability of these reagents in advanced nuclear fuel cycles. Selected features of this chemistry are discussed below, emphasizing Ln/An group separations.

Experimental

Dipicolinic acid derivatives were prepared using two different synthetic pathways.⁵ The first method follows the work by Tang *et al.*⁶⁻⁸ and utilizes radical addition of methanol to the pyridine ring followed by substitution with the desired solubilizing functional group for the –OH group. The second strategy uses direct attachment of the N-donor functional group to the pyridine ring in the 4-position. Addition of the methylene spacer was expected to preserve the Brønsted acidity of the dipicolinate, whereas direct substitution was predicted to result in changes of the proton and metal coordination strength. Using this strategy, it is possible to independently adjust solubility and complex strength. The details of the synthesis and characterization of the complexants are reported in reference 5. Structures are shown in Figure 1.

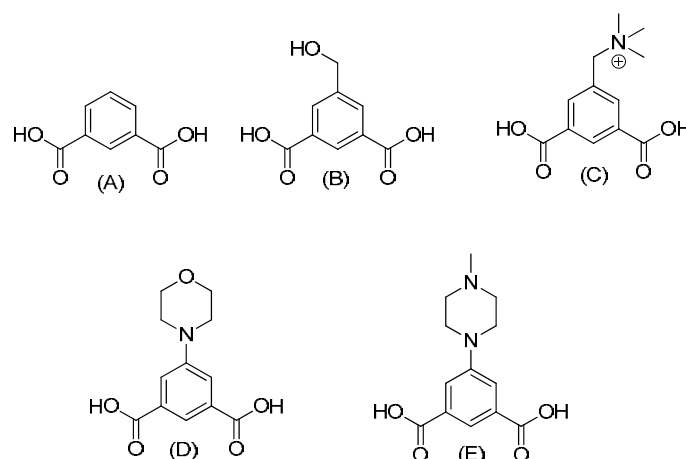


Figure 1 Structure of: **(A)** Dipicolinic acid (DPA), **(B)** 4-(hydroxymethyl) pyridine-2,6-dicarboxylic acid (HMDPA), **(C)** N,N,N-trimethyl-4-pyridinemethanaminium-2,6-dicarboxylic acid (QDPA), **(D)** 4-(4-morpholinyl)-2,6-pyridine dicarboxylic acid (mor-DPA), and **(E)** 4-(N-methylpiperazine-1-yl)-2,6-pyridine dicarboxylic acid (mPIP-DPA).

Solubility Studies

To determine the effect that functionalization has on DPA solubility in acidic aqueous media, solubility studies were performed under conditions representative of the preferred high-acid limit of application for complexants in trivalent An/Ln separation processes. In these studies a known mass of each material was placed in a glass sample vial and small quantities of 1 M HClO₄ were added until the samples completely dissolved. These studies were performed at ~23 °C (RT).

Potentiometric Titrations

Protonation constants of the dipicolinate derivatives were determined by potentiometric titrations on a Mettler-Toledo DL-50 Graphix autotitrator with a Thermo/Ross semi-micro combination pH electrode converted for operation with a 3.0 M NaCl filling solution in the reference compartment. Solution conditions were maintained constant at 25.0(±0.1)°C and 1.0 M total ionic strength (NaClO₄). An inert atmosphere of nitrogen (pre-saturated with water) was used to prevent CO₂ contamination. A mV vs. pH calibration curve was developed based on a strong acid – strong base titration (HClO₄/NaOH at 1.0 M total ionic strength). All titrations were repeated in triplicate. Titration data was fit using the fitting program PSEQUAD.⁹

Distribution Studies

Extractant phases were prepared by dissolving purified (>99%) bis-(2-ethylhexyl) phosphoric acid (HDEHP) in reagent grade *n*-octane. For trans-lanthanide experiments (analyzed by ICP-MS) the total lanthanide metal concentration in the initial aqueous solutions varied between 2 and 20 ppm. Parallel samples also containing either ^{152/154}Eu or ²⁴¹Am were analyzed radiometrically. All experiments were performed at constant ionic strength (1.0 M H/NaClO₄) at 23.0(±1.0)°C. Equilibration was rapid under all conditions. Though lanthanide and Am extraction profiles of all four complexants were evaluated, results are reported only for QDPA due to space limitations.

Results and Discussion

The complexing agents prepared in this investigation share a nearly identical tridentate cation receptor core with dipicolinic acid. The rigid aromatic ring defines the dimensions of the cation binding pocket. Stability constant data from the prior literature¹⁰ establish the existence of complexes having 1:1, 1:2 and 1:3 stoichiometry in the base dipicolinate. The trans-lanthanide pattern of complex stability mirrors that seen in diglycolic acid complexes^{5,10}, though the dipicolinate complexes are notably stronger. In the 1:3 lanthanide-dipicolinate complexes, thermodynamic stability increases from La³⁺ to Eu³⁺ then levels off from Gd³⁺ to Lu³⁺. In contrast with diglycolate, the presence of a soft(er) pyridine nitrogen in a favorable tridentate cation binding pocket offers a potential avenue to An/Ln group selectivity.

The results of the complexant solubility investigation are summarized in Table 1. The low solubility of H₂DPA in acidic solutions is clearly indicated. The sodium salts of HMDPA, QDPA, morDPA and mPIPDPA are seen to be 15-160 times more soluble than DPA. That the sodium salts are more soluble is not very surprising, but the increased solubility of HMDPA, QDPA, and morDPA in solutions of 0.37-0.96 M acid clearly indicates that the functionalization has led to improved solubility of the (X)DPA complexants. In the case of mPIPDPA, the complexant appears to be fully miscible in salt solutions, at least up to 0.5 M. This complexant has the greatest number of basic

donor groups capable of accepting an H^+ ion. The results suggest that the presence of aliphatic N-donors located in a position not associated with cation binding can have a significant effect on complexant (and metal perhaps complex) solubility.

	DPA	HMDPA	QDPA	morDPA	mPIPDPA
Chemical Form	H_2L	Na_2L	$NaL \cdot NaCl$	$NaL \cdot NaCl$	$L \cdot (NaCl)_2$
Mass (g)	0.0081	0.0542	0.0385	0.0476	0.0492
Volume (mL)	16.138	0.708	2.799	0.965	0.257
M.W. (g/mol)	167.12	243.13	318.66	332.65	382.15
[Ligand] (M)	0.003	0.318	0.043	0.148	0.501
$[H^+]_{eq, t}$ (M)	1.006	0.37	0.96	0.70	0.0
$[Na^+]$ (M)	0.0	0.64	0.086	0.30	1.0

Table 1 Experimentally determined solubility of select ligands in 1 M $HClO_4$. dipicolinic acid (**DPA**), sodium 4-hydroxymethylpyridine-2,6-dicarboxylate (**HMDPA**), disodium mono(4-((trimethylammonio)methyl)pyridine-2,6-dicarboxylate) (**QDPA**), sodium 4-morpholinopyridine-2,6-dicarboxylate (**mor-DPA**), and sodium 4-(4-methylpiperazin-1-yl)pyridine-2,6-dicarboxylate (**mPIP-DPA**).

As each of these complexants is likely a weak acid, a complete picture of complexant speciation/solubility in this medium requires consideration of the H^+ affinity of each, which was addressed in the potentiometric titration results (Table 2). In the baseline DPA, the pyridine N atom is likely to be the most basic atom, hence the first protonation reaction of L^{2-} ($pK_2 = 4.62$) is assigned to this atom; the presence of a protonated pyridine N-atom reduces the net basicity of the carboxylate by a factor of about 100 (c.f., $pK_a(\text{benzoic acid}) = 4.0$ under conditions similar to those of this investigation, $pK_1(\text{DPA}) = 2.15$). Substitution of hydroxymethyl at the 4 position results in no net change in either pK_a value. The introduction of a quaternary ammonium group decreases the net Brønsted basicity of the pyridine N-atom by a factor of 10 while apparently altering the basicity of the carboxylate groups minimally. Direct substitution of aliphatic N-atoms significantly increases the acidity of the cation-binding groups of the dipicolinate; the aliphatic ammonium atoms in N-methyl piperazine and morpholine are strongly basic, likely accounting for the significant enhancement of their solubility. The positioning of these rings leaves the N-atoms in a position poorly suited to cation coordination to the lanthanide/actinide ions.

The partitioning of Am^{3+} and lanthanides between 1.0 M HDEHP/n-octane and a 1 M $H/NaClO_4$ solution, 0.1 M H^+ , 0.0077 M QDPA is seen in Figure 1. Under these conditions, a Ln/Am group separation factor of 10 is indicated. Similar patterns of Am/Ln separation have been seen in parallel experiments with the other (X)DPA derivatives under similar conditions. Calculations based on Nd^{3+} and Am^{3+} stability constants suggest that optimization of these systems could produce Am/Nd

separations factors above 1000 for some conditions.⁵

	pK_{a1} (Carboxylic Acid 1)	pK_{a2} (Carboxylic Acid 2)	pK_{a3} (Aromatic N)	pK_{a4} (Aliphatic N1)	pK_{a5} (Aliphatic N2)
DPA		2.15 (± 0.02)	4.62 (± 0.02)		
HMDPA		2.11 (± 0.02)	4.76 (± 0.02)		
QDPA	1.19 (± 0.12)	2.31 (± 0.01)	3.57 (± 0.01)		
mor-DPA			2.07 (± 0.03)	8.40 (± 0.01)	
mPIP-DPA			1.58 (± 0.03)	7.00 (± 0.01)	8.70(± 0.01)

Table 2 Acid dissociation constants for functionalized DPA ligands measured at $T = 25.0 \pm 0.1$ °C, ionic strength held constant at 1.0 ± 0.1 M using NaClO_4 as the supporting electrolyte. Errors in brackets correspond to the $\pm 3\sigma$ uncertainty limit.

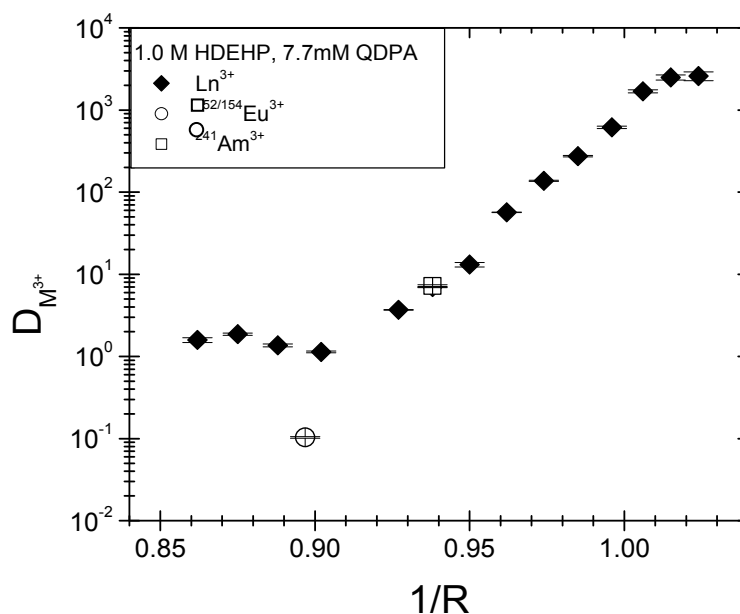


Figure 1 Trivalent f-element extraction of 1.0 M HDEHP (in n-octane) in contact with 0.10 M H^+ , 7.7 mM QDPA, ionic strength of 1.0 M Na/HClO_4 aqueous phases ($\blacklozenge$) Ln^{3+} , analyzed by ICP-MS ($\square$) same sample spiked with $^{152/154}\text{Eu}^{3+}$, analyzed radiometrically, ($\circ$) same sample spiked with $^{241}\text{Am}^{3+}$, analyzed radiometrically.

Conclusion

New derivatives of dipicolinic acid have been developed by functionalization of the pyridine ring at the 4-position on the ring. Adding polar groups in this position markedly increase the solubility of DPA in acidic aqueous media. By inserting a

methylene spacer, the acidity of the ligand can be manipulated independently of aqueous solubility. A successful demonstration of the separation of trivalent actinides from lanthanides has been demonstrated. The primary objective of demonstrating that this strategy will yield improved aqueous solubility of the dipicolinic acid moiety has been established. There is significant potential for improvement and the tunability of acid-base and solubility opens many options.

Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development program, Sigma Team for Minor Actinide Separations.

References

1. Diamond, R. M.; Street, J.; Seaborg, G.T. *J. Am. Chem. Soc.* (1954) 76, 1461-1469.
2. Choppin, G. R. *Radiochim. Acta*, **32**, 43-53 (1983).
3. Ogden, M. D.; Sinkov, S. I.; Meier, G. P.; Lumetta, G.J.; Nash, K.L. *J. Soln. Chem.* **2012**, 201 (41), 2138-2153.
4. Heathman, C. R.; Nash, K. L. *Sep. Sci. Technol.* **2012** 47, 2029-2037.
5. Heathman, C. R. Ph.D. Dissertation, Washington State University, Department of Chemistry, August, 2013.
6. Tang, Rui-ren; Zhao, Qiang; Yan, Zi-er; Luo, Yi-ming. *Synth. Comm.* **2006**, 36, 2027-2034.
7. Buratti, W.; Gardini, G. P.; Minisci, F. *Tetrahedron* **1971**, 27 (15), 3655-3668.
8. Shelkov, R.; Melman, A. *Eur. J. Org. Chem.* **2005**, (7), 1397-1401.
9. Zekany, L.; Nagypal, I. PSEQUAD: A Comprehensive Program for the Evaluation of Potentiometric and/or Spectrophotometric Equilibrium Data Using Analytical Derivatives, In *Computational Methods for the Determination of Formation Constants*, Legget, D.J., Ed.; Plenum, New York, **1985**, pp. 291-308.
10. Martell, A.E.; Smith, R.M.; Motekaitis, R. K. Critically Selected Stability Constants of Metal Complexes, NIST database 46. Version 8.0. **2004**

Effect of the central frames and substituents attached to N atoms on extraction ability of podand-type extractants

Yuji Sasaki^{*1}, Yoshihiro Kitatsuji², Yumi Sugo², Yasuhiro Tsubata², Tomoya Suzuki², Takaumi Kimura², and Yasuji Morita²

The eight amide extractants including podand-types, which introduce oxygen, nitrogen and sulfur donor atoms in their central frame, are synthesized and their *D* values for actinide extraction are compared. The central frame affects greatly on their extractability and it is clear that diglycolamide (DGA) has the highest extractability among extractants used here. In addition, DGA having the different length of alkyl chain or phenyl groups attached to amidic N atoms are obtained and the effect of these substituents is studied. Due to the steric hindrance or hydrogen bond, DGA with long and branched alkyl chains, phenyl group, and CO-NHR group give relatively low *D* values.

Introduction

The extractions and separations of actinides (An) by the novel extractants are reported widely in order to develop the partitioning method of high level radioactive waste containing actinides. However, there are few reports concerning the extractants with the different central frames [1-2], because it includes difficulty for the different organic synthesis. Besides, the forms of the central frame play the important role in actinide extractions, the comparison of the several kinds of extractants is important to understand the best chemical structure. In addition, the selection of the suitable alkyl group attached to their central frames is one of the important factors to develop the promising extractants. Compared to the central frame, effect of the alkyl groups on the extractability is limited to some extent, however, the mismatching choice may lose their potential ability and utility. This paper has focused on the effect of extractants with not only different central frames, but also substituents. The extractants used here are shown in Fig. 1. The diglycolamides (DGA) were used to investigate the effect of the alkyl chain, because of the easy preparation and strong extractability to An [3].

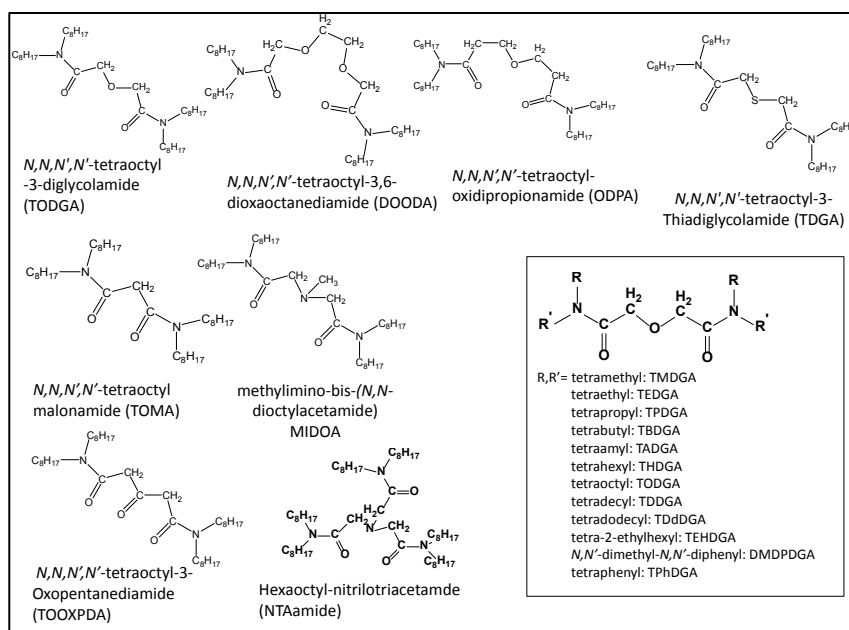


Fig. 1 Extractants used

^{*1} Corresponding Author, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

¹ Author 2, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

Experimental

The diamide extractants, DGA, ODPa, TDGA and TOMA, were synthesized and purified by the same method in the references[1,4]. Other extractants, such as DOODA, MIDOA, TOOXPDA and NTAamide, were obtained from Wako-Pure Chemical Industries. The samples purified were identified by NMR, IR and GC. An extractions using extractants were performed by the method described before[1-3]. Alpha measurements of Am, Pu, U and Np in aqueous and organic phases were done by liquid scintillation counter.

Results and Discussion

Extraction of An(III), (IV) and (VI) by eight extractants

The condition, aqueous phase of 1 M HClO_4 and organic phase of extractants in *n*-dodecane, was used for Am(III), Pu(IV) and U(VI) extractions. This condition gives the sufficient D values for An[5].

The D values for Am(III), Pu(IV) and U(VI) plotted against extractant concentration are shown in Fig. 2(a), (b) and (c). Using the straight lines in Fig. 2, the slopes and the intercept values of y axis (IV,y) are summarized in Table 1. The slope and IV,y values mean the numbers of extractant associated with the extraction reaction and their extractability. From Table 1, the extractions of An need mostly two or three extractants, and the trend of their extractability can be determined as:

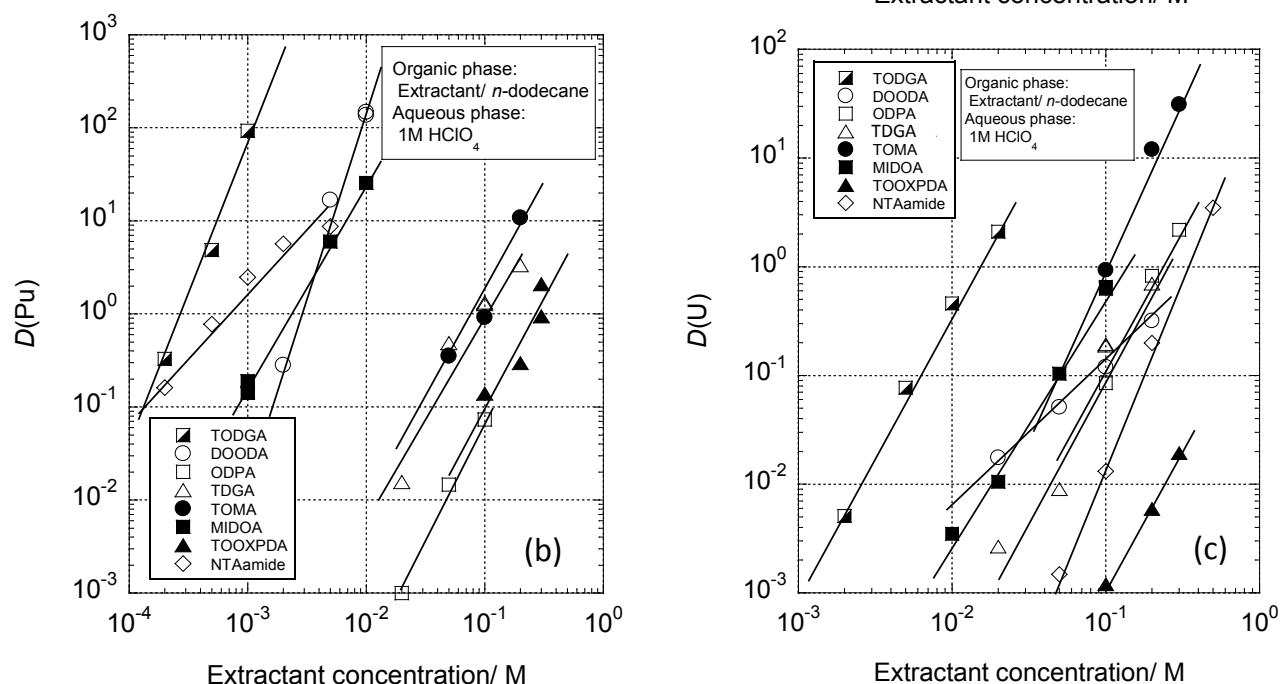


Fig. 2. Relationship between $D(\text{An})$ and extractant concentration, (a): Am, (b): Pu, (c): U

Table 1 Analysis of the straight lines in Fig. 2

	Am		Pu		U	
	slope	IV,y*	slope	IV,y	slope	IV,y
TODGA	4.2±0.4	13.9	3.5±0.4	12.3	2.6±0.1	4.9
MIDOA	-		2.2±0.1	5.8	2.3±0.1	2.1
TDGA	3.2±0.3	2.76	2.4±0.3	2.1	2.6±0.4	1.7
TOOXPDA	-		2.3±0.4	1.4	2.5±0.2	-0.4
ODPA	2.6±0.1	0.13	2.7±0.2	1.6	3.0±0.2	1.9
TOMA	3.8±0.4	1.9	2.5±0.6	2.7	3.2±0.4	3.3
DOODA	5.1±0.4	12.6	3.9±0.1	10	1.3±0.1	0.36
NTAamide	1.2±0.2	0.41	1.3±0.5	4.0	3.4±0.1	1.6

*: IV,y; intercept values of y axis for the straight lines

TODGA > TDGA ≥ DOODA ≥ ODPA > TOMA > NTAamide > MIDOA > TOOXPDA for Am; TODGA > NTAamide ≥ DOODA ≥ MIDOA > TOMA ≥ TDGA > TOOXPDA ≥ ODPA for Pu; and TODGA > TOMA ≥ MIDOA ≥ DOODA > TDGA ≥ ODPA > NTAamide > TOOXPDA for U. The highest extractability for actinides among extractants used in this work can be seen in TODGA. It is clear that extractant with tridentate by three oxygen donor atoms and two five-membered ring chelation is an excellent for the actinide extraction.

The trends of extractability for different oxidation state of An are summarized. In general, An(IV) > An(VI) > An(III) > An(V) or An(VI) > An(IV) > An(III) > An(V) by the bidentate extractant were reported[6,7]. Using IV,y values in Table 1, the trends for each extractant can be determined. Here, $D(\text{Np(V)})$ were also measured and these values were considerably low[2]. The trend, An(III) > An(IV) > An(VI) > An(V), can be appeared in TODGA, TDGA and DOODA, An(IV) > An(VI) > An(III) > An(V) are in MIDOA and TOOXPDA, An(VI) > An(IV) > An(III) > An(V) are in ODPA and TOMA, and An(IV) > An(III) > An(VI) > An(V) is in NTAamide extractions. Bidentate ligands has normally weak reactions with trivalent An, the results in this work support this, too. In addition, extractants showing the podand-type and five-membered chelation have high D values for An(III), except for MIDOA. If we would like to design the novel extractant for MA(III) recovery, this is one of the direction for molecular modelling. In addition, solo-recovery of U(VI) from spent nuclear fuel is one of the important task in the reprocessing study[8,9]. The extractant needs not only high $D(\text{U})$ values, but also high separation factor for U/Pu, extractants employed here are hardly available to use for this purpose.

Extractions of An by twelve DGA extractants

Prior to the solvent extraction, the dissolution tests of DGA compounds obtained are performed. DGA with short alkyl chains (namely TMDGA and TEDGA) have low solubility in organic solvents. DGA having phenyl group, N,N' -dimethyl- N,N' -diphenyl-diglycolamide (DMDPDGA) and TPhDGA (N,N' -tetraphenyl-diglycolamide) has low solubility in most of the organic solvents. From these results, we use chloroform in order to dissolve DGA easily and compare the D values.

The results of An extractions by different 10 DGA extractants are shown in Fig. 3 (aqueous phase: 1 M HNO_3). From Fig. 3, it seems that the $D(\text{An})$ for DGA with short alkyl chain are somewhat higher than those for DGA with long alkyl chain. In order to clear these results, the $D(\text{Am}, \text{Th})$ values for the condition, 0.2M DGA/chloroform and 1 M HNO_3 , are obtained and shown in Table 2. Table 2 indicates that D values decrease gradually with number of carbon atoms in the alkyl chain, which is due to the steric hindrance. $D(\text{Th})$ for TPDGA is lower than that for TBDGA, which might be the reason to have high solubility in aqueous phase. It is clear that D values by TEHDGA and DMDPDGA is low. Phenyl group and branched alkyl chain may have higher steric hindrance than that of normal alkyl chain. In addition to the results described above, we did experiments using N,N' -dioctyl-diglycolamide ($\text{O}(\text{CH}_2\text{CON}(\text{H})(\text{C}_8\text{H}_{17}))_2$). This sample is solid at room temperature and can dissolve well in chloroform. The results of $D(\text{Am}, \text{Th})$ for 0.5 M/ chloroform and 1M HNO_3 are lower than 0.001, which indicates negligibly small extraction. The extractant may have intermolecular hydrogen bond between N(H) and ether or amidic oxygen atoms, which results in low extractability [10].

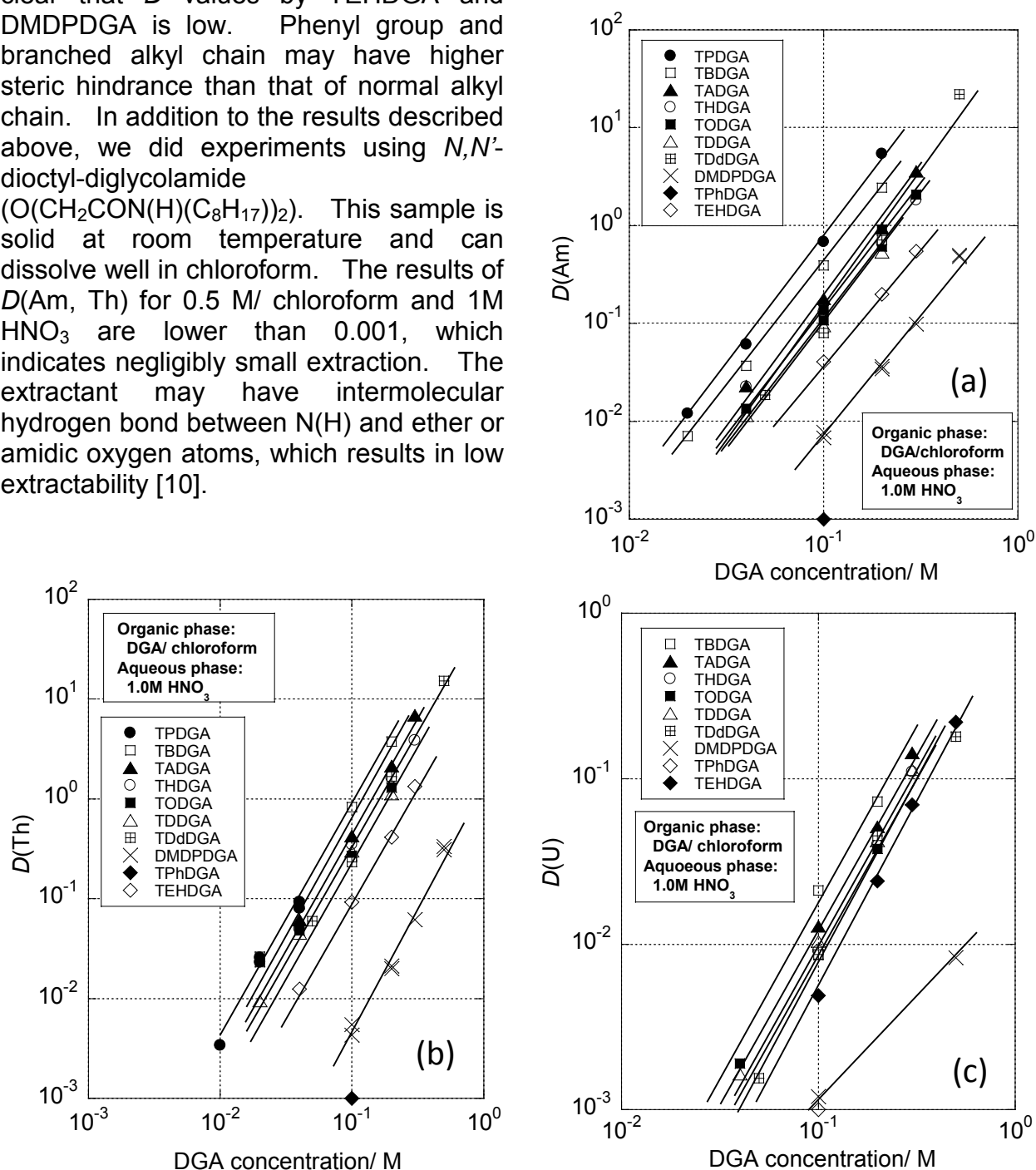


Fig. 3 Relationship between $D(\text{An})$ and DGA concentration, (a): Am, (b): Th, (c): U

Conclusion

The podand-type diamide extractants, which includes oxygen or nitrogen donor atoms introduced into their central frame, are synthesized and examined for the extraction of actinides. It is clear that DGA frame has very high complexing ability with An. DGA having 12 different alkyl groups were employed and investigated for their effect on extraction. The $D(\text{An})$ decrease with length of alkyl chain attached with amidic N atoms. It is clear that the D values by TEHDGA, DMDPDGA with branched alkyl chain and phenyl group, and DGA showing the secondary amide groups are considerably low due to the steric hindrance and intermolecular hydrogen bond.

Table 2 $D(\text{Am}, \text{Th})$ values obtained for the different DGA (Condition: 0.2M DGA/chloroform, 1M HNO_3)

	D	
	Am	Th
TPDGA	5.45	1.48
TBDGA	2.45	3.75
TADGA	0.945	2.13
THDGA	0.661	1.62
TODGA	0.612	1.3
TDDGA	0.536	1.12
TDdDGA	0.713	1.68
TEHDGA	0.199	0.414
DMDPDGA	0.0366	0.0212

Acknowledgments

We acknowledge greatly staff of Wako-Pure Chemical Industries for the organic synthesis and Mr. T. Masaki, M. Ito and Y. Nakahara and Dr. H. Suzuki and N. Shirasu for the An extraction and analysis.

This work was partially supported by MEXT, Grant-in-Aid for Scientific Research (A) (21246146).

References

1. Y. Sasaki and S. Tachimori, *Solvent Extr. Ion Exch.*, **20**, 21-34 (2002).
2. Y. Sasaki, Y. Kitatsuji, Y. Sugo, Y. Tsubata, T. Kimura, and Y. Morita, *Solvent Extr. Res. Develop. Jpn.* **19**, 51-61 (2012)
3. Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solvent Extr. Ion Exch.*, **19**, 91-103 (2001).
4. T.H. Siddall III, M.L. Good, *J. Inorg. Nucl. Chem.*, **29**, 149 (1967).
5. Y. Sasaki, P. Rapold, M. Arisaka, M. Hirata, T. Kimura, C. Hill, G. Cote, *Solvent Extr. Ion Exch.*, **25**, 187 (2007).
6. G.R. Choppin, *Radiochim. Acta*, **32**, 43 (1983)
7. G.R. Choppin, *Sep. Sci. Tech.*, **19**, 911 (1984-1985).
8. S. Suzuki, T. Yaita, Y. Sugo and T. Kimura, *Proceedings of GLOBAL2007*, 1137-1141 (2007)
9. Y. Ban, S. Hotoku and Y. Morita, *Solvent Extr. Ion Exch.*, **29**, 519 (2011).
10. S. Ando, I. Ando, A. Shoji, and T. Ozaki, *J. Am. Chem. Soc.* **110**, 3380-3386 (1988).

New developments with monoamide type extractants

C. Sorel and M. Miguirditchian

CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department,
SMCS, Bagnols-sur-Cèze, F-30207, France

The potentiality of monoamide class extractant for actinides separation was highlighted by Siddall [1] during the 60's and extensive studies were performed in the CEA during the 90's. Monoamides (or N,N-dialkylamides) whose general formula is $RC(O)NR'_2$ show a good stability towards radiolysis and hydrolysis and their degradation products are not troublesome for the separation process [3]. Within this family of extractants, it was shown that the addition of branched alkyl substituent R on the carbon atom alpha to the carbonyl function increases the U(VI) vs An(IV) selectivity.

New investigations have been recently undertaken with DEHiBA (N,N-di-2-ethylhexyl-isobutyramide) to develop an innovative solvent extraction process devoted to the uranium purification. Experimental distribution ratios obtained for nitric acid, uranium(VI), plutonium(III, IV), thorium(IV), neptunium(V, VI), technetium(VII) and other FP's were described with a physicochemical model based on the application of the mass action law on each extraction equilibrium. Deviations from ideal behaviour in aqueous phase were estimated by calculating the activity coefficient of each component according to the "simple solutions" concept based on the outstanding experimental behaviour of isopiestic solutions, (solutions having the same water activity) first pointed out by Zdanovskii and confirmed later by Stokes and Robinson. The equilibrium constants optimised to represent extraction of nitric acid and metals were implemented into the PAREX code. This model was validated by comparing experimental and calculated concentration profiles obtained after a counter-current test performed in laboratory-scale mixer-settlers. With the help of this validated model, an optimised flowsheet was proposed and tested through different pilot tests.

[1] Siddall T.H., Effects of structure of N,N-disubstituted amides on their extraction of actinide and zirconium nitrates and of nitric acid, *J. Phys. Chem.*, **1960**, 64, 1863-1866.

[3] Condamines N., Contribution à l'étude de l'extraction d'acides minéraux et de cations actinides aux degrés d'oxydation (IV) et (VI) par les N,N-dialkylamides, Thèse de doctorat de l'université Paris VI, 1989.

[3] P. N. Pathak, D. R. Prabhu, P. B. Ruikar and V. K. Manchanda, Evaluation of Di(2-éthylhexyl)isobutyramide (D2EHiBA) as a process extractant for the recovery of ²³³U from irradiated Th, *Solvent Extraction and ion Exchange*, 20, 293-311 (2002).

Recovery of Gallium and Indium from Synthetic Leach Solution of Zinc Refinery Residue using Novel Synergistic Solvent Extraction

Sankum Nusen^{1,2}, Torranin Chairuangsr¹, Zhaowu Zhu², Chu Yong Cheng^{2*}

Summary

A synergistic solvent extraction (SSX) system consisting of LIX 63 and Versatic 10 has been developed to recover In and Ga from a synthetic sulphate leach solution of zinc refinery residues. The SSX system was able to selectively extract In and Ga over other metals. About 20-30% Ni, Co and Ge were co-extracted while only very small amounts Zn, Cd, Sb and almost no Mn, Mg and Ca were co-extracted from the synthetic leach solution. Ferric iron was reduced with iron powder and copper removed using LIX 984 before Ga and In extraction to avoid their co-extraction. Ga and In were stripped readily using 0.05 M H₂SO₄. The SSX system consisting of 0.12 M LIX 63 and 0.12 M Versatic 10 in ShellSol D70 was selected for the extraction of In and Ga from synthetic feed solutions containing 1 g/L In and Ga, respectively. At pH 3.0, 86% In and 92% Ga were extracted in a single contact. The synergistic effect on In extraction was significant while no or weak synergistic effect on Ga extraction. The novel SSX system has a great potential for the recovery of In and Ga from leach solutions of zinc refinery residues.

Introduction

Indium and gallium are valuable but scattered elements and one significant source is the zinc refinery residue (Mihaylov and Distin, 1992; Paiva, 2001). After leaching with sulphuric acid in most cases, solvent extraction (SX) is widely studied and used for their separation and purification.

Acidic organophosphorus extractants including M2EHPA (mono(2-ethylhexyl)phosphoric acid), D2EHPA (di(2-ethylhexyl)phosphoric acid), PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) were widely tested for the recovery of In with Fe(III) reduced to Fe(II) and Cu(II) and As(III) cemented with iron powder before SX (Levin et al., 1967; Tomii and Tsuchida, 1981; Aavila et al., 1992; Sato and Sato, 1992; Fortes et al., 2003). High In extraction is obtained with these extractants, but high stripping efficiency can only be achieved with high concentration HCl or HClO₄ solutions (Virolainen et al., 2011; Yang et al., 2013). This is a significant disadvantage of using the above reagents.

Judd and Harbuck (1990) studied the extraction of Ga from leach solutions of zinc plant residues using OPAP (octylphenyl acid phosphate) and isodecanol in kerosene. Overall Ga recovery with this system reached 94%. However, the reagent is not commercially available. Katsura and Abe (1975) reported that after Fe(III) reduction, over 93% Ga and 94% In were co-extracted with 20% Versatic 10 at pH 3.5 and only 0.26% Cu, no Zn, 2.5% Fe(II) and 1.1% Al(III) were co-extracted. Ga and In were stripped with low acidity strip solutions. The separation of Ga and In by acidifying the loaded strip liquor to >2.5 M H⁺ and using two SX circuits is un-economical.

In a process developed by Zhou et al. (1989), D2EHPA was used for the separation of In and iron from the solution and then H106 (a mixture of neo-tridecyl and neo-pentadecyl hydroxamic acid) was used for co-extraction of Ga and Ge. Over 90% In, 94% Ga and 93% Ge were recovered. In this process, further separation of In and Fe(III) is required and H106 is not commercially available.

The aim of the current study is to identify the more efficient and effective SX and SSX systems in terms of extraction and stripping for the recovery of In and Ga from sulphuric acid leach solutions of zinc residues using commercially available reagents.

*Corresponding author email: chu.cheng@csiro.au

¹Department of Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

²CSIRO Minerals Down Under National Research Flagship, Australia

Experimental

To select suitable SX and SSX systems, metal extraction pH isotherm tests were conducted using a synthetic leach solution (Table 1). The solution was prepared by dissolving the required amounts of analytical grade metal sulphates in de-ionised water. Extractants LIX 63 and Versatic 10 and all diluents were used as received, with purities as advised on the relevant MSDS.

All shaking-out tests were carried out in a reactor immersed in a temperature controlled water bath. The pH of the aqueous solution was measured during mixing using a pH electrode and a pH meter. Where necessary, solution pH was adjusted by the addition of 10-100 g/L NaOH or 100 g/L H₂SO₄ solutions.

The aqueous and organic phases of the samples were separated using 1PS separation filter. The organic samples were stripped using 100 g/L H₂SO₄ or 80 g/L NaOH. The loaded strip liquors and aqueous samples from each test point were taken for chemical analysis using ICP-AES.

Table 1. Composition of the synthetic leach solution of typical cementation residue

Elements	Cd	Zn	Co	In/Ga/Ge/Ni/Al/Fe/Cu/Sb/Mn/Mg/Ca
Concentration (g/L)	71.9	17.0	0.90	0.05-0.06

Results and discussion

Selection of an organic system

Scoping tests were conducted with organic systems consisting of M2EHPA, D2EHPA, Ionquest 801, Cyanex 272, Versatic 10, LIX 63 and all combinations thereof to select an effective system for the extraction of Ga and In together in terms of extraction and stripping. The SSX system consisting of LIX 63 and Versatic 10 performed best. With the SSX system containing 0.25 M LIX 63 and 0.20 M Versatic 10 in ShellSol D70, 92% In, 98% Ga and Cu and 94% Fe(III) were extracted at pH 3.5, A/O ratio of 1 and 40 °C (Figure 1). About 20-30% Ni, Co and Ge were also co-extracted while only very small amounts of Zn, Cd, Sb and almost no Mn, Mg and Ca were co-extracted at this pH. Due to very low concentration of Ni, Co and Ge, small amounts of these co-extracted metals would be crowded out or scrubbed in a counter-current operation. The phase separation was fast and no third phase or precipitate was observed in the pH range of 0.2-3.5.

Most importantly, it was found that In, Ga, Cu and Fe(III) were completely stripped from the loaded organic solution with H₂SO₄ solution at pH 1.0 (Figure 2). This also indicates that Fe(III) and Cu must be removed before solvent extraction to prevent their co-extraction. In the current study, over 99.5% Fe(III) was reduced to Fe(II) with iron powder at 70 °C and the re-oxidation of Fe(II) to Fe(III) was prevented by bubbling N₂ gas during extraction. The Cu was eliminated before In and Ga extraction using the organic system consisting of 0.05 M LIX 984N in ShellSol D70 at 40 °C. Over 98% Cu was extracted at pH 2.0 while only 8-11% Ga, In and Fe(III) were co-extracted. After Fe(III) reduction and Cu removal, 97% In and 99% Ga were extracted while only 15% Fe(II) and 12% Ge was co-extracted at pH 3.5 with the organic system consisting of 0.25 LIX 63 and 0.20 Versatic 10 in ShellSol D70 at 40 °C (Figure 3). Almost 100% In and 91% Ga were stripped using 0.05 M H₂SO₄ solution (Figure 4). This is a very significant finding for the separation and recovery of In and Ga from synthetic sulphate solution due to their high extraction at pH 3.5 and very easy stripping using 0.05 M H₂SO₄ solution.

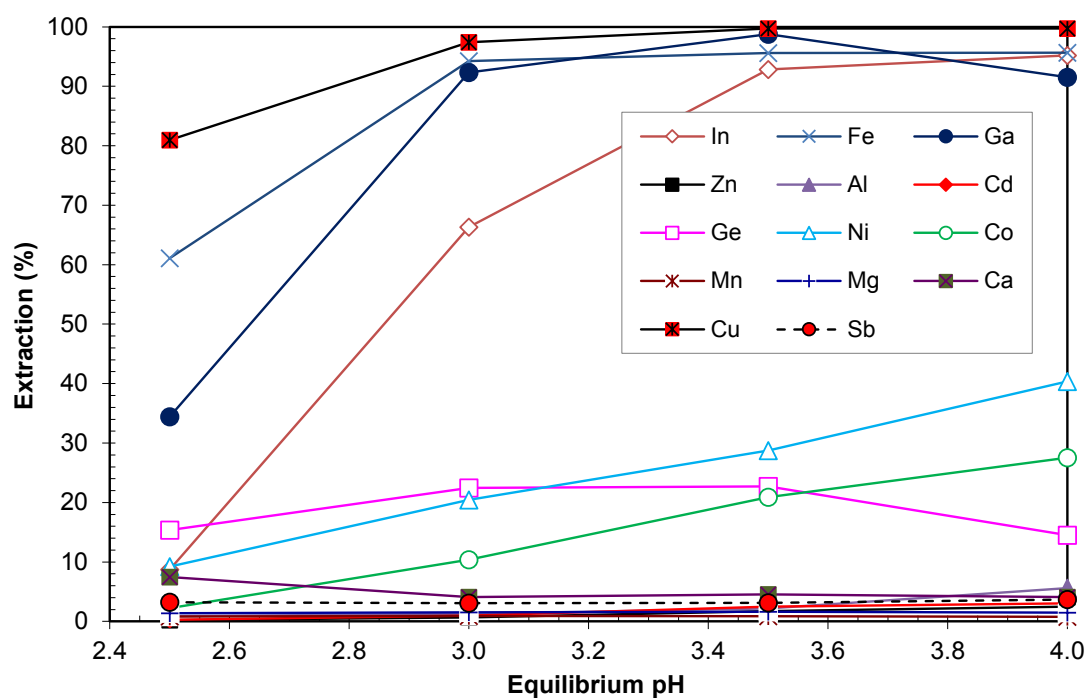


Figure 1. Metal extraction pH isotherms with 0.25 M LIX 63 and 0.20 M Versatic 10.

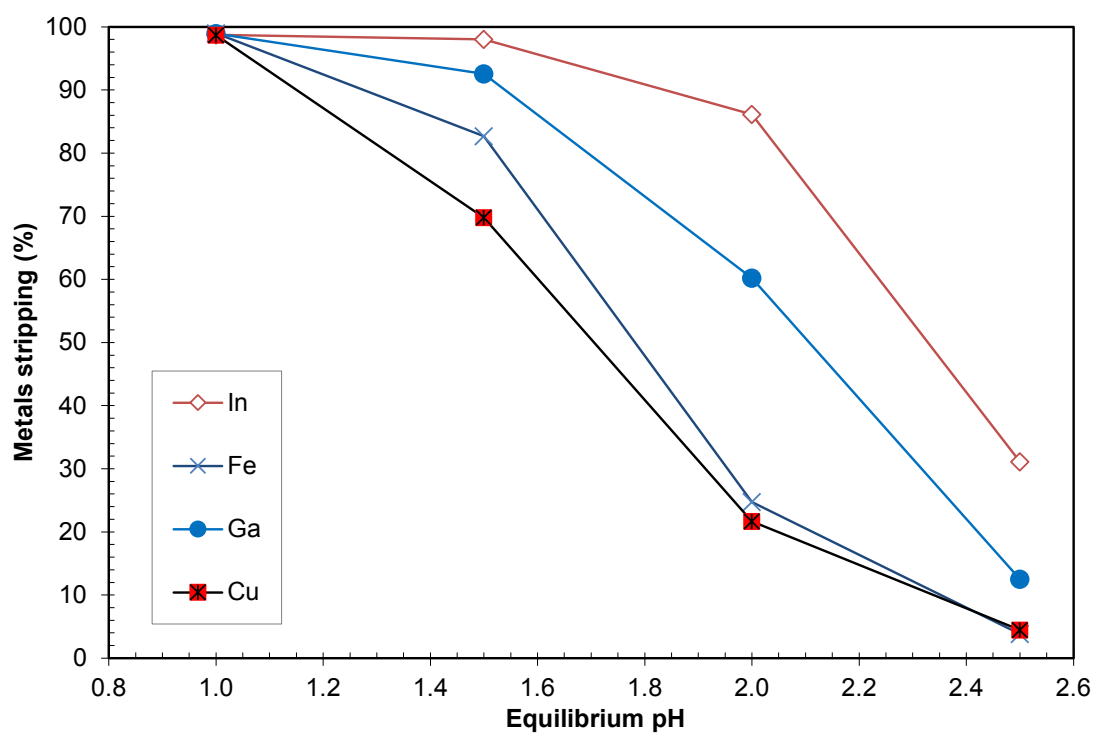


Figure 2. Metal stripping pH isotherms with loaded 0.25 M LIX 63 and 0.20 M Versatic 10.

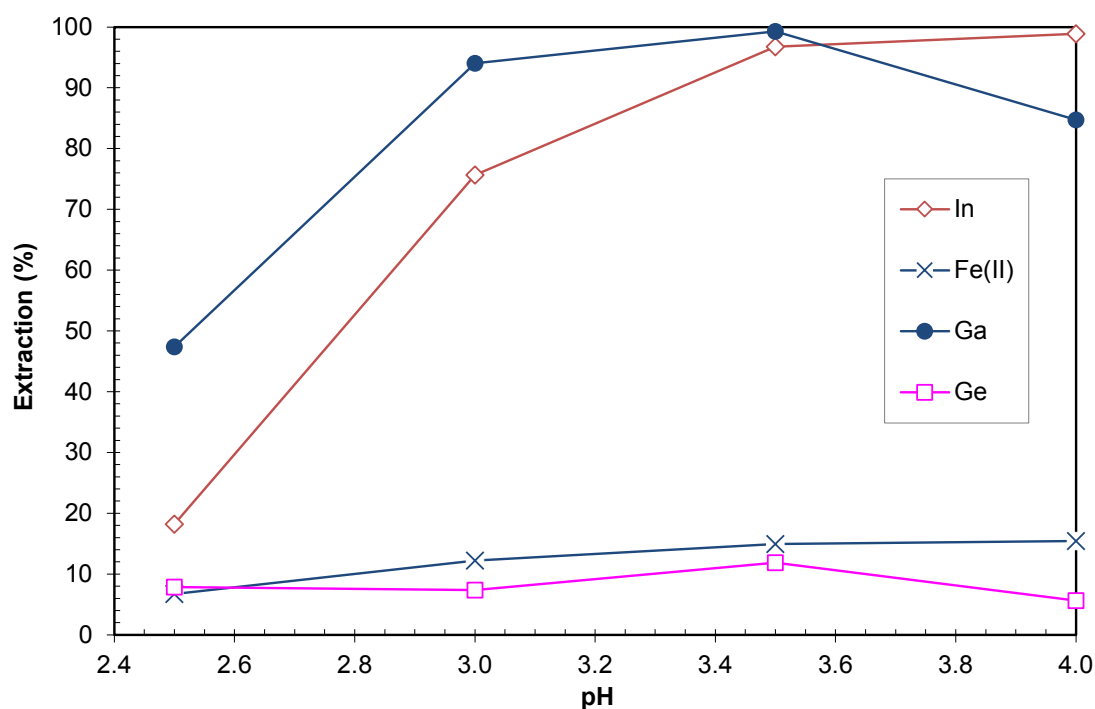


Figure 3. Metal extraction pH isotherms with the 0.25 M LIX 63/0.20 M Versatic 10 organic solution system.

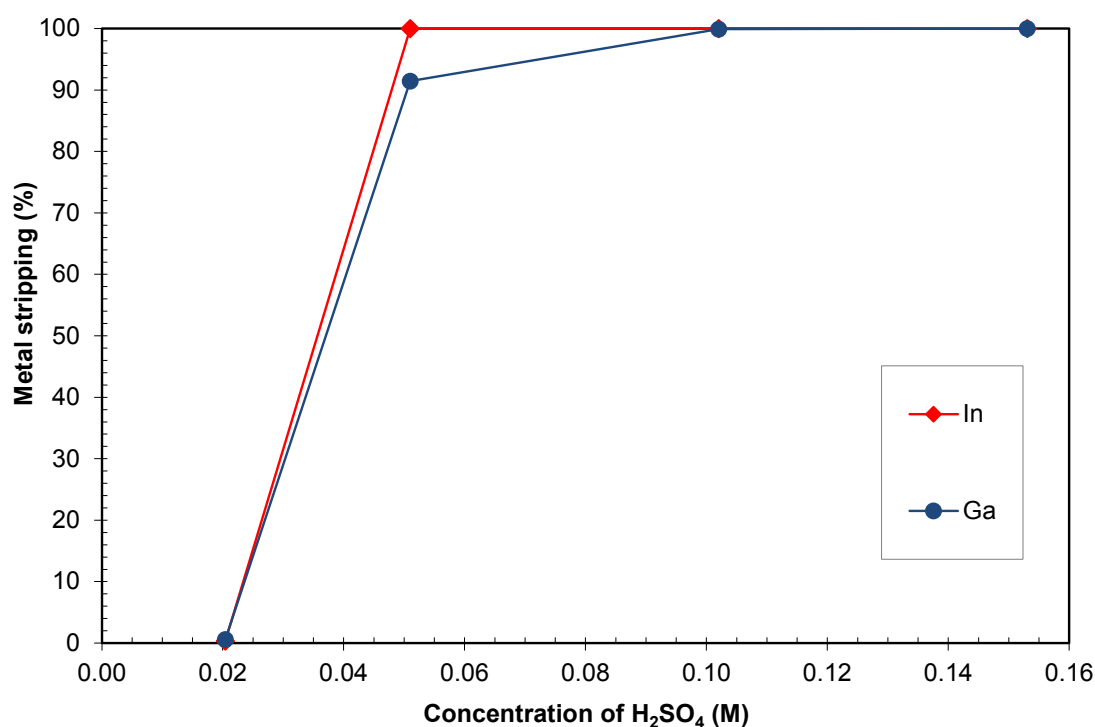


Figure 4. Metal stripping acidity isotherms with the 0.25 M LIX 63 and 0.20 M Versatic 10 system.

Effect of organic system composition

The synergistic effect on the extraction of indium and gallium was determined with two synthetic solutions containing 1 g/L In(III) and 1 g/L Ga(III), separately, and the organic solutions with different fractions of LIX 63 and Versatic 10 in ShellSol D70 for a total concentration of 0.24 M of the extractants at an O/A ratio of 1, pH 3.0 and 40

°C. It was found that over 86% In and 92% Ga were extracted with 50% or 0.12 M LIX 63 and 50% or 0.12 M Versatic 10 (Figure 5). The extraction of indium and gallium with the LIX 63 alone system was 5% and 74%, respectively, and the Versatic 10 alone system 25% and 30%, respectively, suggesting very strong synergistic effect on indium extraction, but weak or no synergistic effect on gallium extraction with the mixed LIX63/Versatic 10 system. The optimum pH for In and Ga extraction was found to be 3.0 with the selected organic composition.

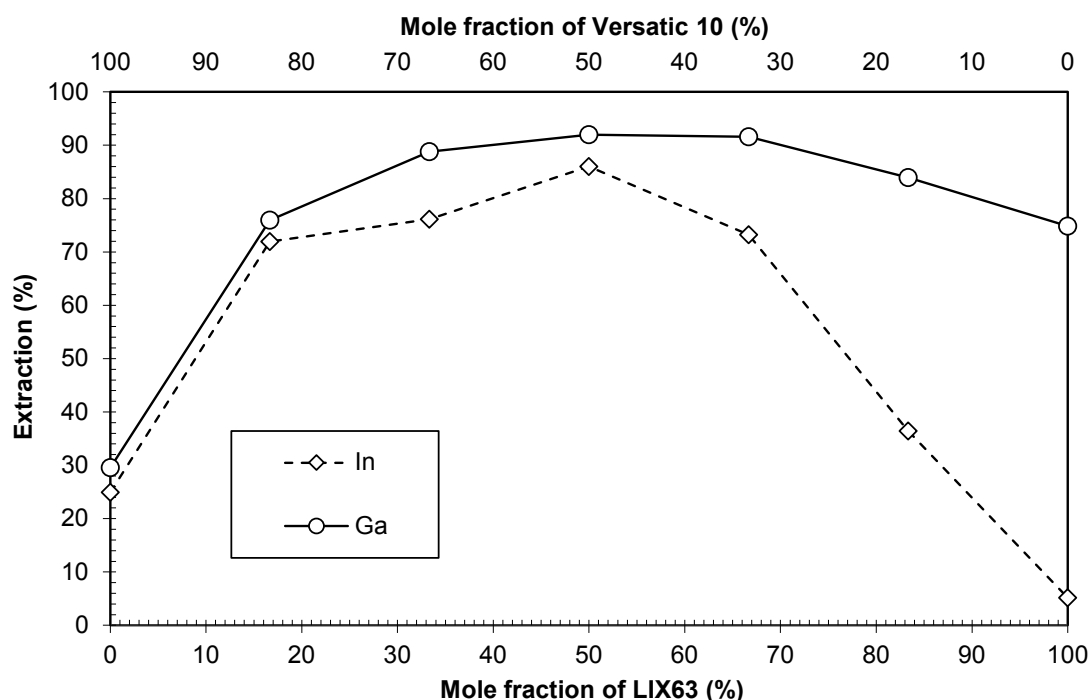


Figure 5. Extraction of indium and gallium with different fractions of Versatic 10 and LIX 63 system.

Conclusions

A mixed extractant system consisting of LIX63 and Versatic 10 was selected and developed to separate and recover In and Ga from synthetic sulphuric acid leach solution of zinc refinery residues. After Fe(III) reduction and Cu removal, 97% In and 99% Ga were extracted while only 15% Fe(II) and 12% Ge was co-extracted at pH 3.5 with the organic system consisting of 0.25 M LIX 63 and 0.20 M Versatic 10 in ShellSol D70 at an A/O ratio of 1 and 40 °C. The small amounts of co-extracted Fe(II), Ge, Ni and Co would be crowded out or scrubbed in counter-current operation. Almost 100% In and 91% Ga were stripped with 0.05 M H₂SO₄ solution.

For synthetic feed solutions containing 1.0 g/L In and Ga, respectively, the selected organic solution composition was 0.12 M LIX 63 and 0.12 M Versatic 10 in ShellSol D70. With the selected organic system, the optimum extraction pH for both In and Ga was 3.0. It was found that the synergistic effect on indium extraction was very significant, but that on gallium extraction was weak or nil with the mixed LIX63/Versatic 10 system. The novel SSX system has a great potential for the recovery of In and, especially Ga from leach solutions of zinc refinery residues.

Acknowledgement

The authors would like to thank Mr Yoko Pranolo and Mr Nicholas Kelly for technical assistance and Dr Keith Barnard for reviewing the manuscript and providing valuable

comments. The support of the CSIRO Minerals Down Under National Research Flagship is gratefully acknowledged. One of authors (S. Nusen) thanks the funding from Thailand Research Fund and Padaeng Industry Public Company Limited through the Royal Golden Jubilee PhD Program (RGJ. -Industry, Grant No. PHD/0111/2552) and also from the Graduate School of Chiang Mai University, Thailand.

References

- Aavila, R. M., Cote, G., Bauer, D., 1992. Recovery of In (III) from Mixed Hydrochloric Acid - Sulphuric Acid Media by Solvent Extraction with Cyanex 301®. *Solv. Extr. Ion Exch.* **10**, 811–827.
- Fortes, M.C.B., Martins, A.H., Benedetto, J.S., 2003. In Recovery from Acidic Aqueous Solutions by Solvent Extraction with D2EHPA: A Statistical Approach to the Experimental Design. *Braz. J. Chem. Eng.* **20**, 121–128.
- Judd, J.C., Harbuck, D.D., 1990. Ga Solvent Extraction from Sulfuric Acid Solutions Using OPAP. *Sep. Sci. Technol.* **25**, 1641–1653.
- Katsura, T., Abe, H., 1975. Solvent Extraction of In and/or Ga. *US Patent 3920450 A*.
- Levin, I.S., Shatalova, A.A., Azarenko, T.G., Vorsina, I.A., Burtovaya-Balakireva, N.A., Rodina, T.F., 1967. Concentration and Separation of In, Ga, Thallium, Antimony and Bismuth by Extraction with Alkylphosphoric acids. *Talanta* **14**, 801–808.
- Mihaylov, I., Distin, P.A., 1992. Gallium Solvent Extraction in Hydrometallurgy: An Overview. *Hydrometallurgy* **28**, 13–27.
- Paiva, A.P., 2001. Recovery of In from Aqueous Solutions by Solvent Extraction. *Sep. Sci. Technol.* **36**, 1395–1419.
- Sato, T., Sato, K., 1992. Liquid-liquid Extraction of In (III) from Aqueous Acid Solutions by Acid Organophosphorus Compounds. *Hydrometallurgy* **30**, 367–383.
- Tomii, K., Tsuchida, H., 1981. Solvent Extraction Recovery Process for In. *US Patent 4292284 A*.
- Violainen, S., Ibane, D., Paatero, E., 2011. Recovery of In from In Tin Oxide by Solvent Extraction. *Hydrometallurgy* **107**, 56–61.
- Yang, J., Retegan, T., Ekberg, C., 2013. In Recovery from Discarded LCD Panel Glass by Solvent Extraction. *Hydrometallurgy* **137**, 68–77.
- Zhou, T., Zhong, X., Zheng, L., 1989. Recovering in, Ge and Ga from Zinc Residues. *JOM* **41**, 36–40.

A new process design for lignite extraction by immersion

*M. Wollmerstädt¹, F. Fehse¹, V. Herdegen^{*1}, H.-W. Schröder¹,
T. Naundorf², J.-U. Repke¹*

Summary

The extraction of lignite is executed today in a belt extractor in industrial scale obtaining the intermediate montan wax. The new proposed process design allows the establishment of immersion for montan wax extraction. The immersion overcomes drawbacks from the percolation in the belt extractor process, also offering some advantages regarding extraction kinetics for example. But new challenges arise concerning material processing for a separation of solid from the miscella. This was achieved on one hand by an agglomeration forming stable granules and on the other hand by a powerful separation step by a filter or a decanter unit. The wax yields in immersion could be uniformly increased to 85 % – 95 % simultaneously at a much shorter operation time of ca. 20 minutes in two different scales of stirred tanks (1L and 50L).

Introduction

In industrial scale, lignite extraction is done nowadays with dried and comminuted particles in a belt extractor. The product montan wax is an amphoteric ester wax and has numerous applications from polishes to cosmetics. The upcoming change in lignite quality will lead to an inefficient extraction due to occurring particle decay.

In the scope of the academic-industrial research project “ibi – Innovative Brown Coal Integration in Central Germany” [1], a new extraction process is developed. The new process in terms of immersion extraction should offer also an intensified mass transport, accompanied by an increase in extraction yield to over 90 %. While comminuted lignite particles would lead to inseparable slurries, only the use of agglomerates with its high mechanical strength enables the application of immersion. For the downstream processing after extraction, a powerful solid-liquid separation is established.

Montan wax extraction by immersion

New Process design

The new proposed process design for the immersion extraction of montan wax from lignite is schematically shown as follows:

^{*1} Volker.Herdegen@tu-freiberg.de; Institute of Thermal, Environmental and Natural Products Process Engineering, TU Bergakademie Freiberg, Leipziger Straße 28, Freiberg/ Germany

²ROMONTA Unternehmensgruppe, Seegebiet Mansfelder Land/ Germany



Figure 1. Schematically process design of the new immersion extraction of lignite

Raw lignite is mined, comminuted and agglomerated in wet state (ca. 45 – 50 wt% moisture content) by the optional addition of an agglomeration additive. Afterwards the wet agglomerates are dried before being extracted in a stirred tank with an organic solvent at elevated temperatures. At the end of extraction period, the leached agglomerates have to be separated from the so-called miscella (loaded solvent). This was simply achieved in the conducted experiments by one-stage filtering in a filter bag. The miscella is afterwards still contaminated with small amounts of suspended ultra-fine solids which can be separated by a decanter or a membrane unit.

Agglomeration of lignite particles

As is well known, the solid pre-treatment strongly influences the solid/ liquid extraction process. This is especially true for natural material extraction. Nowadays, mined lignite from deposit is milled mainly by a hammer mill, dried and sieved until an extractable and conveyable grain size distribution is reached. The drying until specific moisture content in the range of 15 wt% to 20 wt% leads to the mechanical particle strength.

By the new investigated process of lignite treatment, favorable mechanical properties are achieved, which facilitates the set-up of immersion extraction. The new developed preparation is based on comminuting and afterwards agglomeration of the ultra-fine primer particles with an agglomeration additive. The produced granules gain its strength also by drying, as lignite in general does. The favorable agglomerates (shown in Figure 3) can be obtained in different processing chains; exemplary processing chains are shown in Figure 2:

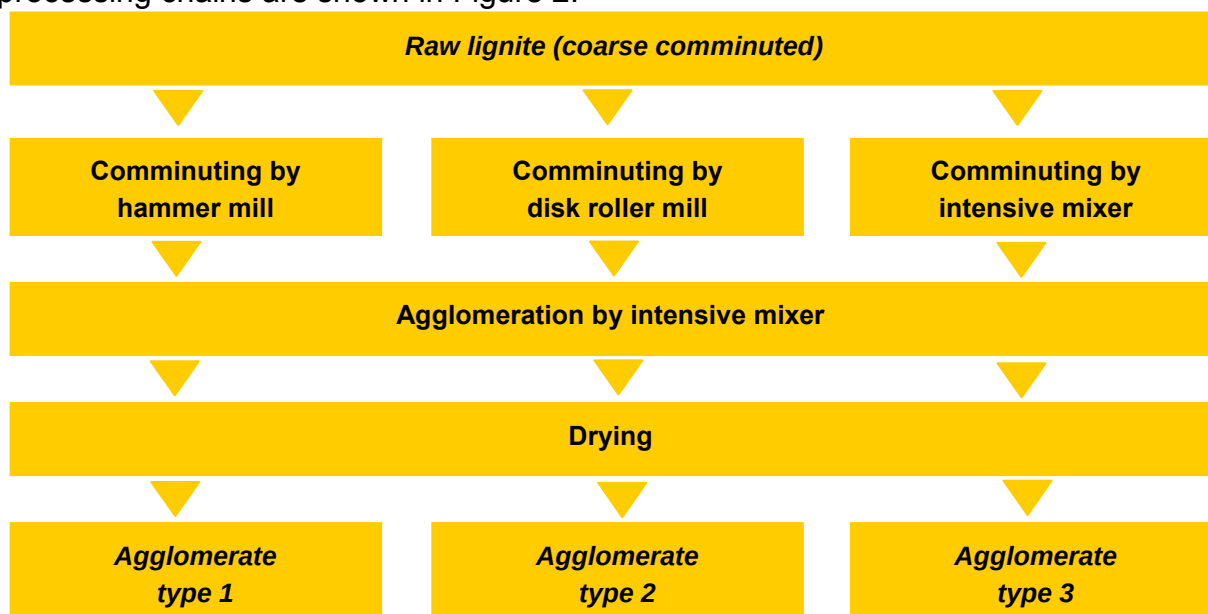


Figure 2. New proposed processing chains for the agglomeration of lignite for immersion

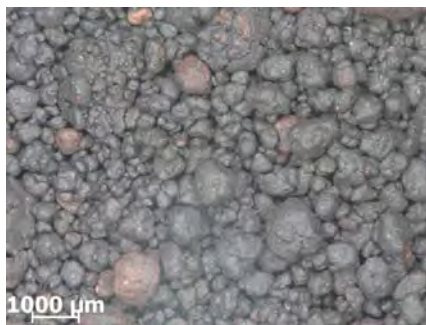


Figure 3. Picture of exemplary agglomerate from lignite by the new proposed processing chains

Details of the different processing chains and of the method of generating lignite agglomerates can be found elsewhere [2, 3]. One advantage of agglomeration is the narrower grain size distribution of agglomerates in comparison to nowadays' feed (see Figure 4).

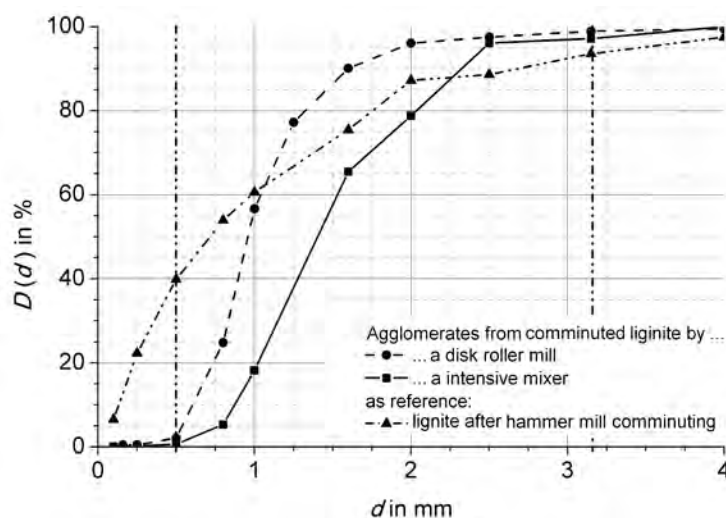


Figure 4. Exemplary particle size distribution of comminuted lignite and agglomerated lignite by two different processing chains (dried to 18 % moisture content)

While state of the art comminuted raw lignite by a hammer mill leads to size distributions after drying of 0/5 mm, the new processing chains (agglomerates after type 2 and 3) allows ranges of 0.5/2 mm, respectively 0.5/3 mm like is shown in the displayed figure. But it is possible to even narrower the distribution ranges and to shift it to lower mean particle sizes, for example 0.5/1 mm. The mentioned set-parameters have to be adapted for the different processing chains, the objective size distribution, and the raw materials.

A second advantage of the agglomerates lies in the higher mechanical strength of the granules and their bulks. The mechanical characteristics are determined by a special stress test [4] and analysis sieving.

Analytical extraction apparatus

At first, an analytical extraction of lignite samples with differing processing was executed in an advanced apparatus of Graefe [5] as reference. The wax extraction

yield after complete leaching as well as the kinetics of extraction can be measured hereby at boiling temperature depending of the particular solvent.

Basic data of maximal extraction yields and extraction kinetics were determined for different processed lignite and various organic solvents. Figure 5 shows the normalized extraction yield of elected organic solvents based on the solvent toluene as standard solvent.

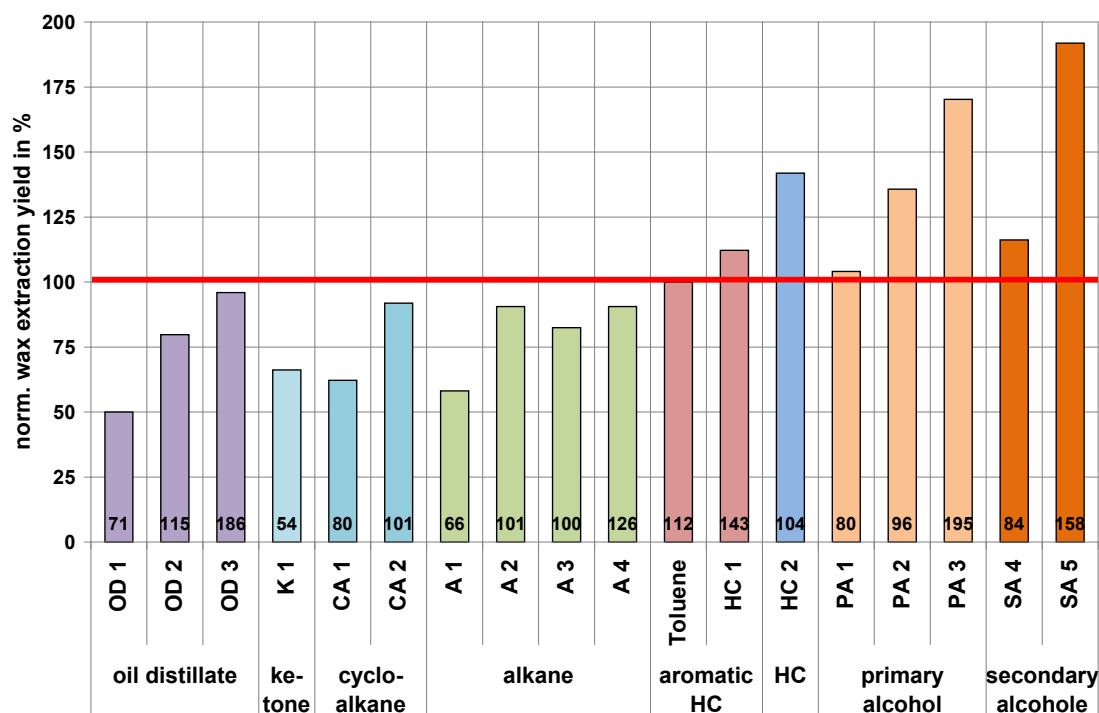


Figure 5. Relative extraction yield of montan wax from lignite of elected organic solvents (sorted by its boiling point and substance class) by analytical extraction of Graefe

It will fall short if only solvents will be considered with wax yields over 100 % (thus more extract than achievable with toluene), because also the wax quality has to be taken into account. So, interesting solvents were selected from above shown solvent screening based on its specific extraction yields, its kinetics and its handling for scale-up investigations in 1L-scale and in 50L-scale later-on.

Extraction kinetics

The extraction kinetic should be increased in a stirred tank compared to ongoing mass transfer in belt extractor. Due to higher solvent velocity, lower boundary layers are formed on the surface of suspended agglomerates and higher transfer rates occurs as a consequence. Besides, the expected higher porosity of the agglomerates and the smaller mean particle size of primary particles forming the agglomerates have also a positive impact on extraction kinetics.

The extraction kinetic, montan wax yield, and the material behavior were investigated systemically in 1L- and 50L-immersion-scale (see Figure 6).



Figure 6. Photos of the two different used laboratory scales of immersion: 1L (left) and 50L (right)

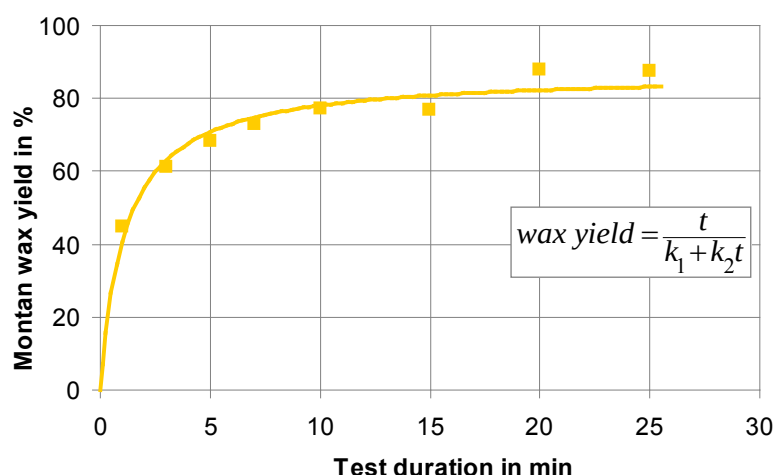


Figure 7. Exemplary extraction curve for one agglomerate in 1L-scale, extracted at 80 °C with toluene; curve by displayed empirical model equation

The following influencing parameters were considered: Solvent, solvent-solid-ratio, extraction temperature, stirrer revolutions, and different particle size distribution.

Figure 7 displays a fitted extraction curve for one agglomerate and toluene at 80 °C for the 1L-scale exemplarily:

In general, the duration of extraction sets could be decreased from 2 h for the industrial extraction process to almost 20 min in single-stage immersion. The extraction process can be described well by an empirical model equation offering a rate constant k_1 and a capacity constant k_2 . The wax yields out of lab-scale extraction (1L and 50L-tank) of the used lignite samples were increased

simultaneously to 85 % – 95 %. The agglomerates, which were produced by the three possible material processing chains, offer a higher stability against mechanical stress and chemical attack. The decay of lignite agglomerates takes mainly place for larger and therefore “weaker” agglomerates; the amount of unwanted and problematic undersize is relatively low.

Solid separation

As last process step, extracted particles have to be separated from the solution. A filter bag with a pore size of 5 µm was very powerful to remove all agglomerates and fine particles from the miscella. For obtaining high montan wax purity after desolventizing, also the remaining suspended ultra-fine particles have to be held out. This could be achieved by using a decanter or a filter unit alternatively. Retention rates of over 90 % and respectively almost 100 % for the filter unit were reached in preliminary experiments. Though, an effective clarification of miscella is established by the mentioned process steps, but detailed results on the two purification devices are still receivable for the ongoing experimental investigations.

Conclusion

The overall process concept and selected experimental results of the new developed process were illustrated, starting from producing lignite agglomerates as important bases for using immersion principle. The agglomeration leads to narrow size distributions and to stabile particles for the following suspension in the organic solvent. The extraction kinetic in the immersion process is largely increased by lower mass transfer resistances down to 20 min compared with 2 h from industrial percolation process. Solvent, solvent-solid-ratio, extraction temperature, stirrer revolutions, and different particle size distribution have been taken into account as influencing parameters and its influence on mechanical properties of the agglomerates. Overall wax yields as high as 85 % to 95 % were achieved based on analytical extraction method. The separation of solids and particulate matters can be set-up by combination of a coarse clarification unit for mainly agglomerates and a device for removing the ultra-fine particles.

Acknowledgements

The research was part of the Growth Core “ibi – Innovative Brown Coal Integration in Central Germany”. The authors are grateful to the partners ROMONTA Unternehmensgruppe and EPC Technology Group and to the Innovation Initiative “Entrepreneurial Regions” (Federal Ministry of Education and Research, Germany) for the financial support.

References

- [1] Website of research project “ibi – Innovative Brown Coal Integration in Central Germany”, <http://ibi-wachstums-kern.de/tl/index.php>, as per march 2014
- [2] Fehse, F., Herdegen, V., Schröder, H.-W., Repke, J.-U., Zielgerichtete Einstellung der Körnung und der mechanischen Stabilität von Braunkohlengranulaten [Specific setting of size distribution and mechanical stability of agglomerates from lignite]. Chemie Ingenieur Technik 2014, 3 (86), 318-327, DOI: 10.1002/cite.201300106
- [3] Fehse, F., Herdegen, V., Schröder, H.-W., Repke, J.-U.: New Processing of Brown Coal for Montan Wax Extraction. International Coal Preparation Congress. Conference Proceedings, Özbayoglu, G. and Arol, A.I. (Ed.). October 1st - 6th 2013, Istanbul. ISBN: 978-605-64231-0-9
- [4] Lehmann, B., Schröder, H.-W., Wollenberg, R., Repke, J.-U., Effect of miscanthus addition and different grinding processes on the quality of wood pellets. Biomass Bioenergy 2012, 44, 150–159.
- [5] Dierichs, A., Ludwig, F., Chemie der Kohle [Chemistry of Coal], VEB Deutscher Verlag der Wissenschaften, Berlin (GDR) 1959.

Lithium Discriminating Extraction with Tripropyl-Monoacetic Acid Derivative of Calix[4]arene

*Keisuke Ohto^{*1}, Hirotoshi Sadamatsu¹, Shintaro Morisada¹, Hidetaka Kawakita¹*

A series of *p*-t-octylcalix[4]arene derivatives with coordinatively-inert propyl and/or ion-exchangeable acetic acid groups were prepared to compare extraction behavior of alkali metal ions. Tripropyl-Monoacetic acid derivative sterically arranged by three propyl groups exhibited selectivity for smaller lithium among five alkali metal ions, while the other ion-exchangeable derivatives prepared in the presence of sodium as a templating ion exhibited sodium selectivity. It completely selectively loaded lithium in the competitive system of alkali metal ions. The complexation behavior was also supported by ¹H-NMR spectra before and after metal loading on the derivative. It was concluded that the coordinatively-inert propyl groups significantly affected the metal selectivity.

Introduction

Calixarenes are macrocyclic compounds prepared by condensation reaction of the corresponding phenol with formaldehyde. Their derivatives have been employed extensively as host compounds in host-guest chemistry and exhibited size-discriminating property due to the specific cyclic framework.^{1,2} In our previous work, it was found that tetraacetic acid derivative of calix[4]arene exhibited high sodium selectivity among three alkali metal ions and simultaneously loaded two sodium ion by allosteric self-coextraction mechanism.^{3,4} Crossed carboxylic acid type of calix[4]arene derivatives containing two longer carboxylic acids (from butanoic to hexanoic acids) and two acetic acids at distal position were also prepared to investigate alkali metal extraction.⁵ Three crossed type of calix[4]arene derivatives exhibited sodium extraction selectivity among three alkali ions, although their extraction abilities were lower compared with calix[4]arene tetraacetic acid derivative. In our recent work, diacetic acid-dipropyl crossed type of calix[4]arene derivative was also prepared to investigate alkali metal extraction.⁶ It also exhibited sodium selectivity. Since *p*-t-octylcalix[4]arene tetrol, a mother compound of such derivatives was originally prepared by using sodium base for templating,⁷ it is easy to expect that most of the calix[4]arene derivatives exhibit sodium selectivity among alkali metals. In this work, the diacetic acid-dipropyl crossed derivative formed 1 : 2, 2 : 3, 1 : 1 (extraction reagent : metal) complexes with lithium, sodium, potassium ions, respectively in the individual extraction system. In the competitive system, sodium and lithium ions were allosterically loaded up to each 100% in this order, whereas potassium ion was hardly extracted. It was concluded that the different stoichiometries was attributed to the size discriminating property of the second metal ion by two coordinatively-inert propyl groups.

^{*1} Corresponding Author, Department of Chemistry and Applied Chemistry, Saga University, 1-Honjo, Saga 840-8502, Japan
ohtok@cc.saga-u.ac.jp

In the present work, monopropyl-triacetic acid, tripropyl-monoacetic acid, and tetrapropyl calix[4]arenes have been newly prepared to compare alkali metal extraction with the previous extraction reagents. The ^1H -NMR spectra study before and after metal loading on the tripropyl-monoacetic acid derivative was also investigated.

Experimental

Materials

Tetraacetic acid⁷ and diacetic acid-dipropyl⁶ derivatives of *p*-*t*-octylcalix[4]arene were prepared in a similar manner to those reported in previous papers. The monopropyl-triacetic acid, tripropyl-monoacetic acid, and tetrapropyl calix[4]arenes were prepared by the synthetic routes shown in Fig. 1.

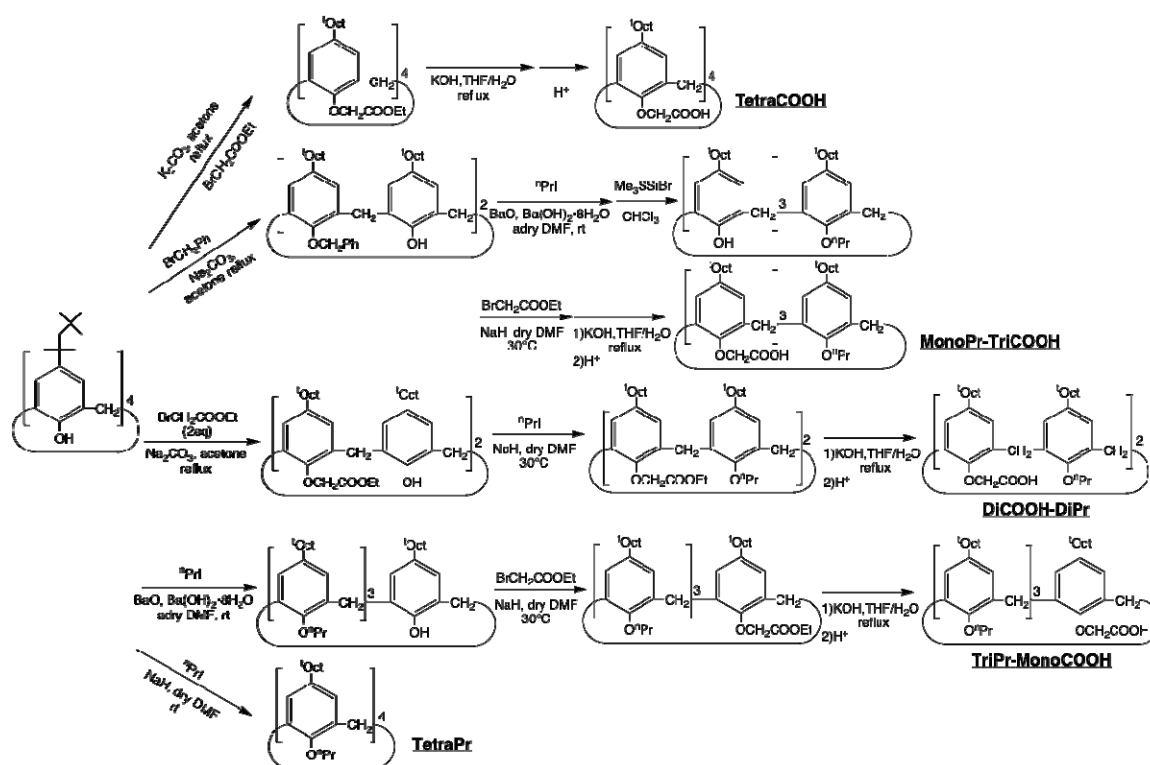


Fig. 1 Synthetic scheme of calixarene derivatives with propyl and/or acetic acid groups and their abbreviations.

Metal Loading

The individual extraction of three alkali ions (lithium, sodium, and potassium ions) was carried out using a conventional batchwise method.⁵ The aqueous solution was prepared by dissolving each alkali hydroxide in 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid) buffer solution to maintain the alkali concentration constant at 0.1 M. The pH was arbitrarily adjusted by adding 0.1 M hydrochloric acid (also to maintain the alkali concentration constant at 0.1 M). The organic solution was

prepared by diluting the extractant in chloroform to 5 mM. Equal volumes (5 cm³) of both phases were added to a test tube and the mixture was shaken at 303 K for 24 h. The pH value of the aqueous solution was measured after the extraction. Furthermore, the equilibrated organic solution (1 cm³) was again mixed with fresh 1.2 M hydrochloric acid (5 cm³) in a teflon-coated bottle. The mixture was shaken at 303 K for 24 h to completely strip the extracted sodium ion. After phase separation, the concentration of sodium ions stripped into the aqueous phase was measured using an atomic absorption spectrometer (AAS, Shimadzu Instruments AA-6800). The sodium extraction was also monitored by ¹H-NMR spectrophotometry. Experimental conditions were nearly the same as those mentioned above except for the use of deuterated chloroform. After equilibrium was reached, the NMR peaks for the extractant used in the organic phase were recorded (using Jeol, JNM-GX300 spectrometer). The competitive extraction of the three alkali metal ions (lithium, sodium, and potassium ions) was also investigated. An aqueous solution was prepared by dissolving these alkali hydroxides in a 0.1 M HEPES solution, with the concentration of each alkali ion being 0.1 M. Subsequent procedures were performed in a similar manner to those described for the individual extraction.

Results and Discussion

Metal Loading

The effects of pH on the loaded percentage of alkali metal ions with the five extraction reagents in individual and competitive systems are shown in Figs. 2(a) – (e) and Figs. 3(a) – (e), respectively. The extraction data for TetraCOOH and DiCOOH-DiPr were referred from the previous papers.^{4,6}

The loaded percentage, %Loading, is defined by eq. (1).

$$\text{Loading}\% = \frac{\text{Amount of alkali metal ion extracted}}{\text{Total amount of extractant}} \times 100 \quad (1).$$

The alkali metal extraction shifted to higher pH region with decrease of the number of acetic acid group in calix[4]arene derivatives due to the decreased complementarity with the same groups. Four ion-exchangeable extraction reagents exhibited pH dependency for alkali metal loading, while the neutral TetraPr hardly loaded any alkali metals in both systems. TetraCOOH and MonoPr-TriCOOH exhibited obvious sodium selectivity, whereas DiCOOH-DiPr exhibited impaired sodium selectivity and TriPr-MonoCOOH finally exhibited lithium selectivity over sodium. Since all molecules of TriPr-MonoCOOH were completely occupied by lithium ion selectively extracted, absolute lithium selectivity was observed in the competitive system. In general, since original calix[4]arene is prepared in the presence of sodium as a templating ion, consequently most of its derivatives exhibit sodium selectivity among alkali metal ions, it is interesting to note that TriPr-MonoCOOH sterically arranged by three propyl groups exhibited selectivity for smaller lithium.

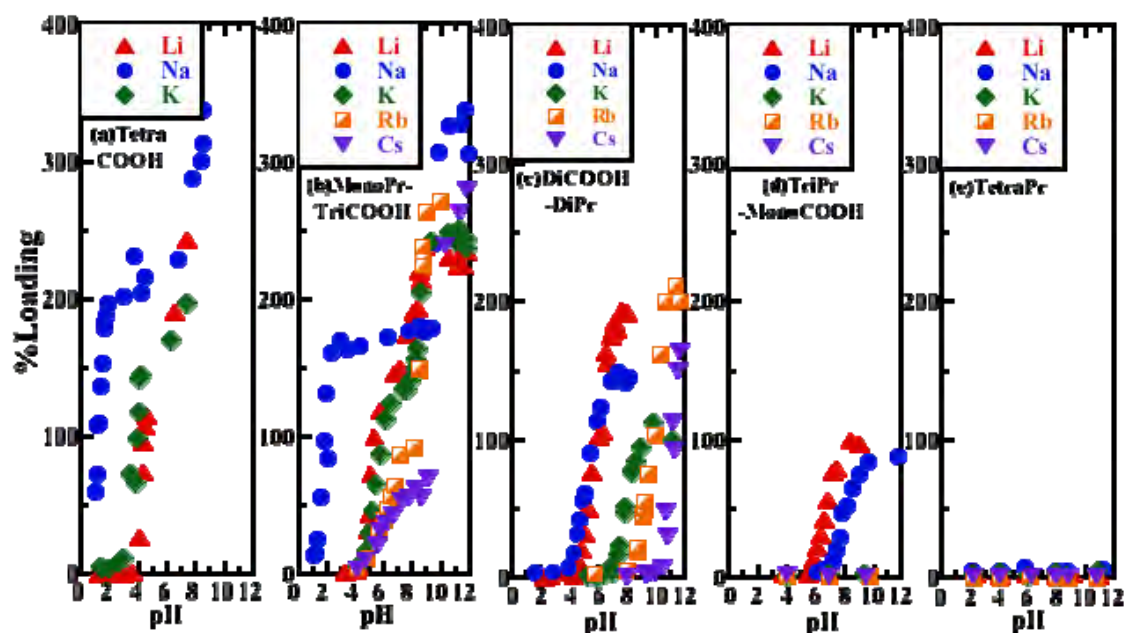


Fig. 2 Effect of pH on alkali metal loading on five calixarene derivatives in individual system.

(a) TetraCOOH⁴, (b) MonoPr-TriCOOH, (c) DiCOOH-DiPr⁶, (d) TriPr-MonoCOOH, (e) TetraPr.

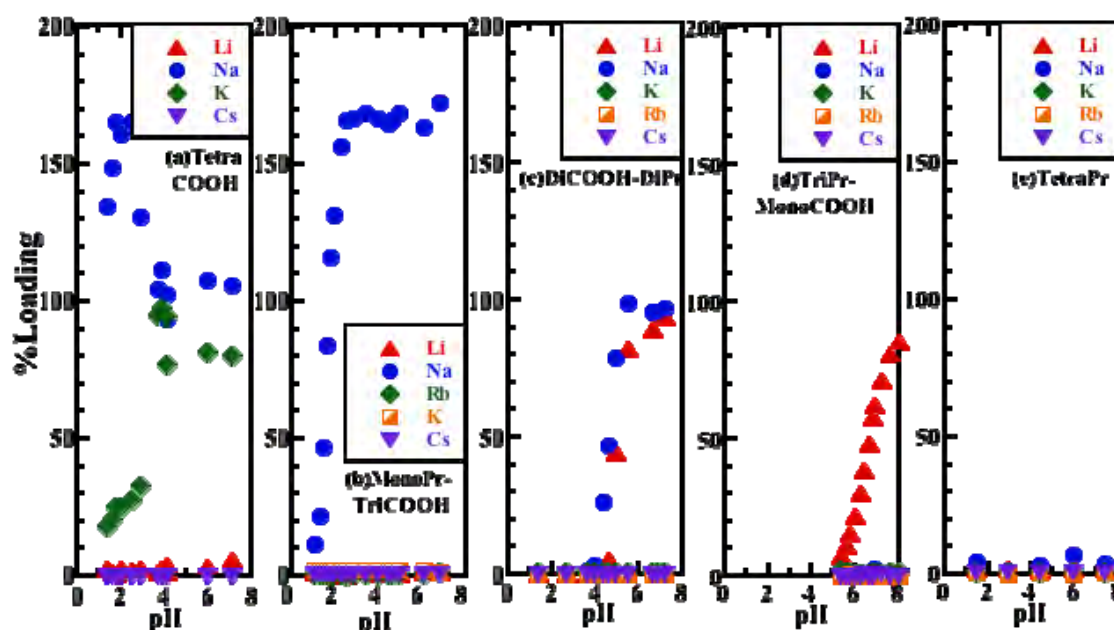


Fig. 3 Effect of pH on alkali metal loading on five calixarene derivatives in competitive system.

(a) TetraCOOH⁴, (b) MonoPr-TriCOOH, (c) DiCOOH-DiPr⁶, (d) TriPr-MonoCOOH, (e) TetraPr.

Similar results for lithium selectivity with mono-ionizable calix[4]arene derivatives were reported by Akabori *et al.*⁸ and Talanova *et al.*⁹ Although the detailed explanation for such specific selectivity was not given, the role of substituted coordinatively-inert propyl groups seems to be meaningful in size-discriminating. That is, TriPr-MonoCOOH substituted with three propyl groups did not saturate the coordination number of metal ions in extracting and incomplete dehydration took

place. Such remaining water molecule(s) would repulsively act with lipophilic groups. It is another specific property for calix[4]arene derivative in cone conformation, whose functional groups direct to the same direction, thus the coordinatively-inert lipophilic groups can be placed on the coordination site made by polar groups. Such concept would be employed to design novel type of the extraction reagents.

¹H-NMR study

It was reported that cyclic structures of calix[4]arenes derivative was changed with metal loading and was observed as shifted peaks in ¹H-NMR spectra.^{4,6} The ¹H-NMR spectra of TriPr-MonoCOOH before and after metal loading were measured. The spectra before and after lithium or sodium loading in both systems together with the shifted percentage of the aryl peaks (%S) and the loading percentage of metal ions (%L) are shown in Fig. 4. The shifted percentage, %S, is defined by eq.(2).

$$\%S = \frac{\text{Integral ratio of aryl peak shifted}}{\text{Total integral ratios of aryl peaks}} \times 100 \quad (2).$$

The ¹H-NMR spectra of TriPr-MonoCOOH in competitive system after metal loading was almost same with that in Li individual system. Selective loading of lithium on TriPr-MonoCOOH shown in Fig. 3(d) was also supported with the result.

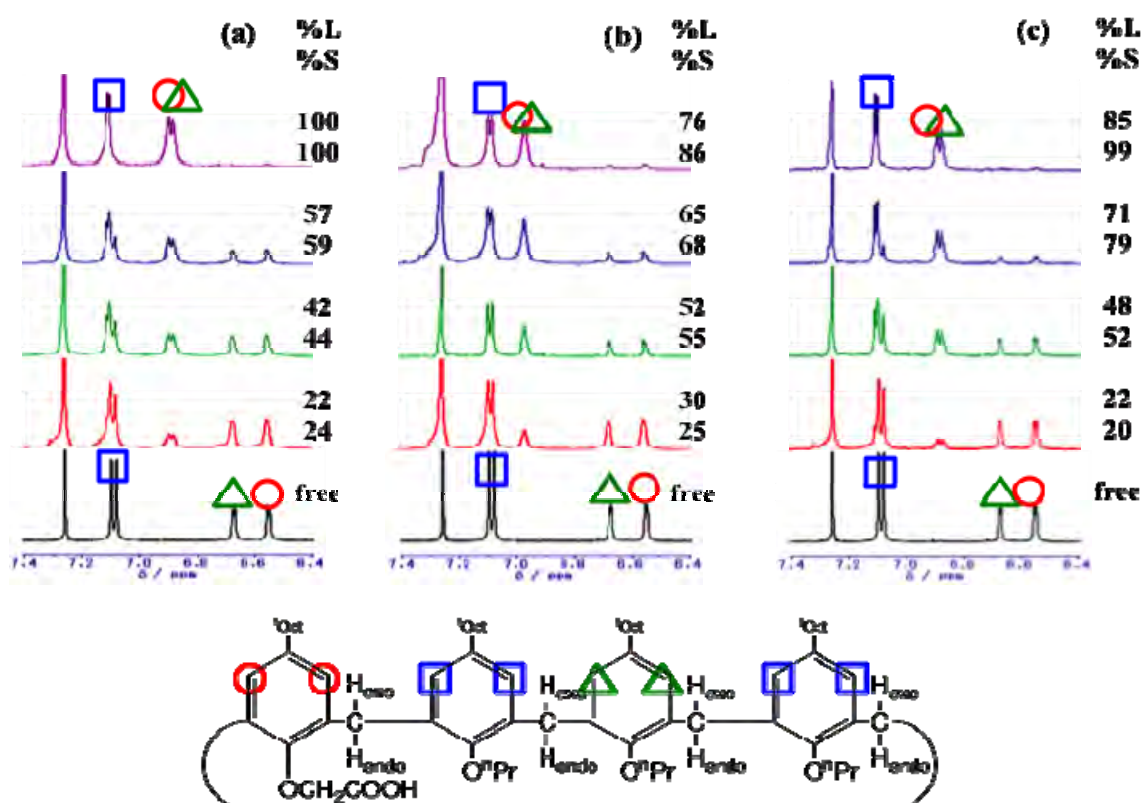


Fig. 4 ¹H-NMR spectra of TriPr-MonoCOOH before and after metal loading. (a) Li individual system, (b) Na individual system, (c) Competitive system.

Asymmetrical elliptic structure as free TriPr-MonoCOOH was changed to more circular-shaped one after metal loading. Compared with Figs. 4(a) and (b), distance between blue-marked peak, and red- and green-marked ones for lithium-loading TriPr-MonoCOOH was broader than that for sodium-loading one. It meant that cyclic structure of the lithium complex was more distorted than that of the sodium one, which was more equivalent and circular-shaped. The distorted structure arranged by three lipophilic propyl groups would affect the size-discrimination for smaller lithium ion.

Acknowledgement

This work was financially supported by “The Environment Research and Technology Development Fund, No. 3K-123022, from the Ministry of the Environment, Government of Japan”.

References

- 1) K. Ohto, Solvent Extr. Res. Dev., Jpn., 17 (2010) 1 - 18.
- 2) K. Ohto, Ion Exch. Solvent Extr., 21 (2013) 81 - 127.
- 3) K. Ohto, H. Ishibashi, K. Inoue, Chem. Lett., (1998) 631 - 632.
- 4) K. Ohto, H. Ishibashi, H. Kawakita, K. Inoue, T. Oshima, J. Incl. Phenom. Macrocycl. Chem., 65 (2009) 111 - 120.
- 5) T. Yoneyama, H. Sadamatsu, S. Kuwata, H. Kawakita, K. Ohto, Talanta, 88 (2011) 121 - 128.
- 6) H. Sadamatsu, T. Yoneyama, S. Morisada, H. Kawakita, K. Ohto, Solvent Extr. Ion Exch., submitted.
- 7) K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, T. Nagasaki, Anal. Sci., 11 (1995) 893 - 902.
- 8) S. Akabori, H. Itabashi, H. Shimura, M. Inoue, Chem. Commun., (1997) 2137 - 2138.
- 9) G. G. Talanova, V. S. Talanov, H. -S. Hwang, B. A. Eliasi, R. A. Bartsch, J. Chem. Soc., Perkin Trans. 2, (2002) 1869 - 1874.

New reagents for uranium(VI) extraction from concentrated phosphoric acid

*Denis Beltrami^{1,2}, Alexandre Chagnes¹, Hamid Mokhtari², Bruno Courtaud²,
Gerard Cote¹*

¹ ENSCP - Chimie ParisTech, Laboratoire d'Electrochimie, Chimie aux Interfaces et Modélisation pour l'Energie (LECIME, UR CNRS 7575), Paris, France

² AREVA Mines, Service d'Etudes de Procédés et Analyses (SEPA), Bessines-sur-Gartempe, France.

Wet Phosphoric Acid (WPA), whose concentration is typically ranging between 4 and 6 mol.L⁻¹, is a strategic source of uranium that can be exploited in spite of the low uranium content (0.1-0.4 g.L⁻¹) and its strong complexing power. Numerous studies concerned the development of synergic mixtures of extractants for the recovery of uranium (VI) from wet phosphoric acid but most of the extractants are not sufficiently selective towards iron. In this paper, the extraction of uranium (VI) from 5.3 mol.L⁻¹ phosphoric acid with a series of phosphoric, phosphinic, dithiophosphoric or dithiophosphinic acid derivatives (0.5 mol.L⁻¹) in mixture with 0.125 mol.L⁻¹ TOPO as well as a series of neutral organosphosphorus synergistic reagents (0.125 - 0.250 mol.L⁻¹) in mixture with 0.5 mol.L⁻¹ bis(2-ethylhexyl) phosphoric acid (D2EHPA) in Isane IP 185 has been investigated. The properties of these molecules in mixtures with TOPO have been compared with other extractants. The replacement of phosphoric acid-type extractant by their phosphinic homologues dramatically decreases the affinity for uranium (VI) whereas the replacement of the phosphoric and phosphinic acid-type extractants by their dithio homologues affects positively the distribution coefficient of uranium (VI). It also appears that hindrance effect is responsible for a significant decrease of the distribution coefficient of uranium (VI). It also appears that the presence of oxygen atoms at the vicinity of the phosphorus atom in the hydrophobic chains of the synergistic reagents lowers significantly the extraction properties of uranium (VI) from concentrated phosphoric acid. Conversely, the increase of the hydrophobicity of the synergistic reagents by increasing the number of carbon atoms in their hydrophobic chains is responsible for an improvement of the extraction efficiency of uranium (VI).

Synthesis of High Purity Didecylphosphinic Acid for Extraction of Heavy Rare Earth

Linyan LI, Shengming XU, Xuejun WANG, Xin LIU

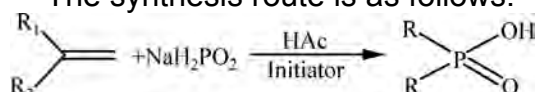
Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China

Introduction

Dialkyl phosphinic acids are an important extractant whose separation and stripping performance for Ni/Co and rare earths is significantly better than other organophosphorus acids such as D2EHPA and PC88A. So far the only commercial extractant of dialkyl phosphinic acid is di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272) because other commercial olefin except diisobutene which provide alkyl is readily to self-polymerize during the synthesis process. Herein, synthesis of high purity didecylphosphinic acid (DDPA) by using branched decene which is the by-product from hexene production and its extraction property for heavy rare earth is reported.

Synthesis

The synthesis route is as follows:



The olefin is the mixture of 2,7-dimethyl octene-1 (50%) and 3-methyl nonene-1 (50%). The synthesis is carried out under atmospheric pressure, while Cyanex 272 is synthesized under high pressure of 30-50 MPa, which is difficult to achieve. The optimal synthesis condition which afford yield of 98.5% and purity of 81% is as follows: $T = 130^\circ\text{C}$, $n(\text{olefin}):n(\text{NaH}_2\text{PO}_2)=2.5:1$, initiator is di-*t*-butyl peroxide.

Purification

The method of copper salt crystallization was used to purify DDPA. The product (71.2% overall yield based on NaH_2PO_2 , 96.7% of purity based on HPLC) was characterized by $^1\text{H-NMR}$, $^{31}\text{P-NMR}$ and ESI-MS. $^1\text{H-NMR}(\delta, \text{ppm}, \text{CDCl}_3)$: 0.89 (m, 15H, 5CH₃), 1.26 (s, 20H, 10CH₂), 1.61 (m, 7H, 3CH, 2CH₂P), 11.79 (s, 1H, OH); $^{31}\text{P-NMR}(\delta, \text{ppm}, \text{CDCl}_3)$: 60.86 (s, P); ESI-MS m/z : 346[M-H]⁻.

Saturated capacity of Tm, Yb and Lu

Extraction condition: HCl medium, $c(\text{DDPA}) = 1\text{mol/L}$; $c(\text{Ln}^{3+}) = 1\text{mol/L}$, O/A = 1:1, contact time = 15min. The extraction tests show that the saturated capacity of Tm, Yb and Lu are about 0.11mol/L which is higher than that of Cyanex 272.

Separation factor(β) for Tm, Yb and Lu

Extraction condition is ditto, and equilibrium pH is about 1.5. The separation factors of P507, Cyanex272 and DDPA for Tm, Yb and Lu are listed as follows:

Extractant/ β	P507	Cyanex272	DDPA
Yb/Tm	1.57	2.91	2.77
Lu/Yb	1.12	1.69	1.62

Stripping acidity for the maximum Lu-loaded complex

To achieve 95% strip rate, the stripping acidity (HCl) for the maximum Lu-loaded complex of P507, Cyanex272 and DDPA is about 5.0, 2.5 and 2.5 mol/L respectively.

Conclusions

DDPA prepared from the by-product from hexene production under mild condition exhibit excellent performance on the separation and stripping of rare earths.

CFD simulation of Mixer-Settler systems; Effect of fluid's volume flow rate on the flow pattern and separation of phases.

*O.Kazemi¹, E. Keshavarz Alamdari^{1, *}*

Summary

In this study, the flow pattern of the fluids and separation behavior of aqueous-organic phases in the Sarcheshmeh Copper Complex-Iran, in presence of several flow rates are investigated using a computational fluid dynamics (CFD) modeling code. In order to verify the simulation and equation set up, the results is compared with Sadeghi et al.'s work. The fluid behavior and field measurement have been studied by solving Navier-stocks equations along with standard K- ϵ turbulence model. Eulerian-Eulerian two phase model is used to model the two phase interactions. Results showed that the fluid's flow rate has a significant effect on the performance of the settler. Reducing flow rate to 1000 m³/h would result a uniform flow pattern. The phase separation becomes more uniform and cleaner and also the dispersion band becomes shorter.

Key Words: Solvent Extraction, CFD, Mixer settler

1. Introduction

Solvent Extraction which is also called Liquid-liquid extraction is the process for separating the components between two immiscible liquids. Solvent Extraction plays an important role in several industries such as; Chemical, Petrochemical and Pharmaceutical and Hydrometallurgy. Mixer settlers are the most used equipments in solvent extraction industries. In mixer-settlers, two immiscible fluids are mixed in a tank and then are fed to the settler for separating the phases by gravity. Several studies are done on mixer settler's performance to increase the phase separation efficiency and achieve a clean phase separation. Some researches investigate effect of settler's geometry on the dispersion pattern [1-7].

The most popular method for increasing the mixer-settler's efficiency is using picket fences. Many studies have investigated the picket fence's effect over the phase separation. Sadeghi showed that setting two rows of picket fences with 1.3 m distance of each other results in more effective phase separation [2].

2-verifying the process simulation's precision

Lack of experimental equipments forced us to check out the equation's accuracy with the other's work. In this regard Sadeghi et. all's work was used as case study for checking accuracy of our equations set up. In their study, the launder of Sarcheshmeh Copper Complex was modeled with Ansys CFX 11. The field measurement was done by solving Continuity and Navier-Stokes equations. In order

¹ Department of mining and metallurgical Eng., Amirkabir University of Technology, Tehran, IRAN

* Corresponding Author, Email: alamdari@aut.ac.ir, Telephone: +98 21 6454 2971

to simulate the turbulence, the standard K- ϵ model was used. They compared the simulation results with the experimental field measurement data and verified the simulation's accuracy. Sadeghi et. al showed that by installing two picket fences without dam in the launder the phase separation becomes more uniform and launder's performance is improved. In this situation the volume fraction of aqueous phase at the upper outlet is 0.17 [3]. In this study, sadeghi's work was repeated and the results were compared. Figure 1 shows the geometry of the launder which was studied. Also, the physical properties of two phases are shown in table 1.

According to Sadeghi and *et al.* [3], the launder's process was studied in steady state and the volume was meshed with 400000 cells. Figure 2 shows the volume fraction of organic phase in settler's volume.

As it is shown in figure 2, the aqueous phase volume fraction at the upper outlet of the settler is about 0.17. It is fully compatible with the results achieved by Sadeghi [3].

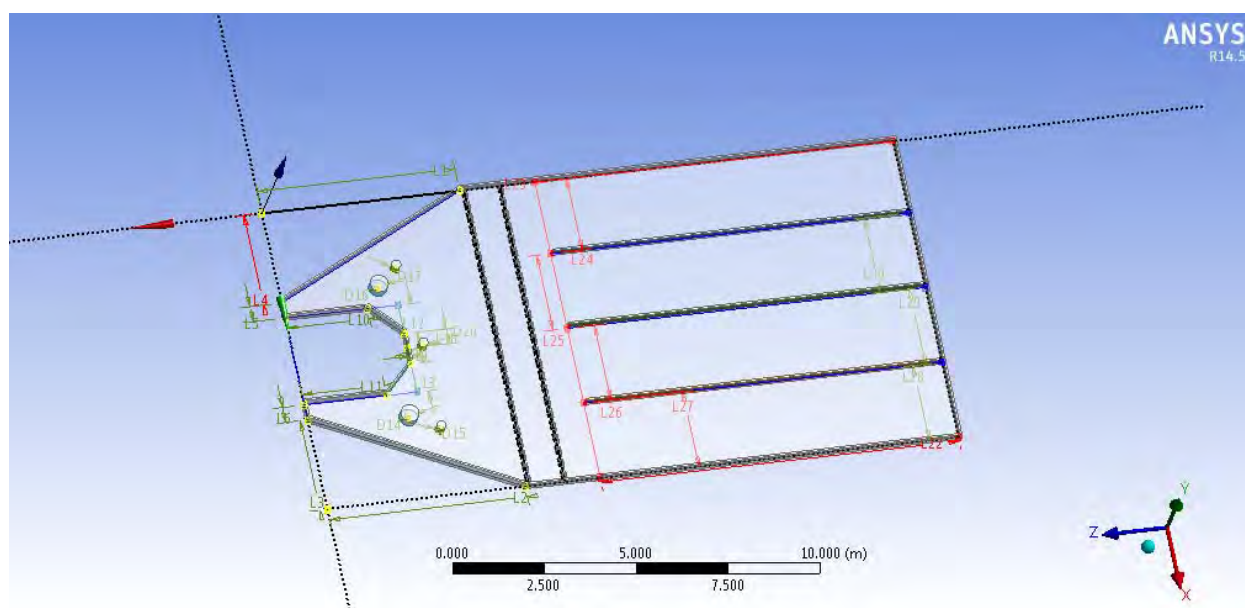


Fig 1. Geometry of launder

Table 1. Physical properties of liquid phases (pH=2, Temperature= 14°C)

Aqueous dynamic Viscosity	Aqueous dynamic Viscosity	Aqueous density	Organic density	Interfacial tension
2.3 mPa.s	3.3 mPa.s	1100 Kg m^{-3}	806 Kg m^{-3}	26.1 mNm $^{-1}$

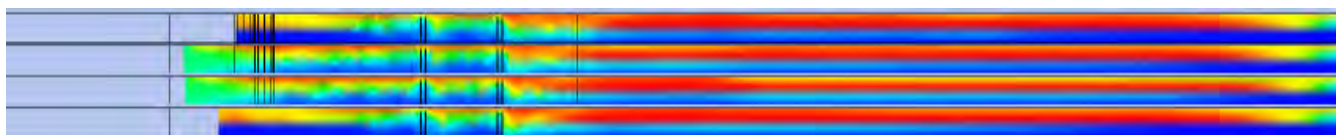


Fig 2. Volume fraction of organic phase in different heights of settler.

3- CFD simulation of separation procedure in settler

In order to evaluate the phase dispersion and fluid flow pattern in the volume of the settler, geometry of settler of Sarcheshme Copper Complex has been simulated with ANSYS Design Modeler. And the drawn geometry has been meshed through ANSYS ICEM with 500000 cells. The mesh independency for this amount of cells has been verified in several simulations. Figure 3 shows the settler's geometry.

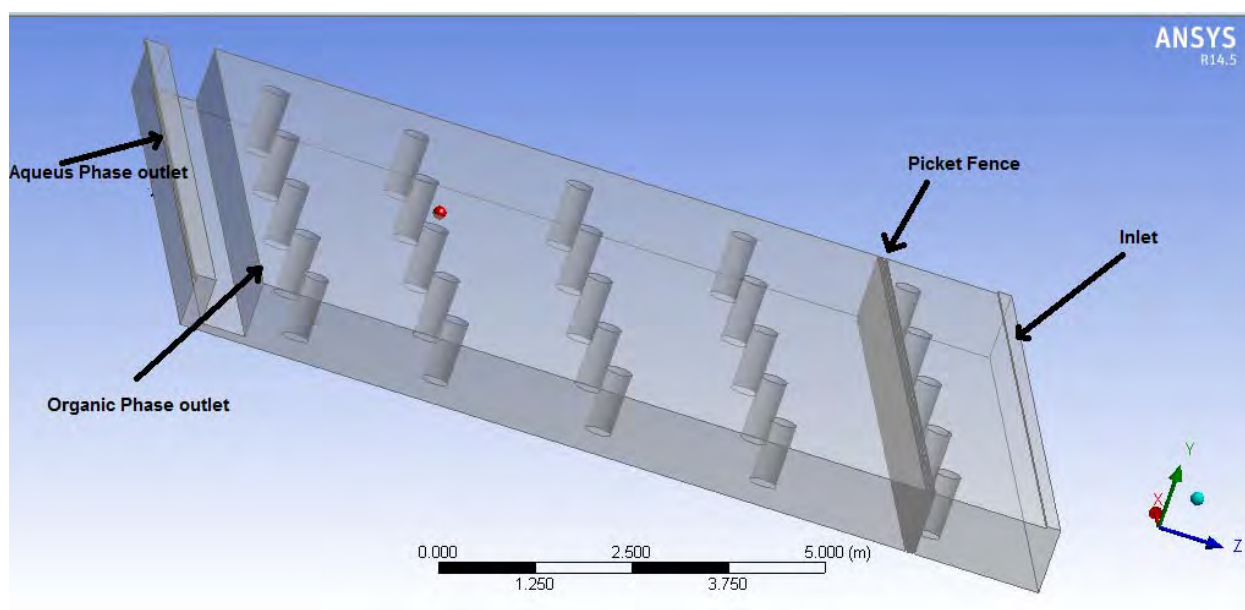


Fig. 3. Geometry of sarcheshmeh copper complex's settler

3.1. Equations

3.1.1. Continuity equations

Continuity equations for the continuous (C) and dispersed (D) phases are as below:

$$\nabla \cdot (\alpha_c U_c) = 0 \quad (1)$$

$$\nabla \cdot (\alpha_d U_d) = 0 \quad (2)$$

Where α and U are volume fraction and velocity vector [3-4].

3.1.2. Momentum equations

For the steady and incompressible time average the time average momentum equations are as follow:

$$P_c [\nabla \cdot (\alpha_c U_c U_c)] = -\alpha_c \nabla P + (\mu_c + \mu_t) \nabla^2 (\alpha_c U_c) + S_{M,c} \quad (3)$$

$$P_d [\nabla \cdot (\alpha_d U_d U_d)] = -\alpha_d \nabla P + (\mu_d + \mu_t) \nabla^2 (\alpha_d U_d) + S_{M,d} \quad (4)$$

Where μ and μ_t are dynamic and turbulent viscosities. P and S_M are pressure and source term respectively.

In order to define the turbulence, standard K- ϵ model has been used. The forces which are included in the source term are drag, buoyancy, lift forces. The drag force between two phases is as follows:

$$F^{drag} = \frac{1}{2} \rho |U_{rel}| U_{rel} A_p C_D \quad (5)$$

U_{rel} is the relative velocity between continuous and dispersed phases. C_D is the drag coefficient and A_p is the projected area of the droplet [3-4].

The buoyancy force is due to the density difference between two phases. This force is zero for the continuous phase and for the dispersed phase could be presented as following form:

$$F_d^{buo} = \alpha_d (\rho_d - \rho_c) g \quad (6)$$

Where ρ_c is reference density. The buoyancy force is zero for the continuous phase since the buoyancy of continuous phase is the buoyancy reference density.

The velocity gradient in the fluid would result in a pressure distribution on the upper and lower surface of droplet. This pressure distribution will cause the lift force. The lift force could be presented in the following form:

$$F_d^{lift} = \alpha_d \rho_c C_L (U_c - U_d) \times \nabla U_c \quad (7)$$

Where the C_L is lift coefficient and according to Sadeghi et al. was set on 0.1. This force is equal for both the phases but opposite in sign.

3.2. Physical domain and calculation procedure

As it is shown in figure 3, dimensions of the settler are 11 m $\times$ 11 m $\times$ 0.9 m. the settler has two outlets for discharging the aqueous and organic phases and one inlet for charging the liquids. For the outlets, Outlet boundary condition has been implemented. Flow rate in the inlet is 1100 m³/h and organic to aqueous phase ration is 0.95. For the upper wall of the settler, free slip wall boundary condition has been implemented [3,18]. The fluids' physical properties were set according to table 1. Figures 4 and 5 show the volume fraction of the Organic phase in the settler.

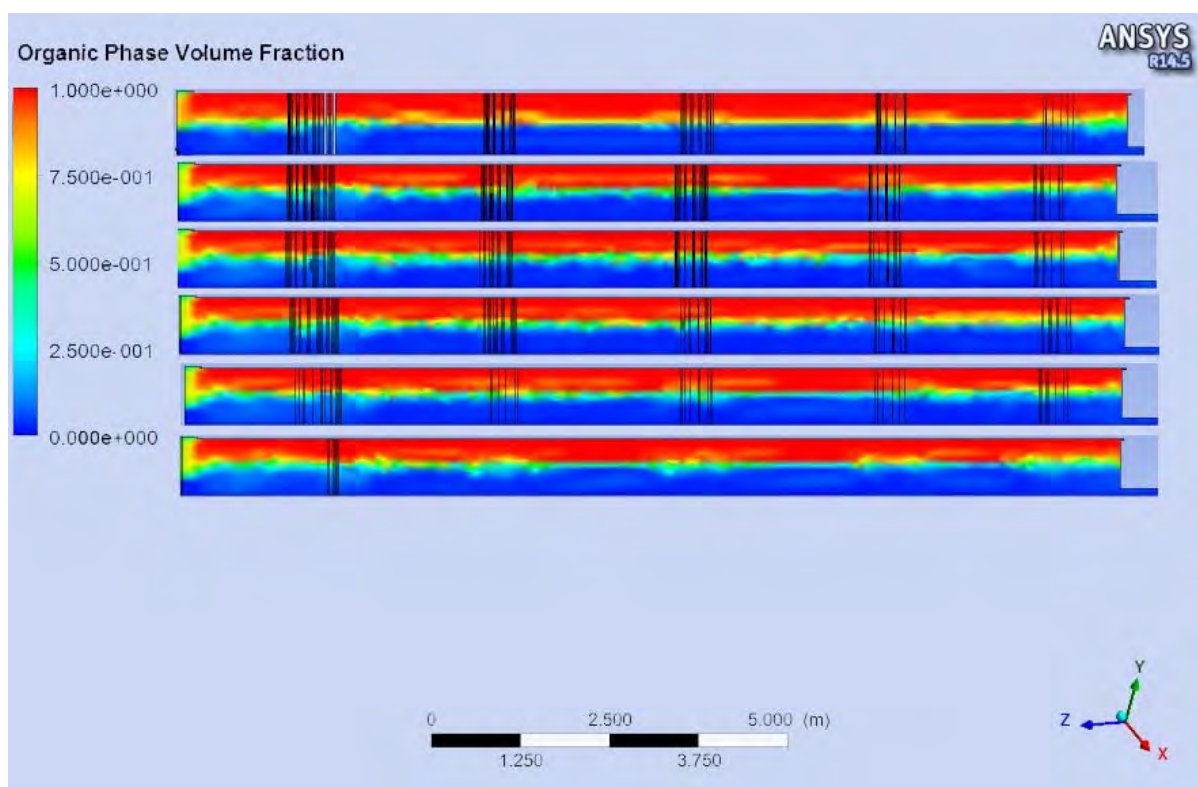


Fig4. Organic phase volume fraction

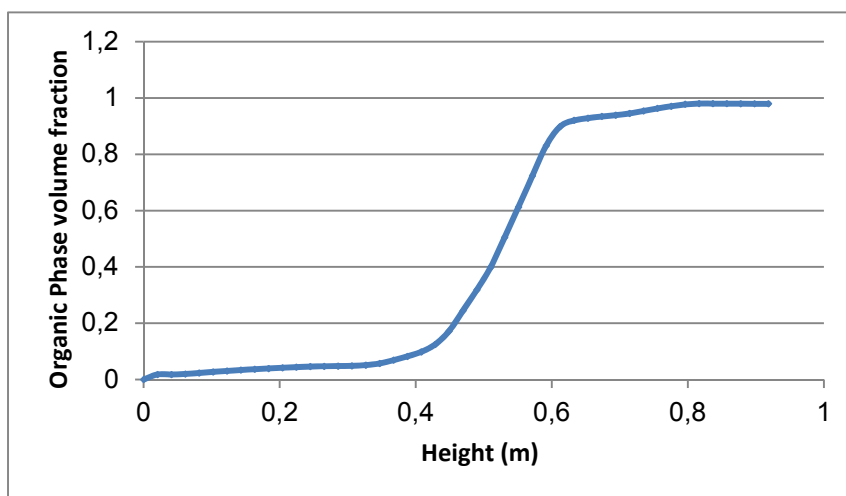


Fig 5. Organic phase volume fraction in different heights of the settler.

In order to investigate the effect of inlet flow rate on the dispersion pattern, the settler process was studied with several flow rates, in steady state. The implemented flow rates are 375, 550, 1000, 1500, 2200 and 3600 m³/h.

4. Results and Discussion

The volume fraction of organic phase in the settler for different inlet flow rate was investigated. Figure 6 to 11 show the dispersion pattern of the liquids in the settler.

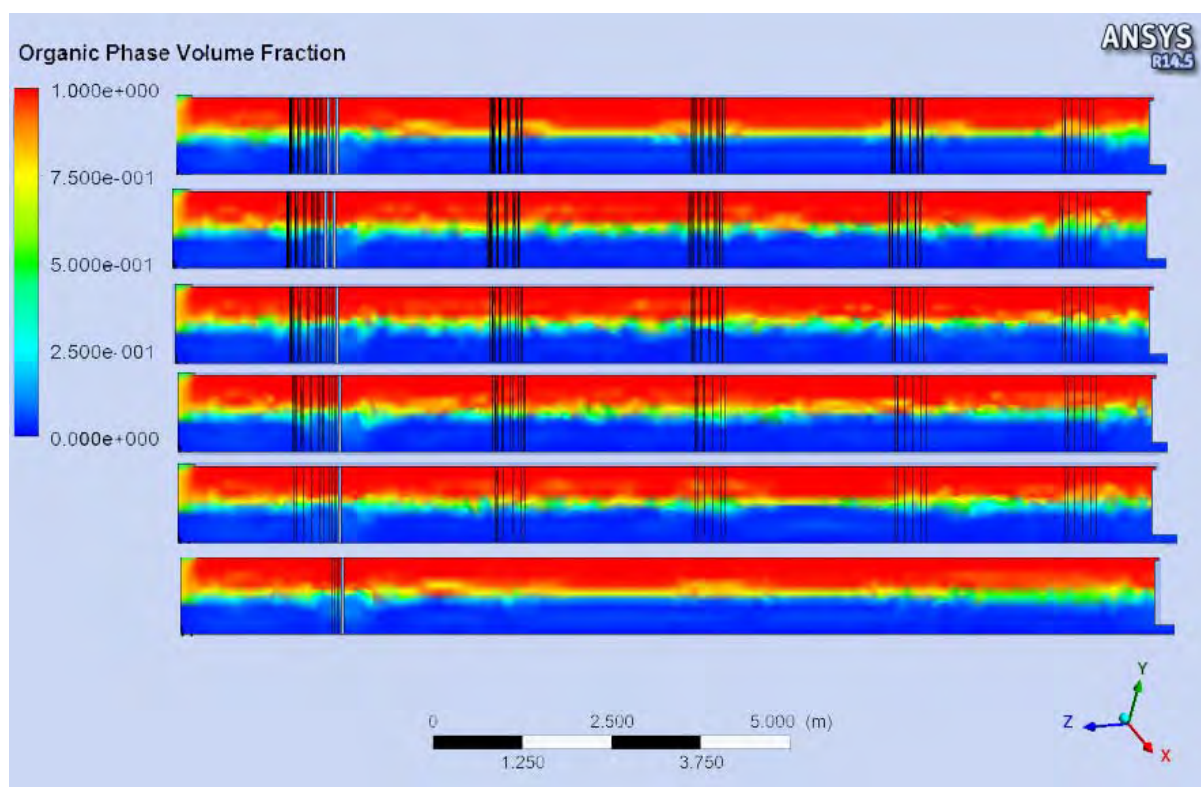


Fig 6. Organic phase volume fraction in the settler with inlet flow rate of 375.

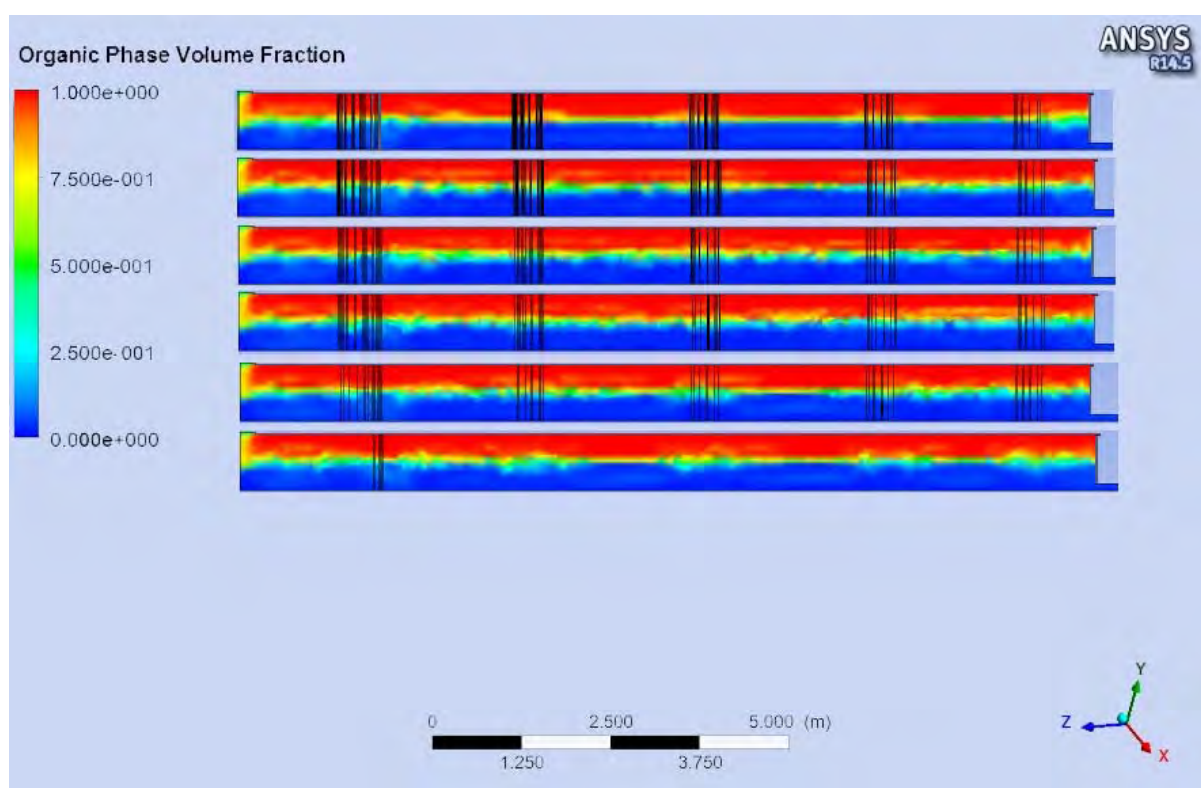


Fig 7. Organic phase volume fraction in the settler with inlet flow rate of 550.

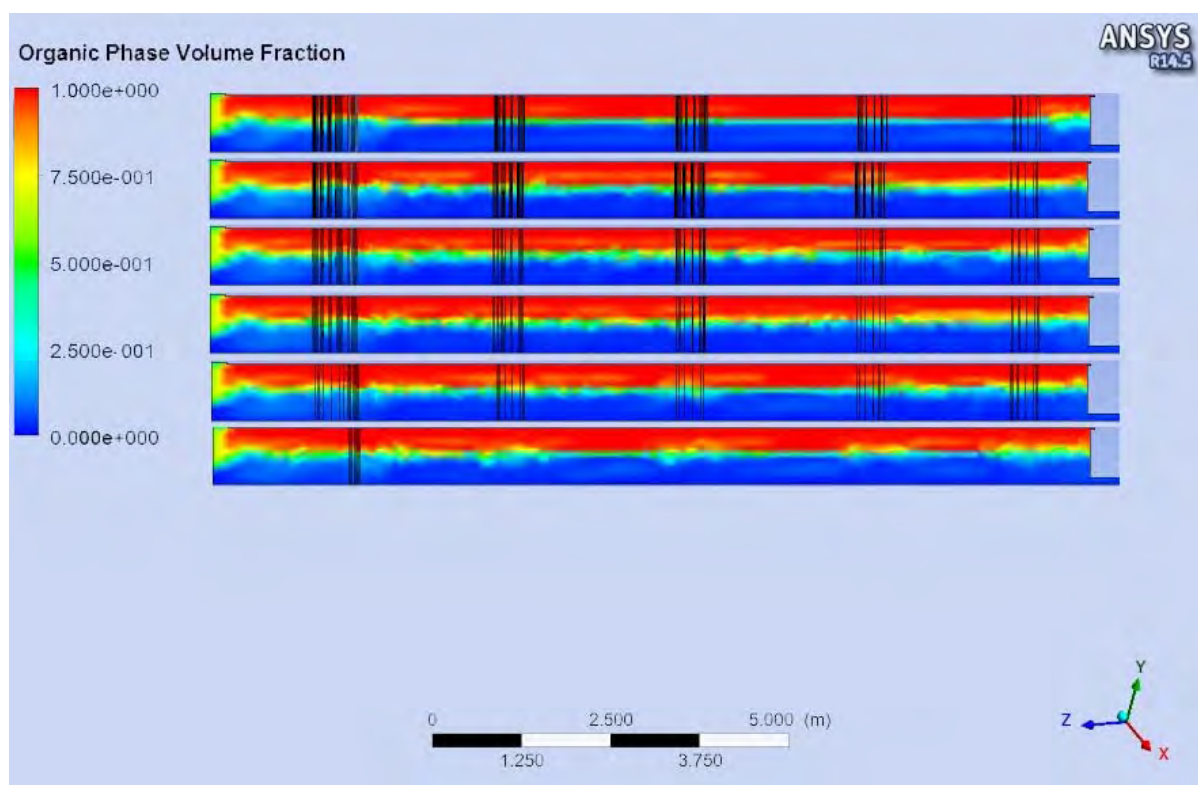


Fig 8. Organic phase volume fraction in the settler with inlet flow rate of 1000.

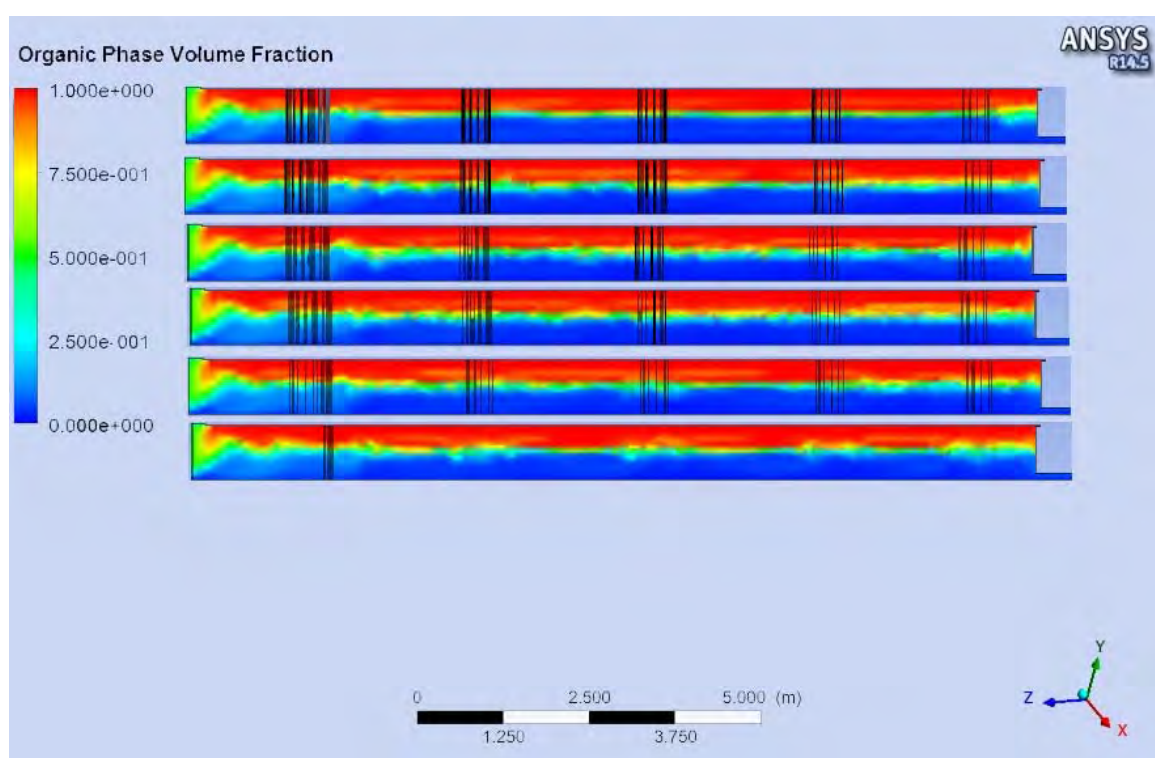


Fig 9. Organic phase volume fraction in the settler with inlet flow rate of 1500.

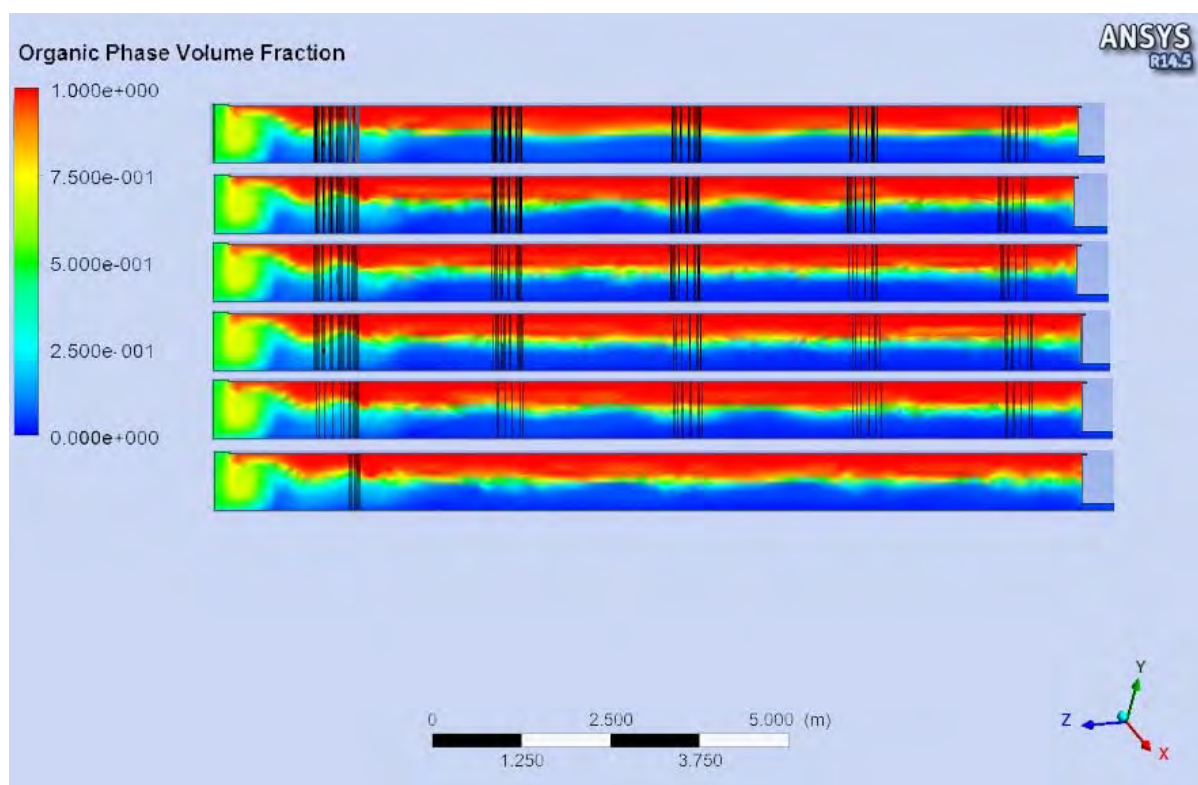


Fig 10. Organic phase volume fraction in the settler with inlet flow rate of 2200.

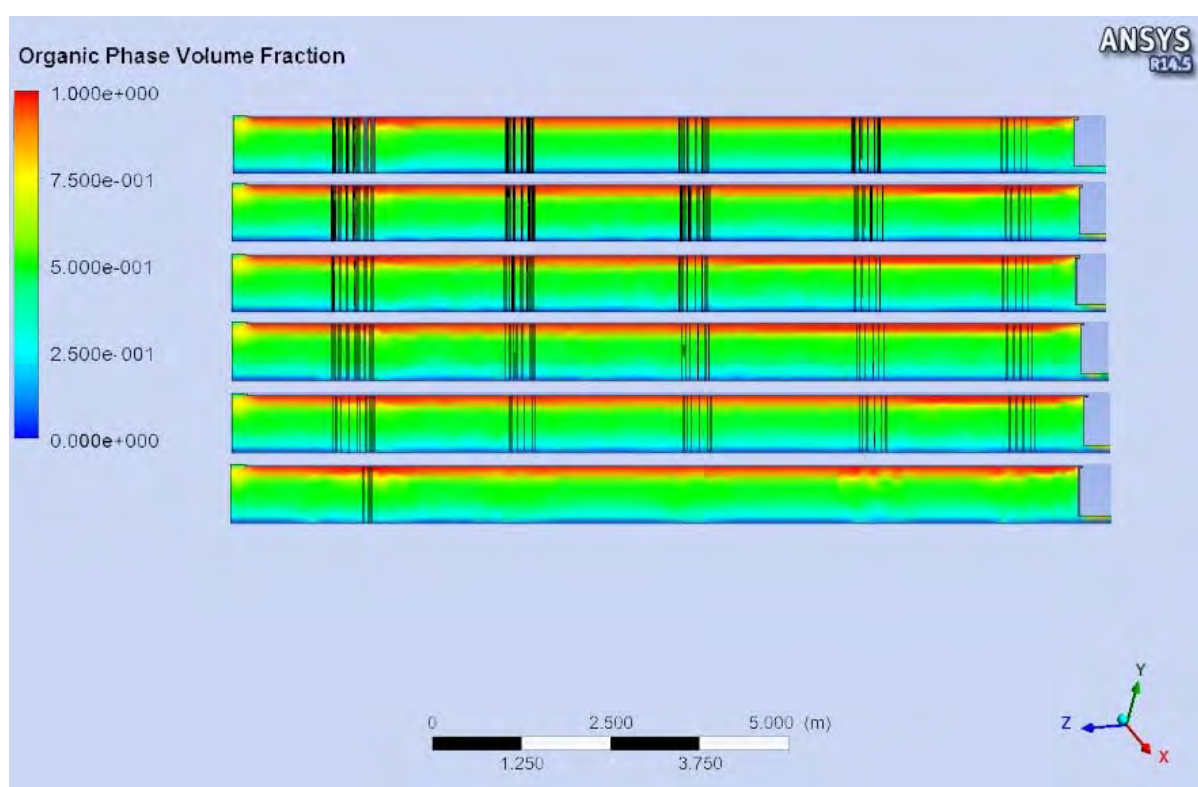


Fig 11. Organic phase volume fraction in the settler with inlet flow rate of 3600.

As it is shown in the figures 5 to 11, the inlet flow rate has a significant effect on the dispersion of the phases in the settler. For explore the effect of the flow rate on the

dispersion of the phases, volume fraction of organic phase in different heights of the settler has been studied. Figure 12 shows the distribution of organic phase in different heights of the settler.

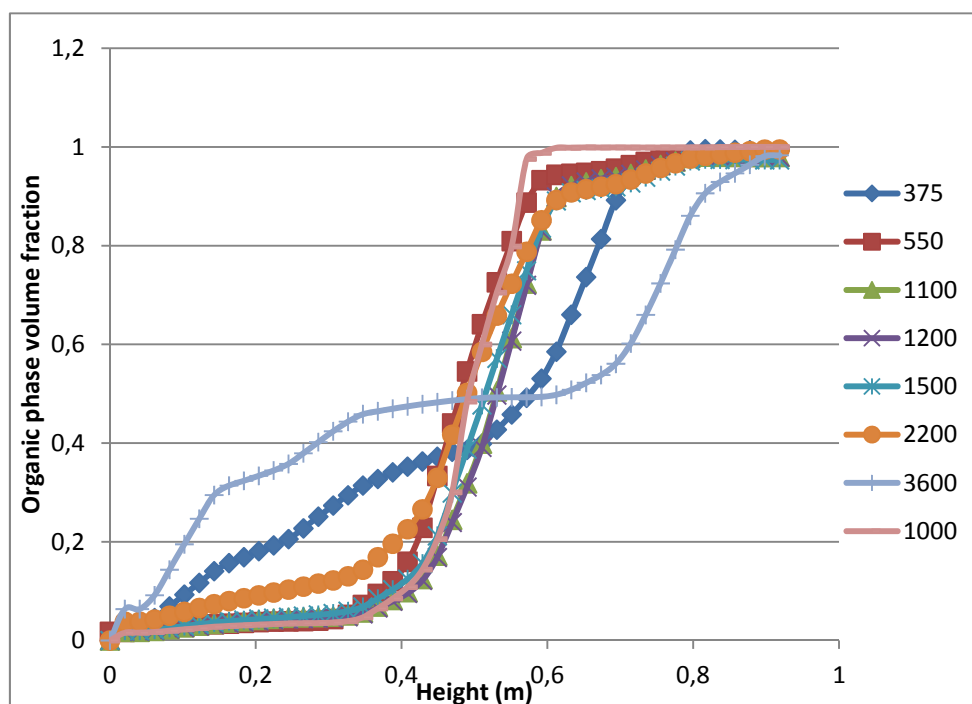


Fig. 12 the distribution of organic phase in different heights of the settler

Figure 12 show that 1000 m³/h is the most effective inlet flow rate, in order to achieve the best phase separation. In this flow rate the dispersion band is effectively thin and the volume fraction of the organic phase reaches to 1, at a lower height, in comparison with the other flow rates. Reducing the flow rate will result in a thicker dispersion band and a non-uniform dispersion of the phases. Whereas, increasing the inlet flow rate would also result in a not suitable phase separation. In which, in 3600 m³/h flow rate, any phase separation will not happen.

5. Conclusion

In this study, a three dimensional computational fluid dynamics has been used for studying the effect of inlet flow rate on the phase separation and performance of the settler of Sarcheshmeh Copper Complex. Thw procedure simulation and setup has been validated with sadeghi et al.'s work. The operational inlet flow rate in Sarcheshmeh is 1100 M³/h. the settler's performance has been studied in presence of several flow rates. The simulation's data and results showed that by increasing the flow rate to 1000 m³/h a more uniform and effective phase dispersion would be achieved. It can be also concluded that CFD is a powerful tool for studying the performance of mixer-settlers, in solvent extraction systems and assessing the other operational parameters with CFD, will result in a significant enhancement in the SX plant's performance without any additional cost.

References

- 1- Mohsen Ostad Shabani, Ali Mazahery, Mehdi Alizadeh, Ali Asghar Tofigh, Mohammad Reza Rahimipour, Mansour Razavi, Alireza Kolahi, Computational fluid dynamics (CFD) simulation of effect of baffles on separation in mixer settler, *International Journal of Mining Science and Technology* 22 (2012) 703–706
- 2- Roohollah Sadeghi, Ali Mohebbi, Amir Sarrafi, Ataallah Soltani, Mazyar Salmanzadeh, Shahram Daneshpojooh, CFD simulation and optimization of the settler of an industrial copper solvent extraction plant: A case study, *Hydrometallurgy* 106 (2011) 148–158
- 3- Roohollah Sadeghi, Ali Mohebbi, Mehdi Baniasadi, CFD modeling of the launder of settler of an industrial copper solvent extraction plant: A case study on Sarcheshmeh copper complex, Iran, *International Journal of Mineral Processing* 98 (2011) 55–65
- 4- Madhvanand N. Kashid and Liubov Kiwi-Minsker Microstructured Reactors for Multiphase Reactions: State of the Art, *Ind. Eng. Chem. Res.* 2009, 48, 6465–6485
- 5- Kankaanpää, T., 2007. CFD procedure for studying dispersion flows and design optimization of the solvent extraction settler, Doctoral Thesis, Helsinki University of Technology, Finland
- 6- Miller, G., 2006. Design of Mixer-settlers to Maximize Performance, Proceedings ALTA Copper 10. Alta Metallurgical Services, Melbourne
- 7- Ritcey, G.M., Ashbrook, A.W., 1984. Solvent Extraction. Principles and Application to Process Metallurgy, Part I. Elsevier Science, Amsterdam, pp. 1–39
- 8- Alan Taylor, REVIEW OF MIXER-SETTLER TYPES AND OTHER POSSIBLE CONTACTORS FOR COPPER SX, ALTA Metallurgical Services
- 9- P., Kuusisto, R., Lyyra, J., Nyman, B., Lindell, E., Ekman, Solvent Extraction — How to Get Over Hard Times Pekkala, The Minerals, Metals & Materials Society, Warrendale, PA, pp. 305–318.
- 10- Simulation Flow in a Static Mixer Using CFX in Standalone, CFX tutorial, tutorial 1, Dec. 2006.
- 11- Mandar TABIB, Graeme LANE, William YANG and M Philip SCHWARZ Seventh, CFD SIMULATION OF A SOLVENT EXTRACTION PUMP MIXER UNIT: EVALUATING LARGE EDDY SIMULATION AND RANS BASED MODELS, International Conference on CFD in the Minerals and Process Industries CSIRO, Melbourne, Australia 9-11 December 2009
- 12- Computational fluid dynamics: A Virtual prototyping tool for materials engineering, *JOM*, Vol. 56, No. 3, 2004, P. 44-48.
- 13- Hirsi, T. Optimization of a settler with the computational fluid dynamics, Master's thesis, Helsinki University of Technology, Espoo 2004.
- 14- S.A. Argyropoulos, CFD- An effective tool for optimizing picket fence geometries, Proceedings of the International symposium, Computer applications in Metals Processing, ed. 40th Annual Conference of Metallurgist of CIM, Toronto, August 2001.
- 15- Xia, J.L., Ahokainen, T., Kankaanpää, T. Nickel droplet settling behavior in an electric furnace, *Metallurgical and Materials Transactions B*, 35B, 2004.
- 16- A. Taylor, M.L. Jansen, SOLVENT EXTRACTION MIXER-SETTLER DESIGN, International Project Development Services Ltd.
- 17- Barena, E. and Mizrahi, J., Trans, Separation mechanism of liquid-liquid dispersions in a deep layer gravity settler: Part I – The structure of the dispersion band, *Instn. Chem. Engrs.*, Vol. 53, 1975.
- 18- Barena, E. and Mizrahi, J. Trans, Separation mechanism of liquid-liquid dispersions in a deep layer gravity settler: Part II – The structure of the dispersion band, *Instn. Chem. Engrs.*, Vol. 53, 1975.

- 19- Barena, E. and Mizrahi, J., Trans. Separation mechanism of liquid-liquid dispersions in a deep layer gravity settler: Part III – The structure of the dispersion band, *Instn. Chem. Engrs.*, Vol. 53, 1975.
- 20- Barena, E. and Mizrahi, J., Trans. Separation mechanism of liquid-liquid dispersions in a deep layer gravity settler: Part IV – The structure of the dispersion band, *Instn. Chem. Engrs.*, Vol. 53, 1975.
- 21- Leng D.E and Calabrese R.V., Immiscible liquid-liquid systems, In the book of Handbook of industrial mixing, science and practice, , John Wiley & Sons Inc., 2004.
- 22- Magiera, R. and Blass, E., Separation of liquid-liquid dispersions by flow through fiber beds, *Filtration & separation*, Vol. 34, 1997.
- 23- Drop coalescence in turbulent dispersions, Liu, S., Li, D., Chemical Engineering Science, 1999.
- 24- Jakobsen, H.A., Lindborg, H., Doraco C. A., Modeling of bubble column reactors: Progress and limitations, *Ind. Eng. Chem. Res.*, 2005.

Experimental and CFD study of drop formation at high jet velocity

E.Sanz, P.Béard, F.Augier, M.Le Moel, D.Leinekugel-Le-Cocq, A.Baudot

IFP Energies nouvelles

Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

Context

Perforated plates are commonly used in solvent extraction processes when low number of theoretical stages are required and/or when an extreme ratio between Extract and Raffinate flow rates is involved, i.e. $E/R > 5$ or $E/R < 0.02$ (Treybal, 1963). However, existing design rules fail for systems with very different densities ($\Delta\rho > 400 \text{ kg/m}^3$). In this operating range, the coalescence of the dispersed phase below (or above) each plate requires a high jet velocity at the orifices (between 1 to 4 m/s), in order to generate a sufficient pressure drop at the plates. The object of this study is the investigation of drop formation for some liquid-liquid systems of interest at high jet velocities, in order to complete existing literature restrained to lower jet velocities (Kumar&Hartland, 1995).

Method and Results

A rectangular mockup has been used to experimentally study the drop formation of heptane in different aqueous solutions of NaOH, and at different initial jet velocities. 3 nozzle sizes have also been tested. Recording and image processing have been used to measure both jet length and drop sizes.

Moreover, 2D and 3D Computational Fluid Dynamics (CFD) calculations have been performed to simulate drop formation in similar conditions. The Volume-Of-Fluid (VOF) algorithm, which is assumed to be pertinent to reconstruct fluid interfaces (Hirt&Nichols, 1981), has been used. Fig. 1 presents a 3D simulation of drop formation from a free jet of heptane into water at 4 m/s through an orifice of 8 mm. Experiments and simulations have been compared to existing correlations. Results have been used to develop a patented perforated plate design.

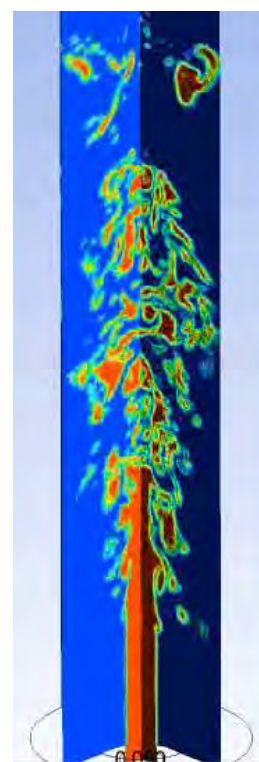


Fig1. CFD-VOF simulation of drop formation at high jet velocity (4 m/s)

HYBRIDISATION OF TAYLOR-COUPETTE REACTORS AND RDC COLUMNS

Enes Aksamija¹

PhD. student, Institute of Chemical Engineering and Environmental Technology, University of Technology Graz, Austria

Matthäus Siebenhofer

Professor and head of the Institute of Chemical Engineering and Environmental Technology, University of Technology Graz, Austria

Taylor-Couette vortices are formed in the gap between concentrically rotating cylinders. They have been subject of investigations for decades and some attempts have been done for implementation in liquid-liquid extraction. Problems with vortex instability at high axial flow rates, high angular velocity differences, high diameter differences of the cylinders and the presence of a second phase made this hydrodynamic phenomenon difficult to apply in liquid-liquid extraction.

Experimentally validated CFD-Simulations of dual phase and single phase flow patterns in the Rotating Disc Contactor (RDC) led to the suggestion that the characteristics of Taylor-Couette flow pattern can seemingly be obtained in a simplified RDC design without stator discs and appropriate rotor disc diameter. As long as the compartment height is large enough to accommodate two toroidal eddies, vortices are dynamically stabilized by the rotor discs, allowing smaller shaft diameters and larger active space in the apparatus. CFD-Simulations show less axial mixing for both phases compared to a state of the art RDC design with stator discs. On the one hand compartments are separated more efficiently by the enlarged rotor discs, on the other hand higher energy dissipation rates caused by the enlarged rotor discs lead to narrower drop size distributions and more uniform axial velocity of the dispersed phase. The geometrical stabilization of the toroidal flow pattern with the rotor discs also induces a straight path of the dispersed phase, minimizing the tendency for vortex inversion, which can be observed in state of the art RDC design.

Mass transfer experiments were performed in a pilot scale RDC100 to quantify optimization in terms of separation efficiency. The height of one transfer unit (HTU) was found to be 40% lower for the simplified internals geometry.

Beside lower investment costs and increased mass transfer efficiency several operation advantages in cleaning, maintenance and assembly may arise from statorless design of RDC extraction columns.

¹ Corresponding author. Institute of Chemical Engineering and Environmental Technology, University of Technology Graz, Inffeldgasse 25C, 8010 Graz, Austria. Phone: +43 316 873 4977. Email: enes.aksamija@tugraz.at

MODELING AND STUDY OF THE DISPERSED PHASE BEHAVIOUR IN A PULSED COLUMN

A. Amokrane¹, S. Charton¹, J. P. Klein², F. Puel²

¹CEA, DEN, F-30207, Bagnols-sur-Cèze, France; tel. +33 4 66796186,
e-mail: abdenour.amokrane@cea.fr, sophie.charton@cea.fr

²Université de Lyon, Université Lyon 1, CNRS, CPE-Lyon, UMR5007, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), F-69622, Villeurbanne, France

The pulsed column is one of the most used apparatus in solvent extraction processes in the nuclear fuel treatment industry. The optimization of solvent extraction operations needs a thorough understanding of the diphasic flow's properties inside the apparatus, especially that of the dispersed phase. In this context, modelling and numerical simulation are powerful tools complementary to the experiments in order to study the dispersed liquid phase behaviour within the pulsed column. In this aim, two approaches are considered, respectively in a Lagrangian and an Eulerian frame.

In the Lagrangian framework, both modeling and monitoring of the drops' residence time distribution (RTD) in the column were undertaken [1]. The experimental results were consistent with those presented in the literature. However, while the pulsation intensity, $A \times f$, is commonly used as the influent parameter, a separate effect of the pulsation amplitude A and frequency f on the RTD was observed. The model we developed held good results compared to the experimental ones.

The Eulerian approach is dedicated to the prediction of the drops behaviour and properties while flowing in the continuous phase. A CFD-PBE coupled model. A water in oil emulsion (W/O) is used in this study.

First, the single-phase flow of the continuous phase (TPH) was investigated. Thanks to PIV measurements [3], a turbulence model relevant to our system and accurately representing the flow turbulent properties in the column has been selected and validated. The breakup and coalescence kernels of the considered W/O system were measured and validated in a separate approach. To achieve this task, a test apparatus providing nearly homogeneous turbulence dissipation, and for which the mean turbulence dissipation ε is correlated to the stirrer's power number, was used. The parameters of the various kernels proposed in the literature and relevant for liquid-liquid systems [4] were adjusted by fitting the Drop Size Distribution (DSD) evolutions monitored in the stirred tank reactor. Values of ε in the range of the pulsed column functioning were studied.

Both the turbulence and the breakage models were implemented in the commercial CFD code ANSYS-Fluent® to perform coupled CFD-PBE simulations [3]. A sensitivity analysis regarding the operating conditions has been performed.

The model holds valuable qualitative information, useful for the understanding and design of the column and there from for the extraction process optimization: interfacial area, holdup, etc.

- [1] Amokrane, A., Charton, S., Lamadie, F., Becker, J., Klein, J.P., Puel, F., 2012, *Study of the dispersed phase behavior in a pulsed column for oxalate precipitation in emulsion*, 9th International conference on CFD in the mineral and process industries, Melbourne.
- [2] Paisant, J.F., Amokrane, A., Lamadie, F., Charton, S., Randriamanantena, T., Duhamet, J., 2013, *Use of synchronised PIV to measure a pulsed flow velocity field in a disc-doughnuts column*, 10th International Symposium on Particle Image Velocimetry -PIV13", Delft.
- [3] Amokrane, A., Charton, S., Sheibat-Othman, N., Becker, J., Klein, J.P., Puel, F., 2013, *Development of a CFD – PBE coupled model for the simulation of the drops behavior in a pulsed column*, Canadian Journal of Chemical Engineering, *accepted*.
- [4] Becker, J., Puel, F., Henry, R., Sheibat-Othman N. 2013, *Investigation of Discrete Population Balance Models and Breakage Kernels for Dilute Emulsification*, Ind. Eng. Chem. Res., 50 (19), 11358–11374.

A modified rotating disc contactor for extraction systems with solid particles

Ze Sun, Hang Chen, Guimin Lu Ping Li, Jianguo Yu**

A modified rotating disc contactor (RDC) was designed based on the CFD-PBM simulation for the processing of extraction systems with solid particles. To prevent the deposition of solid particles on the internals, the key is to eliminate flow dead zones. Meanwhile, to keep the extraction efficiency, a-quater-arcs-shaped internals were proposed. The simulation shows that the dead zones are eliminated effectively while the flow field structure is almost unchanged. The critical parameters of droplet diameter, dispersed phase holdup and axial mixing for the extraction performance are nearly the same. Hence, the modified RDC is considered as an effective improvement for the solid phase processing with high extraction efficiency.

1. Introduction

Extraction is one of the most important operation units in separation engineering. In industry, extraction systems are usually liquid-liquid. However, the extraction faces the challenges from liquid-liquid-solid systems. The solid phase has a series of effects on the operation of extraction columns. Inappropriate treatments will decrease the extraction efficiency, reduce the throughput, and even block the column. So the development of extraction equipments for solid-laden extraction systems is inevitable.

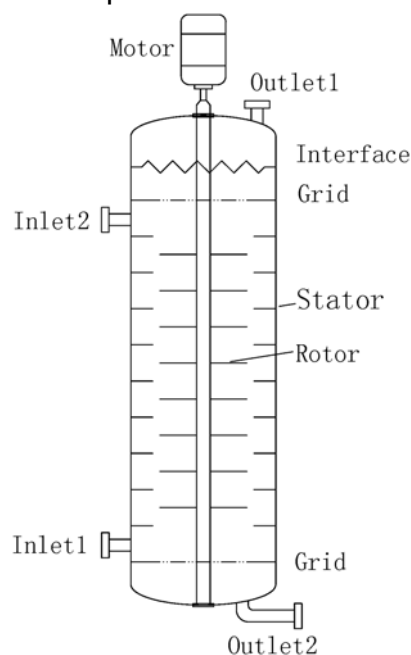


Figure 1. Geometrical structure of a traditional RDC

RDCs are widely used in industry. Figure 1 is the diagram of a RDC. Since Reman et al¹ designed the first RDC, it has been a classical extraction equipment with the advantages of simple geometry, high throughput, and low consumption etc. Another

* To whom correspondence should be addressed. Telephone: 86-21-64252826. Fax: 86-21-64250981. E-mail: Ze Sun: zsun@ecust.edu.cn; Jianguo Yu: jgyu@ecust.edu.cn. National Engineering Research Center for Integrated Utilization of Salt Lake Resource, East China University of Science and Technology, Shanghai 200237, People's Republic of China

significant characteristic of the RDC is its ability for the processing of the solid-laden extraction systems. However, this is only true when the solid concentration is low. The stirring of discs is not strong enough to prevent solid depositing on stators if the solid concentration is high. Zhu et al.² once presented an OTRDC (open turbine rotating disc contactor) to handle the systems with solid particles. In the OTRDC, one side of the stirrer was designed as a pump impeller with three blades. The intensified stirring enhanced its processing capacity at the price of high energy consumption. The well-distributed energy input by the flat rotor discs was destructed because of the asymmetry of the new stirrers.³ In addition, excessive stirring is not beneficial to improve the extraction efficiency and operating throughput.

Hydrodynamics has crucial effects on the performance of extractors. Recently, the development of CFD (Computational Fluid Dynamics) makes the flow field studies more economical and efficient. So it was also applied to the extraction columns and was demonstrated to be valid.⁴ Nevertheless, except the multi-phase flow, the extraction operation also involves complicated droplets coalescence and breakage. Hence, Bart⁵ suggested PBM (Population Balance Model) to simulate these phenomena. As it turns out, coupled CFD-PBM simulation is a useful tool for the highly efficient design of extraction columns.⁶

In this study, based on the elimination of dead zones and flow field structure invariability principles, a modified RDC was proposed for the solid-laden extraction systems. The performance of the new RDC was studied by the CFD-PBM simulation.

2. Mathematical models

2.1 CFD model

The physical model of a pilot-scale RDC was established in Fluent 14.0. Its geometry is the same as the one used by Drumm et al.⁷ The detailed sizes are listed in Table 1. The Eulerian approach and realizable k- ϵ model were used for multi-phase flow and turbulence simulations respectively. Only the drag force was considered as the interphase interaction and it was calculated with the Schiller-Naumann model.

Geometry	Size (mm)
Column diameter	150
Stator opening diameter	105
Rotor disc diameter	90
Shaft diameter	54
Compartment height	30
Stator/disc height	1

Table 1. Geometrical size of the RDC

2.2 PBM model

The PBM model was established based on the conservation equation of a number density function. In this equation, birth and death functions are critical to the description of droplets coalescence and breakage. The model of Luo and Svendsen was usually used to closure them. The elaborate model and theory can be found in references.⁸ Yet, it was found that the original model of Luo and Svendsen overestimated the droplets coalescence rate. Thus, in this study, the coalescence rate was decreased by an empirical factor of 10 suggested by Chen et al⁹.

2.3 Numerical scheme

The mesh size is 0.5 mm. Pressure and velocity boundaries were define at the top and bottom of the column respectively. With the no slip boundary, the rotor was set as a moving wall, while other walls were kept stationary. The method of QMOM was used to solve the PBM model. The equations were discretized by the QUICK scheme. The flow rates of continuous phase (a water/glycerine mixture) and dispersed phase (n-heptane) are 200 L/h and 100 L/h respectively. The agitation rate is 150 rpm. The coupled CFD-PBM simulation has been validated in another paper.

3. Results and discussion

3.1 Modified RDC

The simulated velocity field of the traditional RDC is shown in Figure 2. The vortex structure between the internals is distinct. Due to the structural difference between the circular vortex and rectangular compartment, there are some dead zones in the corners. In this study, the dead zone is defined as the region where the fluid velocity magnitude less than 0.1 m/s. It can be concluded that the dead zones shown in Figure 3 are the main factor which leads to the solid deposition. Hence, the improvement of the column should focus on the elimination of dead zones.

The dead zones are always taken away by increasing the stirring intensity, which will cause more serious axial diffusion. In this study, a-quarter-arcs-shaped internals were designed to eliminate the dead zones. Unlike the OTRDC, the flow field structure in the new column was kept as same as the traditional one, to reduce the negative effects of the modification. The modified RDC is shown in Figure 4.

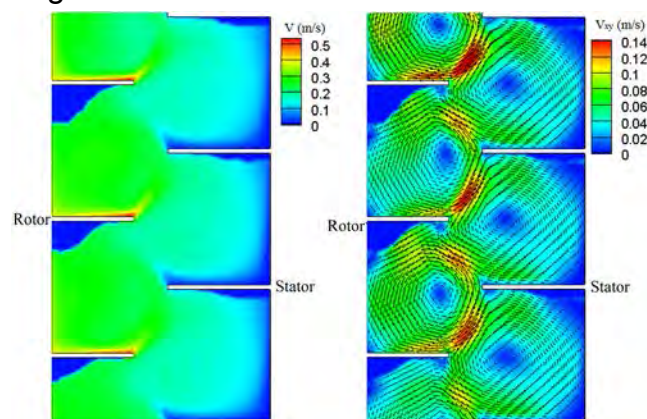


Figure 2. Flow field structure in the traditional RDC, left: velocity field, right: profile velocity field (x,y)

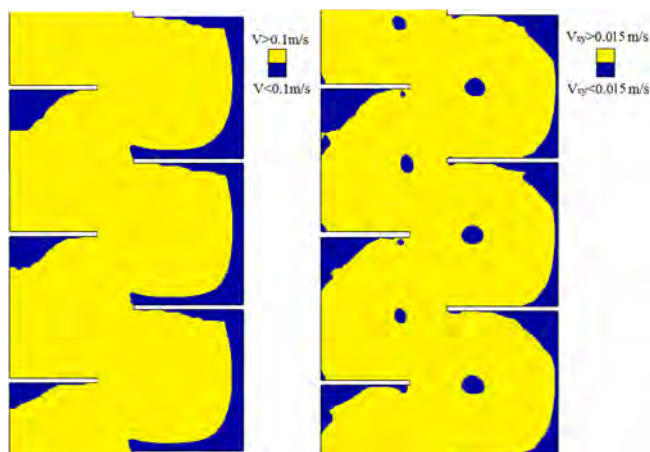


Figure 3. Dead zones in the traditional RDC, left: fluid velocity, right: profile velocity (x,y)

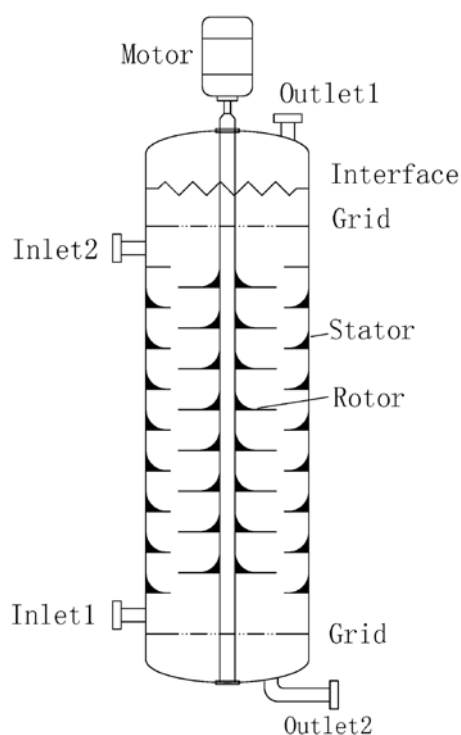


Figure 4. Geometrical structure of the modified RDC

3.2 Flow field of the modified RDC

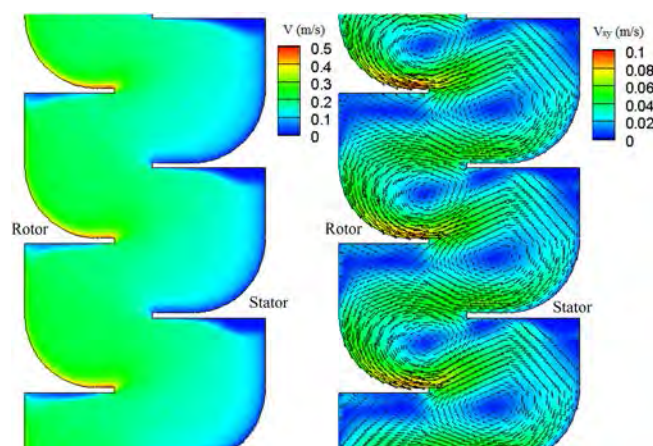


Figure 5. Flow field structure in the modified RDC, left: velocity field, right: profile velocity field (x,y)

Figure 5 displays the flow field of a modified RDC with an arc diameter of 14.5 mm.. There are two obvious characteristics. Firstly, the dead zones on the internals were almost disappeared as shown in Figure 6. This illustrates that the new column is advantageous to avoid the solid deposition. Secondly, the flow field structure was nearly unchanged. Thus, in terms of the hydrodynamic effects, the modification has few effects on the extraction efficiency of the new column.

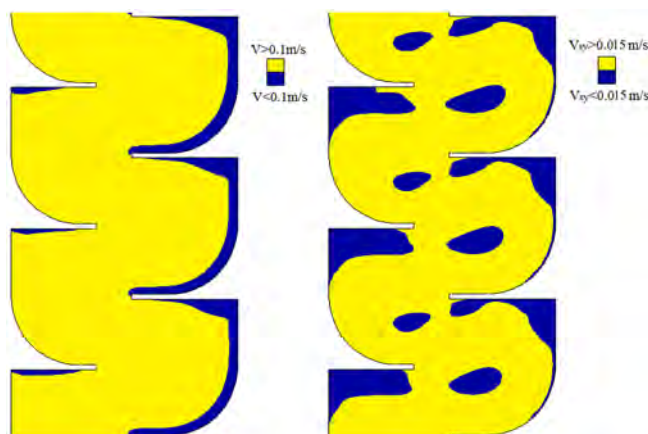


Figure 6. Dead zones in the modified RDC, left: fluid velocity, right: profile velocity (x,y)

3.3 Performance comparison

Droplet diameter, dispersed phase holdup and axial diffusion are three of the most important parameters in extraction columns. By the CFD-PBM simulation, the dispersed phase holdup, droplet diameter and continuous phase axial diffusion coefficient (Peclet number) are 0.14, 1.51 and 5.58 respectively. Compared with the values of 0.11, 1.69 and 6.39 for the traditional RDC. The differences are +21.43%, -11.92% and -14.52%. This comparison indicates that the performance of the modified RDC is almost kept same as the traditional one. The detailed comparison of droplet size distribution and residence time distribution are presented in Figure 7.

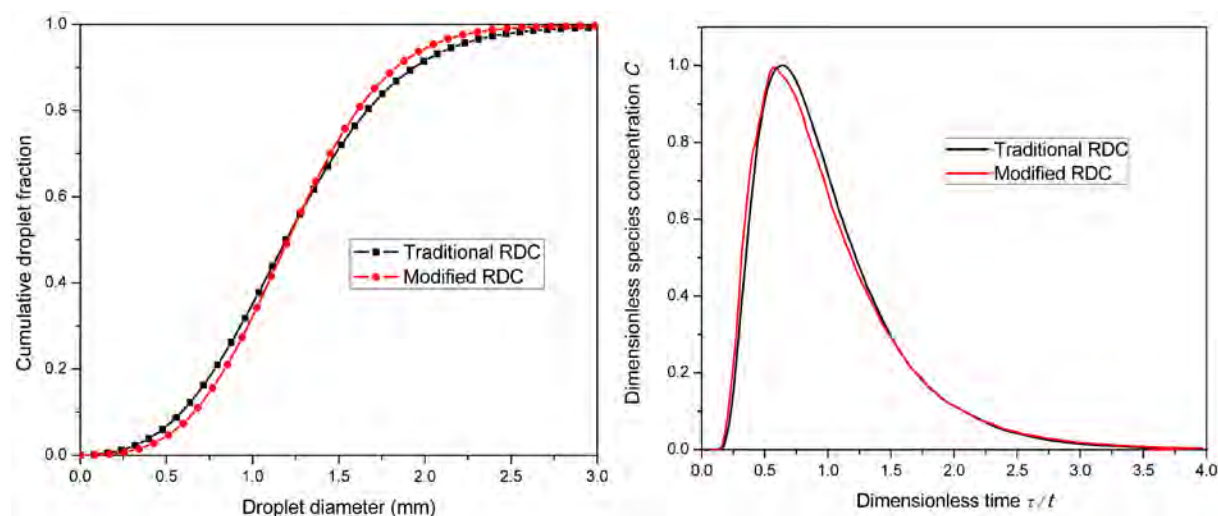


Figure 6. Comparison of droplet size distribution and residence time distribution.

4. Conclusion

RDCs have the problem of solid deposition on internals when they are applied to solid-laden extraction systems. Previous improvements usually focused on the increase of stirring intensity, which is disadvantageous to the extraction efficiency and throughput. In this study, according to the flow field structure of a traditional RDC, flow dead zones are found to be the main cause of solid deposition. Thus a-quarter-arcs-shaped internals were proposed. The results of validated CFD-PBM simulations show that the flow dead zones in the traditional RDC are eliminated effectively by the modification. About the extraction performance, the critical parameter of dispersed phase holdup, droplet diameter and axial diffusion coefficient of the modified RDC are closed to the traditional one. Hence, the modified RDC is considered as an effective equipment for the processing of solid-laden extraction systems with excellent performances. In the future, the new column needs further experimental validations.

Acknowledgement

We acknowledge the financial support provided by the National Natural Science Foundation of China (Grant 21206038), the Specialized Research Fund for the Doctoral Program of Higher Education (New Teachers) (Grant 20120074120014), and the Fundamental Research Funds for the Central Universities..

References

- [1] Reman, G., Van de Vusse, J. Applying RDC to lube extraction. *Petroleum Refiner*. 1955, 34(9): 129-134.
- [2] Zhu, J., Zhang, S., Zhou, X., etc. Hydrodynamics, axial mixing and mass transfer in open turbine rotating disc contactor. *Chem. Eng. Technol*. 1999, 14: 167-177.
- [3] Handbook
- [4] Drumm, C., Bart, H.-J. Hydrodynamics in a RDC extractor: single and two-phase PIV measurements and CFD simulations. *Chem. Eng. Technol*. 2006, 29(11): 1297-1302.
- [5] Bart, H.-J. Extraction columns in hydrometallurgy. *Hydrometallurgy*. 2005, 78: 21-29.
- [6] Hlawitschka, M. W., Bart, H.-J. CFD-Mass transfer simulation of an RDC column. *Computer Aided Chem. Eng*. 2012, 31: 920-924.
- [7] Drumm, C., Attarakih, M., Bart, H.-J. Coupling of CFD with DPBM for an RDC extractor. *Chem. Eng. Sci*. 2009, 64(4): 721-732.
- [8] Luo, H., Svendsen, H. F. Theoretical model for drop and bubble breakup in turbulent dispersions. *AIChE J*. 1996, 42(5): 1225-1233.
- [9] Chen, P., Sanyal, J., Duduković, M. P. Numerical simulation of bubble columns flows: effect of different breakup and coalescence closures. *Chem. Eng. Sci*. 2005, 60, 1085-1101.

Comprehensive Numerical and Experimental Analysis of Copper Solvent Extraction within Y-Y Microreactors

Pedro Ribeiro Martins Bento¹, Omid Kazemi², Sanja Miskovic¹

¹Department of Metallurgical Engineering, University of Utah, Salt Lake City, USA

²Department of Mining and Metallurgy Engineering, Amirkabir University of Technology, Iran

Abstract

Microfluidic or microreactor solvent extraction (SX) is a high-throughput metal extraction method, which has proven to be a promising alternative to conventional large-scale mixer-settler SX process. Within the microreactor, the extraction process is performed through a non-dispersive manner, under laminar conditions, when the reactant phases are brought into contact and form an interface through which the mass transfer occurs. In this way, a large surface area per unit volume is formed, which improves the extraction process. As the available mixing space within the microreactor decreases, the mass transfer in microchannels becomes strongly dependent on diffusion, which further improves the extraction rate. Increased extraction efficiency could be achieved by adjusting several key operational parameters of which only few have been investigated in the past. Through this work, a comprehensive numerical and experimental study, by using computational fluid dynamics (CFD) approach on a series of Y-Y microreactors, is performed. The extraction efficiency of all tested microreactors is investigated by varying several key operational parameters including: phases contact time, microchannel length, interphase liquid/liquid contact surface area, microchannel cross-sectional profile, temperature, existing atomic species, and copper concentration of the aqueous phase at the inlet. For the purpose of experimental analysis, both standard copper aqueous solutions and copper leach solutions are used. A pregnant copper leach solution is produced by sulfuric acid from a flotation copper concentrate composed of chalcopyrite-chalcocite-bornite minerals. The predicted copper concentration gradient and outlet copper concentration of both aqueous and organic phases are validated experimentally by in-line spectrometer and X-ray diffractometry (XRD). The experimental results are found to be in acceptable agreement with the predicted data. The results also show that the contact time, which is determined by the flow velocity and microchannel length, has significant impact on the extraction efficiency – as the contact time increases, separation efficiency improves. Furthermore, for constant flow rates, the efficiency is shown to increase with the solvent to aqueous volumetric ratio increase over the lower range of volumetric ratios. After the critical point is achieved, this trend is found to be reversed for the volumetric ratios higher than the critical value. It is also found that increase in the contact surface area, as well as decrease in the diffusion distance, results in the efficiency increase. Furthermore, the investigation shows that presence of other materials (impurities) reduce the diffusion rate and consequently reduce the efficiency.

Keywords: Solvent Extraction, Microreactor, CFD, Microfluidics, Copper extraction

Simulation of organic drop coalescence in a hypothetical settler: effect of geometry and fluid parameters

Omid Kazemi, Eskandar Keshavarz Alamdar

Dept. of Mining and Metallurgical Eng. Amirkabir University of Technology

Due to increasing world demands to high quality materials and decreasing of rich resources, there is a strong incentive to apply different processes to extraction and processing of metals from low grade ores. The Leaching, Solvent Extraction and Electro winning circuit (LX–SX–EW) is one of the most effective processes for this purpose, Which plays a key role in metallurgical industries.

Liquid–liquid extraction is a process for separating components in solution by their distribution between two immiscible liquids. Solvent extraction is used in numerous chemical industries to produce pure chemical compounds ranging from pharmaceuticals and biomedical to heavy organics and metals in analytical chemistry and in environmental waste purification. It has been used more widely in hydrometallurgy (Copper, Cobalt, Nickel and Zinc). In hydrometallurgy the most applied solvent extraction method is a mixer-settler process, which fits in the group of stage wise equipment. The main ideas in the development of the solvent extraction settler process are to achieve clean phase separation, minimize the loss of the reagents and decrease the surface area of the settlers. In the solvent extraction process, there are two phases: aqueous and organic. Aqueous and organic phases are pumped into a mixer to achieve homogeneous dispersion. After mixing, the dispersion is fed into a settler where the aqueous and organic phases are separated by gravity. The performance of a settler depends on distribution of feed into the settler and feed distribution has a large effect on flow pattern in the settler. Undesirable feed distribution lead to production of macro eddies and circulation flow in the settler. Macro eddies can be eliminated by baffles and packed media. The most common method to make phase separation more effective is to use picket fences, which are installed in different locations in the settler. The idea of the picket fences is to retain a deep and dense dispersion layer in the first part of the settler.

Applying some changes to the circuit to evaluate their effects might be very costly in some cases. So simulating the process in virtual environments could be highly efficient in making improvements by assessing the changes. One of simulation tools which is widely used in metallurgical processes, is Computational Fluid Dynamics (CFD). CFD tools provide the opportunity of simulating and optimizing the fluid's behavior which is a key element in solvent extraction procedure. In this study, geometry of settlers, which are commonly used in copper SX systems has

been optimized to reduce the macro eddies and turbulent flows to increase the efficiency of the settlers and achieve a clean and optimal phase separation. In one step, implementation of two rows of picket fences with optimal distance between rows and its impact on flow pattern have been investigated. The results show that setting these two rows of picket fences help the process to achieve a uniform separation, significantly. Moreover, the effect of changing the ratio of the phases and entrance velocity of mixed fluids into settler has been investigated to achieve the optimal values which would result maximum possible efficiency.

In this study, A computational fluid dynamics simulation based on Eulerian–Eulerian two-phase method have been applied to study the behavior of aqueous–organic dispersion and the flow pattern in the mixer-settlers. The simulations use multiple-size group (MUSIG) model for droplet dispersion and droplet size distribution, which is based on a population balance equation and considers the break-up and coalescence models of the droplets. Moreover, calculation of fluid flow field has been performed by solving the continuity and Navier Stokes equations along with the standard k - ϵ turbulence model. The turbulence model included buoyancy, drag, lift and turbulent dispersion forces. Ansys design modeler has been used to design the geometry of model. And for meshing the produced geometry, the created file has been edited through the CFX mesh method. For meshing, capabilities of Ansys CFX have been used. In order to achieve a fast and reliable result, in the solver setting part, number of maximum interactions has been fixed on 100. And finally, the results are going to be verified with the experimental field measurements (I am now working in this phase and preparing required equipments for experimental measurements).

The Role of Solvent Extraction in Platinum Group Metal Refining – Past, Present and Future

Richard A. Grant^{*1}, Ross J. Gordon¹, Stephen F. Woollam²

Summary

For over 50 years solvent extraction has been a key technology for the refining of the PGM. This paper initially reviews the history of solvent extraction in the PGM refining industries. Despite being a well-established technology research activity in this area has never been stronger with an exponential growth in the number of both literature and patent publications since the Millennium. However a number of the challenges to be faced in the future are outlined and some of the potential options for addressing these are discussed.

Introduction

The refining of the Platinum Group Metals (PGM) presents a number of interesting technical challenges. The PGM concentrates resulting from either Primary production from mines or the recovery from Secondary (recycled) sources contain not only the PGM, Au and Ag but a wide range of base metals (BM). The PGM have similar chemical properties not only to each other but also to many of the accompanying BM. Due to the high value of the PGM the Market requires increasingly rapid refining technology which is highly efficient with minimal recycles whilst meeting the high purities demanded (typically >99.99%).

For over 50 years solvent extraction has been a key technology for the refining of the PGM. This paper reviews the history of solvent extraction in the PGM refining industries. It then outlines a number of the challenges to be faced and discusses some of the potential future options for addressing these.

Past

The PGM are a group of six elements (Ir, Os, Pd, Pt, Rh and Ru) which together with Au and Ag form the Precious Metals. The Conquistadors first encountered Pt in Columbia when panning for Au and named it Platina (little silver) as the silvery metal could not be melted and was therefore of no value. Pt was first identified as an element by Ulloa in 1735 whilst the other members of the group were discovered in the early 1800s.

Initially, demand (mainly for jewellery and specialised industrial applications) was limited and by the 1920s had only reached 25,000ozT (800kg annum⁻¹). The PGM were refined in large scale laboratory equipment using scaled-up analytical gravimetric methods. Demand increased to 250,000ozT by the early 1960s and refining of necessity was carried out on a more industrial scale. Figure 1 shows the scene in a typical refinery which operated manually. Pumps were unreliable and so the reactors were mounted on a series of steps (“cascades”) to allow liquors to be transferred by gravity from one process to the next. Reactors were stirred by hand

^{*1} Johnson Matthey Technology Centre, Sonning Common, Reading, United Kingdom, RG4 7SB. grantra@matthey.com

² Anglo American's Technical Solutions, Johannesburg, South Africa.

using a paddle and heated by sparging with live steam. Process efficiencies for the precipitation-based processes were low and refining times ranged from around 6 months for Pd and Pt to a couple of years for Ir and Rh. Platinosis, an allergic reaction to Pt salts (especially the chloro-complexes), was becoming a significant issue.



Figure 1. Typical PGM Refining Operation at Johnson Matthey, Royston circa 1960

This situation was clearly unsustainable and modern refining technologies were investigated. The similarities between the PGM and nuclear fuel reprocessing industries were identified and this drew attention to the rapidly developing technique of solvent extraction. As a result, a number of the major PGM refiners developed solvent extraction based flowsheets.

The largest platinum producer in the world is Anglo American Platinum (40% of Pt in 2012). In the 1970s, refining was carried out by Matthey Rustenburg Refiners (MRR). This was jointly owned by Johnson Matthey and Rustenburg Platinum Mines (now part of Anglo American) which was set-up as a result of a long-standing relationship dating back to the discovery in 1924 of large deposits of Pt in South Africa by Hans Merensky. The flowsheet developed by MRR¹ is presented in Figure 2. Following extensive piloting, a 300,000ozT Pt annum⁻¹ pre-production plant was established at Johnson Matthey's Royston (UK) operation in 1983. This proved very successful and the decision was taken to build a full-scale solvent extraction refinery at Rustenburg (South Africa). Precious Metal Refiners (PMR) was commissioned in 1989. This is now fully owned by Anglo American Platinum and refines both their entire output and that of a number of joint ventures.

The Pd and Pt solvent extraction sections at PMR are shown in Figure 3. In order to minimize the impact in the unlikely event of a fire, these are dual streamed and sited in separate buildings which are open on three sides for ease of access. The methyl iso-butyl ketone (MIBK) mixer-settlers are also blanketed with nitrogen due to its flash point of 14°C. To give an indication of the compact size of the Solvex equipment each Pt mixer-settler measures 0.3x0.45x1.5m and the design flowrate of feed was 100 L hr⁻¹.

Simultaneously, two other flowsheets were being developed. The first (Figure 2) was developed by INCO and was installed at their PGM refinery in Acton in the UK². The

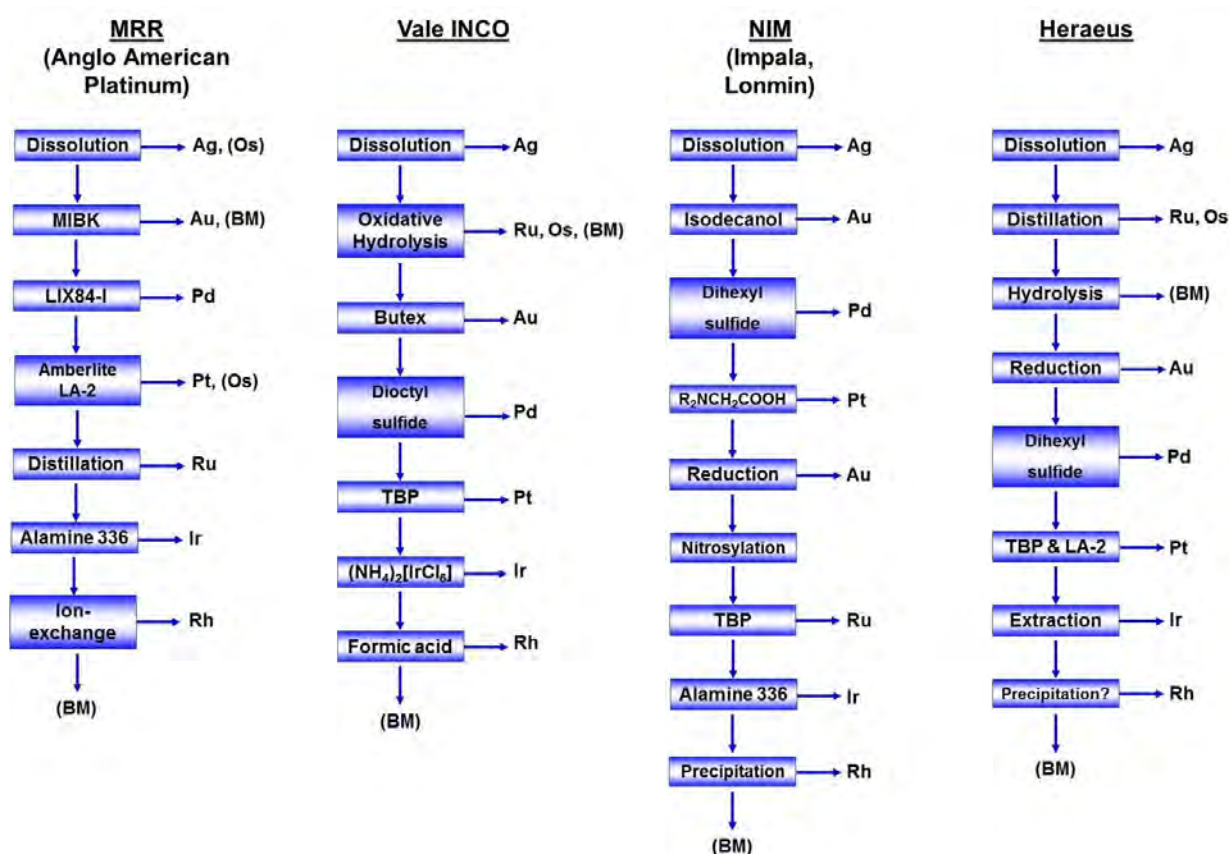


Figure 2. Solvent Extraction flowsheets developed for major PGM refiners.

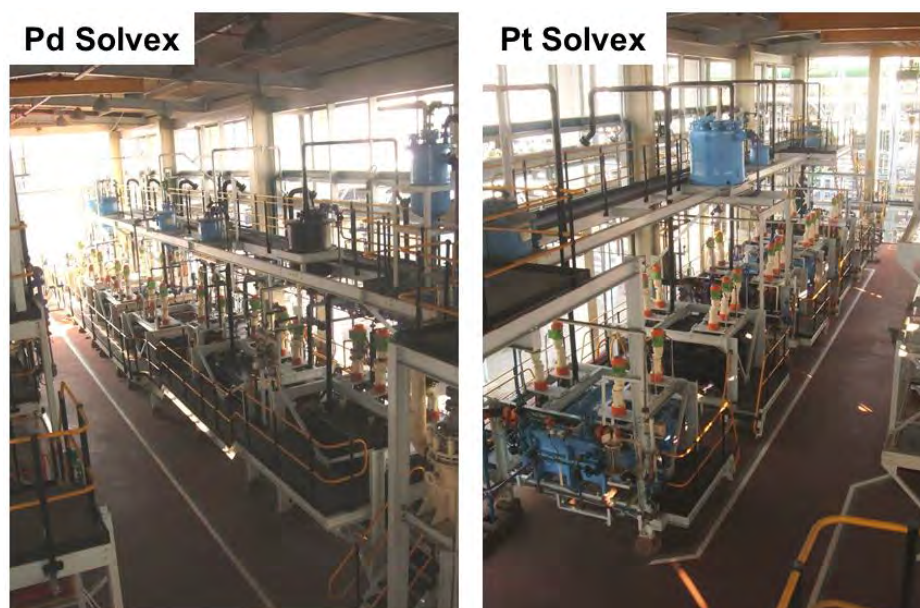


Figure 3. Pd and Pt Solvent extraction plants at Precious Metal Refiners

second³ was developed by the National Institute for Metallurgy (NIM, now MINTEK) in South Africa. This comprised a number of alternative stages utilizing solvent extraction, ion-exchange or precipitation and one option is presented in Figure 2. Variants of this flowsheet were installed by Impala Platinum⁴ at their refinery at Springs and by Lonmin⁵ at Brakpan. Finally in 1993 Heraeus⁶ installed a solvent extraction based refinery at Hanau in Germany primarily to refine the output from Northam Platinum in South Africa.

Present

In the 25 years since the commissioning of PMR, Anglo American Platinum have continued to develop their flowsheet. In the solvent extraction separations, Anglo American Platinum developed a novel mono N-substituted amide extractant⁷. This is a weak-base extractant which offers a very significant improvement over tributylphosphate (TBP) which is employed in the other PGM refining flowsheets in Figure 2. At PMR it was retro-fitted into the Ir solvent extraction stages to replace Alamine 336. Its high oxidative stability resulted in a >50 fold extension in the lifetime of the Ir extractant and a significant increase in the extraction efficiency and selectivity⁸. This amide extractant which is custom manufactured is also exploited by Johnson Matthey at their Royston PGM refinery. In the Pd section, a special formulation (LIX84-A) has been introduced to extend the lifetime of the hydroxyoxime extractant⁹. Further major improvements at PMR include a High Intensity Dissolution process which provides quantitative separation of Os at the start of the flowsheet, and the replacement of the Rh ion-exchange stage by a highly selective precipitation. From 2001 a major expansion was carried out at PMR in anticipation of increasing demand for the PGM. The operation of the Pd, Pt and Ir sections was optimised and a potential threefold increase in production capacity demonstrated. The MIBK solvent extraction of Au, Fe and a number of amphoteric metals was originally carried out using “Oldshue-Rushton” stirred columns. The capacity of these could not be expanded to the same extent and new dual-stream sections were constructed based on glass mixer-settlers manufactured by QVF. However as a result of the prolonged recession, and in particular the reduced demand in Europe for PGM especially for autocatalysts, the expansion of PMR has still to be fully implemented.

There have been no recent publications by Vale INCO on their refining operation. However the section on the Vale website concerning the Vale Acton refinery confirms that they still operate a solvent extraction based flowsheet¹⁰.

The operation of the NIM process by Impala Platinum at their Springs refinery was fairly short lived and they reverted to a conventional precipitation based flowsheet. This has subsequently been replaced by a flowsheet utilising a combination of ion-exchange, molecular recognition technology and precipitation^{11,12} which was commissioned in 1998. Whilst developing this flowsheet, Impala discounted the use of solvent extraction due to concern about the potential risk of fire¹³.

Lonmin also discontinued their refining operation based on the NIM flowsheet and reverted to a conventional precipitation based circuit. Details of their current process are given in reference¹².

Finally Heraeus closed their solvent extraction based refinery when the expanded production from Northam Platinum, for which the plant was constructed, failed to occur. Pd and Pt are now separated by selective precipitation of their potassium salts¹⁴. The same publication reports that Ru is separated by distillation as its volatile tetroxide while Ir and Rh are purified by different precipitation, extraction and ion exchange steps. This may indicate that iridium is still separated by solvent extraction.

The largest PGM refinery in the world, Norilsk Nickel's Krastsvetmet at Krasnoyarsk in Russia, mainly produces Pd due to the much higher Pd:Pt ratio in the Russian ores

(circa 4.5:1) compared with the South African Bushveld deposit (circa 1:2). A recently published flowsheet¹² indicates that this largely employs conventional precipitation techniques with the exception of Ru which is extracted using TBP.

Research activity in PGM solvent extraction

In view of the decreased application of solvent extraction in PGM refining it might be expected that interest in this technology would have peaked and therefore research activity in this area might have decreased. However examination of the literature (Figure 4) shows an exponential increase in the number of publications on PGM solvent extraction since the Millennium. This is not simply due to increased academic activity, as there has been an even stronger growth in patent applications. In the 1960s and 1970s publications in the Russian language predominated. Whilst this has apparently decreased, this is undoubtedly in part due to increasing publication by Russian researchers in the English language. The major area of growth in publications in the literature over the past 13 years has come from Chinese organisations. This again does not simply represent academic research. There has been an even faster rise in patent publications where Chinese publications in the past three years have accounted for 44% of the total activity.

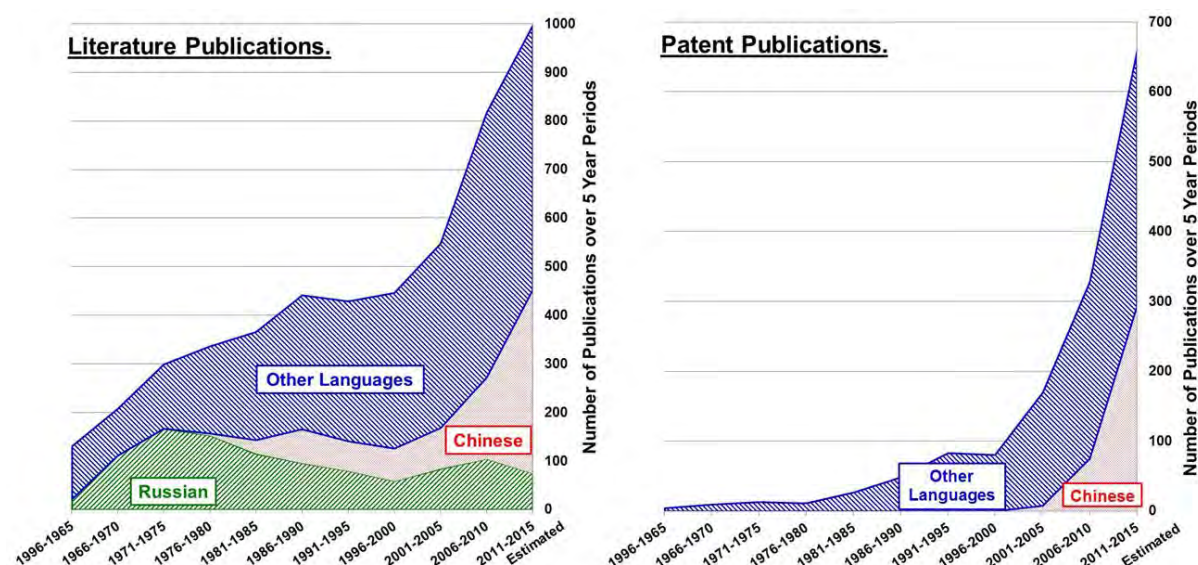


Figure 4. Increase in number of publications on solvent extraction of PGM over the past fifty years.

Future

Although there is currently significant research activity in PGM solvent extraction there are a number of potential challenges to be addressed. Traditionally solvent extraction reagents have been developed by the extractant manufacturers. However there has been a significant contraction in the number of major manufacturers in the Western World from >10 in the 1970s-80s to just 3. This has been accompanied by an even greater decrease in the number of reagents on the market. Whilst innovative applications of the limited number of extractants available will undoubtedly be developed, these reagents are designed for the separation of BM whose extraction chemistries differ significantly from the PGM. However the PGM industry is small with annual production of Pt in 2012 of only 175 tonnes which limits the market for new reagents. The introduction in Europe of the Registration, Evaluation, Authorisation

and restriction of Chemicals (REACH) legislation represents a further potential barrier. The development by Anglo American Platinum and Johnson Matthey of their innovative proprietary amide extractant may be a model for the future.

Another area where future developments will undoubtedly occur is in innovative solvent extraction equipment. The majority of the PGM inventory in conventional mixer-settlers resides in the settlers as does a significant amount of the extractant. Equipment with enhanced coalescence would reduce this. In the longterm innovative developments such as micro-fluidics, which would obviate the requirements for a settler, may find application. However this field is in its infancy and a very long distance from commercialisation.

Acknowledgements

The authors would like to thank Anglo American Platinum Limited and Johnson Matthey for their financial support and for permission to publish this paper.

References

1. MJ Cleare, P Charlesworth, DJ Bryson, *J. Chem. Tech. Biotechnol.* 1979, **29**, 210.
2. JE Barnes, JD Edwards, *Chemistry and Industry* 1982, 6 March, 151.
3. RI Edwards in BH Lucas, GM Ritcey, HW Smith, *Proc. ISEC 77, Toronto, CIM Special Volume 21*, Canadian Institute of Mining and Metallurgy, 1979, p. 24.
4. J Bannon, B Gilmour, L Paton, D Brown, M Jackson, *Who the Hell Wants to be in Platinum?*, Impala Platinum Holdings Ltd, June 2013.
5. LG Floyd, *New Refining Process for Ru, Rh, Ir*, 2nd IPMI Conference, 1978.
6. A Mueller, *Chemische Rundschau* 1993, **46** (38), 9.
7. RA Grant, BA Murrer, US 4726841.
8. RA Grant, RF Burnham, S Collard in T Sekine, S Kusakabe, *Solvent Extraction 1990, Proc. ISEC '90, Process Metallurgy 7*, Elsevier 1992, p 961.
9. SF Woollam, RA Grant in BA Moyer (ed), *Solvent Extraction: Fundamentals to Industrial Applications, Proc. of ISEC 2008*, Tuscon, AZ. Canadian Institute of Mining and Metallurgy, Montreal, Canada, 2008, p 281.
10. Anon, <http://acton.vale.com/RefiningProcess.aspx>, accessed 20/02/2014.
11. WH Black, SR Izatt, JB Dale and RL Bruening, *Precious Metals 2006, Proc. 30th IPMI Conference, Las Vegas*, IPMI, 2006, (cd).
12. FK Crundwell, MS Moats, V Ramachandran, TG Robinson, WG Davenport, *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*, Elsevier, 2011.
13. Stuart Murray, Impala Platinum, *personal communication*.
14. M Grehl, H Meyer, C Nowotny, J Kralik, *Proc. European Metallurgical Conference, EMC 2005*, GDMB Gesellschaft der Metallurgen und Bergleute e. V.

Iron removal and nickel and cobalt recovery from strong chloride leach solution of laterites by solvent extraction

Chu Yong Cheng^{*1}, Zhaowu Zhu¹, Karol Tulpatowicz^{1,2} Yoko Pranolo¹

Summary

Leaching with chloride solutions has advantages of high leaching rate, fast kinetics and the recycling of lixiviant, particularly, HCl. However, the presence of large amounts of Fe(III) in the pregnant leach solution is a challenge for the recovery of cobalt and nickel. In the current study, Fe(III) was removed from a synthetic chloride leach solution of nickel laterites using solvent extraction with N,N-diethyldodecanamide (DEDA). Using an organic system consisting of 30% (v/v) DEDA and 30% (v/v) isodecanol in ShellSol D70, the Fe(III) extraction reached over 90% from a strong chloride solution containing 6 M Cl in a single contact. The selectivity of Fe(III) over all other metals was very high. The Fe(III) extraction increased significantly with the increase in chloride concentration. Water was very effective for stripping Fe(III). After iron removal, aluminium was almost completely precipitated at pH 3 and the co-precipitation of cobalt and nickel was insignificant at this pH. Cobalt and nickel in the raffinate after removal of Fe(III) and aluminium were recovered using SX and SSX systems, respectively. A new process to recover Ni and Co from strong chloride leach solutions of laterites has been developed consisting of four main steps: 1) Removal of Fe(III) using SX with DEDA, 2) Precipitation of aluminium with limestone, 3) Recovery of cobalt and zinc using SX with Alamine 336 and 4) Recovery of nickel using SSX system consisting of Versatic 10/LIX 63/TBP.

Introduction

Processing nickel laterites in chloride media has advantages over sulphate media such as high leach efficiency, high leach kinetics and HCl regeneration (Harris, et al., 2006; McDonald and Whittington, 2008; Kyle, 2010). Leaching processes have been developed using acidic lixiviants containing high concentrations of chlorides (Harris, et al., 2006; Steyl, et al., 2008).

Iron is the major impurity to affect the recovery of nickel and cobalt from chloride leach solutions. Therefore, the removal of iron from leach solutions before nickel and cobalt recovery is critical. Iron could lead to difficult operation or high operating cost if direct precipitation or thermo hydrolysis are employed (Moyes, 2005; Harris, et al., 2006; Harris and White, 2007; Steyl, et al., 2008). Solvent extraction (SX) could be used to remove iron from the leach solution (Gibson and Rice, 1977; Lakshmanan et al., 2013). However, all reagents tested and reported so far have drawbacks, such as poor phase separation, high aqueous solubility etc. In this paper, the removal of Fe(III) using SX with N,N-diethyldodecanamide (DEDA) was studied. DEDA is a commercially available reagent with negligible solubility in water and high flash point (114°C) and stable under normal conditions.

As aluminium could also affect the recovery of nickel and cobalt, precipitation could be carried out to separate it from nickel and cobalt. Cobalt recovery was investigated using SX with Alamine 336 and an SSX system consisting of LIX 63 and Versatic 10 was used to recover nickel in a preferred pH range of 4-5 (Zhu et al. 2012). A process to recover nickel and cobalt was proposed in principle including iron removal by SX, aluminium removal by precipitation and recovery cobalt and nickel by SX and SSX.

*Corresponding author email: chu.cheng@csiro.au

¹CSIRO Minerals Down Under National Research Flagship, Australia

²RMDSTEM Limited, Australia

EXPERIMENTAL

A synthetic chloride leach solution of nickel laterites was prepared containing 20 g/L Fe(III), 10 g/L Al, 5 g/L Ni, 2 g/L Mn(II), 30 g/L Mg, 0.5 g/L Co, Zn, Cr(III) and Cu by dissolving the corresponding AR grade metal chloride salts in de-ionised water. N,N-diethyldodecanamide (DEDA, 98% purity), Alamine 336, LIX 63, Versatic 10, Isodecanol and ShellSol D70 were purchased or provided by reagent companies and used as received without further treatment, with purities as advised on the relevant MSDS.

All shake-out tests for SX and SSX were carried out in a reactor immersed in a temperature controlled water bath at 40 °C. The pH of the aqueous solution was measured during mixing using a pH electrode and a pH meter. The aqueous and organic phases of the samples were separated for chemical analysis using ICP-AES.

Aluminium precipitation was carried out in a glass jar immersed in a water bath at 40°C. The pH adjustment was achieved by adding fine limestone powder. Metal precipitation was calculated based on the metal concentration in the aqueous solution.

RESULTS AND DISCUSSION

Chloride concentration effect on Fe(III) extraction with the DEDA organic system

The organic solution consisting of 30% (v/v) DEDA and 30% isodecanol in ShellSol D70 and the synthetic feed solution with various initial chloride concentrations were used for the investigation of the effect of chloride concentration on Fe(III) extraction at an A/O of 1:1 and 40 °C (Zhu et al. 2014). Chloride concentrations were increased by adding CaCl₂. The Fe(III) extraction at various chloride concentrations is shown in Table 1. The extraction of Fe(III) was significantly increased with the increase in chloride concentrations. With the initial chloride concentration of 265 g/L (~7.5 M Cl), nearly 99% Fe(III) was extracted in a single contact. As the chloride concentration dropped to 42 g/L (~1.2 M Cl), only 2.4% Fe(III) was extracted. The significant dependence of Fe(III) extraction on chloride concentration can be used to extract and strip Fe(III).

Table 1: Effect of chloride concentration on Fe(III) extraction (Zhu et al., 2014)

Cl ⁻ concentration (g/L)	42	74	138	201	265
Fe(III) Extraction (%)	2.4	13.4	51.2	83.4	98.9

pH effect on Fe(III) extraction with the DEDA organic system

The organic solution consisting of 30% DEDA and 30% isodecanol in ShellSol D70 was contacted with the synthetic leach solution containing 213 g/L Cl at an A/O of 1:1 and 40 °C at various pH values to study the effect of pH on Fe(III) extraction (Figure 1, Zhu et al. 2014). Amongst the 10 metals involved, only Fe(III) was significantly extracted (90%) in the pH range tested. The extractions of other metals were very low (<0.5%) except that of zinc (~3%). Therefore, iron separation from all other metals could be readily achieved using the DEDA system. This again indicates that the extraction of Fe(III) is basically dependent upon the chloride concentration and the effect of the presence of other metals at the levels found in laterite leach solutions on iron extraction is negligible.

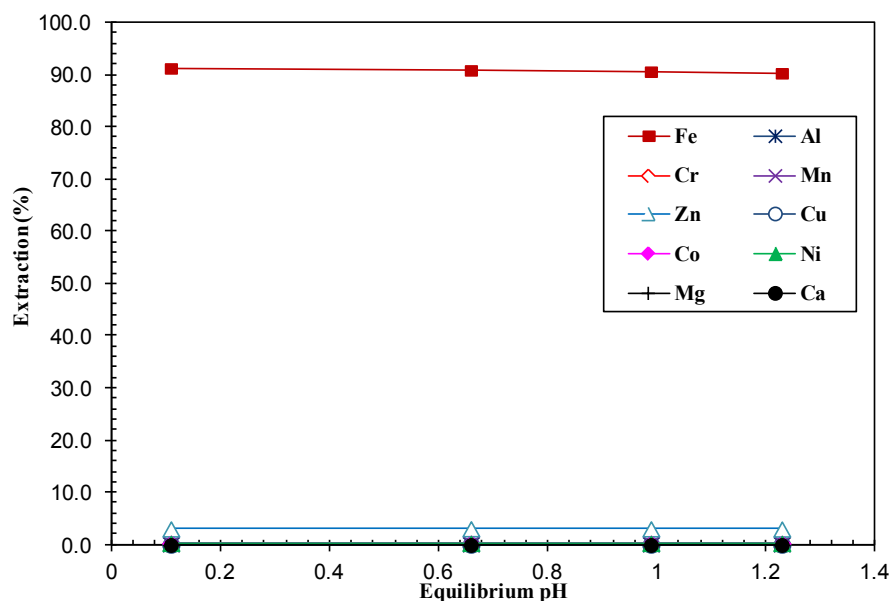


Figure 1: Metal extraction pH isotherms with the DEDA/Isodecanol system (Zhu et al., 2014)

Stripping Fe(III) from the loaded DEDA organic system

Stripping Fe(III) from the loaded organic solution using water was very effective, with over 99% stripped at an O/A of 1 and 40 °C. The loaded strip liquor will be subjected to hydrolysis to recover the HCl for recycling and hematite for safe disposal.

pH effect on Al removal by precipitation with limestone

The removal of Al from the synthetic solution after iron removal was studied by precipitation with fine limestone powder. Metal precipitations were calculated at various equilibrium pH measured at 50 °C (Figure 3). It was found that Al precipitation was almost completed at pH 3.0 with 28% Cu, 10% Zn and 1-2% Ni and Co co-precipitated or entrained, indicating a very good separation of Al from Ni and Co.

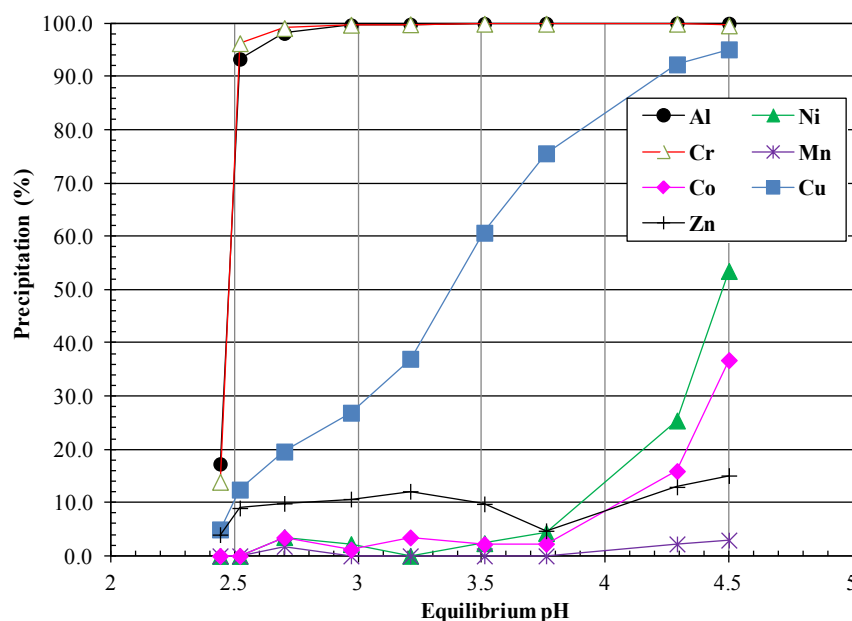


Figure 3: Metal precipitation from chloride solution of Ni laterite with limestone at 50 °C.

Temperature effect on Al removal by precipitation with limestone

The precipitation of Al and Ni from the synthetic aqueous solution was assessed under various pH values and temperatures (Figure 4). Again, the aluminium precipitation was almost completed at pH 3.0 with no significant Ni co-precipitation in temperature range of 25 - 70 °C, indicating that the temperature effect on Al precipitation and its separation from Ni is insignificant. Taking consideration of high energy consumption in higher temperatures and difficulty in filtration in low temperatures, the Al precipitation should be conducted at a moderate temperature of 40 °C.

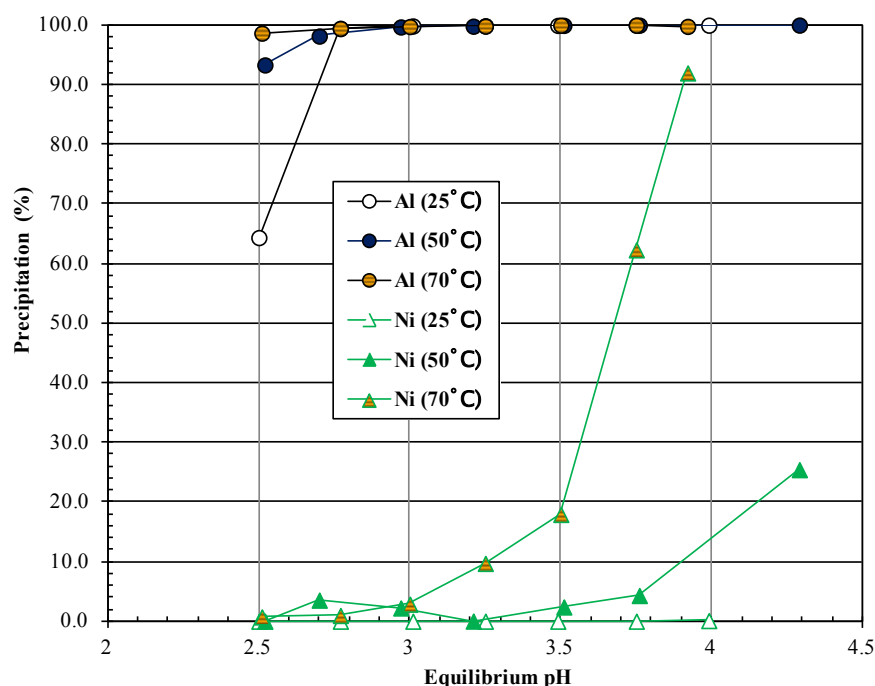


Figure 4: Al and Ni precipitation under various pH values and temperatures

A new process to recover Ni and Co from chloride leach solution

A new process to recover Ni and Co from strong chloride leach solution of laterites has been developed consisting of the following main steps: 1) Removal of Fe(III) using SX with DEDA, 2) Precipitation of Al with limestone, 3) Recovery of Co and Zn using SX with Alamine 336 (Figure 5, Zhu et al., 2012), and 4) Recovery of Ni using SSX system consisting of Versatic 10/LIX 63/TBP (Figure 6, Zhu et al., 2012). In Step 1, the loaded strip liquor from water stripping is subjected to hydrolysis to regenerate HCl and to convert Fe(III) to harmless hematite for disposal. In Step 3, the loaded strip liquor from water stripping can be subjected to Zn and Mn removal using D2EHPA (Cheng, 2000). Co can be recovered from the resultant solution by precipitation or electrowinning. In Step 4, the loaded strip liquor from stripping using low concentration H_2SO_4 is subjected to electrowinning of nickel. The raffinate containing large amount of CaCl_2 is recycled for leaching. To meet the mass balances of Mn, Mg and Ca, some raffinate from Step 4 is bled and treated with limestone to precipitate Mn and Mg. The resultant solution is further treated by acidification using H_2SO_4 to precipitate extra Ca as gypsum for disposal.

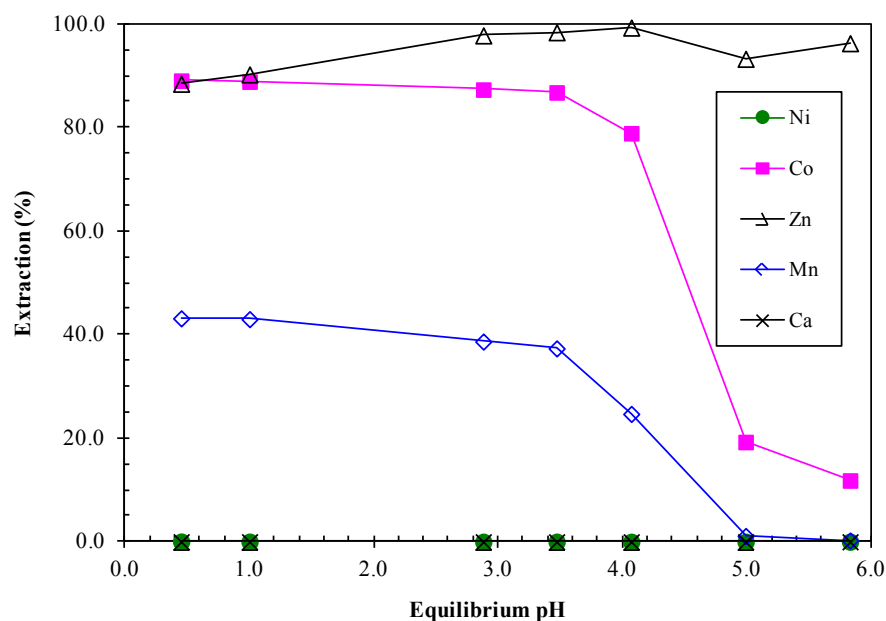


Figure 5: Extraction pH isotherms with Alamine 336 SX system

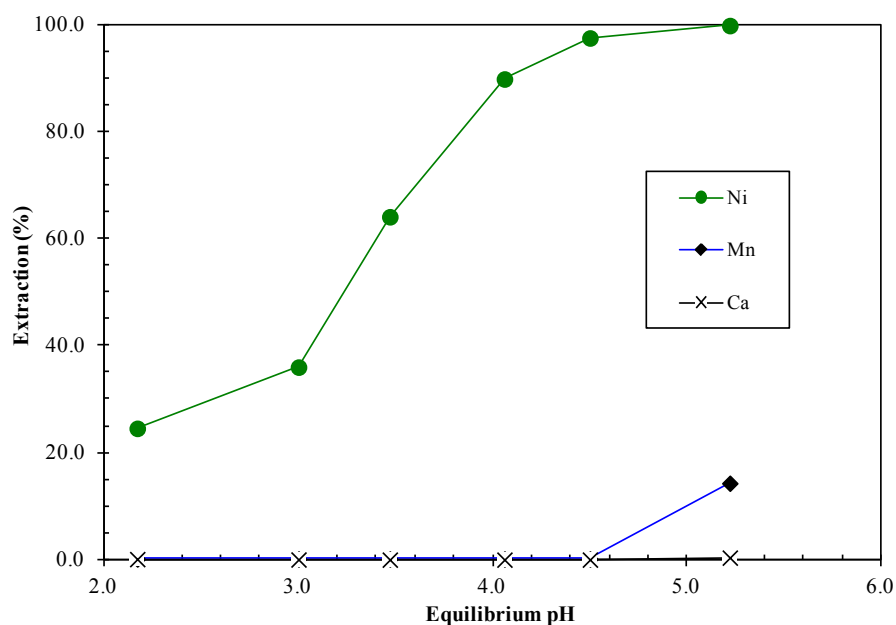


Figure 6: Extraction pH isotherms with SSX system consisting of Versatic 10/LIX 63/TBP.

CONCLUSIONS

An organic system consisting of N,N-Diethyldodecanamide (DEDA) and isodecanol was found to be very effective for the removal of Fe(III) from strong chloride leach solutions. It is shown that the DEDA and isodecanol system could be used to effectively extract > 90% Fe(III) from solutions containing more than 200 g/L Cl in a single contact. The extraction increased almost linearly with the increase in chloride concentration. The extraction selectivity of Fe(III) over metals tested including Ni, Co, Cu, Zn, Al, Cr, Mn, Mg and Ca was very high. The effect of pH and temperature on Fe(III) extraction was insignificant. Fe(III) can be readily stripped using water.

At pH 3.0, the Al precipitation was almost completed with no significant Ni and Co co-precipitation. There was no effect of temperature on Al precipitation and its separation from Ni and Co.

A new process to recover Ni and Co from strong chloride leach solutions of laterites has been developed consisting of the following main steps: 1) Removal of Fe(III) using SX with DEDA, 2) Precipitation of Al with limestone, 3) Recovery of Co and Zn using SX with Alamine 336 and 4) Recovery of Ni using SSX system consisting of Versatic 10/LIX 63/TBP.

ACKNOWLEDGEMENTS

The authors would like to thank Drs Keith Barnard and Goutam Das for reviewing the paper and providing valuable suggestions. Mr Nicholas Kelly and Mr Karl Bunney are thanked for their assistance in test work. The support of the CSIRO Minerals Down Under National Research Flagship is gratefully acknowledged.

REFERENCES

- Cheng, C. Y., 2000. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA, *Hydrometallurgy*, **56**: 369-386.
- Gibson, R.W. and Rice, N.M., 1977. A hydrochloric acid process for nickeliferous laterites. In Cooper, W.C. and Mihaylov, I. (Eds.), *Hydrometallurgy and Refining of Nickel and Cobalt*, Vol. 1. C.I.M., Montreal, 247-261.
- Harris, B.G., White, C.W. and Demopoulos, G.P., 2006. Iron control in high concentration chloride leach processes, in iron control technologies. *Proceedings of the Third International Symposium on Iron Control in Hydrometallurgy*, 36th Annual CIM Hydrometallurgical Meeting, Montreal, October 1-4, 2006, p. 445
- Harris, B.G. and White, C.W., 2007. process for recovering iron as hematite from a base metal containing ore material. WO2007071020A1.
- Kyle, J., 2010. Nickel laterite processing technologies-where to next? *ALTA 2010 Nickel/Cobalt/Copper Conference*, 24 -27 May, Perth, Western Australia.
- Lakshmanan, V.I., Sridhar, R., Chen, J., de Laat, R., Halim, M.A. and Roy, R., 2013. Extraction of nickel, cobalt and iron from laterite ores by mixed chloride leach process. *TMS 2013 142nd Annual Meeting & Exhibition*, March 3-7, 2013. San Antonio, Texas, USA.
- McDonald, R.G. and Whittington, B.I., 2008. Atmospheric acid leaching of nickel laterites review. Part II. Chloride and bio-technologies. *Hydrometallurgy*, **91**, 56–69.
- Moyes, J.A., 2005. The Intec nickel laterite process. *ALTA Nickel/Cobalt Conference*, 16-18 May, Perth, Western Australia.
- Steyl, J.D.T., Peiser, M., Smit, J.T., 2008. Atmospheric leach process for nickel laterite ores. In: Young, C.A. et al.(Eds.), *Hydrometallurgy 2008. Proceedings 6th International Symposium*, SME, 541-550.
- Zhu, Z., Zhang, W., Pranolo, Yoko and Cheng, C.Y., 2012. Separation and recovery of copper, nickel, cobalt and zinc in chloride solutions by synergistic solvent extraction. *Hydrometallurgy*, **127-128**, 1-7.
- Zhu, Z., Tulpatowicz, K., Pranolo, Yoko and Cheng, C.Y., 2014. Fe(III) removal from a synthetic chloride leach solution of nickel laterite by N,N-Diethyldodecanamide. *Minerals Engineering* (In press).

Extraction of Cobalt from a Liquor Rich in Nickel by Liquid Surfactant Membrane and Liquid-Liquid Extraction Techniques

*Adriane Salum^{*1}, Estêvão M. R. Araújo¹, Tânia L. S. Miranda¹,
Cibele Konzen¹, Julio C. Balarini¹,*

The aim of the present work was the selective removal of cobalt from a synthetic solution containing 50 g.L⁻¹ of nickel, 5.0 g.L⁻¹ of cobalt and 11.3 g.L⁻¹ of sodium, simulating the conditions of an industrial plant, using Liquid Surfactant Membranes (LSM) and Liquid-Liquid Extraction (SX) techniques, in order to obtain a nickel rich liquor. For each technique, temperature, pH of the feed phase, extractant concentration and phases ratio were investigated. For the LSM technique, other variables were also investigated: surfactant concentration and concentration of sulphuric acid in the internal phase. Then, the operating conditions were experimentally chosen. After this, a multistage operation was performed in order to promote the complete removal of cobalt using both techniques. The chosen conditions for the LSM system were: membrane phase comprising 1.1% w/v (9.4 g.L⁻¹) Cyanex[®] 272, 2.0% v/v ECA 4360, 96.8% v/v Escaid[™] 110; volumetric ratios: external phase (EP)/internal phase (IP) = 5/1 and membrane phase (MP)/internal phase (IP) = 1/1; internal phase composed of a H₂SO₄ solution (1.5 mol.L⁻¹) with 0.05 mol.L⁻¹ Li₂SO₄ (tracer); permeation time = 40 min; initial pH of the external phase = 4.5 and temperature = 40 °C. For the SX system: 12% w/v Cyanex[®] 272, pH 5.0 and 50°C, using tridecanol as modifier. Comparing the results in these conditions, it follows that, for the SX, the cobalt recovery reached 99.9% with a recycle of this element equivalent to 2.50 kg per kg of Co in the feed. The extraction process required 10 stages: 4 for the extraction step, 2 for scrubbing and 4 for the stripping one. It was necessary 120 g of extractant per litre of treated liquor. In the LSM system, 5 stages were used, with a total of 5.5 g Cyanex[®] 272 per litre of treated liquor and a Co recovery of 99.5%. In addition to the reduced consumption of the extractant and the non-use of a modifier, other advantage of the LSM process in relation to solvent extraction is the use of higher phases ratio (external phase/membrane phase = 10/1 (LSM) and aqueous phase/organic phase = 1/1 (SX)), besides the use of a single equipment for extraction and stripping process in LSM. In the LSM system, an extraction of 1.8% of Ni still occurred after 5 stages, but with a further stage, the two processes will probably present similar selectivity and substantial savings in reagent is likely to favour the use of the LSM technique.

Introduction

The solvent extraction (SX) is the most widely used process for separating nickel and cobalt. Ion exchange resins can also be used, but this technique is more expensive. Another alternative to the traditional solvent extraction is the liquid surfactant membranes technique (LSM), which in comparison with the former presents higher extraction capacity with high selectivity, lower reagents consumption and others. [1-3]

The LSM consists of three different phases (water/oil/water or oil/water/oil) in which an emulsion formed by two of them is dispersed into the third one. The three phases are commonly referred as external (EP), membrane (MP) and internal (IP) phases, and in comparison to the SX they correspond to the feed, solvent and stripping

^{*1} Adriane Salum: salum@deq.ufmg.br, +55 (31) 3409-3676/ 3409-3678

Department of Chemical Engineering, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil

solution phases, respectively. The membrane phase contains a surfactant, an amphiphilic compound responsible for stabilizing the emulsion obtained from the mixture of the membrane and the internal phases, an extractant and a diluent.

Then, in this work, the objective was to study both techniques (LSM and SX) in order to remove cobalt selectively from a synthetic solution containing 50 g.L⁻¹ of nickel, 5.0 g.L⁻¹ of cobalt and 11.3 g.L⁻¹ of sodium, to obtain a nickel rich liquor, simulating the conditions of an industrial plant. The extractant CYANEX[®] 272 and the solvent Escaid[™] 110 were used for both techniques. In the LSM system, the surfactant was ECA 4360 and the modifier in the SX system was 1-tridecanol.

All the experiments were performed in batch scale.

Experimental

Reagents

In this work, NiSO₄·6H₂O (Vetec, 98.0% purity), CoSO₄·6H₂O (Dinâmica, 99% purity), NaOH (Vetec, 97% purity) and H₂SO₄ (Vetec, 95% purity) were used to prepare the feed phase and the stripping solution; and CYANEX[®] 272 (Cytec, 85% purity), Escaid[™] 110 (Exxon Chemicals Ltd.), ECA 4360 (Paramins) and 1-tridecanol were used to prepare the organic phases: membrane and solvent phases.

Synthetic Liquor Preparation

The feed phase in both processes (LSM and SX) was an aqueous solution containing 50.0 g.L⁻¹ of Ni⁺², 5.00 g.L⁻¹ of Co⁺² and 11.3 g.L⁻¹ of Na⁺. The pH was adjusted to 4.5 (LSM) and to 5.0 (SX) as previously defined [4-5].

Liquid Surfactant Membrane Procedure

The membrane phase was composed of 1.1% w/v CYANEX[®] 272 (9.4 g.L⁻¹) and 1.8% w/v ECA 4360 in Escaid[™] 110. All the reagents were used without further purification. The inner phase (stripping solution) was composed of a solution 1.5 mol.L⁻¹ H₂SO₄ containing Li₂SO₄ 0.05 mol.L⁻¹ (Li⁺ as a tracer). All the concentrations were previously defined [4, 6].

Firstly, the primary emulsion (PE) was prepared by adding the inner phase (IP) and the membrane phase (MP) using a high shear emulsifier. The phases ratio IP/MP was equal to 1/1. The conditions in the emulsification step were 13,000 rpm and a time of 5 minutes.

The initial synthetic solution was contacted with a fresh primary emulsion five times in a cross-current arrangement, as shown in Figure 1.

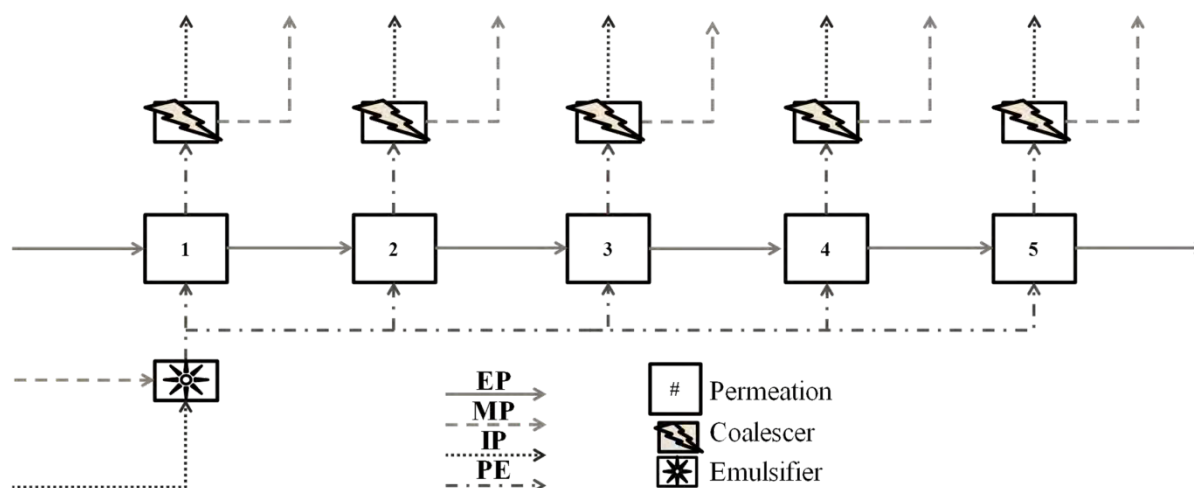


Figure 1 – Esquematic flowsheet for the LSM operation

Each permeation experiment consisted in contacting a liquor and a fresh primary emulsion (phases ratio EP/PE = 5/1), for 40 minutes at 40°C and with a stirring speed of 205 rpm. The feed of each stage was the raffinate (the depleted external phase) of the previous one (the final stripping solution in the previous stage). At the end of the permeation, the raffinate and the loaded primary emulsion was transferred to a settler. When the phases were separated, the loaded emulsion was sent to an electrostatic coalescer to separate the inner and the membrane phases. The pH in the permeation step was controlled by dripping a solution of NaOH 9.0 mol.L⁻¹ into the reactor.

The operating conditions for the LSM system are in Table 1.

Table 1 – Conditions used in the LSM experiments.

Parameters		Levels
Phases ratio MP/IP (membrane phase/inner phase)		1/1
Phases ratio FP/PE (feed phase/ primary emulsion)		5/1
Temperature (°C)		40
Permeation time (min)		40
Permeation stirring speed (rpm)		205
Emulsification stirring speed (rpm)		13,000
H ₂ SO ₄ concentration at inner phase (mol.L ⁻¹)		1.5
ECA 4360 concentration at membrane phase (%w/v)		1.8
CYANEX® 272 concentration at membrane phase (%w/v)		1.1
1 st Step	External phase volume (mL)	200
	Primary emulsion volume (mL)	40
2 nd Step	External phase volume (mL)	190
	Primary emulsion volume (mL)	38
3 rd Step	External phase volume (mL)	180
	Primary emulsion volume (mL)	36
4 th Step	External phase volume (mL)	170
	Primary emulsion volume (mL)	34
5 th Step	External phase volume (mL)	160
	Primary emulsion volume (mL)	32

The concentrations of Co^{2+} and Ni^{2+} in the final external and internal phases were determined by atomic absorption spectrometry (GBC – model Avanta PM). The adopted response variables were the cobalt and nickel percent extraction and the cobalt and nickel recovery (%), which were calculated using Equation (1) and (2).

$$\% \text{ Extraction} = \left(1 - \frac{\text{metal mass in the raffinate}}{\text{metal mass in the initial feed phase}} \right) \cdot 100 \quad (1)$$

$$\% \text{ Recovery} = \left(\frac{\text{metal mass in the final inner phase}}{\text{metal mass in the initial feed phase}} \right) \cdot 100 \quad (2)$$

Solvent Extraction Procedure

The solvent used was 12% w/v CYANEX[®] 272 and 5% w/v 1-tridecanol solution in Escaid[™] 110, the phases ratio A/O was 1/1 and the contact time 10 minutes. The loading cobalt experiments (extraction) were carried out at 50°C and pH of the feed phase 5.0. The pH was controlled by the addition of NaOH 1.0 mol.L⁻¹ solution. These conditions were based on Cytec data [5] and on a previous work [4].

In the scrubbing experiments, it was used CoSO_4 solution, containing 30 g.L⁻¹ Co^{2+} , a ratio phases A/O equals to 1/5 and temperature of 25 °C. For the stripping, the strip solution was H_2SO_4 0.25 mol.L⁻¹ containing 20 g.L⁻¹ Co^{2+} as CoSO_4 , the temperature was 40 °C and a ratio phases A/O of 1/5 was used.

The counter-current operation system was composed of 4 extraction, 2 scrubbing and 4 stripping stages based on Cytec data [5].

With these results the mass balance could be performed across the system.

Results and Discussion

Liquid Surfactant Membranes

The LSM experiments were carried out in 5 stages aiming the depletion of cobalt using the cross-current system.

A cobalt extraction of 98.4% and 99.6% for the 4th and 5th stages was achieved respectively and the cobalt recovery in the same stages were 89.6% and 90.6%, as can be seen in the Figure 2 and Table 2. The nickel extraction and recovery were always less the 2%. An additional stage lead to a raffinate practically free of cobalt (99.8% of Co extraction).

Using liquid surfactant membrane technique, a cobalt extraction of 99.6%, with a Co (recycled) /Co (feed) ratio of 0.122, consumed 5.5 g of Cyanex[®] 272 per one litre of treated liquor, in 5 complete cycles, for a external phase/membrane phase ratio

equals to 10/1 per stage. Then, for the treatment of one litre of liquor, it was necessary 1.17 g of Cyanex[®] 272 per gram of recovered cobalt, which proves that the LSM system is selective showing a high extraction of the interested metal (cobalt).

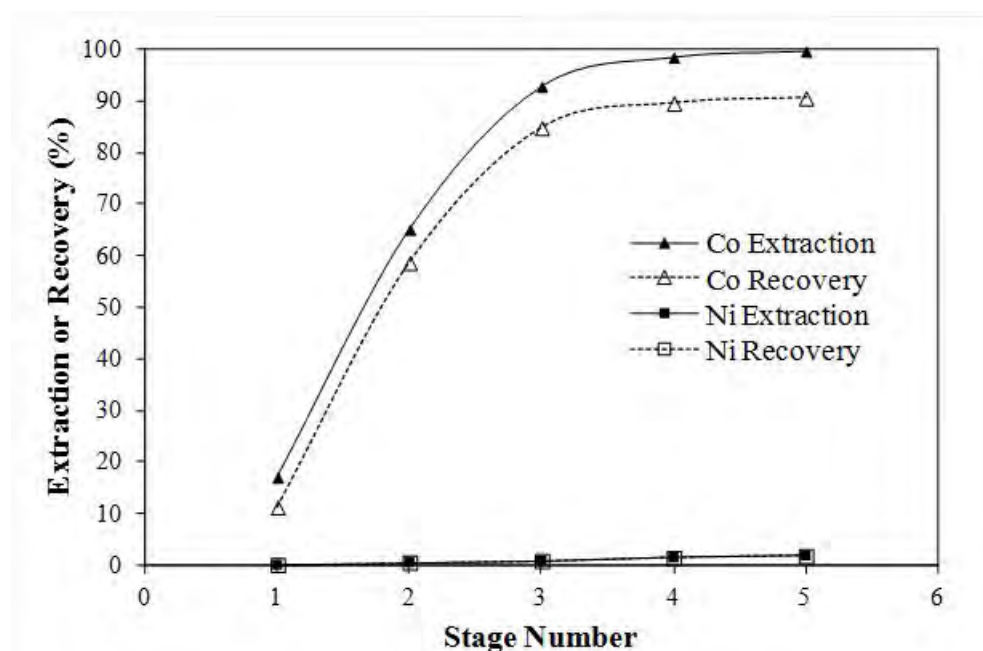


Figure 2 – Extraction and recovery results to the LSM system

Table 2 – Extraction and recovery results for cobalt and nickel for each stage using liquid surfactant membrane.

Stage	Extraction (%)		Recovery (%)	
	Co	Ni	Co	Ni
1	17.1	0.1	11.3	0.1
2	65.1	0.6	58.7	0.6
3	92.8	0.9	84.8	0.9
4	98.4	1.5	89.6	1.5
5	99.6	1.8	90.6	1.8

Solvent Extraction

Using four extraction stages a cobalt extraction of 99.9% was achieved. The calculated streams of a continuous system are shown in Figure 3. The solvent extraction technique proved be highly selective, but it was necessary to use a great amount of cobalt salts to perform the scrubbing and the stripping stages.

For the solvent extraction operation, with a ratio phases A/O of 1/1, using a Cyanex[®] 272 concentration of 12% w/v, the Co recovery was 99.9%, with a Co (recycled)/Co (feed) ratio of 2.50, in 10 stages (4 extraction, 2 scrubbing and 4 stripping) and it was used 120 g of Cyanex[®] 272 per one litre of treated liquor (25.07 g per gram of recovered cobalt).

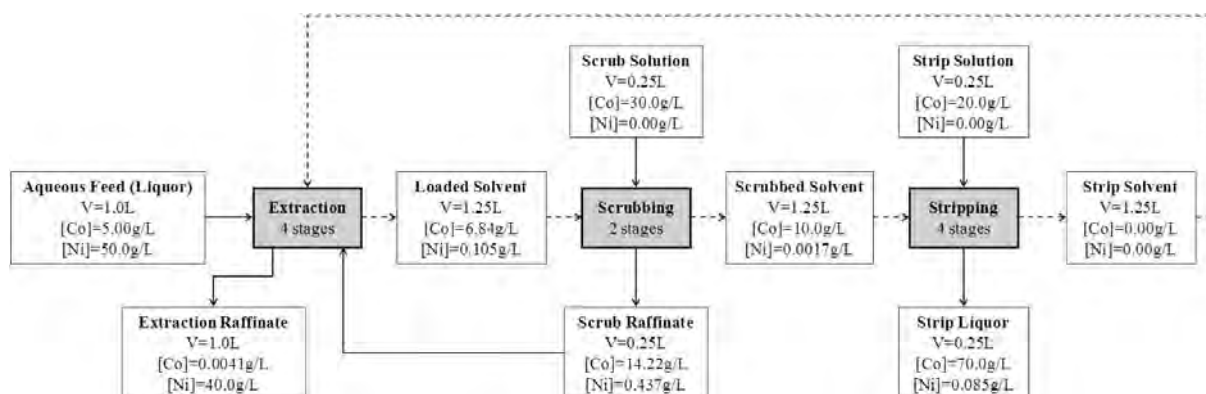


Figure 3 – Streams in the solvent extraction system, considering the basis for calculation of 1 litre of feed phase.

LSM and SX comparison

In the solvent extraction, it is necessary to proceed the loading of the solvent while in the liquid surfactant membrane the extractant acts as a carrier. Thus, the amount of extractant and, consequently, the organic phase volume are larger for the SX technique. The equipment size for the SX is also larger than for LSM, since the extraction and stripping stages are carried out separately in the former. Some other comparisons between the two techniques investigated in this work and their parameters are shown in Table 3.

Table 3 – Liquid Surfactant Membrane and Liquid Extraction comparison.

Parameters	LSM	SX
Emulsification Stages	1	0
Permeation Stages	5	4
Scrubbing Stages	0	2
Stripping Stages	0	4
Demulsification Stages	5	0
Total Settling Stages	10	10
Co Extraction (%)	99.6	99.9
Ni Extraction (%)	1.8	0.01
Co Recovery (%)	90.6	99.9
Ni Recovery (%)	1.8	0.01
Co circulating charge (Co (recycled)/Co (feed))	0.09	2,50
Organic phase to treat 1L of liquor (L)	0.5	1.0
Extractant per litre of liquor (g)	4.7	102
Mass of extractant per gram of extracted cobalt (g)	0.94	20.4

Conclusions

This study aimed to obtain a liquor rich in nickel and almost cobalt-free.

Both techniques proved to extract nearly all the present cobalt (more than 99%) with high selectivity.

Comparing both techniques used in this study, it can be concluded that the LSM process requires less amount of solvent than the classical solvent extraction. It was necessary around 20 times more extractant in solvent extraction process than in LSM (120 g of Cyanex[®] 272 and 5.5 g per one litre of treated liquor, respectively). Another advantage of the LSM process was the high phases ratio liquor/organic phase (external phase/membrane phase = 10/1) while the A/O ratio in the solvent extraction was 1/1. Additionally, extraction and stripping occur simultaneously in a single equipment in LSM systems.

The LSM technique can be attractive for the application in cobalt / nickel separation (and for the extraction of other metal species), which can be competitive in this separation from the solvent extraction process.

References

- [1] **Kumbasar, R. A. & Kasap, S.** (2009) *Selective separation of nickel from cobalt in ammoniacal solutions by emulsion type liquid membranes using 8-hydroxyquinoline (8-HQ) as mobile carrier*. Hydrometallurgy 95, p. 121-126.
- [2] **Kumbasar, R. A. & Sahin, I.** (2008) *Separation and concentration of cobalt from ammoniacal solutions containing cobalt and nickel by emulsion liquid membranes using 5,7-dibromo-8-hydroxyquinoline (DBHQ)*. Journal of Membrane Science 325, p. 712-718.
- [3] **Kumbasar, R. A. & Tutkun, (2008) O.** *Separation of cobalt and nickel from acid leach solutions by emulsion liquid membranes using Alamine[®] 300 (TOA) as a mobile carrier*. Desalination 224, p. 201-208.
- [4] **Araújo, E. M. R.** (2012) *Tratamento de licor sulfúrico rico em níquel visando à remoção de cobalto*. Dissertation. Chemical Engineering Department, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil. 125p. (in Portuguese).
- [5] **Cytec Industries Inc.** (2008) *Cyanex[®] 272 Extractant*. Solvent extraction brochures. <<https://www.cytec.com>>
- [6] **Salum, A.** (1998) *Estudo da permeação de cobalto e da separação cobalto/níquel em meio sulfúrico, com CYANEX[®] 272, pela técnica de membranas líquidas surfatantes*. PhD Thesis. Mining and Metallurgy Department, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil. 258p. (in Portuguese).

Separation and Purification of Zirconium with Amines from Sulphuric Acid System: A Review

*V.I. Lakshmanan¹, R. Sridhar¹, Z. Jankovic¹, M.A. Halim^{*1}*

Summary

Zirconium is being used as a high-technology material for industrial applications due to its excellent thermal, electrical, chemical and optical properties. Solvent extraction process is used for separation and purification of zirconium in sulphate media from different value metals including hafnium, uranium, niobium, rare earths and titanium. Efficient recovery of zirconium using solvent extraction is extremely complicated due to the fact that zirconium forms poly-nuclear complexes in sulphate solution. This polymerization is more favorable in low concentration of free acid and at high concentration of zirconium. Understanding the aqueous chemistry of zirconium species, separation technology and complex-formation reactions are most important for selecting appropriate organic media and optimization of separation conditions. In this paper, solvent extraction technique for zirconium separation and purification with amines from sulphate solution is reviewed. The solution chemistry of zirconium species and separation mechanisms are discussed to illustrate the better understanding of the process steps.

Introduction

Zirconium (Zr) is mainly produced from zircon (ZrSiO_4), which is found in the beach sands along with rutile, ilmenite, and monazite. Zirconium also occurs in several minerals including baddeleyite, kosnarite and Eudialyte. Zirconium dioxide is mainly used in piezoelectric crystals and as pigment in the ceramic industry. High purity metallic Zr is used in nuclear reactor due to its low neutron cross section, outstanding mechanical and chemical resistance and excellent thermal conductivity. The concentration of Hf in nuclear grade Zr should be no more than 30 mg/L [1]. Amongst various techniques, solvent extraction is quite popular for separation of Zr from other metals including Hf, Ti, Fe, rare earths and Nb. Currently, TBP(tri-butyl phosphate)/ HNO_3 , MIBK(methyl isobutyl ketone)/ $\text{NaSCN}/\text{HNO}_3$ and TBP/ HCl solvent extraction processes are used for separation of Zr, but the downstream contain high concentration of ammonium, cyanide and by-products of organic [2, 3].

A literature survey reveals that amine-based extractants are often chosen for the separation and purification of Zr(IV) [4-6]. The primary amine (Primene-JMT) was used by El-Yamani et al. [7] in the separation of Zr(IV) from Hf(IV) in H_2SO_4 medium. Shimizu [8] found the suitable extraction conditions of different metals including Zr(IV) from ammonium sulphate solution with the secondary amine (Amberlite LA-2) in xylene. Generally, the tertiary amines are better extractant than the primary or secondary amines [9, 10]. Sato and Watanabe[11] investigated the extraction of Zr(IV) from sulphate solutions using di-n-octylamine, tridodecylamine, trioctylamine, and tris (2-ethylhexyl) amine. The comparison of Zr extraction from sulphate solution with tri-n-laurylamine, tri-n-octylamine, di-n-nonylamine, primene-JMT and p-dodecylaniline has been performed [12]. MacDonald [13] developed a computer simulation process for separation of Zr from Hf in sulphuric acid medium using Alamine 336. In this paper, separation and purification of Zr with amine extractants in sulphuric acid solution are evaluated, and the solution chemistry and mechanism of extraction, stripping and organic regeneration are discussed.

¹Process Research ORTECH Inc., 2350 Sheridan Park Drive, Mississauga, ON, L5K 2T4, Canada;

*Email: halim@processortech.com

Solution Chemistry of Zirconium

Understanding the solution chemistry of Zr species has played an important role for the development of solvent extraction process steps. In solution, Zr exists exclusively in a +4 oxidation state and is believed to attain coordination numbers of 7 and 8 [14]. Paramonova and Voevodskii [15] concluded that, at least two processes occur simultaneously in sulphate solutions, the formation of sulphate complexes and hydrolysis. They suggested that the complex formation is related to the presence of hydrolysed Zr species with a positive (ZrSO_4^{2+}) or a zero charge ($\text{Zr}(\text{SO}_4)_2$) and the absence of negatively charged species at concentrations of H_2SO_4 lower than 0.5 M. The predominant form of Zr(IV) is the $\text{Zr}(\text{SO}_4)_3^{2-}$ at around 1 M of H_2SO_4 .

Etinson and Petrov [16] concluded that Zr compounds in aqueous solution are characterized by their high degree of hydrolysis as well as their tendency to form various complex ions and polymer compounds. Consideration of hydrolysis and polymerisation of Zr is necessary because these phenomena directly affect the extraction of Zr. Yagodin et al. [17] reported that Zr sulfate may hydrolyse at less than 2 M of H_2SO_4 . Richens [14] reported that due to the high charge/radius ratio, Zr(IV) ion strongly hydrolyses in water, leading to the formation of poly-nuclear species with oxygen containing bridges. Recent publications [18] reported that the Zr is hydrolysed to form dimer ($\text{Zr}_2(\text{OH})_6^{2+}$ and $\text{Zr}_2(\text{OH})_7^+$), trimer ($\text{Zr}_3(\text{OH})_4^{8+}$ or $\text{Zr}_3(\text{OH})_5^{7+}$) and tetramer ($[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$) in aqueous solution. Under certain conditions, Zr forms extremely stable polynuclear compounds that are not in equilibrium with monomer form [8]. The extent of polymerisation depends on different parameters including aging, temperature, acidity, and concentration of Zr [14]. The polymerisation reaction of Zr(IV) is increased with decreasing acidity of solution. Yagodin et al. [17] reported that poly-nuclear compound $\text{Zr}_2(\text{SO}_4)_7$ is formed in a solution containing 1-1.5 M of Zr(IV). Moreover, Baglin and Breger [19] reported that in strong sulphuric acid solution, the sulphate ion can displace hydroxyl group to form other products.

Table 1 Commonly used different type of amines for solvent extraction study.

Extractant/Diluent	Molecular formula	Reference
Primary amines		
Primene JMT	$\text{RNH}_2 (\text{R} = (\text{CH}_3)_3\text{C}(\text{CH}_2\text{C}(\text{CH}_3)_2)_4)$	[7, 20]
Secondary amines		
Di-cyclohexylamine	$\text{C}_6\text{H}_{11}\text{-NH-C}_6\text{H}_{11}$	[21]
Di-n-octylamine	$[\text{CH}_3(\text{CH}_2)_7]_2\text{NH}$	[11]
Di-n-nonylamine	$[\text{CH}_3(\text{CH}_2)_8]_2\text{NH}$	[7, 20]
Tertiary amines		
Tri-n-octylamine (Alamine 336)	$[\text{CH}_3(\text{CH}_2)_7]_3\text{N}$	[11]
Tri-n-dodecylamine	$[\text{CH}_3(\text{CH}_2)_{11}]_3\text{N}$	[11]
Tris-(2-ethylhexyl)amine	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2]_3\text{N}$	[11]
Quaternary ammonium salts		
Tri-caprylmethylammonium chloride (Aliquat 336/Adogen 464)	$[\text{CH}_3(\text{CH}_2)_7]_3\text{N}^+(\text{CH}_3)\text{Cl}^-$	[7, 22]

Extraction of Zirconium (IV) with Amine Extractants

The most commonly used amine extractants in solvent extraction process steps include primary amines, secondary amines, tertiary amines and quaternary

ammonium salts. The amine extractants used for Zr(IV) solvent extraction study are listed in Table 1.

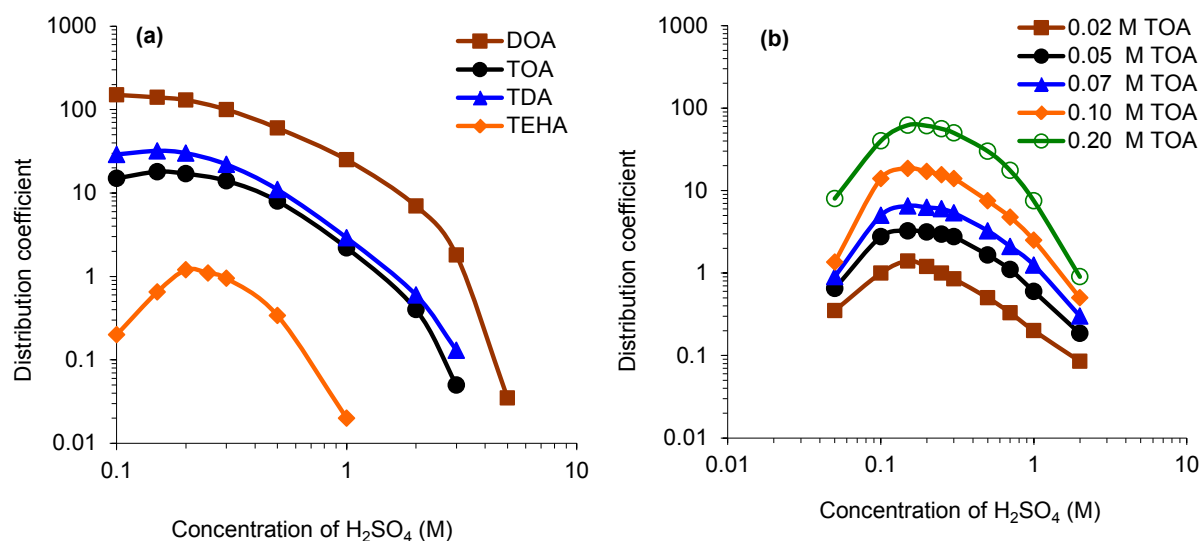


Fig. 1 Extraction of zirconium (IV) from sulphuric acid solutions with (a): 0.1 M solutions of different amines in chloroform and (b): different concentrations of TOA in chloroform [11].

Effect of H_2SO_4 Concentration on Zirconium Extraction

Several studies have been carried out for Zr(IV) extraction from different concentrations of H_2SO_4 solutions with amine extractants. Different extraction behaviours in H_2SO_4 solutions were observed for tertiary amines (Tri-n-octylamine (TOA), Tri-n-dodecylamine (TDA) and Tris-(2-ethylhexyl)amine (TEHA). The distribution coefficients of Zr(IV) curve as a function of acidity are shown in Fig. 1(a, b) with tertiary amines [11]. Sato and Watanabe [11] reported that the increase in distribution coefficient at low acidities is ascribed to salting-out of sulphuric acid, while the decrease at higher acidities results either acid for association with these amines or from the formation of less extractable complexes. In contrast, distribution coefficient is decreased with increasing the concentration of H_2SO_4 in both Primene-JMT and Adogen 464, which is shown in Fig. 2(a, b) [7, 22]. These studies suggest that the decreasing of distribution coefficient with increase in sulphate ion concentration is due to the formation of inextractable anionic species presumably $\text{Zr}(\text{SO}_4)_3^{2-}$ and/or $\text{Zr}(\text{SO}_4)_4^{4-}$.

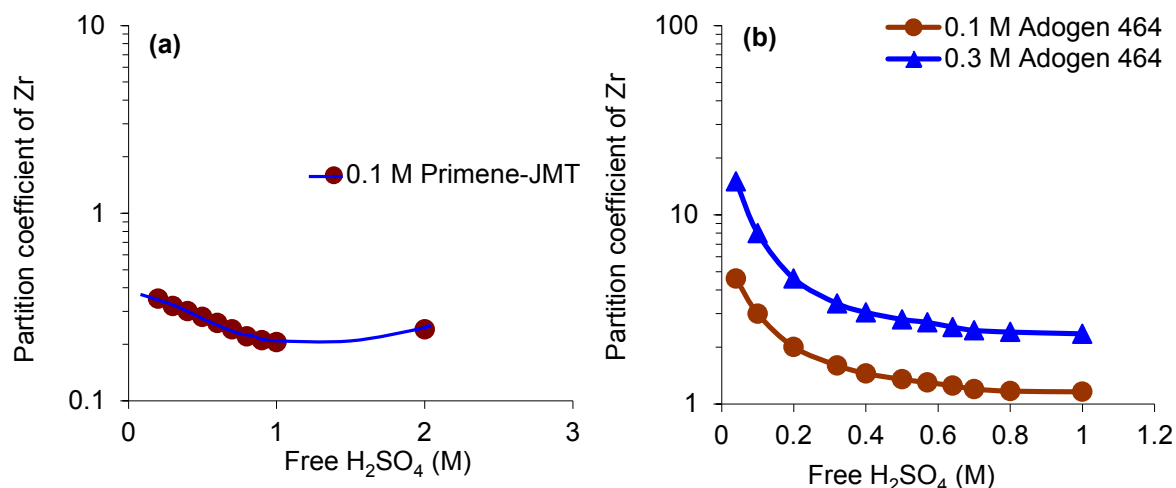
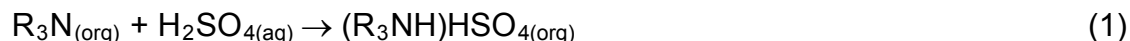
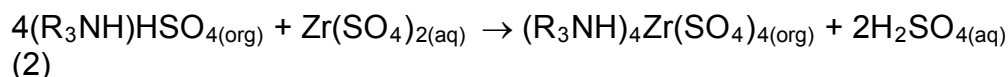


Fig. 2 Extraction of zirconium (IV) from sulphuric acid solutions with (a): 0.1 M solution of Primene-JMT in kerosene and (b): 0.1 M and 0.3 M of Adogen 464 in kerosene [7, 22].

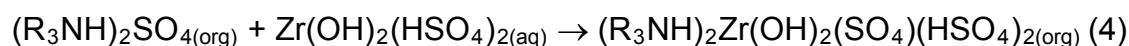
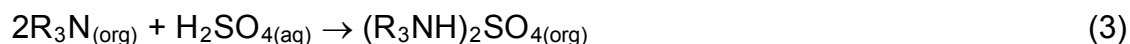
The following extraction mechanism is proposed for nonhydrolysed Zr sulphate extraction with tri-n-octylamine: neutralised tri-n-octylamine in organic solution reacts in the presence of excess H_2SO_4 solution according to the reaction:



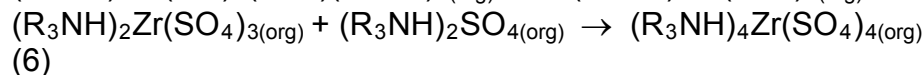
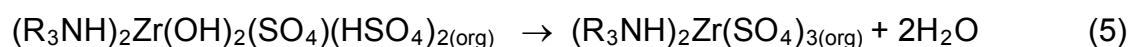
in which R_3N represents the tertiary amine. The extraction equilibrium corresponds to the reaction:



Extraction of polymeric hydrolysed zirconium sulphate with tertiary amine is possible through the destruction of this polymer into the monomeric hydrolysed zirconium sulphate (for an example, $\text{Zr}(\text{OH})_2(\text{HSO}_4)_2$). At the moment of formation of monomer, the coordination sphere of such a complex is not saturated; therefore, their extraction at the first stage follows the additional mechanism [23]:



Then a slow decrease in the rate of Zr hydrolysis in the organic phase occurs, which is shown in reactions (5) and (6).



Extraction of stable hydrolysed polymers is also possible following the exhaustion of hydrolyzed monomers and destruction of unstable multinuclear complexes in conformity with the extractability series of Zr sulphate by TOA: nonhydrolysed complexes > hydrolysed monomers > stable hydrolysed polymers [17, 23].

Table 2 Stripping of Zr(IV) from loaded amines by different solution at the A/O ratio of 1.

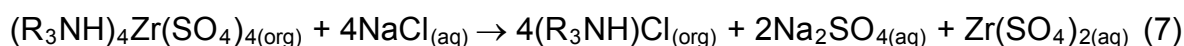
Extractant		Diluent	Stripping solution	Stripping (%)	Reference
Name	Conc. (M/%)				
Primene-JMT	0.25 M	BDR-Z*	0.75 M HNO_3	71	[20]
			1.0 M HNO_3	98	
			2.0 M HNO_3	Complete	
	0.25 M	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
N-n-Octylaniline	3%	Xylene	0.5 M HNO_3	Complete	[24]
Di-n-nonylamine	0.25 M	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
Tri-n-octylamine	10%	Kerosene	1.0 M Na_2CO_3	Complete	[25]
	0.25 M%	Benzene	4.0 M NaCl + 0.5 M HCl		[12]
	10%	Kerosene	1.5 M NaCl + HCl	Complete	[26]
Alamine 336	10%	Kerosene	4.0 M NaCl + 0.5 M HCl	Complete	[27]
	10%	Kerosene	10% HCl	--	[28]

Tri-n-laurylamine	0.25 M%	Benzene	4.0 M NaCl + 0.5 M HCl	--	[12]
Adogen 464	0.2 M	Kerosene	0.5 - 1.0 M HNO ₃	Complete	[22]
Aliquat 336	0.2 M	Kerosene	0.5 - 1.0 M HNO ₄	Complete	[29]

BDR-Z: Mixture of aliphatic hydrocarbons.

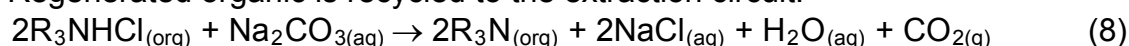
Impurities Scrubbing and Zirconium (IV) Stripping

MacDonald et al. [26] reported that the Hf content of the Zr-bearing organic phase can be decreased to any desired level by multistage counter-current extraction followed by scrubbing with dilute sulphuric acid solution. Takahashi et al. [30] reported that the separation of Zr from most of the elements including Al, Ca, Co, Fe, Mn, Ti, V and rare earths is possible in extraction stages with tri-n-octylamine in paraffin. Zr(IV) can be completely stripped from Alamine 336 in kerosene by three stage counter-current stripping with NaCl-HCl solution [26]. Stripping can be shown by the following reaction [30]. Stripping of Zr(IV) from loaded amines by different aqueous solutions is summarised in Table 2.



Organic Regeneration and Uranium Removal

MacDonald et al. [26] reported that in process leach solution when U and Zr are present, they are loaded together to organic phase. If the chloride ion activity is high enough in Zr stripping solution, Zr is selectively stripped over U from the loaded organic phase. Uranium remaining in the Zr-depleted organic phase can be removed by the following reaction with Na₂CO₃ solution in the organic regeneration stages [30]. Regenerated organic is recycled to the extraction circuit.



Conclusion

Separation of Zr by solvent extraction with amines from sulphate system is summarised by the following steps:

- (1) Due to the high charge/radius ratio, Zr(IV) ion is strongly hydrolysed to form poly-nuclear species including dimer, trimer and tetramer in aqueous solution.
- (2) The polymerisation of Zr(IV) is increased with increasing aging, temperature and concentration of Zr, and with decreasing acidity of solution.
- (3) The distribution coefficient is increased at low acidities due to salting-out of sulphuric acid, while decreases at higher acidities results either association with amine or formation of less extractable Zr(IV) complexes.
- (4) Stable hydrolysed polymers are also possible to extract with amines by the exhaustion of hydrolyzed monomers and destruction of unstable complexes.
- (5) Zirconium (IV) can be selectively extracted over most of the metals with Alamine 336 while Hf can be scrubbed from Zr-loaded organic by controlling the O/A phase ratio.
- (6) Zirconium followed by U can be selectively stripped from loaded Alamine 336 with NaCl-HCl and Na₂CO₃, respectively. An overall flowsheet for separation

and purification of Zr from sulphuric acid solution with tertiary amine (Alamine 336) in kerosene is shown in Fig. 3.

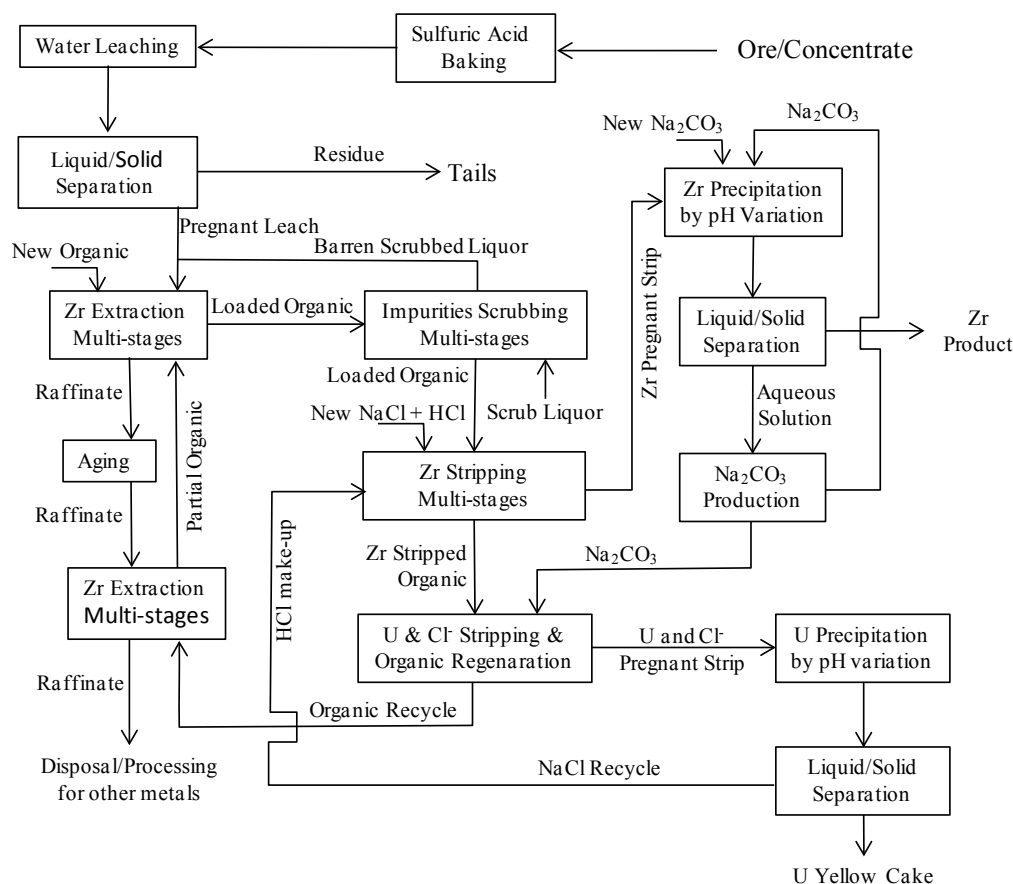


Fig. 3 Flowsheet for separation and purification of zirconium from sulphuric acid solution with tertiary amine (Alamine 336) in kerosene.

References

1. Voit DO. US Patent # 51320106, 1992.
2. M. Taghizadeh [†], M. Ghanadi, E. Zolfonoun. J. Nucl. Mat., 412, 2011, 334–337.
3. G. Gopi Krishna, R. Sudarshan Reddy, P. Raghunath, K. Bhanuprakash. M. Lakshmi Kantam, and B. M. Choudary. J. Phys. Chem. B. 108, 2004, 6112-6120.
4. Yang, X. J.; Pin, C., Anal. Chem. 71, 1999, 1706.
5. Karve, M. A.; Khopkar, S. M., Anal. Sci., 8, 1992, 237.
6. Yang, X. J.; Pin, C.; Fane, A. G., J. Chromatogr. Sci. 37, 1999, 171.
7. El-Yamani, I.S., Farah, M.Y., Abd El-Aleim, F.A., Talanta, 25, 1978, 523.
8. Shimizu, T., Bunseki Kagaku, 17, 1968, 1187.
9. Sato, T., Watanabe, H., Anal. Chim. Acta, 54, 1971, 439.
10. Green, H., Talanta, 20, 1973, 139
11. Sato, T.; Watanabe, H., J. Inorg. Nucl. Chem. 36, 1974, 2585.
12. Schroetterova, D., Nekovar, P., Marika, M., J. Radioana. Nucl. Chem. 150, 1991, 325.
13. MacDonald, D. J., Sep. Sci. Technol. 16, 1981, 1355.
14. Richens, D. T., The Chemistry of Aqua Ions, John Wiley & Sons: Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, 1997; pp 207-220.
15. Paramonova, V.I., Voevodskii, A.S., ZhNkh, 1, 1956, 347.
16. Elinson. S. V., Petrov. K. I., Analytical chemistry of zirconium and hafnium, Israel program for scientific translations, Jerusalem, 1969.
17. Yagodin, G. A., Sinefribova, O. A., Chekmarev, A. M., International Solvent Extraction Conference Proceedings, 3, 1974, 2209-2233.

18. Niny R., Marian N. Holerca, Vojislava P., J. Chem. Theory Comput. 4, 2008, 145-155.
19. Baglin, F.G., Breger, D., Inorg. Nucl. Chem. Letters. 12, 1976, 173-177.
20. Schrotterova, D., Nekovar, P., Mrnka, M., Bousa, M., J. Radioana. Nucl. Chem., 163(1), 1992, 29-36.
21. Cerrai, E., Testa, C., Energia Nucleare, 6 (11), 1959, 707-716.
22. El-Yamani, I.S., El-Aleim, F.A. Abd, J. Radioana. Nucl. Chem., 88(2), 1985, 201-208.
23. Yagodin, G. A., Sinegribov, O. A., Processes for zirconium-hafnium and niobium-tantalum. Handbook of solvent extraction, Chapter 25,14, 1983, 811-812.
24. Rajmane, Sargar, N.M., Mahamuni, S.V, J. Serb. Chem. Soc., 71, 2006, 223-234.
25. Takeshi Otsuka, United States Patent # 3658466, Apr. 25, 1972.
26. MacDonald, D. J., Henry, H. G., Bauer, D. J., Purification of Zirconyl Sulfate by Solvent Extraction. Report of investigations, United States Department of the Interior, Bureau of Mines, 8849, 1984.
27. David J. MacDonald, Helen G. Henry, United States Patent # 4381287, Apr. 26, 1983.
28. Brown, P.M., Hard, A.R., Harbuck, D.D., Green, G.K., United States Patent # 7282187B1, October 16, 2007.
29. El-Yamani, I.S., Farah, M. Y., El-Aleim, F.A. Abd, J. Radioana. Chem., 45(2), 1978, 125-133.
30. Takahashi, M., Miyazaki, H., Katoh, Y, Proceeding of Sixth International Symposium on Zirconium in the Nuclear Industry, Edited by Franklin D.G and Adamson R.B., 1982, 45-56.

Development of novel extractants with amino acid structure for highly effective recovery and separation of nickel and cobalt ions

Yuzo Baba¹, Fukiko Kubota¹, Noriho Kamiya^{1,2}, Masahiro Goto^{*1,2}

Summary

We developed novel amic acid type extractants with the glycine or sarcosine moiety *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) and *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]-sarcosine (D2EHAS). These extractants were prepared by a simple two-step reaction and were readily soluble in aliphatic organic solvents. The extraction behavior of Ni²⁺, Co²⁺, and Mn²⁺ using D2EHAG and D2EHAS in *n*-dodecane was investigated compared with that of conventional extractants such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). The novel extractants extracted Ni²⁺ and Co²⁺ preferentially with a high selectivity over Mn²⁺. The metal ions could be back-extracted quantitatively using 1 mol dm⁻³ sulfuric acid. The extraction mechanism of the three metal ions with D2EHAG and D2EHAS was investigated, and results suggest that one divalent metal ion is extracted with two extractant molecules. These extractants were expected for industrial application.

Introduction

In recent years, there are much attention for cobalt and nickel because of their increased application in cutting edge industries such as batteries (such as Li-ion batteries and nickel-metal hydride batteries), magnetic materials, and catalysts. [1,2] Their stable supply is of worldwide concern and used products that contain cobalt or nickel have been highlighted as possible secondary resources [1] as opposed to using natural resources [2]. Therefore, the development of highly efficient techniques for the separation and recovery of these metals is a serious issue.

Solvent extraction is used widely for the separation and purification techniques of metal ions either in the area of analytical chemistry, or on an industrial scale [3]. It displays a number of advantages compared with other competitive techniques such as ion-exchange, adsorption, and precipitation, such as its easy operation using simple equipment and small amounts of reagent, the ability to operate in a continuous mode and achieve high sample throughput. In the solvent extraction process, separation performance is influenced by the used extractant properties. However, many metal combinations exist that are difficult to separate from one another. A variety of extractants have been designed for the separation of critical metals such as rare earth metals [4], precious metals [5,6] transition metals such as nickel (Ni²⁺), cobalt (Co²⁺) and so on. The selective extraction of Ni²⁺ and Co²⁺ from impurity metals such as zinc, magnesium and calcium has been examined [7]. However, difficulties still remain for their separation from manganese (Mn²⁺), which

*Corresponding Author: M. Goto, Tel.: +81-92-802-2806, E-mail address: m-goto@mail.cstm.kyushu-u.ac.jp
(Presenting Author: Y. Baba, Tel.: +81-92-802-2808, E-mail address: y_baba@mail.cstm.kyushu-u.ac.jp)

¹ Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

² Center for Future Chemistry, Kyushu University, Fukuoka, Japan

often coexists in large amounts in natural and secondary resources [8,9]. Commercial organophosphorous extractants, such as PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) [10], D2EHPA (di-(2-ethylhexyl) phosphoric acid) [11] and Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) [10,11] are typically used in hydrometallurgy, however the separation of Ni^{2+} and Co^{2+} from Mn^{2+} using these extractants is difficult because they are selective for Mn^{2+} .

Few extractants can separate Ni^{2+} and Co^{2+} from Mn^{2+} effectively, and novel extractants to meet such a requirement are strongly desired.

In this study, we have developed two new amic acid type extractants for the selective separation of Co^{2+} and Ni^{2+} from Mn^{2+} . One is a glycine derivative, *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) (Fig. 1 (a)) and the other is a sarcosine (*N*-methyl glycine) derivative, *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]sarcosine (D2EHAS) (Fig. 1(b)). These two extractants contain a carboxyl group and a nitrogen atom derived from an amino acid structure in the molecule. Furthermore, we have designed the new extractants without a phosphorus atom, because extractants containing P-atoms often generate secondary wastes [4].

In this work, we investigate the extraction behavior of D2EHAG and D2EHAS for Co^{2+} , Ni^{2+} and Mn^{2+} compared with some typical commercial extractants, such as D2EHPA, 2-methyl-2-ethylheptanoic acid (Versatic 10), and bis-(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), and discuss the potential use of the novel extractants for the separation and recovery of Co^{2+} , Ni^{2+} from Mn-containing resources.

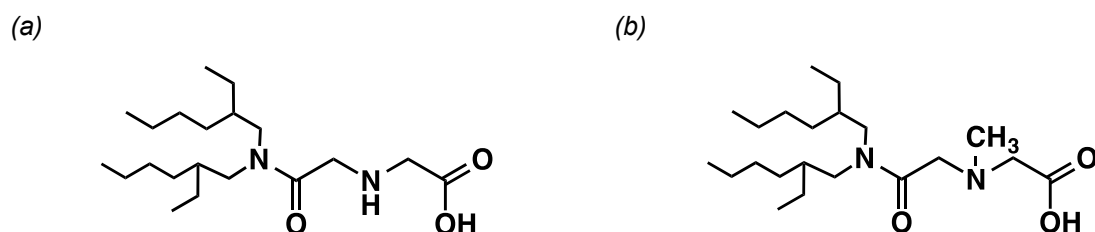


Fig. 1 Molecular structures of novel amic acid type extractants. (a) D2EHAG, (b) D2EHAS.

Experimental

Reagents

D2EHAG and D2EHAS were synthesized by simple two step reactions in our laboratory [12]. The commercial extractants D2EHPA, Versatic 10, and Cyanex 301 were supplied by the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), Mitsubishi Chemical Co., (Tokyo, Japan) and Cytec Industries Inc. (New Jersey, USA), respectively. Cobalt(II)sulfate heptahydrate (> 99.0%), nickel(II)sulfate hexahydrate (> 99.0%) and manganese(II)sulfate pentahydrate (> 99.0%) were also from Kishida Chemical Co., Ltd. (Osaka, Japan). Special grade *n*-dodecane was used as organic solvent. All other reagents and solvents were of analytical grade and were used as received.

Extraction procedure

The extracting organic phase was prepared by dissolving D2EHAG or D2EHAS in *n*-dodecane, which is similar in properties to that of the industrial solvent kerosene. An organic phase containing a commercial extractant such as D2EHPA, Versatic 10, Cyanex 301 was prepared for comparison with the novel extractants. An aqueous solution containing 0.1 mmol dm⁻³ metal ions was prepared by dissolving their sulfates in 0.1 mol dm⁻³ H₂SO₄ or (NH₄)₂SO₄. The aqueous feed solution pH was adjusted by mixing these aqueous solutions and/or adding 28 wt% ammonia solution.

Equal volumes (5 cm³) of the aqueous and organic solutions were mixed in a sealed tube by vortex mixer and then shaken gently for more than 1 h to attain extraction equilibrium at 298K. After phase separation, the metal ions in the organic phase were stripped using H₂SO₄ solution. The metal concentrations in the aqueous phase for the extraction and stripping tests were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 5300, Perkin Elmer Co, Waltham, Ma, USA). The pH was measured using a pH meter (HM-30R, DKK-TOA Co, Tokyo, Japan). The extent of extraction and stripping of the metal ions and the distribution ratio, extraction *E* [-], and stripping *S* [-], distribution *D* [-] ratios were calculated using Eqs. (1), (2), and (3):

$$E = \frac{[M]_{org,eq}}{[M]_{aq,init}} = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,init}} \quad (1) \quad S = \frac{[M]_{aq,strip}}{[M]_{org,init}} \quad (2) \quad D = \frac{[M]_{org,eq}}{[M]_{aq,eq}} = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,eq}} \quad (3)$$

([M] : metal ion concentration, *aq* : aqueous phase, *org* : organic phase, *init* : initial state, *eq* : after equilibration, *strip*: stripping phase at equilibrium.)

Results and discussion

Extraction behavior of metal ions with novel extractants

The extraction of Co²⁺ and Mn²⁺ from the aqueous feed phase with the conventional industrial extractants in *n*-dodecane is shown in Fig. 2(a) as a function of aqueous phase equilibrium pH. The organophosphorus extractant, D2EHPA, extracted Mn²⁺ preferentially over Co²⁺ as shown in Fig. 2 (a) and similar results were also reported for PC-88A and Cyanex 272 [10]. The industrial monocarboxylic acid extractant, Versatic 10 [13], extracted Co²⁺ and Mn²⁺ at around neutral pH and a high selectivity among the metal ions was not observed. Cyanex 301 which includes a sulfur atom, is the only conventional extractant capable of extracting Co²⁺ selectively over Mn²⁺. Because of its very high affinity to Co²⁺, however, a high temperature (60 °C) and high acid concentration (over 5 mol dm⁻³ HCl) are required to strip the metal ions from the extracting phase [14], and extractants include sulfur atoms are easy to be affected by the oxidation [15].

As shown in Fig. 2(b), D2EHAG extracted the metal ions selectively in the following order: Ni²⁺ > Co²⁺ >> Mn²⁺. Nickel and cobalt ions could be extracted satisfactorily and they were separated from Mn²⁺ under acidic conditions. A similar extraction

behavior was observed for D2EHAS as for D2EHAG and the separation of Ni^{2+} and Co^{2+} from Mn^{2+} was achieved at lower pH compared with D2EHAG under the same experimental conditions, although the selectivity between Ni^{2+} and Co^{2+} was suppressed (Fig. 2(c)). The extraction behavior of Co^{2+} and Mn^{2+} was compared with that of the conventional extractants.

The high selectivity for Ni^{2+} and Co^{2+} with D2EHAG compared to that with Versatic 10 may be attributed to the amine structure ($-\text{NH}-$) in the center of the D2EHAG, because Ni^{2+} and Co^{2+} , which are a soft acid compared with Mn^{2+} , have a higher affinity to softer nitrogen than oxygen, according to the hard and soft acids and bases rule. The high extraction and separation performance of D2EHAG could be attributed to a chelate effect by the tridentate structure of the D2EHAG formed by the amide and amino acid groups. The novel extractants have a high selectivity for Ni^{2+} and Co^{2+} over Mn^{2+} compared with that of the conventional extractants. In the extraction with D2EHAS, which introduced a methyl group to the nitrogen atom in the amine structure, the selectivity of Co^{2+} and Ni^{2+} toward Mn^{2+} was enhanced, although the selectivity between Ni^{2+} and Co^{2+} decreased compared with that of D2EHAG. The difference in $\text{pH}_{1/2}$ (half-extraction pH values), $\Delta\text{pH}_{1/2}$, between Co^{2+} and Mn^{2+} with

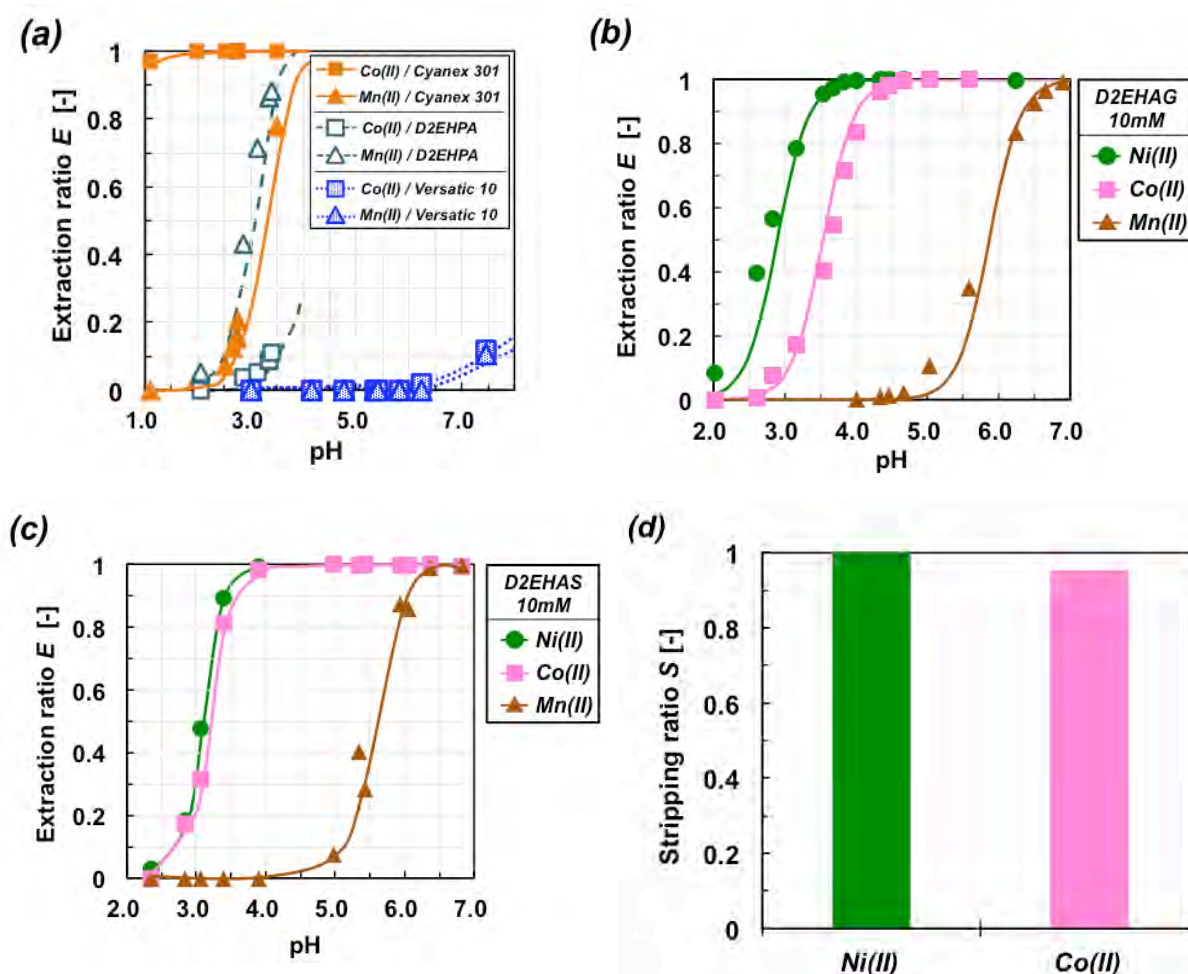
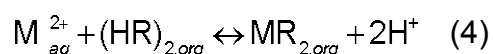


Fig. 2 (a)-(c) Extraction behavior of metal ions with ((a) conventional extractants (100 mmol dm^{-3} Cyanex301, 50 mmol dm^{-3} D2EHPA, and 100 mmol dm^{-3} Versatic 10, solvent: n -dodecane); (b) 10 mmol dm^{-3} D2EHAG in n -dodecane; (c) 10 mmol dm^{-3} D2EHAS in n -dodecane). (d) Stripping ratio of metal ions using 1 mol dm^{-3} H_2SO_4 . ($[M]_{\text{aq,init}} = 0.1 \text{ mmol dm}^{-3}$)

D2EHAG and D2EHAS was approximately 2 and that between Co^{2+} and Ni^{2+} with D2EHAG was over 0.5. Therefore, the novel extractants, D2EHAG and D2EHAS, can be applied for the recovery of Ni^{2+} and Co^{2+} from leach solution of electronic wastes such as lithium ion batteries, or of Mn-rich natural ore even in the presence of large amounts of Mn^{2+} . The separation of Ni^{2+} and Co^{2+} was also possible using D2EHAG. In preliminary investigations, it was confirmed that 1 mol dm^{-3} D2EHAG was soluble in the aliphatic organic solvent *n*-dodecane. The extraction capacity of the metal ions was considered to be high enough for practical use. Therefore, these novel extractants show potential for use in industrial processes as a new extractant. To our knowledge, this is the first report discussing the achievement of the mutual separation of Ni^{2+} , Co^{2+} and Mn^{2+} with high efficiency, especially for Co^{2+} and Ni^{2+} from Mn^{2+} , by solvent extraction with a single extractant.

Slope analysis and loading test was conducted to clarify the extraction mechanism of the divalent metal ions with the novel extractants (data not shown).

Based on the slope analysis and results from the loading test, the extraction equilibrium equation of the metal ions with D2EHAG is expressed by Eq. (4):



Stripping behavior

The stripping of metal ions from the extracting phase was also conducted. Fig. 2(d) shows the stripping ratio, *S*, for the metal ions from the extracting phase prepared by extraction at $\text{pH}_{\text{eq}} = 4.35$, where only Ni^{2+} and Co^{2+} were extracted efficiently. As shown in Fig. 2(d), quantitative recovery and separation of Ni^{2+} and Co^{2+} from Mn^{2+} was achieved (Ni^{2+} : 100%, Co^{2+} : over 95%) using 1 mol dm^{-3} H_2SO_4 . Mn^{2+} was not extracted in the pH range and accordingly Ni^{2+} and Co^{2+} could be recovered to the stripping phase. Here, it is noted that the stripping of Co^{2+} was possible, despite its stripping being difficult for the conventional systems using a commercial extractant such as 2-hydroxy-5-nonylacetophenone oxime (LIX 84I), because of the oxidation of divalent cobalt (Co^{2+}) to trivalent cobalt (Co^{3+}) ions [16]. The pink octahedral Co^{2+} complex in the organic phase disappeared, and the stripping phase changed to the light pink cobalt ion.

Conclusions

Novel amic acid extractants D2EHAG and D2EHAS which have alkylamide and glycine (or sarcosine) derivatives were developed for the separation of Co^{2+} and Ni^{2+} from Mn^{2+} . Several typical commercial extractants such as D2EHPA, PC-88A and Cyanex 272 are selective for Mn^{2+} against Ni^{2+} and Co^{2+} , whereas the newly developed extractants were found to extract Ni^{2+} and Co^{2+} preferentially with high selectivity over Mn^{2+} from a sulfuric acid solution. The high affinity of D2EHAG and D2EHAS for Co^{2+} and Ni^{2+} is considered to be because of the carboxyl and amine groups in their molecular structures. Quantitative stripping of Co^{2+} and Ni^{2+} from the extracting phase was achieved using 1 mol dm^{-3} H_2SO_4 , despite the stripping of Co^{2+}

often being difficult in conventional extraction systems such as using Cyanex 301. The target ions Ni^{2+} and Co^{2+} were separated satisfactorily from Mn^{2+} through the extraction and stripping steps. Thus, the novel extractants D2EHAG and D2EHAS are useful for the recovery of important metals such as Co^{2+} and Ni^{2+} from a Mn^{2+} rich solution derived from secondary as well as natural resources.

Acknowledgement

We thank Sumitomo Metal Mining (SMM) Co., Ltd. for their financial support of this research. Y. Baba was supported by Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

References

1. T. Suzuki, T. Nakamura, Y. Inoue, M. Niinae, J. Shibata (2012), *Sep. Purif. Technol.*, **98**, 396-401.
2. C. Williams, W. Hawker, J. W. Vaughan (2013), *Hydrometallurgy*, **138**, 84-92.
3. A.M. Wilson, P.J. Bailey, P.A. Tasker, J.R. Turkington, R.A. Grant, J.B. Love (2014), *Chem. Soc. Rev.*, **43**, 123-134.
4. K. Shimojo, N. Aoyagi, T. Saito, H. Okamura, F. Kubota, M. Goto, H. Naganawa (2014), *Anal. Sci.*, **30**, 263-269.
5. H. Narita, K. Morisaku, M. Tanaka (2008), *Chem. Commun.*, **2008**, 5921-5923.
6. Y. Baba, A. Arima, S. Kanemaru, M. Iwakuma, T. Oshima (2011), *J. Chem. Eng. Jpn.*, **44**, 686-691.
7. P.E. Tsakiridis, S.L. Agatzini (2004), *Miner. Eng.*, **17**, 913-923.
8. W. Zhang, C.Y. Cheng (2007), *Hydrometallurgy*, **89**, 137-159.
9. W. Zhang, C.Y. Cheng (2007), *Hydrometallurgy*, **89**, 160-177.
10. F. Wang, F. He, J. Zhao, N. Sui, L. Xu, H. Liu (2012), *Sep. Purif. Technol.*, **93**, 8-14.
11. D.S. Flett (2005), *J. Organomet. Chem.*, **690**, 2426-2438.
12. Y. Baba, F. Kubota, N. Kamiya, M. Goto (2014), *Ind. Eng. Chem. Res.*, **53**, 812-818.
13. K. Shimojo, A. Nakai, H. Okamura, A. Ohashi, H. Naganawa (2013), *Anal. Sci.*, **29**, 147-150.
14. P.E. Tsakiridis, S.L. Agatzini (2004), *Hydrometallurgy*, **72**, 269-278.
15. G.S. Groenewold, D.R. Peterman, J.R. Klaehn, L.H. Delmau, P. Marc and R. Custelcean (2012), *Rapid Commun. Mass Spectrom.* **26**, 2195-2203.
16. S. Nishihama, N. Sakaguchi, T. Hirai, I. Komasaawa (2000), *Ind. Eng. Chem. Res.*, **39**, 4986-4990.

Recovery of Ni and Cd from spent Ni - Cd batteries by acid leaching and a synergistic solvent extraction system using D2EHPA and Cyanex 302

Ataollah Babakhani¹, Nastaran Heidari¹, Fereshteh Rashchi^{*1}, Ehsan Vahidi²

Summary

Due to the presence of heavy metals (Cd, Ni, Co) in the electrode materials and their possible landfill leaching, disposal of spent Ni – Cd batteries as municipal solid waste has a significant role in environmental problems. Therefore, recycling of Ni – Cd batteries is improving in order to decrease environmental concerns over risks of soil contamination and water pollution. In this study, a physical separation following by a hydrometallurgical process has been investigated and the following sequential stages were proposed: dismantling, leaching in sulfuric acid, and separation of Ni(II) and Cd(II) from sulfate leach liquor using solvent extraction.

At the first step, steel cases of AA size spent Ni-Cd batteries were opened and anode materials were disaggregated from steel support plaques. The advantage of this method is removing steel plaques in advance and preventing dissolution of Fe(III) in leach liquor. At the leaching process by sulfuric acid, effect of influential parameters on extraction efficiencies of Cd and Ni from anode material of spent Ni-Cd were studied. The experimental results revealed that under optimal leaching conditions (sulfuric acid concentration: 2 M, T: 65°C, t: 90 min, L/S:10 mL/g, and rpm:500), the final leach liquor contained 52.67 gr/L Cd and 7.72 gr/L Ni.

In the solvent extraction process, the results imply that cadmium extraction with D2EHPA involves co-extraction of nickel; thus, synergistic effect of D2EHPA and Cyanex 302 diluted in kerosene was investigated for separation of cadmium and nickel from leach liquor with the aim of increasing separation efficiency and reducing the reagent cost. The operation variables, pH (0.25–4.0), ratio of D2EHPA: Cyanex 302 (9:1, 7:1, 5:1) at ambient temperature were studied. As a result, increasing the ratio of Cyanex 302 to D2EHPA in the organic phase caused a left shifting of the extraction isotherm of cadmium and a right shifting of the extraction isotherm of nickel. Optimum parameters in separation process were found with a ratio of Cyanex 302 to D2EHPA 5:1 in which Cd had a 100% extraction rate at pH=2 and less than 5% Ni extraction at this pH.

Introduction

Advanced technology continuously leads to a variation in lifestyle and increasing utilization of portable devices [1]. This technological innovations leads to increase the number and variety of portable electronic devices (such as cell phones, laptops, cameras) which use rechargeable batteries [2]. Therefore, management of spent batteries which consider as hazardous wastes due to their high levels of metals is so important from both environmental and economical aspects [3-5]. Nickel-Cadmium batteries (Ni-Cd) which are an example of typical rechargeable batteries have been greatly replaced by Ni-MH and Li-ion batteries because of their technological and environmental preferences [6]. However Ni-MH and lithium batteries are more expensive and Ni-Cd batteries are still used in many countries [7-8]. Besides, new application of Cd in solar energy systems has brought about an increasing demand of the production of cadmium from secondary sources [9-13].

Several processes based on hydrometallurgy, pyrometallurgy or a combination of them are utilizing to recover nickel and cadmium from spent batteries [10]. Currently, various companies such as INMETCO (USA), SAFTAB (Sweden), ACCIREC GmdH (Germany), and SNAM (France) are applying pyrometallurgical processes to recycle Ni-Cd batteries. [11]. Espinso and Tenorio was investigating a method for recycling Ni- Cd batteries involved cadmium distillation, whereas coal applied as reducing agent. In spite of the existence of some industrial processes, this study was a fundamental study on a pyrometallurgical method and resulted in cadmium with

¹ School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, PO Box 11155/4563, Tehran, Iran, (rashchi@ut.ac.ir)

² Department of Civil and Environmental Engineering, University of South Florida, Tampa, FL 33620, USA

99.92% purity and an Ni-Co alloy [12]. In comparison with pyrometallurgical processes which are often accompanied with high air emissions and high energy demand, hydrometallurgical processes have so many advantages such as complete recovery, high purity of recovered metals, low energy requirements and no air emissions [13]. Therefore, hydrometallurgical methods are employed in several researches for recycling of spent batteries in order to be optimized and industrialized considering its advantages.

In hydrometallurgical methods, the first step after dismantling and crushing is acid leaching of active materials of the batteries. After leaching of valuable metals, subsequent separation of metal ions is carried out by several techniques, like electrochemical [6, 14], chemical precipitation [15] and solvent extraction [2]. Some bio hydrometallurgical routes to treat spent batteries have also been proposed [16, 17].

Different hydrometallurgical stages have been investigated in details by various researchers. Several investigations have focused on different leaching conditions by H_2SO_4 [4, 6, 13, 14, 18] or HCl [2, 19] as leaching agent to increase metal extraction efficiency and enhance selectivity of different metal ions. Furthermore, several novel hydrometallurgical processes have been developed with particular attention to solvent extraction methods due to its high selectivity in separation stage. Solvent extraction of leach liquor of Ni-Cd batteries has been studied by Cyanex 923 (a mixture of four trialkyl-phosphine oxides ($\text{R}_3\text{P}=\text{O}$, $\text{R}_2\text{R}'\text{P}=\text{O}$, $\text{R}'_3\text{P}=\text{O}$, $\text{R}'_2\text{R}\text{P}=\text{O}$, where R = hexyl and R' = octyl)) [19], Cyanex 272 [5,19], Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) [5], Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid) [5, 20], Tops 99 (an equivalent of di-2-ethylhexyl phosphoric acid) [5] and PC 88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) [21]. Mixture of extractant (synergism) was applied to the separation of nickel-cadmium system by Reddy et al. [22]. They found that in the separation of nickel and cadmium species from sulfate solutions, a mixture of TOPS 99 and Cyanex 471 X performs a clear separation of cadmium from nickel. Addition of Cyanex 471 X suppressed the co-extraction of Ni drastically from 2.03 to 0.28%. Thus, compared to the solvent extraction with sole extractants, separation of Cd over nickel was more efficient with mixture of extractants in a synergistic system. Babakhani et al. studied the synergistic effect of Cyanex 302 on solvent extraction of nickel and cadmium from sulfate solution with D2EHPA with the aim of increasing separation efficiency. As a result, satisfactory separation has been found with a Cyanex 302 to D2EHPA ratio of 0.1 M: 0.5 M [20].

This study examines the leaching of spent batteries with sulfuric acid followed by solvent extraction separation of metals from leach liquor. In the present investigation, Synergistic solvent extraction of Ni and Cd from leach liquor was performed by D2EHPA and Cyanex 302 diluted in kerosene.

Experimental

The experimental work adopted in this study consisted of the following steps: (i) Dismantling of batteries in order to separate components of spent Ni-Cd batteries; (ii) Metal characterization of the internal content of spent Ni-Cd batteries; (iii) leaching of active electrode materials of the anodes with sulfuric acid; (iv) solvent extraction with the mixtures of D2EHPA and Cyanex 302 in different ratios (9:1, 7:1, 5:1)

Dismantling and metal characterization of spent NiCd batteries

Different brands of spent Ni–Cd batteries (AA-size) with a mean weight of 22 g were dismantled into separate various components of the cell such as anode, cathode, separator, steel case and plastic parts. The steel case was opened using a lathe machine to cut the ends of the cylindrical batteries and a cutting tool to cut the steel case axially. The rolled electrode plates were carefully withdrawn and the separator part between anode and cathode was removed. The internal contents of 3 random batteries (including the grids that support the active material) were weighed. The electrodes were then dried in a drying oven for 24 h at 100°C. The anodes and cathodes were then disaggregated from the steel support plaques by a mixer separately and sieved to 177 microns (-100 mesh). The ground cathodes and anodes were qualitatively analyzed by X-ray fluorescence (XRF) Spectrometer, Brucker (model AXS-S4). Then, to characterize different phases X-ray diffraction method (XRD) was applied by a Philips (model PRO-PW1730). A sample of the sieved anode were then dissolved in aqua-regia and its metal composition (Cd and Ni) was analyzed by atomic absorption spectrometry (AAS) using a Unicam (model 939) Atomic Absorption Spectrometer.

Leaching test

The leaching experiments were performed at atmosphere pressure in a 1L pyrex reactor equipped with a reflux condenser, with four necks for mechanical stirrer, condenser, thermometer, and the inlet of the sample. The solution in the reactor could be heated up indirectly by a hot plate through a water bath. In a typical leaching experiment, 100 mL sulfuric acid of predetermined concentration was taken in the glass reactor. As soon as the temperature of the solution reached the desired value, weighed amounts of sample was added and mixture was agitated with a mechanical stirrer using a plastic blade at 500 rpm. Temperature and time were evaluated as operation variables. After a specific leaching time a glass funnel equipped with a paper filter was used for filtration. The slurry was filtered and a sample of aqueous solution was submitted to atomic absorption spectrometer (AAS) to analyze Cd and Ni. All tests were carried out in duplicate.

Solvent extraction procedure

Bench scale studies were carried out by mixing equal volume (50 mL) each of aqueous solution and organic extractant with the help of mechanical stirrer for specified time (10 Min). The concentration of the extractant in the organic phase (D2EHPA- Cyanex 302 mixtures) was 1 M. The aqueous to organic phase ratio (A/O) of 1:1 was applied in all tests. A pH-meter was used to monitor pH during the experiments. In order to obtain the extraction isotherms, the required pH for the aqueous feed was adjusted with NaOH or H₂SO₄ solution. After the pH was stable, the phases were allowed to separate then a sample was taken, transferred to a separatory funnel, and allowed to disengage. The metal concentration in the aqueous phase was estimated directly after suitable dilutions by AAS.

Results and discussion

Sample Characterization

Mineralogical and chemical analyses of the ground anode were done by XRD and XRF. The XRD pattern and the major compounds present in the sample were shown in Fig. 1. The XRD result revealed that the major phases in the anode are nickel hydroxide (Ni(OH)₂), cadmium oxide (CdO), metallic nickel (Ni) and cadmium hydroxide (Cd(OH)₂). Table 1 represents the chemical analysis of the anode, obtained by XRF.

As mentioned in Table 1, the spent batteries contained ca. 55 percent by weight CdO (ca. 48% Cd) and ca. 38% NiO (ca. 30% Ni).

Leaching experiments

The effect of residence time on leaching efficiency data in 25°C, 45°C and 65°C represented in Fig. 2., show that in 25°C, the efficiency of nickel dissolution increased from 4.5% in 15 min leaching time to 10.5% in 120 min, while in 65°C the efficiency of nickel dissolution increased from 6% in 15 min to 27% in 120 min. At the same time, the dissolution of cadmium can be achieved completely in all examined temperature within 120 min of leaching time. From these results, it seems that, extending time of leaching have more effect on dissolution of nickel in higher temperatures.

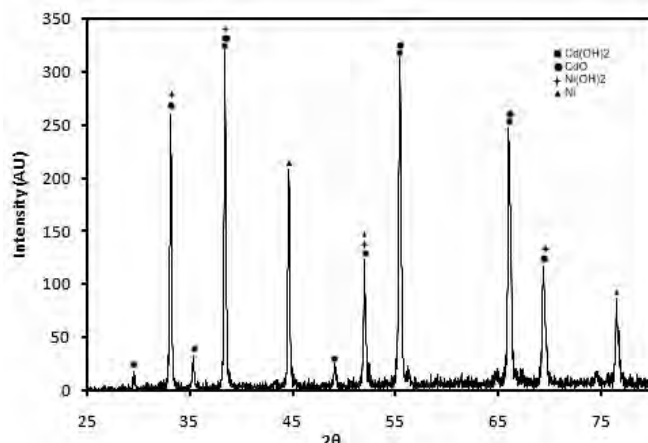


Figure 1. XRD pattern of the ground anode of spent Ni-Cd batteries.

Table 1. Major compounds in the ground anode, wt.%.

Compound	Wt%
MgO	0.76
Al ₂ O ₃	0.12
SO ₃	0.16
K ₂ O	2.6
Fe ₂ O ₃	0.13
NiO	37.6
CdO	54.8

From another point of view, studying the effect of temperature on leaching efficiency of nickel and cadmium in 120 minutes leaching time are represents in Fig. 3. It can be observed that in the studied leaching condition ($H_2SO_4=2M$, $t=120min$, $rpm=500$), increasing temperature has a negligible effect on dissolution of cadmium; however, leaching efficiency of nickel increased from 10.5% in 25°C to 27% in 65°C.

The different behavior of dissolution of nickel and cadmium probably belongs to metallic Ni of anode material which was not soluble in those conditions of acidity and temperature.

Considering leaching at 2M acid concentration, residence time of 120 min, agitation rate of 500 rpm and L/S of 10 mL/g, resulted in 52.67 gr/L Cd and 7.72 gr/L Ni.

Solvent extraction

Fig. 4. illustrates the percentage of cadmium and nickel ions extracted as a function of equilibrium pH using D2EHPA in kerosene at 25 °C and A/O phase ratio of 1:1. As it can be seen from the extraction isotherm, cadmium extraction with D2EHPA involves co-extraction of nickel [20].

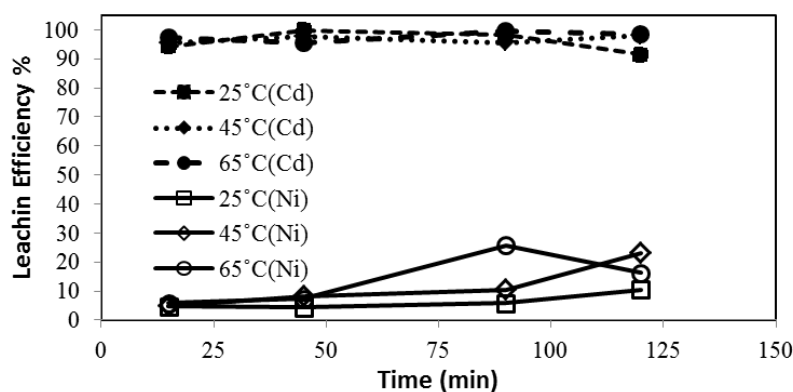


Figure 2 – Effect of residence time on leaching efficiency in in 25°C, 45°C and 65°C (2M acid concentration, agitation of 500 rpm and L/S=10 mL/g)

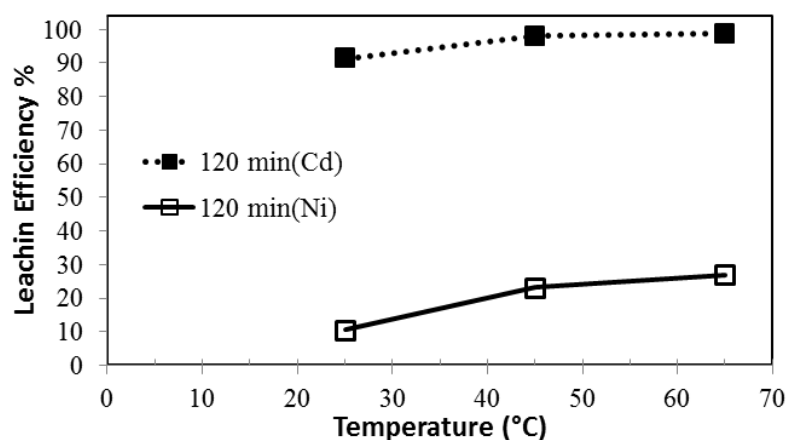


Figure 3 – Effect of temperature on leaching efficiency (2M acid concentration, residence time of 120 min, 500 rpm and L/S= 10 mL/g)

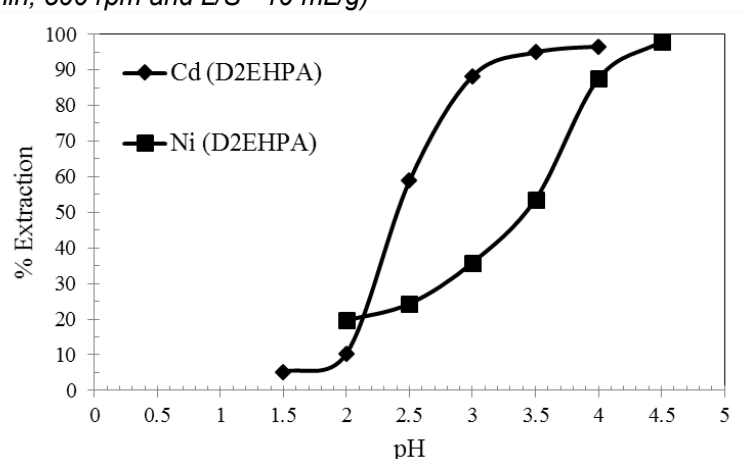


Figure 4. Effect of equilibrium pH on extraction of cadmium and nickel using D2EHPA at 25°C and A/O ratio of 1:1

To decrease the co-extraction of Ni and increase the selective extraction of Cd, mixed extractant systems consisting D2EHPA and Cyanex 302 in kerosene were applied. Fig. 5 shows the percentage of cadmium and nickel ions extracted as a function of pH at different D2EHPA to Cyanex 302 ratios (9:1, 7:1, 5:1) at 25 °C. It illustrates significant synergistic shifts of cadmium and nickel isotherms due to the addition of Cyanex 302 to D2EHPA. As can be seen in the figure, by increasing the ratio of Cyanex 302 to D2EHPA, the cadmium extraction curve shifted more to the left and that of nickel to the right. In other words, addition of Cyanex 302 to D2EHPA significantly improves the separation of cadmium over nickel.

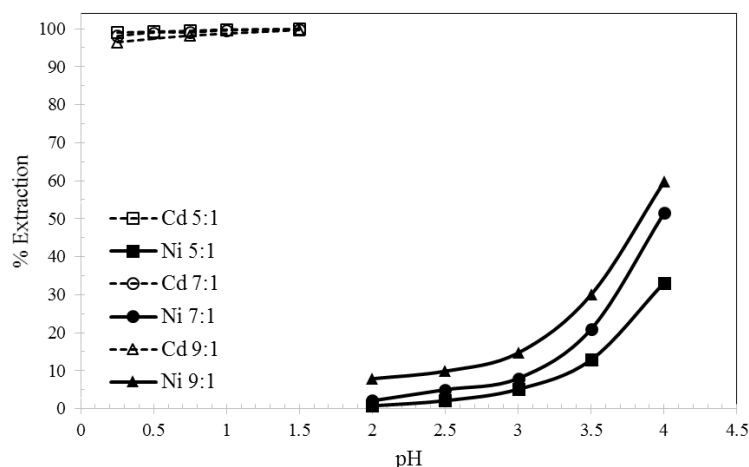


Figure 5. Effect of additions of Cyanex302 to D2EHPA on the extraction of Cd and Ni at 25°C and A/O ratio of 1:1.

Conclusions

- 1- In the studied leaching conditions, increasing temperature has a negligible effect on dissolution of cadmium, and the dissolution of cadmium can be achieved completely in all examined temperatures within 120 min of leaching time.
- 2- In the studied leaching condition ($\text{H}_2\text{SO}_4 = 2 \text{ M}$, $t = 120 \text{ min}$, $\text{rpm} = 500$), increasing temperature has a negligible effect on dissolution of cadmium; however, leaching efficiency of nickel increased from 10.5% in 25°C to 27% in 65 °C.
- 3- Adding Cyanex 302 to D2EHPA caused a synergistic effect and shifted the extraction curve of cadmium and nickel to the left and right, respectively.

References

1. L. E. O.C. Rodrigues, M.B. Mansur, *Journal of Power Sources*, Vol. 195, 2010, pp. 3735-3741.
2. A.Fernandes, J.C.Afonso, A.J.Bourdut Dutra, *Journal of Power Sources*, Vol. 220, 2012, pp. 286-291.
3. M. S. Safarzadeh, M. Bafghi, D. moradkhani, M. Ojaghilkhchi, *Minerals Engineering*, Vol. 20, 2007, pp. 211–220.
4. C. Nogueira, F. Margarido, *Waste Management*, Vol. 27, 2007, pp. 1570–1579.
5. B. R. Reddy, D. N. Priya, *Separation and Purification Technology*, Vol. 50, 2006, pp. 161-166.
6. M. B. J. G. Freitas, S. F. Rosalem, *Journal of Power Sources*, Vol. 139, 2005, pp. 366-370.
7. C.J. Rydh, M. Karlstrom, *Resources, Conservation and Recycling*, Vol. 34, 2002, pp. 289-295.
8. C. J. Rydh, B. Svard, *Science of the Total Environment*, Vol. 302, 2003, pp. 167-174.
9. R. K. Pandey, S. Mishra, S. Tiwari, P.Sahua, B. P. Chandra, *Solar Energy Materials and Solar Cells*, Vol. 60, 2000, pp. 59-72.
10. D. C. R. Espinosa, A. M. Bernardes, J. A. S. Tenório, *Journal of Power Sources*, Vol. 135, 2004, pp. 311–319.
11. G. Pistoia, J. Wiaux, S. Wolsky, *Used Battery Collection and Recycling*, Elsevier, 2001.
12. D. C. R. Espinosa, J. A. S. Tenorio, *Journal of Power Sources*, Vol. 157, 2006, pp. 600–604.
13. L. Pietrelli, B. Bellomo, D. Fontana, M. Montereali, *Waste Management*, Vol. 25, 2005, pp. 221–226.
14. E. Rudnik, M. Nikiel, *Hydrometallurgy*, Vol. 89, 2007, pp. 61–71.
15. K. Provazi, B. A. Campos, D. C. R. Espinosa, J. A. SoaresTenório, *Journal of Waste Management*, Vol. 31, 2011, pp. 59-64.
16. N. Zhu, L. Zhang, C. Li, C. Cai, *Waste Management*, Vol. 23, 2003, pp. 703-708.
17. C. Cerruti, G. Curutchet, E. Donati, *Journal of Biotechnology*, Vol. 62, 1998, pp. 209-219.
18. C. Nogueira, F. Margarido, *Hydrometallurgy*, Vol. 72, 2004, pp. 111–118.
19. B. R. Reddy, D. N. Priya, *Journal of Power Sources*, Vol. 161, 2006, pp. 1428-1434.
20. A. Babakhani, F.Rashchi, A. Zakeri, E. Vahidi, *Journal of Power Sources*, Vol. 247, 2014, pp. 127-133.
21. B. R. Reddy, D. N. Priya, J.R. Kumar, *Hydrometallurgy*, Vol. 74, 2004, pp. 277–283.
22. B. R. Reddy, S. V. Rao, D. N. Priya, *Separation and Purification Technology*, Vol. 59, 2008, pp. 214-220.

Homogeneous liquid-liquid extraction of metals with ionic liquids

Bieke Onghena, KU Leuven, Heverlee (Leuven), Belgium; Koen Binnemans, KU Leuven, Heverlee (Leuven), Belgium

Ionic liquids (ILs) are intensively studied for use in solvent extraction. Attractable properties such as negligible vapor pressure, non-flammability, broad liquidus range and high thermal stability, makes ionic liquids interesting replacements for the environment damaging volatile organic solvents (VOCs). However, most ionic liquids are characterized by a high viscosity, which is a serious drawback for use in solvent extraction. Due to their high viscosity, a large energy input and long mixing times are required to reach equilibrium conditions.

Homogeneous liquid-liquid extraction (HLL) with ionic liquids is introduced as a modified solvent extraction technique to cope with these problems. HLL makes use of solvents showing thermomorphic behavior in combination with water. This means that the phase behavior of the IL-water mixture is temperature-dependent. Heating of the extraction mixture above the critical temperature or cooling below it (depending on the type of phase behavior) leads to the formation of one homogeneous phase, which eliminates the need for intense stirring during the mixing stage of the extraction. In this homogeneous stage, extraction is no longer kinetically hindered by a barrier interphase. As a result the extraction equilibrium is reached practically instantaneously. During the settling stage, the temperature is changed in such a way that the two phases are reformed.

The scope of our work was to find an efficient homogeneous liquid-liquid extraction system to extract metal ions with a critical temperature close to room temperature (hence little energy is required to reach the homogeneous stage). The ionic liquid [Hbet][Tf₂N], with an upper critical solution temperature (UCST) of 55.5 °C, was shown to extract Ga, Sc, In and the most important rare earths with high extraction efficiencies in combination with betaine as extractant.¹ The extracted metals were stripped from the loaded ionic liquid phase with hydrogen chloride. At the end of the extraction, pure ionic liquid was recovered, which could be used for new extractions.

¹ Vander Hoogerstraete, T.; Onghena, B.; Binnemans, K. Homogeneous Liquid-Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid. *J. Phys. Chem. Lett.* **2013**, *4* (10), 1659-1663.

Extraction of Zn(II), Cd(II), Hg(II) and Co(II) by a high quaternary ammonium salts

*Alena E. Trofimenko, PhD-student Belarusian State University, Minsk, Belarus,
trofimenko.ee@gmail.com;*

Alexandr L. Gulevich, Prof. Dr., Belarusian State University, Minsk, Belarus

Summary

Anion-exchange extraction of Zn(II), Cd(II), Hg(II) and Co(II) thiocyanate complexes using solutions of high quaternary ammonium salts (QAS) with different structure in various organic solvents has been investigated. It is found that metals extracted in the form of doubly charged thiocyanate complexes $\text{Me}(\text{SCN})_4^{2-}$. Conditional exchange constants of doubly charged thiocyanate complexes with the picrate anion were experimentally determined using the direct and inverse extraction schemes and functional dependence of their logarithms on pSCN was established. Concentration exchange constants were calculated with aid of SCM Mathematica, taking into account the interference of free thiocyanate anions. It was established that extractability of metal complexes decreases in a row: $\text{Zn}(\text{SCN})_4^{2-} > \text{Co}(\text{SCN})_4^{2-} > \text{Cd}(\text{SCN})_4^{2-} > \text{Hg}(\text{SCN})_4^{2-}$ and does not correlate with their stability for all examined QAS and organic solvents. It was determined that saturated hydrocarbons (hexane) demonstrate the strongest differentiating ability among tested organic solvents for QAS. And QAS with short hydrocarbon substituents (triethyl) have the largest value of exchange constants.

Introduction

Anion-exchange extraction by QAS solutions is applied for isolation and extractive-spectrophotometric determination of metals in a form of anions of metal-complex acid [1]. Of particular interest are M-SCN complexes. Depending on the nature of metal ion they can be either thiocyanato (M-SCN) or isothiocyanato (M-NCS) complexes, that differ dramatically in their extractability [2]. Much research has been done on complex formation in aqueous and nonaqueous solutions [3], however, only stability constants and some thermodynamic characteristics of complexation were determined, ignoring the problems of extractive isolation of metal complexes.

There is no information about quantitative characteristics of extraction such as exchange constants and distribution coefficients in the reference and scientific literature for the majority of metals. Influence of organic solvent and nature of QAS on the extractability of the most metal complexes have not been investigated. This restricts the development of new more selective methods of extraction and analytical determination of metals in a form of anionic complexes.

Experimental part

Reagents

Table 1 summarizes QAS, synthesized at the Belarusian State University, which were used as an anion exchanger.

Table 1. High quaternary ammonium salts (QAS)

IUPAC name	Abbreviation	Structural formula
Trinonyloctadecylammonium iodide	TNODA	$(C_9H_{19})_3C_{18}H_{37}N^+I^-$
3,4,5-Tris(dodecyloxy)benzyltriethylammonium bromide	TE	
3,4,5-Tris(dodecyloxy)benzyltributylammonium bromide	TB	
3,4,5-Tris(dodecyloxy)benzyltrilaurylammonium bromide	TL	
3,4,5-Tris(dodecyloxy)benzyltricetylammmonium bromide	TC	

Conversion of initial bromide and iodide QAS into required anionic forms (picrate, zinc- and cobalt-thiocyanate) was carried out by liquid-liquid/solvent extraction with photometric control of conversion completeness.

Toluene p.a. and hexane p.a. were additionally purified from sulphur-containing impurities by the treatment with 70% sulphuric acid. Chloroforme p.a. was washed with distilled water before use to remove stabilizer impurities. Octanol-1 was additionally distilled under vacuum over alkali.

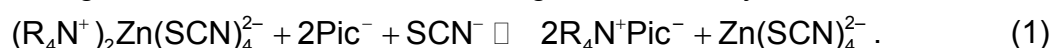
Starting aqueous solutions of Zn(II), Co(II), Cd(II) and Hg(II) were prepared from corresponding sulfates and nitrates (p.a.) line. Accurate concentration of Hg(II) and Zn(II) was determined by complexometric titration.

Apparatus

Absorbance measurements and registration of absorption spectrum were carried out on spectrophotometer Solar PV 1251.

Procedure

Extraction of highly-extractable Zn(II) and Co(II) thiocyanate complexes was investigated using inverse extraction on the background of thiocyanate anions:



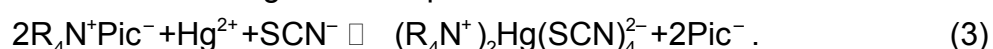
Conditional exchange constant was calculated according to the equation (1)

$$\tilde{K}_{2Pic^-}^{Zn(SCN)_4^{2-}} = \frac{[(R_4N^+)_2Zn(SCN)_4^{2-}] \cdot [Pic^-]^2}{[R_4N^+Pic^-]^2 \cdot [C_{Zn}]_{aq}} = \frac{(C_{0,QAS} - 0,5 \cdot [R_4N^+Pic^-]) \cdot (C_{0,Pic^-} - [R_4N^+Pic^-])^2}{0,5 \cdot [R_4N^+Pic^-]^3}, \quad (2)$$

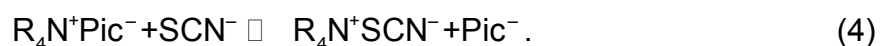
where $[C_{Zn}]_{aq}$ - total equilibrium concentration of all Zn-species in aqueous phase, $C_{0,QAS}$ - initial concentration of QAS in organic phase, C_{0,Pic^-} - initial concentration of picrate anions in aqueous phase, $[R_4N^+Pic^-]$ - equilibrium concentration of picrate in organic phase.

Background thiocyanate anions did not shift anion-exchange equilibrium (1) significantly and did not influence the values of conditional exchange constants $\tilde{K}_{2Pic^-}^{Zn(SCN)_4^{2-}}$ because of low values of their exchange constants with picrate-anion ($K_{Pic^-}^{SCN^-} = 10^{-4} - 10^{-3}$).

Extraction of more hydrophilic Cd(II) and Hg(II) thiocyanate complexes was examined by a direct scheme using QAS in a picrate form:



Concentration of QAS in all experiments exceeded the initial concentration of metal and was $1 \cdot 10^{-3}$ M. Concentration of thiocyanate anions was higher than concentration of metal cation and reached 1,0 M. In this case, the background thiocyanate anions make substantial contribution to the equilibrium concentration of picrate anions due to competitive reaction



Calculations showed that proportion of picrate anions displaced by reaction (4) in general/total amount of picrate anions in the flow of the main anion-exchange reaction (3) is rather significant and for 1,0 M solution of KSCN run up to 77% rel.

It is incorrect to calculate conditional exchange constants of Hg(II) and Cd(II) thiocyanate complexes by equilibrium picrate anions concentrations in aqueous phase. In this case, concentration exchange constants are calculate by algorithm [4] with subsequent recalculation to conditional exchange constant by equation

$$\tilde{K}_{2Pic^-}^{M(SCN)_4^{2-}} = K_{2Pic^-}^{M(SCN)_4^{2-}} \cdot \frac{M(SCN)_4^{2-}}{M(SCN)_4^{2-}}, \quad (5)$$

where $\alpha_{M(SCN)_4^{2-}}$ - molar fraction of extractable thiocyanate complex.

Results and Discussions

Investigated metal cations form with thiocyanate anions a number of complexes $M(SCN)_i^{2-i}$, where $i=1 \div 4$. Molar fractions (distribution function) of metal complexes are defined the corresponding stability constants β_i and equilibrium thiocyanate anions concentration in aqueous phase. Previously [2] it was found that this metals are extracted in the form of double-charged anions $M(SCN)_4^{2-}$ by solutions of QAS. Since double-charged complexes are the most saturated with ligand, there molar fraction increases with the thiocyanate concentration. This leads to the increase in conditional exchange constants with the increasing of initial concentration of thiocyanate anions (Figure 1).

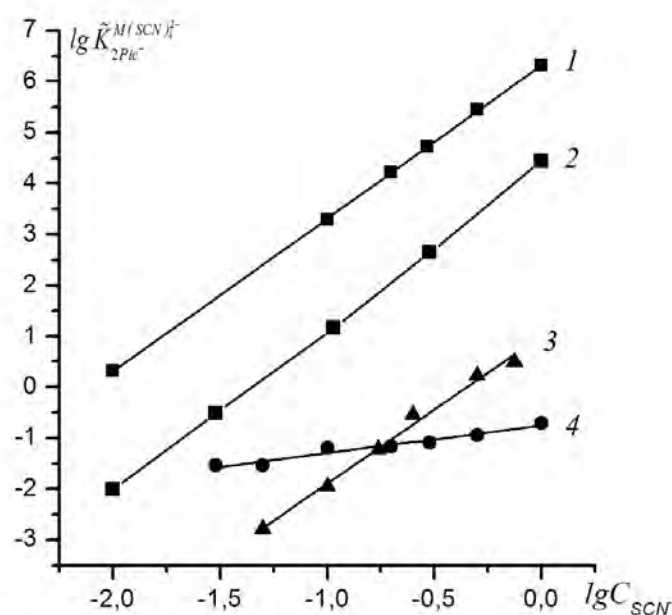


Fig. 1. Effect of thiocyanate concentration in aqueous phase on conditional exchange constants of metal complexes. Metals are: 1 – Zn, 2 – Co, 3 – Cd, 4 – Hg.

All the metals are extracted in the form of doubly-charged metal-complex anions $M(SCN)_4^{2-}$, to compare the extractability of these metals it is necessary to use concentration exchange constant (Table 2).

Table 2. Concentration exchange constants of thiocyanate metal-complexes with picrate anion and logarithm values of total stability constants of complexes $M(SCN)_4^{2-}$

Cation	$K_{2Pic^-}^{M(SCN)_4^{2-}}$	$lg K_{2Pic^-}^{M(SCN)_4^{2-}}$	$lg \beta_4$
Zn^{2+}	$(2,5 \pm 0,3) \cdot 10^6$	6,40	3,02
Cd^{2+}	$2,10 \pm 0,10$	0,32	2,91
Hg^{2+}	$0,16 \pm 0,02$	-0,81	21,2

As shown in Table 2 the correlation between stability and extractability is negligible. The most stable Hg(II) thiocyanate complexes were the least extractable. And conversely, much less stable Zn(II) thiocyanate complexes have a very high extractability. Due to this feature it is used in membranes of highly-selective $Zn(SCN)_4^{2-}$ electrodes [5]. This observation can be explained by the structure of the thiocyanate complexes. Zinc is coordinated through the nitrogen atom, whereas mercury and cadmium - via the sulfur atom in thiocyanate anion [3].

Organic solvent of QAS is an important factor that affects the extractability of metal-complexes. It was established that addition of hexane to toluene solution of picrate TNODA lead to an increased extractability of thiocyanate complexes. As an

example, Figure 2 shows the dependence $\lg K_{2\text{Pic}^-}^{\text{Zn}(\text{SCN})_4^{2-}} - \lg C_{0,\text{SCN}^-}$ for zinc thiocyanate complexes. Conditional exchange constant for zinc increased by 0,5 orders of magnitude, whereas for cadmium and mercury – by one order of magnitude, using 90 vol.% hexane in toluene. Thus, increase in hexane proportion lead to the differentiation of bulk properties for studied metal-complexes and picrate-anions.

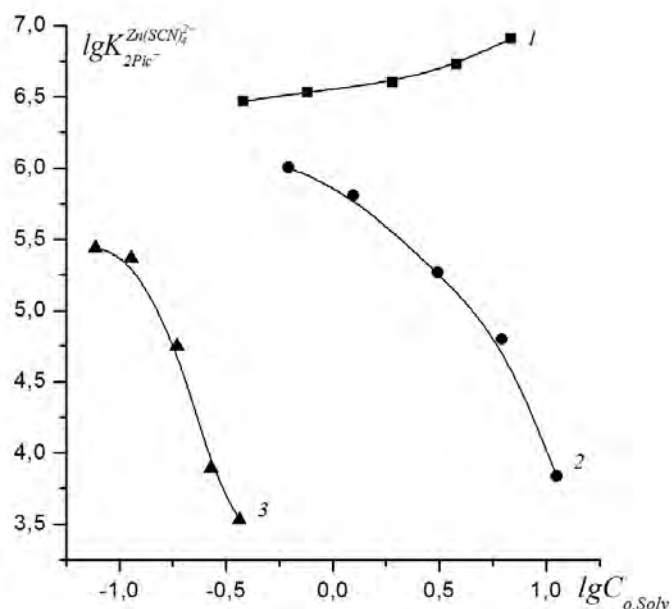


Fig.2. Influence of hexane (1), chloroform (2) and *n*-octanol (3) additives on the extractability of zinc thiocyanate complexes by toluene solutions of TNODA picrate

Addition of «acidic» organic solvents – chloroform and *n*-octanol – in all occasions lead to reduction in extractability of thiocyanate complexes. Octyl alcohol content was recalculated to a monomeric form that is better corresponds to an actual extraction system.

The observed change in extractability was presumable determined by the nature of negative charge distribution on the surface of metal-complexes and picrate. Metal-complex anions have lower electron density, therefore solvation of picrate anions decreased in a greater degree upon dilution of toluene with hexanes, which lead to the increase in extractability of metal-complex anions.

For thiocyanate anions reverse effect was observed: addition of «acidic» solvents sharply increased the extractability of thiocyanate anions by picrate TNODA. Hexane addition had little effect on the extractability of thiocyanate anions. Thus, optimal solvent for the extraction is hexane. Using this solvent observed maximum differentiation in exchange properties in the triple system: $\text{M}(\text{SCN})_4^{2-} - \text{SCN}^- - \text{Pic}^-$. «Acidic» solvents - chloroform and higher alcohols not only reduced the affinity of cobalt and cadmium thiocyanate complexes to the picrate TNODA, but at the same time sharply facilitated competitive extraction of background thiocyanate anions.

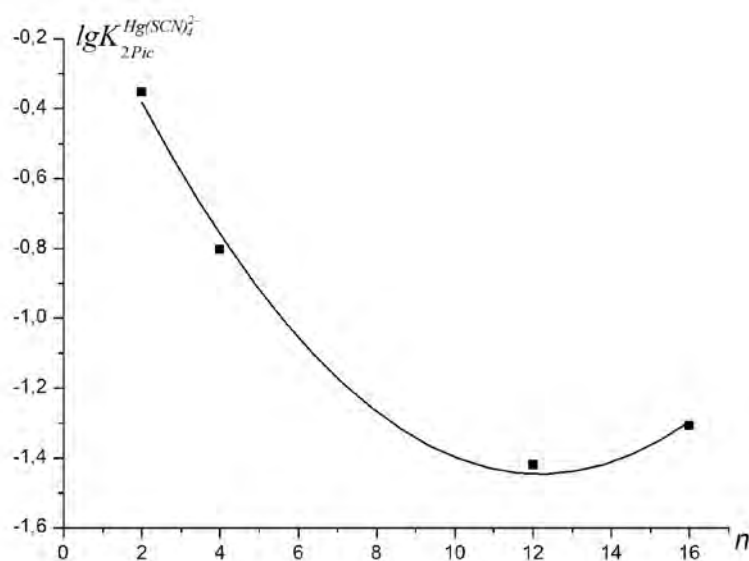


Fig.3. Dependence of concentration exchange constants $\lg K_{2Pic}^{Hg(SCN)_4^{2-}}$ on the number of carbon atoms in substituent

It was found that extractability of all investigated anions by picrate form of QAS decreased with increasing length of hydrocarbon substituent. As an example, Figure 3 shows the dependence of concentration exchange constants for mercury thiocyanate complexes on the number of carbon atoms in substituent.

From triethyl to tricetyl substituent logarithms of exchange constants decreased by 0.4 - 1.0 log units for all studied metals.

References

1. E.M. Rakhman'ko, G.L. Starobinets, V.V. Yegorov, A.L. Gulevich. Analytical application of high molecular quaternary ammonium salts // *Frezenius J. Anal. Chem.* 1989. Vol.335. №1. P.104-110.
2. I.V. Kachanovich., T'yu Van Bien, E.M. Rakhman'ko. Anion-exchange extraction of thiocyanate complexes of some metals using salts of didecylaminoethyl- β -tridecylammonium in the neutral ambient. *J. of the Inorganic Chemistry.* 1994. Vol. 39. No.2. P. 347-352. (rus.)
3. Abraha Banta, Gordon A. Parker, Dennis G. Tuck. Critical survey of stability constants of complexes of thiocyanate ion // *IUPACPure & Appl. Chem.* 1997. Vol. 69. No. 7. P. 1489-1548.
4. A.L.Gulevich, A.E Trofimenko. Anion-exchange extraction of cadmium // *Vestnik BSU.* 2013. Ser. 2. No.1. P. 40-43. (rus.)
5. E.M. Rakhman'ko, U.V. Matveichyk., V.V. Yasinetskii, L.S. Stanishevskii. $Zn(SCN)_4^{2-}$ -selective electrodes based on higher quaternary ammonium salts (QAS) // *Zhurn. neorgan. khimii.* 2013. V. 68. №4. P. 355-362. (rus.)

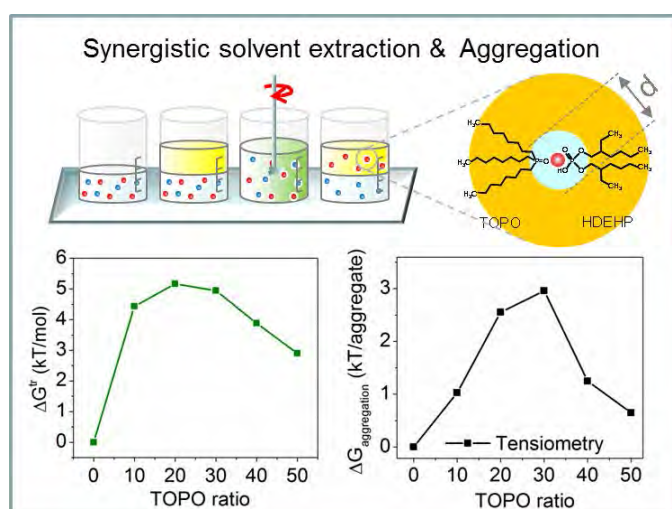
About the origin of “synergism” in ion selectivity in metal salt extraction by microemulsions

S. Dourdain, I. Hofmeister, J-F. Dufrêche, R. Turgis, A. Leydier, S. Pellet-Rostaing and Th. Zemb

Institute for Separation Chemistry of Marcoule, Bagnols sur Ceze, France

In solvent extraction, a concentrated solution of mixed salts is contacted with a reverse microemulsion. Some salts are selectively extracted. When mixed surfactants are used in the formulation of the microemulsion, “synergism” of yet unknown origin emerges: when, for a defined formulation of the solvent phase, there is an increase of distribution coefficients for some salts from a mixture. The origin of synergism is a mystery in chemical engineering because modelling implies complexation and not micellisation. In order to achieve predictive modelling, aggregation number, coordination numbers and complexation numbers must be distinguished.

To determine the origin of this synergy, we determine free energy of co-assembly in mixed aggregates. Aggregation in any point of a phase diagram is followed not only structurally by SANS, SAXS and SLS, and also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates. Using the industrially used couple HDEHP/TOPO forming mixed reverse aggregates, and the representative couple U/Fe¹, we show that there is no peculiarity in the aggregates microstructure when the maximum of “synergism” is obtained. We compare the free energy of aggregation necessary to form mixed aggregates



containing extracted ions in their polar core, to the free energy of extraction difference between target and non-target ions. This allows us to propose a general mechanism at the basis of ion selectivity used industrially for metal recovery.

Fig. 1 Aggregation and transfer energy correspondence in and out of synergism.

Operational Features Related to Copper SX Wash Stages

*Hans Hein^{*1}, Ricardo Hein¹*

Summary

The objective of the paper is a better understanding of how copper, acid, total iron, ferric, chloride and nitrate behave in SX wash stages. The evaluation is based on two SX plants in Chile with information collected three to five years ago. Since then those plants have improved their operation significantly. One of the plants operates with a single wash stage and high nitrate concentration in PLS. The second plant uses two wash stages per SX train under high chloride presence in PLS. All information provided is related to SX wash stages and an overall view of plant operation is not the purpose of the present paper. Aspects considered are wash efficiency, chemical and physical iron transfer in organic, copper/iron selectivity, aqueous in organic entrainment, unit copper transfer and others. The results of the work are based on SX plant data, treating a subject where little has been published.

Introduction

Roughly 50 to 60% of existing copper SX plants worldwide are using a wash stage per SX train. Only a few of them operate with two wash stages per SX train, in view of extremely high chloride concentration in PLS and to obtain high quality copper cathodes at reasonable electrolyte bleed.

Usually a wash stage has a similar size in comparison to extraction and stripping stages. Almost all of them take the electrolyte bleed to the wash stage [1], replacing partially or completely the addition of fresh sulfuric acid.

Only few papers have been published in the past on the subject, e.g., by Kordosky et al. [2] and by Virnig & Olafson [3]. The second paper is related to a patent, where Fe(III) is reduced to Fe(II) in the wash solution recycle for improving iron stripping [4]. The first author [5] presented a wash stage paper in 2005 dealing with copper transfer, iron stripping and physical transfer of chloride and manganese.

The objective of the present paper is to allow a better understanding of how certain parameters like copper, acid and Fe(III) concentrations in the wash solution impact copper transfer and iron stripping based on flows of organic and wash solutions.

Two case studies are illustrated. One of them considers a single wash stage per SX train at high nitrate and chloride concentrations in PLS, whereas the other includes two wash stages per SX train at extremely high chloride concentration in PLS.

Case study on a single wash stage

The first case study considers a plant with five PLS flows in parallel, where only the PLS flow to extraction stage E1 is characterized, since the other PLS flows virtually do not impact wash stage conditions. The nitrate level reaches 15.0 g/l and the chloride level 9.8 g/l in PLS. The Fe(III) concentration, as shown on Table 1, is rather low.

* Corresponding Author

¹ Oryxeio Ingeniería Limitada,
José Miguel Carrera PC 48, El Noviciado, Pudahuel, Santiago, Chile
contact@oryxeio.com

SX configuration		SX reagent	
Multiple series-parallel 7E-1W-1S (5 PLS flows)		Concentration:	23.5 v/v%
Oxide PLS		Reagent:	LIX 84-I
Copper:	2.67 g/l Cu	Organic viscosity:	3.31 cP
Acid:	1.29 g/l H ₂ SO ₄	Operational parameters	
pH:	1.97	Cu net transfer in organic:	0.323 g/l Cu / %reagent
Chloride:	9.8 g/l Cl	Aq. in LO entrainment:	259 ppm
Nitrate:	15.0 g/l NO ₃	Organic flow:	25800 m ³ /d
Total iron:	2.04 g/l FeT	Loaded organic in E1:	9.08 g/l Cu
Ferric:	0.46 g/l Fe ³⁺		8.8 ppm Fe
Manganese:	3.3 g/l Mn	Stripped organic:	1.35 g/l Cu
Sulfate:	131 g/l SO ₄		0.7 ppm Fe
Viscosity:	2.55 cP	Reverse osmosis water consumption	
Density:	1.23 g/cm ³	Wash stage W1:	319.5 m ³ /d
		Unit water consumption:	1.66 m ³ /ton Cu

Table 1: Plant data on single wash stage case study.

Figure 1 shows an aqueous in organic entrainment flow as a bypass. In reality, the bypass corresponds to aqueous droplets not coalesced in the wash stage, which move forward in the washed loaded organic to the stripping stage.

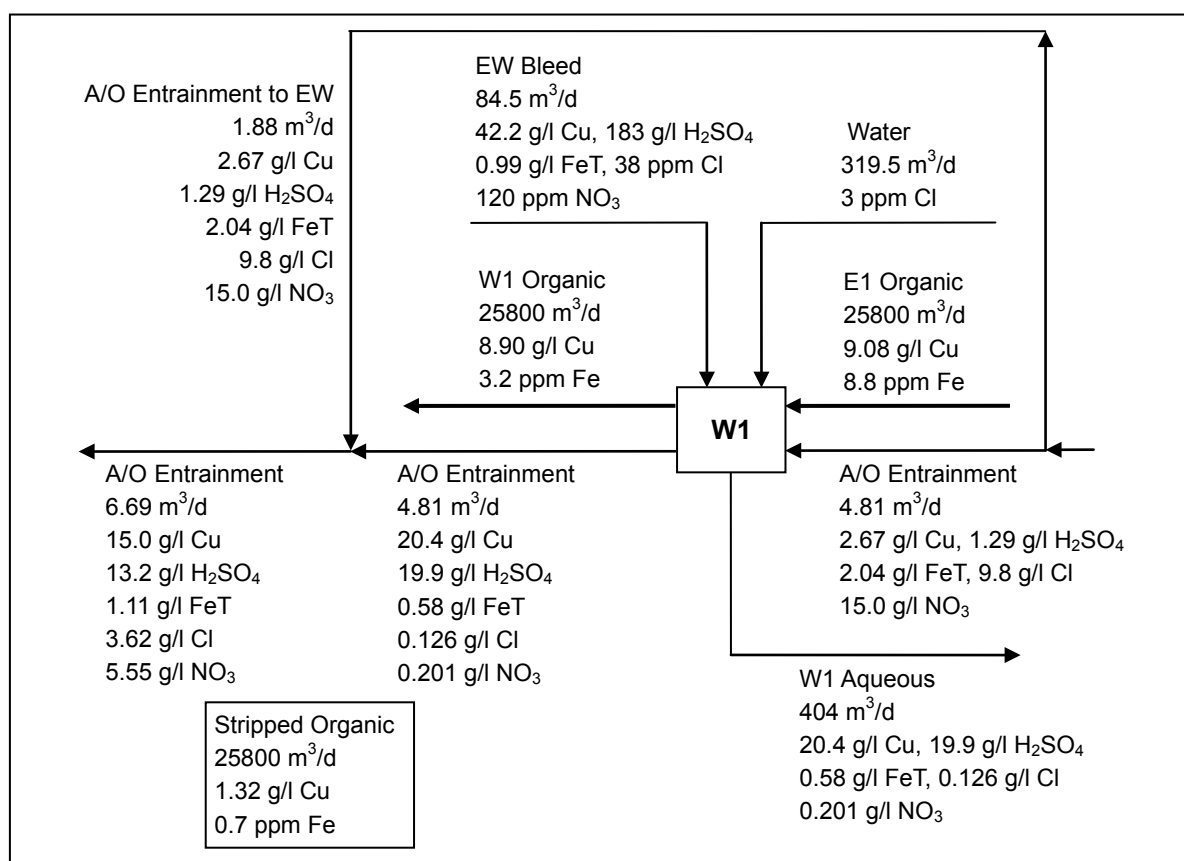


Figure 1: Single wash stage flow diagram.

On Figure 2, the material balance for copper, acid, total iron, chloride and nitrate is determined on aqueous solutions, whereas the material balance on organic solutions is presented for copper and iron.

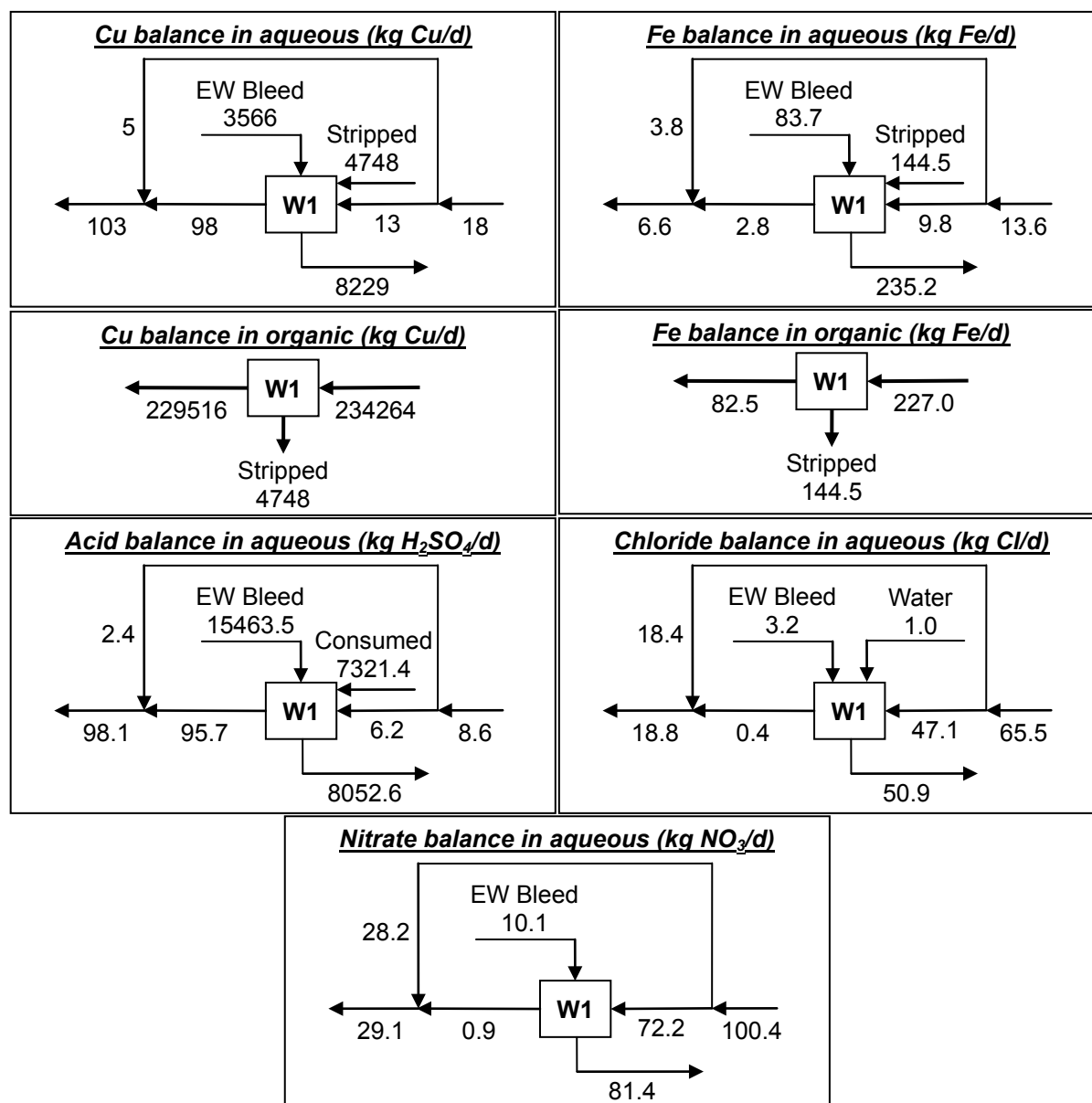


Figure 2: Copper, total iron, acid, chloride, and nitrate material balances in aqueous and organic.

Iron			
Chemical wash efficiency W1:	69.1%	Total iron in PLS:	2.04 g/l FeT
Physical wash efficiency W1:	46.2%	Ferric iron in PLS:	0.46 g/l Fe ³⁺
Global wash efficiency W1:	62.9%	Total iron in electrolyte:	0.99 g/l FeT
Cu/Fe selectivity E1:	940	Ferric iron in electrolyte:	0.83 g/l Fe ³⁺
Cu/Fe selectivity W1:	3030		
Chloride			
Wash efficiency W1:	63.1%	Chloride in electrolyte:	38 ppm Cl
Chloride in PLS:	9.8 g/l Cl		
Nitrate			
Wash efficiency W1:	71.0%	Nitrate in electrolyte:	120 ppm NO ₃
Nitrate in PLS:	15.0 g/l NO ₃		
Copper			
Copper production:	192000 kg Cu/d	Copper recycle in EW bleed:	1.9%
Copper extraction:	195600 kg Cu/d	Copper recycle calculated:	2.9%
Copper in PLS:	2.67 g/l Cu	Copper in stripped electrolyte:	42.2 g/l Cu

Table 2: Results on single wash stage case study.

Wash stage efficiencies are different for iron, chloride and nitrate. In Table 2 these wash efficiencies are indicated, besides of copper/iron selectivities before and after wash stage W1. In this particular plant chloride is the critical element, as a chloride concentration of 30 ppm Cl would be desirable in the electrolyte. The aqueous in organic entrainment shown as a bypass is significantly high and this is a side effect of high nitrate concentrations in PLS. For many years the plant was unable to operate its extraction mixers in organic continuous due to the nitrate effect.

As known, a significant amount of chloride and nitrate being transferred to electrowinning gasifies as chlorine and nitrogen oxides in the electrolytic cells.

Case study on two wash stages

The second case study deals with a PLS of 64 g/l chloride, 216 g/l sulfate and a viscosity of 4.85 cP. As noticed on Table 3, the nitrate and manganese levels are reasonably low at 1.9 and 1.8 g/l respectively, whereas magnesium reaches 32 g/l.

SX configuration Conventional series-parallel 3E-2W-1S		SX reagent <i>Concentration:</i> 14.0 v/v% <i>Reagent blend:</i> 44.7% ketoxime LIX 84-I 55.3% aldoxime LIX 860N-I <i>Organic viscosity:</i> 2.99 cP	
Oxide PLS <i>Copper:</i> 3.35 g/l Cu <i>Acid:</i> 5.92 g/l H ₂ SO ₄ <i>pH:</i> 1.25 <i>Chloride:</i> 64.0 g/l Cl <i>Total iron:</i> 20.0 g/l FeT <i>Ferric:</i> 7.6 g/l Fe ³⁺ <i>Aluminum:</i> 14.6 g/l Al <i>Magnesium:</i> 32.0 g/l Mg <i>Sodium:</i> 34.1 g/l Na <i>Manganese:</i> 1.8 g/l Mn <i>Nitrate:</i> 1.9 g/l NO ₃ <i>Sulfate:</i> 215 g/l SO ₄ <i>Viscosity:</i> 4.85 cP <i>Density:</i> 1.284 g/cm ³		Operational parameters <i>Cu net transfer in organic:</i> 0.320 g/l Cu / %reagent <i>Aq. in LO entrainment:</i> 173 ppm <i>Organic flow:</i> 16800 m ³ /d <i>Loaded organic in E1:</i> 6.72 g/l Cu 29.2 ppm Fe <i>Stripped organic:</i> 2.15 g/l Cu 2.2 ppm Fe	
		Purified water consumption <i>Wash stage W1:</i> 42 m ³ /d <i>Wash stage W2:</i> 23 m ³ /d <i>Total W1+W2:</i> 65 m ³ /d <i>Unit water consumption:</i> 0.89 m ³ /ton Cu	

Table 3: Plant data on two wash stages case study.

Nowadays, a great concern in northern Chile is water availability. The evaluated SX plant uses sea water and additional chloride is generated in leaching, mainly from atacamite. Further chloride level increase in leach solutions is caused by water evaporation. Purified water is generated from sea water being added to wash stages and electrowinning. The second wash stage receives all the electrolyte bleed and purified water is added to both wash stages. One advantage of two wash stages is a diminished consumption of water, besides of cobalt savings at lower EW bleed.

On Figure 3 all flows related to both wash stages are shown, including concentrations for copper, acid, total iron and chloride. On Figure 5 (left) a McCabe-Thiele diagram reflects the fact that W1 is loading, whereas W2 is stripping copper. Figure 4 summarizes material balances related to copper, acid, total iron and chloride in aqueous solutions, and to copper and iron in organic solutions.

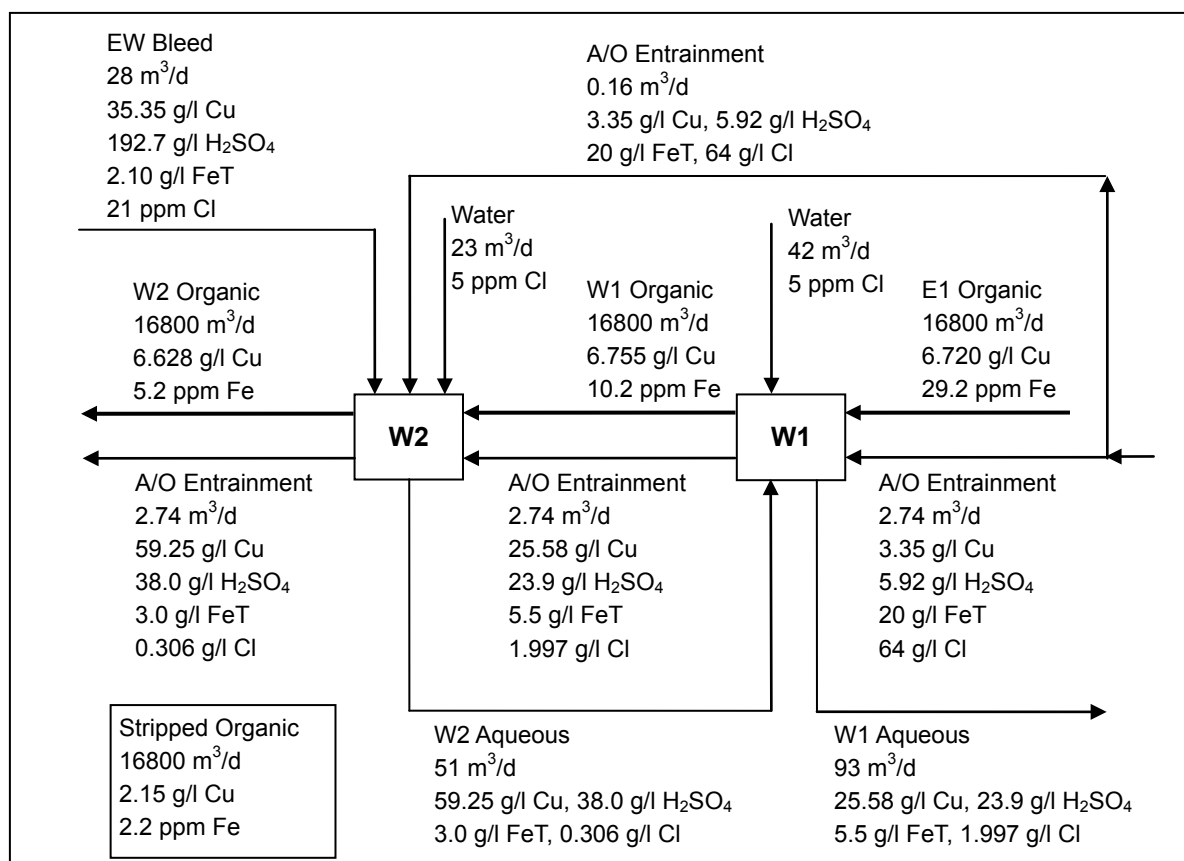


Figure 3: Two wash stages flow diagram.

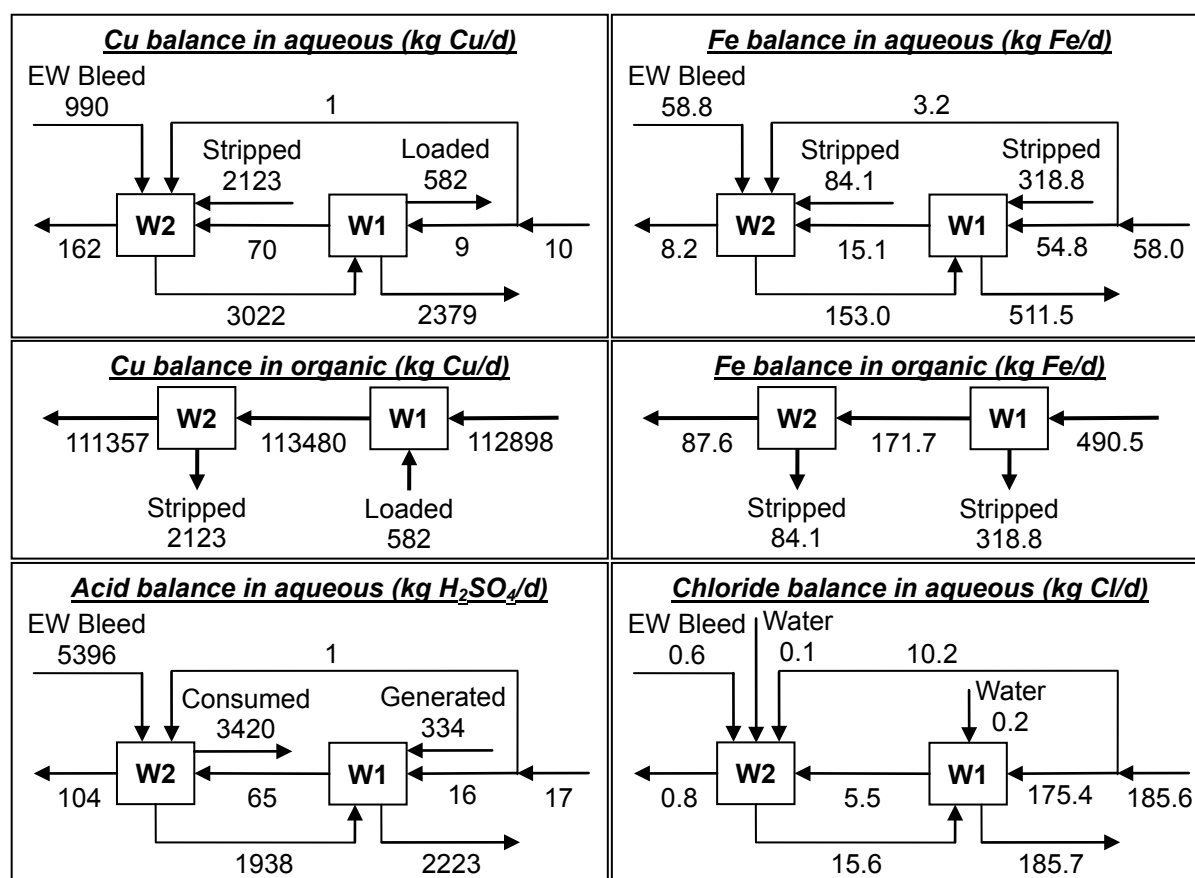


Figure 4: Copper, total iron, acid, and chloride balances in aqueous and organic.

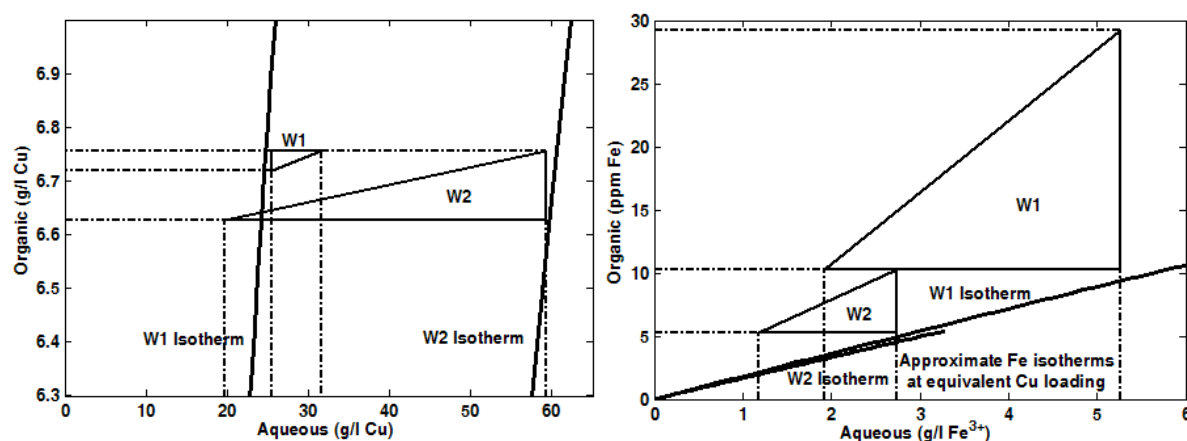


Figure 5: Copper loading and stripping (left) and iron stripping (right) in wash stages.

Iron			
Chemical wash efficiency W1:	70.3%	Chemical wash efficiency W1+W2:	88.8%
Physical wash efficiency W1:	68.4%	Physical wash efficiency W1+W2:	85.9%
Global wash efficiency W1:	70.1%	Global wash efficiency W1+W2:	88.5%
Cu/Fe selectivity E1:	230		
Cu/Fe selectivity W1:	660	Cu/Fe selectivity W1+W2:	1270
Total iron in PLS:	20.0 g/l FeT	Total iron in electrolyte:	2.10 g/l FeT
Ferric iron in PLS:	7.6 g/l Fe ³⁺	Ferric iron in electrolyte:	1.80 g/l Fe ³⁺
Chloride			
Wash efficiency W1:	91.5%	Wash efficiency W1+W2:	99.6%
Chloride in PLS:	64.0 g/l Cl	Chloride in electrolyte:	21 ppm Cl
Copper			
Copper production:	73003 kg Cu/d	Copper extraction:	75382 kg Cu/d
Copper loaded in W1:	582 kg Cu/d	Cu stripped in W2:	2123 kg Cu/d
Cu in electrolyte recycle:	990 kg Cu/d	Copper in EW bleed:	1.36%
Total Cu recycled:	2379 kg Cu/d	Copper recycle incl. W1+W2:	3.16%
Copper in PLS:	3.35 g/l Cu	Copper in stripped electrolyte:	35.35 g/l Cu

Table 4: Results on two wash stages case study.

On Table 4, wash efficiencies on chloride and iron are shown for both wash stages, besides of copper/iron selectivities. Unlike copper, iron is stripped in both wash stages. Figure 5 (right) represents a sort of McCabe-Thiele diagram related to iron, indicating iron isotherms at equivalent copper loading.

The SX plant operated for many years with a single wash stage at increased EW bleed, without achieving chloride concentrations below 30 ppm Cl in the electrolyte. Since a second wash stage was installed, the chloride inconveniences in electrolyte disappeared completely and both purified water and cobalt sulfate consumption rates decreased.

References

1. S. M. Olafson, R. G. Lewis & G. A. Kordosky, US Patent 4957714, "Solvent Extraction Process" (1990).
2. G. Kordosky, S. Olafson & C. Hahn, "Iron control strategies in copper solvent extraction plants, the case for a wash stage", ALTA 2000.
3. M. J. Virnig & S. M. Olafson, "Improved iron scrubbing with a wash stage", ALTA 2002.
4. M. J. Virnig & G. T. Fisher, US Patent 6599414, "Solvent Extraction Processes for Metal Recovery" (2003).
5. H. Hein, "Importance of a wash stage in copper solvent extraction", HydroCopper 2005.

Americium and Curium Separations

Bruce A. Moyer, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

Separation of minor actinides has been an active research area worldwide toward achieving closed nuclear fuel cycles that reduce the heat and radiotoxicity burden on geologic repositories, reduce the consequences of potential disruptive events involving repositories, and increase energy utilization of nuclear fuel. Simple and efficient americium and curium separations, from lanthanides and from each other, are regarded as major technical challenges requiring new technology. The Sigma Team for Minor Actinide Separations (STMAS) in the USDOE Fuel Cycle Research and Development program has been formed to develop new science and technology to achieve these goals. Accordingly, integrated hypothesis-driven research mainly within the paradigm of aqueous reprocessing of used oxide nuclear fuel dissolved in nitric acid is being pursued. Questions being addressed deal with principles of selectivity through various means including aqueous-phase complexation, soft-donor extractants, higher oxidation states of americium, and ion exchange. Explicit attention is also paid to the question of robustness of chemical systems under conditions relevant to future technology implementation. This paper reviews the goals of the STMAS, significance of achieving these goals, STMAS scientific thrusts to address the above aims and questions, recent highlights of achievements, and future direction.

This submission has been authored by a contractor of the U. S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U. S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for the U. S. Government purposes.

This research was sponsored by the Fuel Cycle Research and Development Program, Office of Nuclear Energy, U. S. Department of Energy.

A New Appraisal of Wastes from an Aqueous Solvent Extraction Based Reprocessing Facility

*Chris Phillips^{*1}, William Willis¹, Robert Carter¹, Stephen Baker².*

Summary

As part of its work for the US Government Department of Energy's (DOE) Global Nuclear Energy Partnership project, EnergySolutions designed a solvent extraction based reprocessing facility to recycle the components of the stockpile of used nuclear fuel (UNF) that is currently stored at all nuclear reactor sites in the U.S.A (US). This 'NUEX' facility and its technology was a development of the third generation technology used for the Thermal Oxide Reprocessing Plant (THORP) at the Sellafield site in England, where the pioneering Hanford and Savannah River sites in the US are considered first generation, and plants such as the Magnox, UK and Marcoule, France reprocessing plants are considered second generation. The NUEX facility was based on the well-proven PUREX process of dissolving the UNF in nitric acid and using a solvent of tri-N-butyl phosphate carried in a kerosene diluent to extract uranium and plutonium away from other transuranic species and the fission products. Novel redox/complexing reagents are used to effect uranium - plutonium partial separation.

The NUEX facility was designed to meet expected U.S. environmental and nuclear regulations so it was designed to produce no liquid waste discharges, with all process water recirculated to the maximum extent possible and with capture of the volatile fission products carbon-14, krypton-85, iodine-129 and tritium for encapsulation in solid waste forms. The main vitrified high level waste product, together with the krypton-85 and tritium wasteforms, was designed to capture over 99.9% of the radioactivity present in the original UNF, with the remaining <0.1% distributed principally between grouted wasteforms and compacted UNF zircaloy and stainless steel hardware. With these advances in waste treatment, and ability to keep some uranium, and optionally neptunium, with the plutonium at all points through the process for proliferation resistance, the NUEX facility can be considered fourth generation.

Recently, the DOE has commissioned EnergySolutions and others to carry out a new appraisal of the wastes from such a reprocessing facility, using a set of standard assumptions for design, UNF properties, allowable wasteforms and regulatory climate. This paper describes the results from this appraisal as an up-to-date guide on the wastes that can be expected from a modern fourth generation solvent extraction based reprocessing facility.

Introduction

As part of their past work funded by the US Department of Energy (DOE) for the Global Nuclear Energy Partnership (GNEP), several industry groups, including one led by EnergySolutions, developed conceptual designs and process flowsheets for a US facility to recycle used nuclear fuel (UNF) from the US fleet of Light Water Reactors (LWRs). The aqueous-based facility designed by the EnergySolutions team is based on the well-proven "PUREX" process of dissolving the UNF in nitric acid and using a solvent of tri-N-butyl phosphate carried in a kerosene diluent to extract uranium and plutonium away from other transuranic species and the fission products. Novel redox/complexing reagents are used to effect uranium-plutonium partial separation so that pure plutonium is not produced anywhere in the process, but is instead always mixed with some uranium (and optionally neptunium). The process is capable of processing UNF at a rate of 5 tonnes per day, at burn-ups up to 50 GWD per tonne of UNF and a minimum of 5 years out-of-reactor cooling. The facility was designed to produce (i) a pure uranium stream which was to be re-enriched and re-used in LWRs, or used directly in heavy water moderated reactors, (ii) a mixed uranium-plutonium (and optionally neptunium) stream which was to be converted directly into Mixed Oxide (MOX) fuel and re-used in LWRs, (iii) an optional separated minor actinide (americium and curium) stream that was to be formed into targets and burned in either thermal or fast neutron reactors so as to keep these long lived heat-emitting species out of the waste repository, and (iv) a high level waste stream which would be vitrified ready for

¹ EnergySolutions, 2345 Stevens Drive, Richland, WA, 99354, USA, cjphillips@energysolutions.com

² UK National Nuclear Laboratory, Warrington, Cheshire, England

permanent disposal. The facility was based on third generation European recycling technology (on a scale where the pioneering US Hanford and Savannah River facilities are first generation) and, with further improvements enabled by continually improving technology, would be fourth generation. It was capable of being built and put into use on a short timeframe (<20 years) in the US and was also part of an overall plan that would bring fast neutron reactors into the scheme over a longer 50+ year timeframe.

As part of this design work, the EnergySolutions team estimated all primary and secondary wastes that such a recycling facility would produce. These comprise (i) the vitrified high level waste, plus captured krypton-85 and tritium (containing over 99.9% of all the radioactivity in the UNF), (ii) Class C and Remote Handled Greater Than Class C wastes (containing almost all of the rest of the radioactivity, and formed of the UNF zircaloy cladding plus salt wastes and certain other captured volatile fission products), and (iii) secondary wastes from, for example, facility maintenance and cleanup work.

Differences between these waste estimates, those made by the other industry teams, and ones made by some of the US National Laboratories were recognized and could be traced to a range of differing assumptions made by each team in their bases of design for the recycling facility and in the assumed regulatory climate.

To address and better understand these differences in waste estimate generation when analyzing various potential future fuel cycle options, DOE placed contracts with EnergySolutions and with another industry team to conduct a study to determine more precisely waste arising from a UNF recycle facility using a common set of high-level assumptions, and with review support provided by US National Laboratories. The work that the EnergySolutions team carried out under this task order is described here, and a summary of the waste estimates produced is provided.

Waste Estimating Scenarios

Estimates were made of wastes arising from two UNF reprocessing scenarios:

- (i) Reprocessing of LWR uranium oxide fuel at a burnup of 50 GWD/tonne and an out-of-reactor cooling time of 5 years.
- (ii) Reprocessing of LWR uranium oxide fuel at a burnup of 50 GWD/tonne and an out-of-reactor cooling time of 50 years.

Scenario (ii) recognizes that, given the reality in the US of extended UNF storage times prior to reprocessing, a new reprocessing facility might reprocess existing long-cooled UNF for a substantial period of time, and thus benefit from the decay of several shorter half-life fission products that otherwise complicate waste treatment. However, scenario (i) recognizes that, should a reprocessing facility be constructed, it will likely be desirable for it also to have a capability to process shorter-cooled UNF. This UNF is likely to be stored in water-filled pools, and reprocessing it first leaves in place the longer-cooled UNF that is already safely contained in the dry storage casks that are now in routine use by the US power utilities.

Basis of the Reprocessing Waste Estimate

The basis of the waste estimates produced by this work was EnergySolutions' "NUEX" reprocessing chemical flowsheet (Figure 1). This flowsheet and the process equipment to operate it [1, 2] is a fourth generation development of the "PUREX" solvent extraction reprocessing technology pioneered in the 1940s and 1950s by the Hanford and Savannah River sites in the U.S.A. NUEX is itself built upon the third generation reprocessing technology developed for the Thermal Oxide Reprocessing Plant (THORP) at Sellafield in the United Kingdom [3]. THORP is an industrial scale reprocessing plant capable of processing 5 tonnes of UNF per day and producing three main outputs (uranium trioxide, plutonium dioxide and fission product vitrified waste).

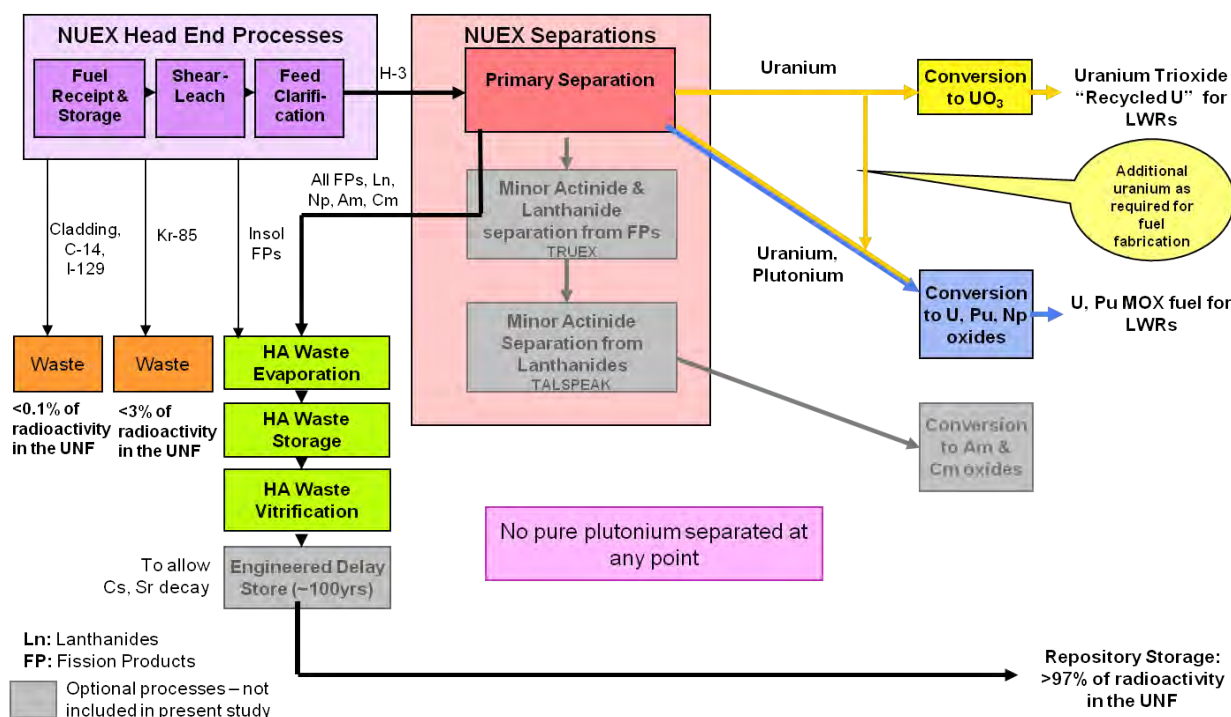


Figure 1: The NUEX Reprocessing Flowsheet

The NUEX flowsheet differs from that of THORP in three main respects:

- Pure plutonium is not separated at any point in the process but instead stays mixed throughout the process with some uranium. This is a fissile material security measure [4, 5], the uranium mixed with the plutonium making it less attractive for potential weapons production.
- The gaseous fission products iodine-129, carbon-14, krypton-85 and hydrogen-3 (tritium) are all captured and consigned as waste. For the GNEP study this was in recognition of the anticipated regulatory environment for any new reprocessing facility in the U.S.A. For the present study it served to allow assessment of the waste impact associated with this capture. In THORP only the I-129 and C-14 are captured, with the Kr-85 allowed to disperse into the atmosphere from a tall stack and the tritium discharged to the ocean, both allowed under UK regulatory limits that were in place when THORP was designed and commissioned.
- Process water is recycled to the maximum extent possible by sending it to reagent make-up instead of using fresh water. A small daily purge discharge is still required to limit the build-up of radioactivity and to manage tritium. This is treated by ion exchange so that the residual radioactivity in the water is low enough for it to be grouted in cement and consigned as low level (Class A in the US) waste.

Wastes from the NUEX Process

A depiction of the wastes from all parts of the NUEX process is shown in Figure 3 and the main wastes are listed below:

- Empty canisters used to contain the UNF assemblies
- UNF storage pool filters and ion exchange materials for water treatment
- Worn-out blades used for shearing the UNF assemblies before dissolution
- UNF cladding 'hulls' left after the oxide fuel has been dissolved in nitric acid
- Undissolved fission products and fuel cladding particles separated from the dissolver product solution – sent to vitrification with the fission product waste
- Dissolver off-gases containing the gaseous fission products. The carbon-14 and iodine-129 are captured on solids, the krypton-85 is compressed and stored until it has

decayed and the tritium is recycled to the dissolver product liquid and recycles with the process water until purged.

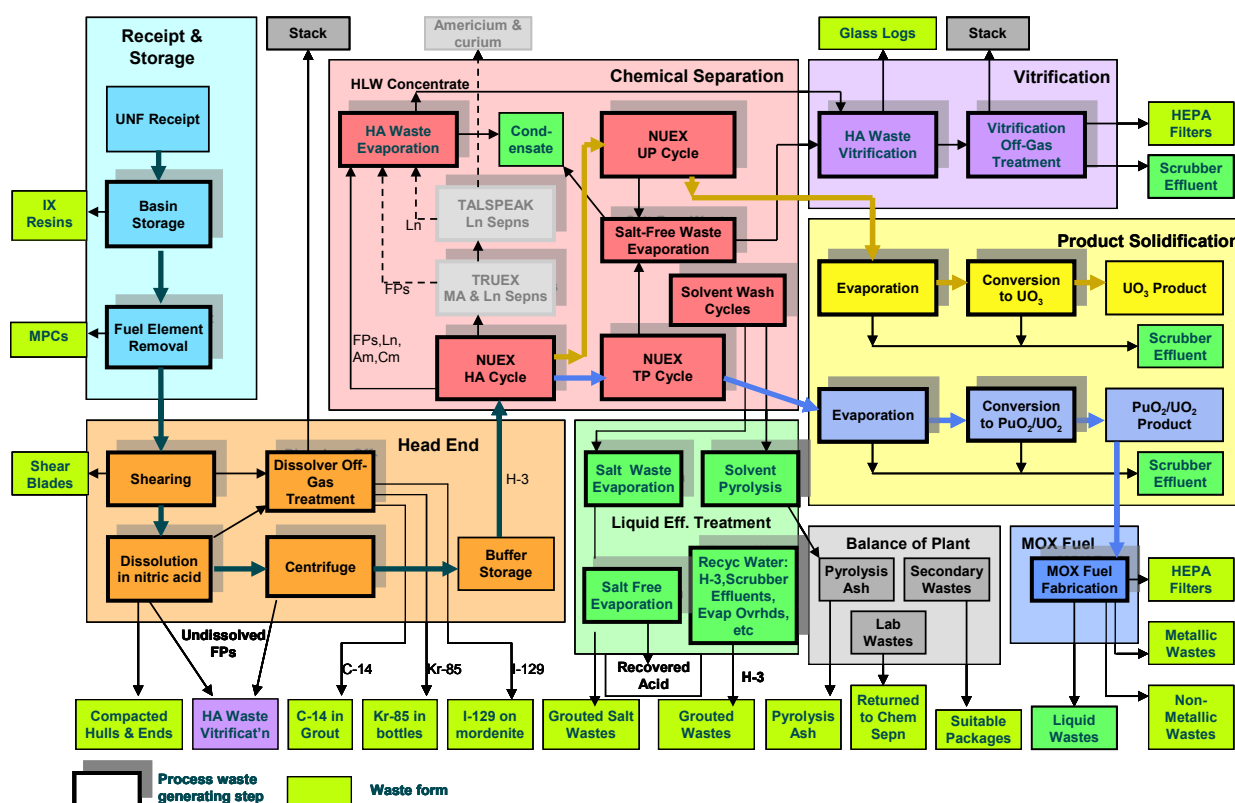


Figure 2: Wastes Generated by the NUEX process

- Highly active waste from the HA cycle of chemical separation by solvent extraction. This contains the fission products, the lanthanides, and the transuranics. This stream is evaporated to small volume and then vitrified to provide a permanent waste form.
- Aqueous wastes from the uranium and uranium/plutonium purification stages of solvent extraction. Because the reagents used in NUEX are 'salt free' these wastes can also be sent to vitrification.
- 'Salt wastes' from solvent washing with sodium carbonate and hydroxide. These low activity (Class A) wastes cannot be vitrified and are instead concentrated and grouted in cement for disposal.
- Ash from the pyrolysis of solvent purged from the process to prevent excess unwashable degradation products building up in the solvent stock.
- Miscellaneous items of mechanical equipment from maintenance operations and filters from off-gas and ventilation air filtration.

Waste Estimating Methodology

The waste estimating process was carried out in two ways, depending on whether waste was *Process Waste* (that is arising directly from the operation of the unit processes, dependant on the number of operating days and the amount of UNF processed per operating day) or *Maintenance and Clean-up Wastes* (that is disposal of failed equipment, materials contaminated during maintenance operations, routine change-out of ventilation filters, general housekeeping wastes that are radioactively contaminated etc).

For process wastes use was made of the dynamic flowsheet model that was developed during the GNEP work. This model was developed using a combination of first principles equilibrium and rate chemistry for the reprocessing processes, and the decontamination factors and reaction extents that have been observed in practice during the operation of

THORP at Sellafield in the UK. Except for the HLW vitrified glass waste form, the U.S. Code of Federal Regulations Chapter 10, Part 61 (10CFR61) was used as the primary basis for determining waste classification from the model results.

For Maintenance and Clean-up Wastes, it was recognized that the arisings of these are not generally dependent on UNF processing rates or even the number of processing days per year. For any large reprocessing facility of 800 to 1000 tonnes per year capacity these wastes are likely to arise at a similar rate, and the best indication of the amounts of such waste will be actual operating experience. Therefore the documented experience from the THORP plant, from the start of its hot operation in 1994 to the present time was drawn upon, with the emphasis on later years during periods of steady operation.

Results of the Waste Estimating Process

The distribution of radioactivity among the classes of waste from a 5 year cooled 50GWD/tonne UNF processing plant are shown in Table 1 by both Group and US Classification. The 10CFR61 code classifies waste into classes of increasing radioactivity from Class A through Greater than Class C (GTCC) and also defines both remote handled and contact handled GTCC wastes. Highly active waste is uniquely classified as that waste arising from the first cycle of PUREX solvent extraction.

Table1: Wastes from a 5 tonne/day Reprocessing Plant for 5 & 50 year cooled, 50GWD/tonne UNF (beginning with a UNF canister of volume 10.9m³ and containing 10 tonnes of UNF)

Waste Form & Classification	Volume Processed/Produced per 2 Days*		Radioactivity as % of that in the UNF	Initial to Final Volume Ratio		Comments
	5 yr Cooled	50 yr cooled		5 yr Cooled	50 yr Cooled	
Group 1 Wastes						
HLW Glass HA	2.3 m ³	1.2 m ³	97.1	4.6	8.5	This group gives a volume decrease. Achievable volume decrease limited for 5yr cooled fuel by 14,000 watt/canister limit for HLW glass
Krypton-85	9.5 L	9.1 L	2.7			
Tritium Class B	49 L	49 L	0.11			
Sub Total	2.35 m ³	1.28 m ³	99.92			
Group 2 Wastes						
Salt Conc. Class C	19.4 m ³	19.4 m ³	0.046	0.51	0.51	This group gives a volume increase – caused by the salt concentrate – but radioactive load is small
Carbon-14 Class C	112 L	112 L	0.018			
Clad Hulls RH-GTCC	1.76 m ³	1.76 m ³	0.009			
Iodine -129 GTCC	49 L	49 L	0.000013			
Sub Total	19.45 m ³	19.45 m ³	0.073			
Group 3 Wastes						
TRU-bearing maintenance wastes GTCC	1.35 m ³	1.35 m ³	0.000987	0.23	0.23	This group gives a volume increase, dominated by the IX media, the canisters and the Class A maintenance wastes. But radioactivity associated with this waste is very low indeed
Maintenance wastes Class C	1.08 m ³	1.08 m ³				
UNF Canisters Class A	10.9 m ³	10.9 m ³				
IX Media Class A	21.3m ³	21.3m ³				
Solvent Pyrolysis Ash Class A	1.07 m ³	1.07 m ³				
Maintenance wastes Class A	11.13 m ³	11.13 m ³				
Sub Total	46.87 m ³	46.87 m ³	0.000987			

*Including canisters

Table 1 also shows, in the “Initial to Final Volume Ratio” column, the change in volume of the waste between the UNF canister containing 10 tonnes of UNF (2 days of processing) and the final waste form resulting from 2 days of reprocessing

Commentary on the Waste Estimates

It can be seen that, for 50 year cooled fuel, 99.92% of the radioactivity in the UNF contained in the 10.9m³ volume canister is transferred to the HLW glass, krypton storage bottles and tritium grout drums (Group 1 Wastes), which have a combined volume of 1.28m³. This is a volume reduction of some 8.5-fold from the original UNF canister, for the waste that must ultimately be stored in a geologic repository. The equivalent volume reduction for 5 year cooled fuel is lower at 4.6-fold, due to an imposed watts/canister heat limit for the vitrified waste. This heat limit arises from the requirement to maintain a maximum center line temperature for the glass in the 600 mm diameter canister when the canister is placed in the geologic repository. This limit could be increased by delay-storing the canisters above ground for ~100 years to let the heat-producing cesium and strontium fission products decay and/or using a smaller diameter canister.

The Group 2 and 3 wastes show a volume increase, rather than decrease from the volume of the original UNF canister, but the amounts of radioactivity they contain (respectively 0.073% and 0.001%) are very small indeed. These waste volumes and radioactivity amounts from a modern fourth generation reprocessing plant effectively defeat the sometimes heard criticism that reprocessing spreads radioactivity into a large number of difficult-to-deal-with wastes.

Conclusions

This work has provided waste estimates from reprocessing of 50 GWD/tonne, 5 year and 50 year cooled UNF based on an initially defined set of assumptions, established to aid in understanding the differences in waste estimates that have hitherto been apparent. The work has shown that, with a modern fourth generation reprocessing plant such as NUEX, which has been designed to limit the production and volume of wastes, it is possible to get the vast majority (>99.9%) of the radioactivity in the UNF into waste forms that occupy only about one eighth of the volume of the original UNF assemblies. Over 97% of the radioactivity is encapsulated in the HA waste vitrified product, a robust waste form arguably much more suitable for consignment to a geologic repository than UNF assemblies that were not designed for this purpose.

References

1. C. Phillips and S.T.Arm, “Recycling of Used Nuclear Fuel: Bringing Well-Established Solvent Extraction Processes into the 21st Century”, International Solvent Extraction Conference, ISEC 2011, Santiago, Chile, October 3-7 2011.
2. S.T.Arm, C.Phillips and A.Dobson, “Industrial Application of GNEP Solvent Extraction Processes”, International Solvent Extraction Conference, ISEC 08, Tucson, Arizona, U.S.A., September 15-19 2008.
3. C.Burrows, C.Phillips and A.Milliken, “The Thermal Oxide Reprocessing Plant at Sellafield – Lessons learned from 10 years of Hot Operations”, Waste Management 06 Conference, Tucson, Arizona, U.S.A, February 26 – March 2, 2006.
4. C.Phillips and S.T.Arm, “The Use of Innovative Designs to Provide Enhanced Proliferation Security in a Modern Used Nuclear Fuel Recycling Facility”, Pacific Northwest International Conference on Global Nuclear Security – the Decade Ahead, Portland, OR, USA, April 11-16, 2010.
5. C.Phillips and S.T.Arm, “Closing the Nuclear Fuel Cycle in the 21st Century While Minimizing Proliferation Risk”, University of Utah 2nd National Conference on Nuclear Materials Detection, Salt Lake City, May 2-4 2011.

On-Line Monitoring Of Used Nuclear Fuel Separation Processes Using Near Infrared Spectroscopy

*Ko Nee^{*1}, Sam Bryan², Tatiana Levitskaia², Mikael Nilsson¹*

Applying spectroscopic tools to a process stream have been intensively investigated in various industries due to the capability for detecting certain chemical components and physical characteristic of a system rapidly and noninvasively. Moreover, using spectroscopy can provide a response in near real time. The complicated behavior of used nuclear fuel separation processes, e.g., chemical speciation, temperature variation, and proliferation concerns, requires a well-secured monitoring system to provide precise information of the process streams. In our study, chemometric models that respond to the components in our samples were trained and validated to establish a model with good prediction accuracy. In our system, 95 aqueous phase samples that are composed of varied sodium nitrate, nitric acid, and neodymium nitrate concentrations were prepared for chemometric model calibration. Near infrared spectral data of the samples were collected at room temperature. The data was analyzed and chemometric models were developed and validated using partial least square on PLS-Toolbox. Finally, an extraction process using a single stage contactor at our laboratory was tested to observe how our chemometric models would predict the metal ion extraction in a process.

1. Introduction

When used nuclear fuels are discharged from a power plant, they still contain many useful elements, such as uranium, plutonium, and minor actinides, which can be recycled for extended energy production and other industrial applications. Separation and reuse of nuclear fuel has both ecological and economical advantages through partition and transmutation of radioactive isotopes that otherwise would require long storage time [1]. Due to the sensitive nature of the nuclear material involved in used nuclear fuel reprocessing, the security of these separation processes is extremely important. The International Atom Energy Agency (IAEA) has declared in their objective of safeguards that early detection of diversion of significant quantities of nuclear material is extremely important [2]. In order to achieve a secure process for used nuclear fuel separation accountability of the material in the process is critical. Traditional grab sampling techniques and laboratory analysis are time consuming and can cause delayed feedback to the operators and possible interruptions in the continuous operation. Therefore, in our study, we investigated the possibility of applying near infrared spectroscopy in combination with chemometric techniques for monitoring separation processes in a rapid, non-destructive way. Spectroscopy has been widely utilized in many monitoring applications due to the advantage of the fast and non-destructive way of analysis. Spectral analysis on metal ions has been studied for the past decades and has been used for chemical process monitoring [3]–[7]. Moreover, in work from Bryan et al. the use of spectroscopic tools for chemical streams have been demonstrated for nuclear fuel separation systems [3]–[6]. The solvent extraction process involves complex chemistry and possible added challenges such as inconsistent flow rates, changes in speciation and chemical conditions etc. In order to accomplish a real time on-line monitoring system, large amount of well-analyzed data are required for training the models. This study involved

training chemometric models using partial least square (PLS) analysis. The PLS models were then validated by the extraction of trivalent neodymium (Nd(III)) with di-(2-ethylhexyl) phosphoric acid (HDEHP) by a single stage centrifugal contactor. The results of applying chemometric models for our simulated used nuclear fuel separation process and the HDEHP extraction efficiency of the single stage centrifugal contactor are discussed.

2. Experimental

2.1 Sample preparation for chemometric model calibration

95 samples composed of different combinations of concentrations of nitric acid (HNO_3 , 0 M to 6 M), sodium nitrate (NaNO_3 , 0 M to 3 M), and neodymium nitrate ($\text{Nd}(\text{NO}_3)_3$, 0 M to 0.038 M) were prepared. Ultrapure water ($>18\text{M}\Omega$) was used to dilute all aqueous solutions to the desired concentrations. Samples containing HNO_3 were prepared from diluting 70% concentrated stock supplied by MacronTM Chemical. Samples containing NaNO_3 were prepared from a standardized stock solution of filtered and recrystallized NaNO_3 (Fisher Scientific). Samples containing Nd(III) were prepared from 99.9% neodymium (III) nitrate hexahydrate, supplied from Alfa Aesar. All solutions were analysed for H^+ , Na^+ , NO_3^- and Nd^{3+} concentration. The final Nd(III) concentration was standardized using an Olis upgraded Cary 14 UV/VIS/NIR Spectrophotometer at 794.5nm at room temperature. Acid concentrations were determined by acid-base titration by a Metrohm 836 Titrando auto-titrator. The concentrations of Na^+ and NO_3^- were determined by a Metrohm 850 ion chromatography, supplied by Metrohm USA Inc.

2.2 Sample preparation for chemometric model validation

An aqueous phase was prepared by dissolving neodymium nitrate hexahydrate to a final Nd(III) concentration of 0.0376 M in 0.1 M HNO_3 with 0.9 M NaNO_3 . Organic phase was prepared by diluting 0.2M HDEHP₂ in n-dodecane. Organic phase was contacted with 0.1M HNO_3 and 0.9 M NaNO_3 during the pre-equilibration step to avoid volume change during the extraction. During the extraction process aqueous and organic solutions were fed simultaneously to the respective inlets of a BXP-012 annular centrifugal contactor, supplied by Rousselet Robatel. The rotor speed was initially set to 4500 revolutions per minute (rpm) then changed to 3500 rpm. The syringe's injection flow rate was changed from 2ml/min to 1ml/min. Changes were made to flow rates and pump speed in an attempt to optimize the performance and obtain clean phases, i.e. free of entrainment. Aqueous and organic products were collected from the heavy phase and light phase outlets of the contactor separately. The aqueous phase concentrations of acid, Nd(III), Na^+ , and NO_3^- were determined as detailed above.

2.3 Near Infrared spectroscopy

The NIR spectra of all samples were collected using an Olis upgraded Cary 14 UV/VIS/NIR spectrophotometer scanning from 850 nm to 1350 nm with a resolution of 0.5 nm. Air was used as reference for all the samples.

2.3 Chemometric model calibration and validation

Partial least square (PLS) analysis was applied in our chemometric modeling. All the data were compiled using MatLAB from Mathworks, Inc. PLS Toolbox, supplied by Eigenvector Research, was applied for building PLS models for each chemical component, i.e. HNO_3 , NaNO_3 , $\text{Nd}(\text{NO}_3)_3$ and total ionic strength. The spectral data preprocessing method used 1st derivative and 2nd polynomial Savitsky-Golay, followed with mean centering and variance scaling for removing any bias among the variable and ensuring equal weight were contributed from each variable [5]. The pretreated spectral data was then loaded to the X block of PLS Toolbox. The Y block of PLS Toolbox contained a matrix of composition information of 95 samples. The Venetian Blind method was used for cross validation. After model calibration was finished, aqueous phase NIR spectra from the centrifugal contactor extraction and the aqueous component information were used for model validation. The accuracy of the model prediction for each component was determined by R-square (R^2), Root Mean Square Errors Cross Validation (RMSECV) and Root Mean Square Errors Prediction (RMSEP). R^2 represent ratio of predicted values versus measured values. RMSCV and RMSEP were calculated for the prediction power of model. RMSECV is the errors calculated from fitting PLS model from Venetian blind cross validation and RMSEP is the errors calculated by the validating data set.

3. Results and discussion

Selected NIR spectra from the calibration data set are shown in Fig.1.

3.1 Near infrared spectroscopy

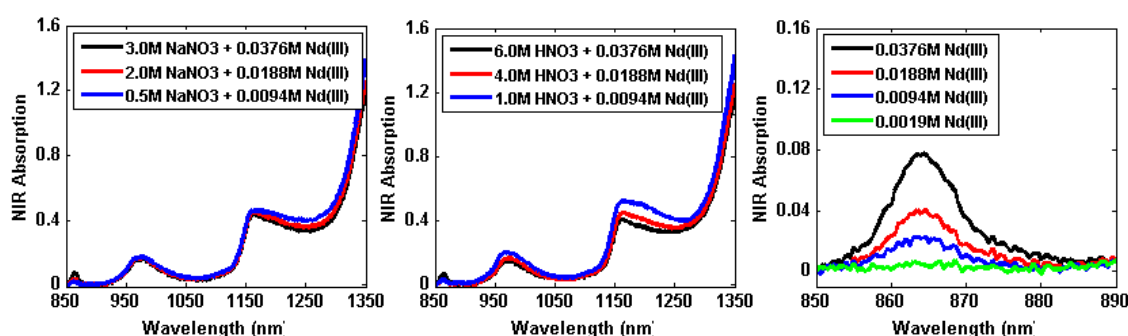


Figure 1: (Left) 4 M HNO_3 with varied NaNO_3 and Nd(III) concentrations. (Center) 3 M NaNO_3 with varied HNO_3 and Nd(III) concentrations. (Right) Varied Nd(III) concentration.

Previous studies have demonstrated that the OH bonding of surrounding water molecules can be disrupted or enhanced when changing temperatures

and adding certain ions to the solution [8]–[12]. Therefore, as indicated in Fig.1, when increasing both NaNO_3 and HNO_3 , NIR absorbance at 1250 nm and 1150 nm was weakened due to the disruption of OH bonding in water. Due to the weak absorbance at 975 nm, the absorbance change at this region is more difficult to be observed. As shown in Fig1, Nd(III) absorption at 865 nm increases with Nd concentration which was expected according to Beer-Lambert's Law.

The results show that changes in chemical composition of the aqueous phase can be observed in the NIR spectra. Consequently, NIR can be a useful tool used for monitoring aqueous system that involves changes in the chemical composition. The result also suggests that NIR spectroscopy can be advantageous for providing information for building chemometric models for on-line monitoring of aqueous systems.

3.2 Solvent extraction by a single centrifugal contactor

Fig. 2 and Table 1 below show the results of the PLS model of each component in the aqueous solution.

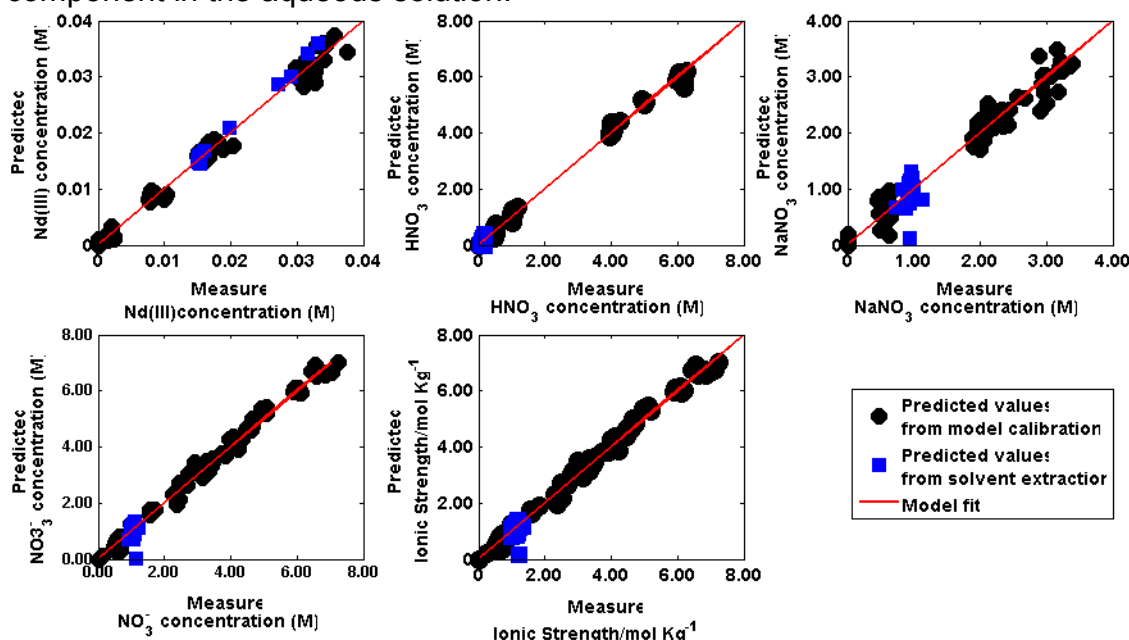


Figure 2. Results of the PLS models. (Top Left) Nd(III). (Top Center). HNO_3 . (Top Right) NaNO_3 . (Bottom Left) NO_3^- . (Bottom Right) Ionic strength.

Table 1: Results of the PLS models

	Nd(III)	HNO_3	NaNO_3	NO_3^-	Ionic Strength
Latent Variables	3	5	5	5	5
RMSCV (M)	0.00126	0.172	0.256	0.256	0.256
RMSP (M)	0.00197	0.106	0.263	0.309	0.294
R^2	0.989	0.994	0.953	0.988	0.988

Black closed circles in Fig. 2 represent the predicted values from the model from the calibration set. The blue closed circles represent the predicted values from the validation set. Table 1 indicates the model's result and shows that both Nd(III) and HNO_3 have lower errors compared to NaNO_3 , NO_3^- and ionic

strength. Moreover, the validation errors (RMSP) are lower than the RMSCV for both Nd(III) and HNO_3 . The objective of this study was to investigate the possibility of monitoring the aqueous phase in a solvent extraction process using the combination of NIR and PLS models. The data below in Fig. 3 shows the results from the predicted and measured concentration of HNO_3 and Nd(III) in the aqueous phase from the centrifugal contactor run. The measured values versus predicted results by the PLS models from the centrifugal contactor are shown below.

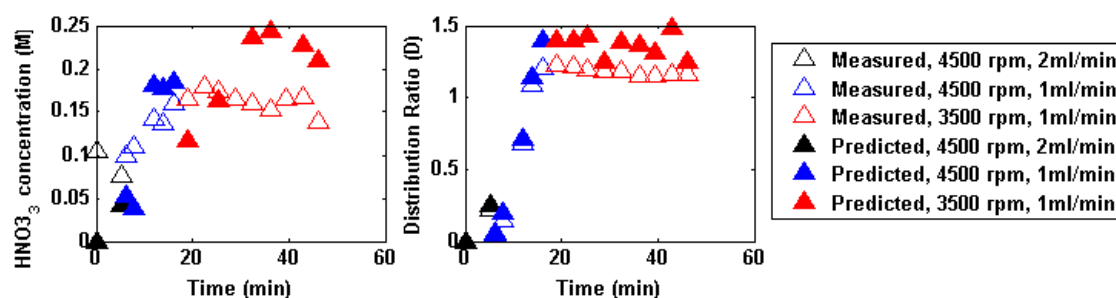


Figure 3: Aqueous phase results from the contactor. (Left) HNO_3 . (Right) Nd(III) distribution ratio (D)

Fig. 3 is the result of the aqueous outlet of the contactor at an assigned rpm and inlet flow rate (ml/min). The deviation between actual measured concentration and the predicted concentrations of HNO_3 is observed in Fig. 3. Distribution ratios (D) indicate the extraction efficiency for a solvent extraction process. Results of D from the actual measurement and from the prediction are shown in Fig. 3. D values were calculated from the ratio between the concentrations of Nd(III) in organic phase and aqueous phase. Organic phase Nd(III) concentrations were calculated by taking the difference in the initial Nd(III) concentration in the aqueous phase to the aqueous Nd(III) concentration at the corresponding time. Fig. 3 shows that equilibrium of Nd(III) extraction with HDEHP was achieved after 20 min. Moreover, due to RMSEP of Nd(III) being fairly small, the discrepancy in D values between measured and predicted is smaller compared to the difference observed for HNO_3 .

3. Conclusion

From our results NIR spectra demonstrated strong correspondence toward Nd(III), HNO_3 and NaNO_3 . Therefore, NIR can be suitable for monitoring those chemical species in aqueous solutions. However, prior to implementing an online monitoring system, a large amount of well-analyzed data that respond to the physical and chemical conditions of the process should be collected. Our calibrated PLS models were validated using the aqueous outlet from Nd(III) extraction with HDEHP from a single stage centrifugal contactor. The results from the solvent extraction show a discrepancy between actual measured concentration and model predicted concentration due to the errors from the models. Although deviations between measurement and prediction were noticed the overall trends in HNO_3 , Nd(III) concentration was accurately modeled. Thus NIR spectroscopy coupled with PLS models may be useful in

online monitoring of solvent extraction processes due to the rapid and noninvasive analysis method.

4. Acknowledgement

This project was funded by the National Nuclear Security Administration (NNSA) through the Department of Energy (DOE). The work is carried out under the SUCCESS PIPELINE consortium.

5. References

- [1] F. Baumgartner and L. Finsterwalder, "On the transfer mechanism of Uranium (VI) and plutonium (IV) nitrate," vol. 503, no. 11, pp. 108–112, 1969.
- [2] IAEA, "THE STRUCTURE AND CONTENT OF AGREEMENTS BETWEEN THE AGENCY AND STATES REQUIRED IN CONNECTION WITH THE TREATY NON-PROLIFERATION OF NUCLEAR WEAPONS," vol. 153.
- [3] S. a. Bryan, T. G. Levitskaia, a. M. Johnsen, C. R. Orton, and J. M. Peterson, "Spectroscopic monitoring of spent nuclear fuel reprocessing streams: an evaluation of spent fuel solutions via Raman, visible, and near-infrared spectroscopy," *Radiochim. Acta*, vol. 99, no. 9, pp. 563–572, Sep. 2011.
- [4] S. Bryan, T. Levitskaia, and A. Casella, "Spectroscopic On-Line Monitoring for Process Control and Safeguarding of Radiochemical Streams in Nuclear Fuel Reprocessing Facilities," *Adv. Sep. Tech. Nucl. Fuel Reprocess. Radioact. Waste Treat.*, 2011.
- [5] A. J. Casella, T. G. Levitskaia, J. M. Peterson, and S. a Bryan, "Water O-H stretching Raman signature for strong acid monitoring via multivariate analysis," *Anal. Chem.*, vol. 85, no. 8, pp. 4120–8, Apr. 2013.
- [6] C. a Schroll, S. Chatterjee, W. R. Heineman, and S. a Bryan, "Semi-infinite linear diffusion spectroelectrochemistry on an aqueous micro-drop," *Anal. Chem.*, vol. 83, no. 11, pp. 4214–9, Jun. 2011.
- [7] K. Binnemans and C. Görrler-Walrand, "On the color of the trivalent lanthanide ions," *Chem. Phys. Lett.*, vol. 235, no. 3–4, pp. 163–174, Mar. 1995.
- [8] J. Collins, "Change in the Infra-Red Absorption Spectrum of Water with Temperature," *Phys. Rev.*, vol. 26, no. 6, pp. 771–779, Dec. 1925.
- [9] G. Choppin and K. Buijs, "Near- Infrared Studies of the Structure of Water. II. Ionic Solutions," *J. Chem. Phys.*, vol. 39, no. 8, pp. 2042–2050, 1963.
- [10] K. Buijs and G. R. Choppin, "Near-Infrared Studies of the Structure of Water. I. Pure Water," *J. Chem. Phys.*, vol. 39, no. 8, p. 2035, 1963.
- [11] H. Yamatera, B. Fitzpatrick, and G. Gordon, "Near infrared spectra of water and aqueous solutions," *J. Mol. Spectrosc.*, vol. 14, no. 1–4, pp. 268–278, Jan. 1964.
- [12] V. S. Langford, A. J. McKinley, and T. I. Quickenden, "Temperature Dependence of the Visible-Near-Infrared Absorption Spectrum of Liquid Water," *J. Phys. Chem. A*, vol. 105, no. 39, pp. 8916–8921, Oct. 2001.

The radiation chemistry of CMPO

Stephen P. Mezyk,^{1*} Bruce J. Mincher,² M. Nilsson,³ J. Pearson,³ J.A. LaVerne⁴

¹Department of Chemistry and Biochemistry, California State University at Long Beach, 1250 Bellflower Blvd, Long Beach, CA 90840, USA

²Aqueous Separations and Radiochemistry Department, Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415-4107, USA

³Department of Chemical Engineering and Materials Science, University of California Irvine, Irvine, CA 92697-2575, USA

⁴Department of Physics and Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

Summary:

The actinide/lanthanide ligand CMPO (octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide) was subject to gamma irradiation using ^{60}Co γ -rays, and alpha-irradiation using a He-ion beam, ^{244}Cm isotopic α -rays, and by He and Li ions created by the n,α reaction of ^{10}B in a nuclear reactor. Post-irradiation samples were analyzed for the decrease in CMPO concentration, the appearance of degradation products, and the effects on americium solvent extraction. The -G-value for the radiolytic degradation of CMPO was much lower for alpha irradiation as compared to gamma, and was dependent upon the presence of nitric acid and oxygen during irradiation, with both providing protection from radiolytic degradation. The -G-value does not depend on the γ -ray dose rate, or the CMPO concentration. Effects on solvent extraction performance were independent of the change in CMPO concentration, but rather related to the nature of the degradation products. The main CMPO products were identified by ESI-MS, and were different for CMPO irradiation performed in the presence of nitric acid.

Introduction

The compound octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) (Fig. 1) is a strong Lewis base that was designed to partition the trivalent actinides and lanthanides from acidic solutions of high-level nuclear waste. It has also been proposed as a solvent extraction ligand in the treatment and recycling of used nuclear fuel. The irradiation of any solvent extraction ligand

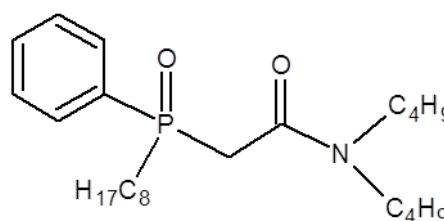
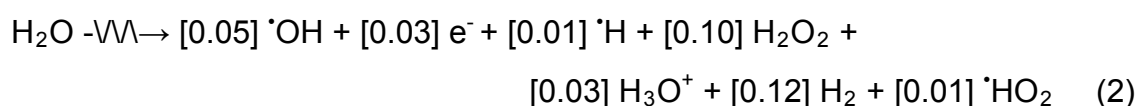
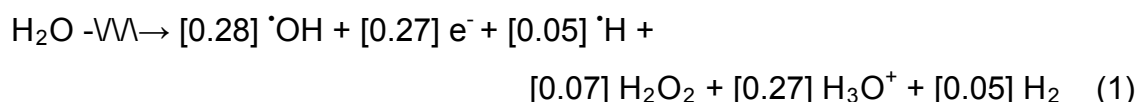


Figure 1. The structure of octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).

in an organic diluent in contact with a radioactive aqueous phase exposes that ligand to numerous radiolytically-produced reactive species. These reactive species are created by the decomposition of water, nitric acid and the organic diluent. Thus, successful deployment of CMPO for fuel cycle applications will depend on its radiolytic stability under these conditions.

Among the major reactive species produced by radiation are the oxidizing $\cdot\text{OH}$, $\cdot\text{NO}_2$, and $\cdot\text{NO}_3$ radicals from water and nitric acid radiolysis, the reducing solvated electron e^-_{sol} and $\cdot\text{H}$ atom, produced by water and organic diluent radiolysis, and various carbon centered radicals produced from the organic diluent.^[1] In contact with dissolved nuclear fuel, CMPO is exposed to both low linear energy transfer (LET) β/γ radiation from fission product decay and high-LET α radiation from actinide decay. The LET of the incident radiation influences the amounts of the reactive species produced during diluent radiolysis.^[2] For example, the yields of the primary reactive species in the radiolysis of water for low-LET electron beam irradiation are shown in Eq. 1,^[3] in comparison to the yields for high-LET radiation shown in Eq. 2:^[4]



These equations present a list of radiolytic products and are not intended to be stoichiometric. The numbers shown in brackets are absolute yields (G-values) given in $\mu\text{mol J}^{-1}$. From these two equations it can be seen that the yields of the products favor increased production of the molecular species such as H_2O_2 and decreased production of the radical species such as $\cdot\text{OH}$ radical as the LET increases. This change is due to the deposition of larger amounts of energy in a small volume along the path of the higher LET radiation, which results in high localized concentrations of radicals, allowing for their recombination into molecular species prior to reaction with the ligands.^[5] Therefore, it might be expected that the $-G_{\text{CMPO}}$ -value and products of CMPO degradation would be different for the two radiation types.

The adverse effects of γ -irradiation on the solvent extraction properties of CMPO-containing solutions have previously been investigated by Simonzadeh et al.,^[6] Logunov et al.,^[7] and Chiarizia and Horwitz.^[8] In contrast, almost no work has been done on the α -radiolysis of CMPO, mainly due to the radiological control difficulties associated with the handling of α -emitters and of analyzing post-irradiation, α -emitter contaminated samples. Only Buchholz et al.^[9] performed α -irradiation of a CMPO-containing solution; however, neither degradation yields nor products analyses were obtained.

Therefore, we have investigated both the γ and α -radiolysis of this compound in dodecane under a variety of conditions, using various steady-state sources. The γ irradiations were performed using a ^{60}Co irradiator, the α irradiations were done by the isotopic α -source ^{244}Cm as well as with a He-ion beam and with He/Li ions generated by the reaction of neutrons with ^{10}B . The effects on $-G_{\text{CMPO}}$ and the solvent extraction performance of these irradiated solutions were compared to degradation products analyses.

Experimental Methods:

Gamma-ray irradiations:

These irradiations were conducted at the Idaho National Laboratory (INL) by ^{60}Co irradiation of 0.1 M CMPO/dodecane solutions, either as neat organic solutions, or as organic solutions in contact with an equal volume of an aqueous phase of varying nitric acid concentration. Samples were irradiated in sealed glass scintillation vials to a series of absorbed doses determined by their duration in the irradiator. An additional series of samples was irradiated with continuous air sparging, using room air delivered by a diaphragm pump through a syringe needle inserted into septum-capped scintillation vials. The INL irradiator was a Nordion GammaCell 220E (Ottawa, Canada) with a center-line sample chamber dose rate of 6.2 kGy h^{-1} at the time of these experiments, as determined by standard decay-corrected Fricke dosimetry.

Isotope α -irradiations: ^{244}Cm

Samples of 0.1 M CMPO/dodecane were α -irradiated in a glovebox using ^{244}Cm at the Idaho National Laboratory, Idaho Falls, ID, USA. Curium-244 decays by emission of a 5.8 MeV α -particle with an 18.1-y half-life. These irradiations were performed by dissolving 0.6 mg of ^{244}Cm in 0.1 M HNO_3 and then contacted with the CMPO/dodecane solution with constant stirring for amounts of time appropriate to deliver the desired absorbed dose. Absorbed doses in J kg^{-1} (Gy) were calculated based on the α -particle energy, the calculated number of decays occurring for the duration of the irradiation, and the solution mass. The dose rate varied from $1.1\text{--}1.4 \text{ kGy h}^{-1}$, depending on the volume irradiated. The irradiations were performed at room temperature in sealed 20 mL scintillation vials with about 10 mL of headspace. The vials were opened intermittently for sampling purposes and thus these samples are considered to have been aerated during the irradiation.

α -irradiations: He-ion beam

He-ion beam irradiations were performed at the University of Notre Dame, IN, USA. Helium ions were produced using a 9 MV FN-Tandem Van de Graaff generator with a 20 keV duoplasmatron source.^[10] The α -particle energy was selected by varying the accelerator terminal voltage to provide sufficient initial particle energy such that after passing through the cell window the energy incident to the sample was 5.0 MeV to simulate the α -particle energies produced by actinide decay. Since penetration of the ions in the solution is low, samples were continuously and vigorously stirred at room temperature to ensure uniform dose deposition to the entire sample and bubbled throughout the irradiation with air or argon to achieve aerated or deaerated conditions, respectively.

α -irradiations: ^{10}B (n, α) ^7Li

In a novel high-LET radiolysis technique reported by Pearson et al.,^[11] He ions were generated by neutron-induced fission of ^{10}B nuclei. The reaction, shown in Eq. 3,

produces He ions with an energy of about 1.4 MeV and Li ions with an energy of about 0.85 MeV. Neutrons were generated using the University of California, Irvine TRIGA® Mark I reactor with the samples irradiated in a sample carousel at a flux of $8.0 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ at 250 kW power for 2 h. Different absorbed doses to these 0.1 M CMPO/dodecane samples were achieved by varying the total boron concentrations to values of 0, 0.03, 0.06, 0.09, 0.12, or 0.15 M using bis(pinacolato)diboron, to generate high-LET dose rates of 0, 43, 86, 129, 171, or 213 kGy hr^{-1} , respectively. Background corrections for gamma (estimated at 40 kGy h^{-1}) and neutron absorbed doses were performed by irradiating CMPO samples that contained no added boron. Alpha dosimetry was performed using the standard Fricke dosimeter, modified by the addition of boric acid.^[12, 13] The temperature of the reactor-irradiated samples did not exceed 31°C.

CMPO analysis by HPLC

The concentration of CMPO in dodecane was determined by high performance liquid chromatography (HPLC) with UV detection at 220 nm, after the method of Elias et al.^[11] Briefly, samples in dodecane were diluted 1:100 with 2-propanol to ~1 mM, then analyzed using a Supelcosil C-18, RP, 25 cm, 4.6 mm x 5 μm column and guard column. The eluent solutions used were either 30 mM 60:40, pH 2.7 phosphate buffer/alcohol mix or 60:40 0.1% formic acid at pH 2.7/alcohol mix, where the alcohol mix was 3.6% 1-octanol in 2-propanol. The flow rate was 1 mL min^{-1} . The column temperature was 50°C, and the run time was 35 min. Acid-contacted samples required separate calibration due to the formation of an equilibrium $\text{CMPO} \cdot \text{HNO}_3$ complex^[13,14] in dodecane that decreased the apparent concentration of CMPO by UV detection. Reported concentrations were the means of triplicate determinations. The relative standard deviation for the method was reported to be < 1%.

Solvent extraction experiments

Irradiated CMPO/dodecane solutions were used in Am solvent extraction experiments. Equal volume, pre-equilibrated, room temperature ($21 \pm 2^\circ\text{C}$) extraction contacts of 1 min duration were performed from ^{243}Am traced 2 M HNO_3 . The irradiated solutions were diluted to nominal 0.016 M CMPO (based on the pre-irradiation concentration of 0.1 M) with fresh dodecane prior to use. Following contact, 1 mL aliquots of each phase were removed for γ -ray counting, with the Am activity determined at 74.7 keV. The loaded organic phase was next stripped with an equal volume of 0.1 M HNO_3 and aliquots of these phases were also removed for γ -counting.

For α -irradiated samples only, a single determination was performed at each absorbed dose due to the small amounts of material available, and the organic phases were not pre-equilibrated prior to extraction to minimize loss of any water-soluble radiolysis products. For radiolysis product-amended samples, the extractions were performed in triplicate with the mean values reported, and triple 1-min pre-equilibration contacts were performed.

Results and Discussion:

Typical data for CMPO loss induced by γ irradiation as measured by HPLC are shown in Figure 2, for α irradiation are shown in Figure 3. These data demonstrate that the loss is condition-dependent, but under both conditions minimal loss is observed for aerated, acidic-contacted solutions. Some minor loss from the reactor data are seen in Figure 3.

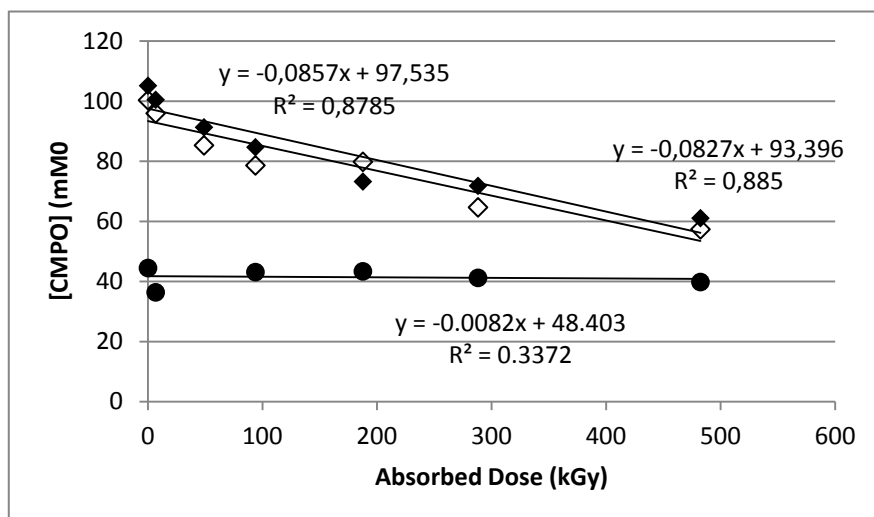


Figure 2. The γ -radiolytic decrease in CMPO concentration for aerated samples in the absence of the aqueous phase (closed diamonds); in contact with an equal volume of 0.1 M HNO₃ (open diamonds); in contact with an equal volume of 2 M HNO₃ (closed circles). Duplicate irradiations for the 2 M acid contacted samples provided an RSD of $\pm 15\%$.

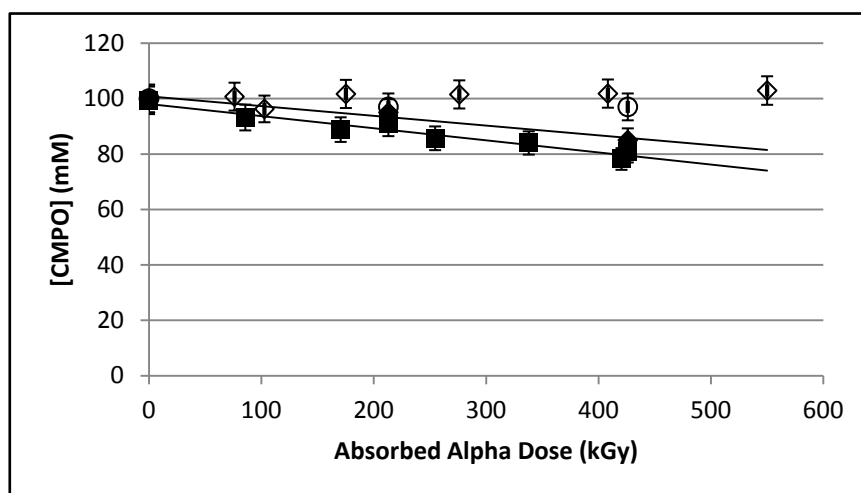


Figure 3. The change in CMPO concentration under various conditions of alpha (high LET) irradiation. Cm irradiation in the presence of 0.1 M HNO₃ (open diamonds); Reactor He/Li irradiation in the presence of 0.1 M HNO₃ (closed diamonds); Normalized reactor He/Li irradiation in the presence of 3 M HNO₃ (open circles); and reactor He/Li irradiation with no aqueous phase (closed boxes). Error bars shown are $\pm 5\%$ in CMPO concentration.

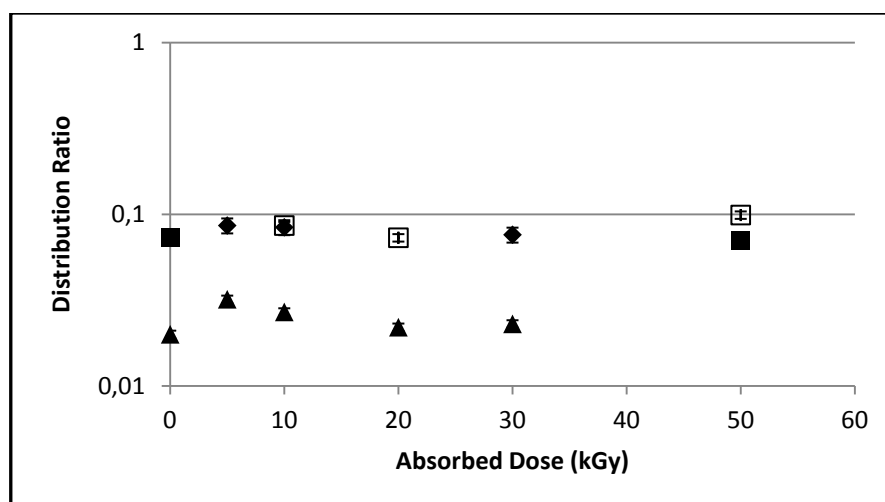


Figure 4. The solvent extraction distribution ratios of Am from 2 M HNO₃, for initially 0.1 M CMPO/dodecane irradiated using the He-ion beam: aerated (closed diamonds); deaerated trial 1 (open boxes); deaerated trial 2 (closed boxes); pre-equilibrated with 3 M HNO₃ (closed triangles). The CMPO concentration was diluted to 0.016 M with fresh dodecane prior to extractions.

In addition, information on solvent extraction and CMPO degradation mechanisms were also measured in this study. Typical solvent extraction data for He ion beam irradiation are shown in Figure 4, demonstrating that minimal dose effects occurred under these conditions, consistent with the loss measurements shown previously. These data, along with other mass spectrometric product identification will be presented.

References:

- Mincher, B.J.; Mezyk, S.P. *Radiochim. Acta* **2009**, 97, 519–534.
- Burns, W.G.; Sims, H.E. *J. Chem. Soc. Faraday Trans.* **1981**, 77, 2803–2813.
- Buxton, G.V.; et. al., *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886.
- LaVerne, J.A. *Radiation Chemical Effects of Heavy Ions*. In: Mozumder, A.; Hatano, Y. **2004**, Marcel Dekker, New York, pp. 403–429.
- Spinks J.W.T.; Woods, R.J. *An Introduction to Radiation Chemistry 3rd Edition*, **1991**, John Wiley and Sons, New York, NY.
- N. Simonzadeh, A.M. Crabtree, G.F. Vandegrift, *Radiolysis and hydrolysis of TRUEX-NPH solvent*. Argonne National Laboratory Report ANL-90/14, July **1992**.
- M.V., Logunov, et. al. *Radiochemistry*, **2006**, 48, 55–61.
- R. Chiarizia, E.P. Horwitz, E.P. *Solvent Extr. Ion Exch.*, **1986**, 4, 677–723.
- B.A. Bucholz, et. al. *Sep. Sci. Technol.*, **1996**, 31, 2231–2243.
- Dhiman, S.; La Verne, J.A. *J. Nuc. Mat.* **2012**, 436, 8–13.
- Pearson, J.; et. al. *J. Radioanal. Nucl. Chem.* **2012**, 292, 719–727.
- Pearson, J.; Jan, O.; Wariner, A.; Miller, G.E.; Nilsson, M. **2013**, *J. Radioanal. Nucl. Chem.* 258, 1401–1409.
- Elias, G.; Groenewold, G.S.; Mincher, B.J.; Mezyk, S.P. *J Chromatography A* **2012**, 1243, 47–52.
- Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S.; Riddle, C.L.; Olson, L.G. **2013**, *Solvent Extr. Ion Exch.* 31, 715–730.

Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel

M. Nilsson^{1}, A. Braatz¹, A. Jackson¹, P. Zalupski², R. Ellis³, M. Antonio³*

Advanced fuel cycles all over the world rely heavily on successful chemical separation of various elements in used nuclear fuel. Numerous solvent extraction processes have been developed for the recovery and purification of metal ions from this used material. However, under certain conditions such as high metal loading or extensive degradation of the extraction reagents the extraction systems may behave different from classical solvent extraction theory. This may result in severe problems with the predictability of process operations. In several of these separation systems the challenge of predictability comes down to a lack of a fundamental understanding of the chemical interactions. One chemical interaction of particular interest is the formation of reverse micelles and large aggregates that has been observed during solvent extraction. In our work, we are studying the effect and relationship of extensive aggregate formation with enhanced extraction of metal ions, i.e. synergistic extraction. Our studies so far have shown that relationships do exist between these two effects in some, but likely not for all, synergistic extraction systems. The studies show the importance of combining and comparing several different analytical techniques, such as metal ion extraction, physicochemical measurements and colligative properties, spectroscopic measurements, thermodynamics studies and structural investigations by for example SAXS and EXAFS. We will present here some recent work on combinations of neutral and acidic extraction reagents exhibiting synergistic extraction of metal ions. For example, we have observed from our analysis of X-ray scattering data that using tributyl phosphate (TBP) and dibutyl phosphoric acid (HDBP) a relationship between metal and water uptake and size of aggregates exist. The combination of TBP and HDBP was also studied by fluorescence showing that when the two reagents are present in different ratios the coordination environment around metal ions appear to change suggesting the formation of mixed complexes. Overall, the results do not disagree with classic understanding of extraction synergy although there appears to be additional chemical interactions that may affect the distribution of metal ions prompting further studies.

Introduction

Nuclear energy is good for production of base load power, although management of the waste is essential to avoid potential catastrophe. One option for managing this material is recycling the used fuel. Liquid-liquid extraction is the benchmark technique for separation of used nuclear fuel and is currently the only technology that is used for this purpose in industry scale in the so called PUREX (Plutonium Uranium Reduction EXtraction) process.[1,2] The PUREX process relies on tri-n-butyl phosphate, TBP, to selectively extract U and Pu away from the fission and corrosion products as well as other minor actinides. TBP, a neutral extractant, coordinates to metal ions through a solvation mechanism[3], recovering the neutral metal nitrate species via displacement of water molecules from the inner-coordination sphere, favored by high nitric acid concentrations, see Equation 1.



A bar over a species denotes that it is present in the organic phase.

* Corresponding Author, Tel.: +1-949-824-2800; fax: +1-949-824-2541. Email address: nilssonm@uci.edu

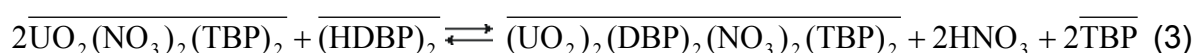
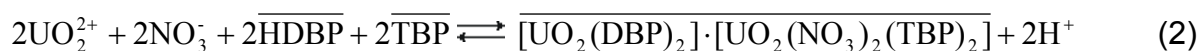
¹ University of California Irvine, Department of Chemical Engineering and Materials Science, Irvine, CA 92697-2575, USA

² Idaho National Laboratory, Aqueous Separations and Radiochemistry Department, Idaho Falls, ID, USA

³ Argonne National Laboratory, Chemical Sciences & Engineering Division, Chicago, IL, USA

The exact composition of the extracted complex may vary depending on the metal and the diluent. The examples given by Irving and Edgington[3] for U(VI), i.e. UO_2^{2+} , extraction suggest $n=2$ and $m=2$.

Since the development of the PUREX process, a large variety of extraction reagents have been studied and different combinations of reagents have been tested to improve efficiency and separation factors. Some combinations of reagents result in enhanced extraction compared to the use of each reagent alone. This enhanced extraction effect is commonly referred to as synergistic extraction and has been observed in systems combining neutral phosphorus containing reagents with acidic extractants,[3-5] and other related systems.[6] These studies often explain synergism as increased dehydration of the metal ion improving its extraction into the organic phase. Some studies have shown that combining TBP and dibutyl phosphoric acid (HDBP) results in enhanced extraction of metal ions compared to using each reagent alone.[7-9] Hahn and Vander Wall[7] suggested two possible mechanisms for the extraction of U(VI) using a combination of TBP and HDBP:



More recent works, pioneered by Osseo-Asare, have taken a different approach, explaining synergistic extraction as a reverse micelle enhanced extraction in systems containing combinations of reagents where at least one displays surface active properties.[10] In these studies, the systems were modeled based on the assumption that the formation of reverse micelles result in increased solubility of metal ion complexes in the organic phase. Early on it was observed that TBP would, under certain conditions, form a heavy organic phase (known as ‘third phase’)[11] causing disruptions in the process. In the early 1990s, Osseo-Asare[12] postulated that the third phase formation from TBP was due to reverse micelles in the organic phase that would grow into large aggregates until they formed a separate phase.

Here we present some of the recent results from an ongoing study [13, 14] of the synergistic extraction system of TBP/HDBP focusing on the possible role of reverse micelles in the extraction of metal ions.

Experimental

Stock solutions of Eu^{3+} and Dy^{3+} were created identically as previous work [14]. The solutions were standardized for metal ion concentration, acidity and excess nitrate concentration as described in Anderson, et al. Aqueous solutions were prepared by dilution of the stock solutions to obtain working solutions consisting of 10^{-4} M Dy^{3+} and 10^{-3} M Eu^{3+} in 0.2 or 2 M HNO_3 . Organic solutions of n-dodecane containing a total of 1 M extractant (TBP + HDBP) in varying molar ratios (4:0, 3:1, 2:2, 1:3, and 0:4; TBP:HDBP) were prepared. Chemicals were obtained from the same sources as in previous work [14]. Extraction experiments were carried out by contacting equal

volumes of aqueous phase containing Dy or Eu with organic solution of varying mole ratios of TBP/HDBP. For the dysprosium experiments, aliquots of each phase was taken after contact and sealed in polyethylene vials (NAA grade supplied by LA Container Inc.). The samples were taken to the UC Irvine TRIGA® reactor for irradiation and activation of the dysprosium followed by analysis using a high purity germanium (HPGe) detector. The water content in the organic phase after extraction was analyzed using a Karl-Fischer titrator, Metrohm model 831 KF Coulometer. The organic solutions containing TBP/HDBP and Eu after contact were taken for fluorescence spectroscopy. A Fluoromax-4 spectrophotometer from HORIBA Scientific, Ltd. and quartz fluorescence cuvettes from Starna Cells, Inc. were used to carry out all determinations.

SAXS Measurements

SAXS data for the organic phases from the experiments with 2 M HNO₃ and 0.2 M HNO₃ with Dy³⁺ were collected at beamline 12-ID-C at the Advanced Photon Source (APS).[15] More details of the experiments and the SAXS analysis are found in previous work from our group [13].

Results and Discussion

Figure 1a (left) show how the distribution ratios of Dy³⁺ varies with the TBP:HDBP mole ratio. The dotted lines in Figure 1a represent a possible extraction trend for additive behavior of the two reagents. Figure 1b (right) show the water uptake in the organic phase at the various mole ratios of TBP/HDBP. For the low acid system (square markers), a non-linear trend for both water and Dy³⁺ uptake is observed, indicating a pronounced synergistic effect between the TBP and HDBP extractants. At high acidity (triangle markers), the trend for Dy³⁺ and water extraction is more linear so that, at this condition, only a weak synergistic effect, if any, is produced by the TBP-HDBP mixture. Figure 1b also shows the concentration of water in the organic phase before contact with an aqueous phase, i.e. blank. It can be seen that the water content in the organic phases is very low before contact.

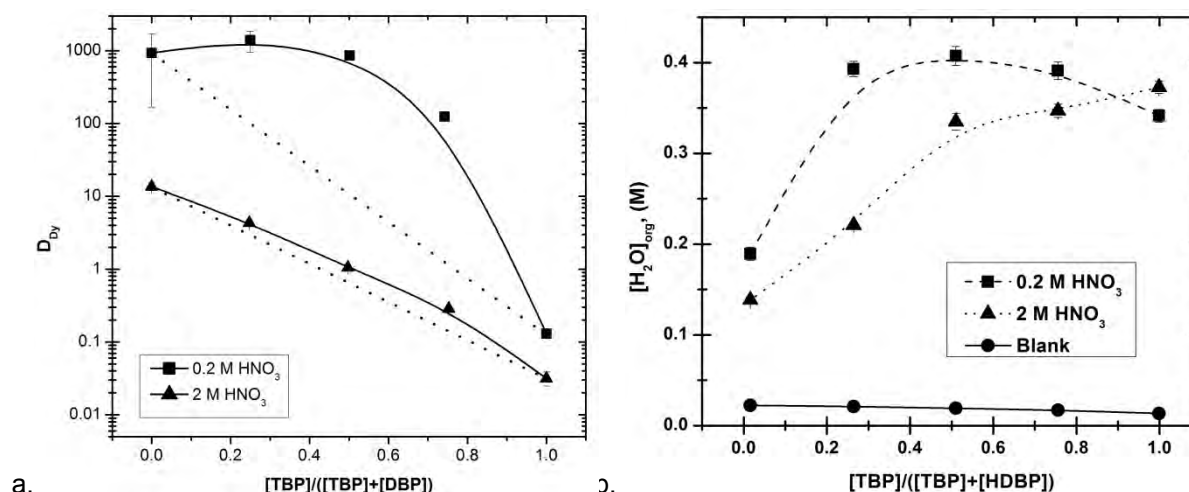


Figure 1. a. Distribution ratios of dysprosium, and b. water concentration in organic phase, from contacting 2 M HNO_3 (triangles) or 0.2 M HNO_3 (squares) with organic phases containing varying ratios of TBP and HDBP at a constant, 1 M, total concentration of extracting reagent. The closed circles are water content in blank, non-pre-equilibrated (or “dry”) organic phases. The error bars represent standard deviations from triplicate measurements. The lines in the figure do not represent best fits to the data but are there to guide the eye of the reader. The dotted lines in the left figure (a) indicate a non-synergistic extraction trend. (Figures reproduced from data in [13]).

Metrical information about the aggregates observed in the SAXS data is provided in Figure 2 in terms of R_g values, which are plotted as a function of the mixing ratio of the extractants. For 100% HDBP, the aggregates formed upon extraction of 2 M HNO_3 (12.7 Å) are smaller than those from 0.2 M HNO_3 (15.4 Å), whereas for 100% TBP the trend in R_g is reversed, with the aggregates formed upon extraction of 0.2 M HNO_3 (11.7 Å) being smaller than those formed upon extraction of 2 M HNO_3 (15.6 Å). This trend in aggregate size correlates with organic phase water content (Figure 1b) and is consistent with the formation of reverse micelles.

Figure 3 shows the fluorescence spectra of Eu at both acid concentrations. The spectra were collected at an excitation wavelength of 395 nm. It can be seen that the fluorescence peak intensities increase when a mixture of TBP and HDBP is used. The maximum peak intensity is seen for the 2:2 mixture of TBP/HDBP. This maximum intensity with a mixed organic system cannot be directly correlated to metal ion concentration in the organic phase. The results for Eu extraction follow trends that are similar to Dy extraction. Hence a maximum extraction should occur at a HDBP:TBP ratio of 75:25 although the extraction of Dy at 100% HDBP is, within errors, equally high. Furthermore, the extraction at 2 M HNO_3 indicates a more linear increasing trend with increasing HDBP ratio, which should result in a linear increase in intensity in the fluorescence spectra. At low acid, there is a significant change in morphology in the largest peak at 612 nm. This has been observed by Zhang, et al. in varying nitric acid concentrations for the complexation of europium with HDBP alone [16]. This is likely due to a change in the complexes formed in the organic phase as HDBP is an efficient extractant at low acid and the mixture of TBP/HDBP may interact to enhance the extraction, as indicated in the distribution data for low acid.

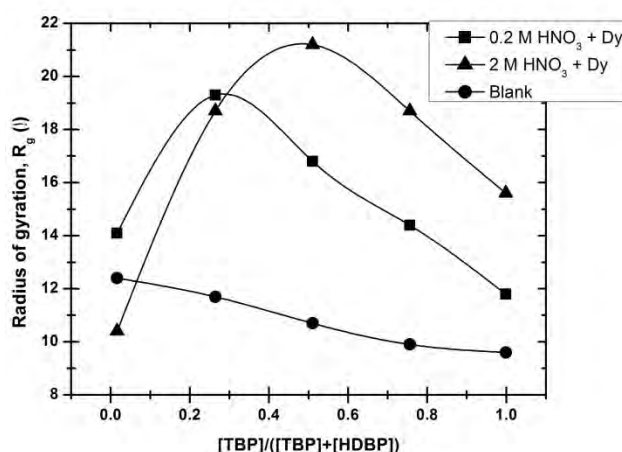


Figure 2. Radius of gyration (in Å) calculated from the SAXS measurements of organic solutions containing varying ratios of TBP and HDBP with constant, 1 M, extractant concentration, contacted with 2 M HNO_3 (triangles) or 0.2 M HNO_3 (squares) containing 10^{-4} M Dy^{3+} . The filled circles refer to blank, non-pre-equilibrated (or “dry”) organic phases. (Figure reproduced from data in [13]).

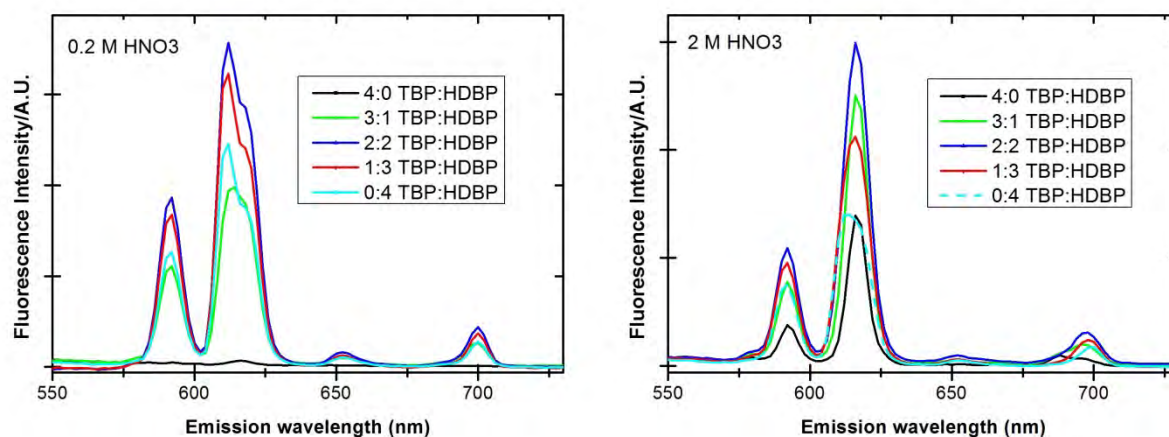


Figure 3: Fluorescence spectra for organic solutions of varying TBP/HDBP ratios in *n*-dodecane contacted with 10^{-3} M Eu in 0.2 M HNO_3 (left), and 10^{-3} M Eu in 2M HNO_3 (right). (Figures reproduced from data in [17]).

The trends observed in metal ion extraction using low acid indicate a synergistic behavior when combining TBP and HDBP. While this is in line with previous studies suggesting mixed complexes the increase in water uptake is not consistent with increased dehydration of the metal ion and suggests the formation of reverse micelles. The X-ray scattering data support the prediction that reverse micelles form and furthermore show that the size of the aggregates change as the ratio between TBP and HDBP vary with the largest aggregates forming for the mixtures rather than the end members. The fluorescence data suggests a change in morphology of the extracted metal ions as the ratio of TBP and HDBP change and neither support nor conflict with any suggested extraction mechanisms, whether it is by mixed complexes or by reverse micelles. Further studies are underway to probe this system in more detail.

Conclusions

Although previous studies of synergistic extraction of metal cations using combinations of neutral and acidic reagents explain the enhanced extraction by increased dehydration of the metal ion and the formation of mixed extractant complexes, our evidence for the increased water extraction coupled with the aggregate formation suggests a reverse micellar aspect to synergism in the system containing TBP and HDBP. It is quite possible that both of these phenomena contribute to our system behavior. We cannot yet provide a definitive answer as to the nature of extraction in this system or the exact complex formed during extraction but work is currently underway to provide further insight into the extraction behavior of the TBP-HDBP system with trivalent lanthanides.

Acknowledgements

The authors wish to thank the U.S. Department of Energy through the Nuclear Energy University Program, NEUP Contract No. 120569 and DE-NE0000156 for financial support for the experiments and the HPGE detector, respectively. The work at Argonne and the use of the Advanced Photon Source are supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences, under contract No DE-AC02-06CH11357. The authors wish to thank the UC Irvine TRIGA® Reactor Facility for use of the reactor for neutron activation analysis.

References

1. Lanham, W.B.; Runion, T.C. ORNL-479, Oak Ridge National Lab.: TN, 1949.
2. Herbst, R.S.; Baron, P.; Nilsson, M. In Advanced separation techniques for nuclear fuel reprocessing and radioactive waste treatment; Nash, K.L., and Lumetta, G.J. Ed.; Woodhead Publishing: Philadelphia, PA., 2011, 141-173.
3. Irving, H.; Edgington, D.N. J. Inorg. Nucl. Chem. 1960, 15(1-2), 158-170.
4. Irving, H.M.N.H. In Solvent extraction chemistry: Proceedings of the international conference held at Gothenburg, Sweden, 27 August-1 September 1966; Dyrssen, D., Liljenzin, J.O., Rydberg, J. Ed.; North-Holland Pub. Co.: Amsterdam, 1967, 91-110.
5. Zangen, M. J. Inorg. Nucl. Chem. 1963, 25(8), 1051-1063.
6. Hagström, I.; Spjuth, L.; Enarsson, Å., et al. Solvent Extr. Ion Exch. 1999, 17(2), 221-242.
7. Hahn, H.T.; Vander Wall, E.M. J. Inorg. Nucl. Chem. 1964, 26(1), 191-202.
8. Dyrssen, D.; Kuča, L. Acta Chem. Scand. 1960, 14, 1945-1956.
9. Schmidt, O.V.; Zilberman, B.Ya., et al. Radiochemistry 2003, 45(6), 596-601.
10. Osseo-Asare, K.; Keeney, M.E. Sep. Sci. Technol. 1980, 15(4), 999-1011.
11. Alcock, K.; Grimley, S.S., et al. Trans. Faraday SOC. 1956, 52, 39-47.
12. Osseo-Asare, K. Adv. Colloid Interface Sci. 1991, 37(1-2), 123-173.
13. Ellis RJ, Anderson TL, et al. (2013) J. Phys. Chem. B., 117, 5916-5924
14. Anderson TL, Braatz A, et al. (2013) Solvent Extr. Ion Exch. 31, 6, 617-633
15. Seifert, S.; Winans, R.E., et al. J. Appl. Crystallogr. 2000, 33(3), 782-784.
16. Zhang P, Kimura T (2006) Solvent Extr. Ion Exch. 24, 149-163
17. Braatz A, Nilsson M (2013) Submitted to J. Radioanal. Nucl. Chem.

Development of the Actinide-Lanthanide Separation (ALSEP) Process

*Gregg J. Lumetta^{*1}, Tatiana G. Levitskia², Brian M. Rapko², Jennifer C. Carter², Cynthia M. Niver², and Artem V. Gelis³*

Summary

Separating the minor actinide elements (Am and Cm) from acidic high-level raffinates arising from the reprocessing of irradiated nuclear fuel is an important step in closing the nuclear fuel cycle. Most proposed approaches to this problem involve two solvent extraction steps: 1) co-extraction of the trivalent lanthanides and actinides, followed by 2) separation of the actinides from the lanthanides. The objective of our work is to develop a single solvent-extraction process for isolating the minor actinide elements. We report here a solvent containing N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) combined with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) that can be used to separate the minor actinides in a single solvent-extraction process. T2EHDGA serves to co-extract the trivalent actinide and lanthanide ions from nitric acid solution. Switching the aqueous phase chemistry to a citrate buffered solution of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid at pH 2.5 to 4 results in selective transfer of the actinides to the aqueous phase, thus affecting separation of the actinides from the lanthanides. Separation factors between the lanthanides and actinides are approximately 20 in the pH range of 3 to 4, and the distribution ratios are not highly dependent on the pH in this system.

Introduction

Separating the minor actinide elements (Am and Cm) from used nuclear fuel remains a significant technical challenge. However, considerable effort continues worldwide to develop the technologies required to separate these elements—driven by the prospect of destroying them in fast reactors to reduce their long-term radiotoxicity.^[1-2] To date, some of the most promising options involve two separate separation cycles for isolating the minor actinides from acidic high-level-waste raffinate. The first cycle is designed to separate the minor actinides and the trivalent lanthanide fission products together as a group. A second process cycle is then used to separate the minor actinides from the lanthanide elements. A number of such approaches have been investigated and these have recently been reviewed.^[1]

To reduce the complexity associated with the separations needed to close the fuel cycle, a number of efforts have been directed at combining the two separation cycles described above into a single solvent-extraction process.^[3] These efforts are based on the hypothesis that two extractants can be combined into a single solvent, yet still chemically operate separately from one another. Our early efforts in this research area were directed at combining the bifunctional neutral extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) with the acidic extractant bis-(2-

^{*1} Gregg J. Lumetta, Pacific Northwest National Laboratory, Richland, Washington, USA; gregg.lumetta@pnnl.gov

² Pacific Northwest National Laboratory, Richland, Washington, USA

³ Argonne National Laboratory, Argonne, Illinois, USA

ethylhexyl)phosphoric acid (HDEHP).^[4-6] CMPO is known to efficiently extract trivalent lanthanides and actinides from HNO_3 solutions,^[7] whereas HDEHP is known to be effective at separating the trivalent actinides from the trivalent lanthanides by application of a polyaminocarboxylate to retain the minor actinides in the aqueous phase while the lanthanides are extracted.^[8] The performance of the combined CMPO/HDEHP solvent system was complicated by strong interactions between the two extractant molecules in the organic phase. Therefore, alternative extractant combinations were sought. Replacing HDEHP with the related acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) resulted in some improvement because the interaction between CMPO and HEH[EHP] was considerably weaker than that between CMPO and HDEHP.^[9] However, even more favorable systems were discovered when diglycolamide (DGA) extractants were used instead of CMPO.

The combination of a DGA-type extractant with an acidic extractant is now referred to as the Actinide-Lanthanide SEParation (ALSEP) concept. In this paper we summarize some important aspects of the process chemistry for the preferred ALSEP solvent formulation—0.05 mol/L *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) plus 0.75 mol/L HEH[EHP] in *n*-dodecane. Included in the discussion are 1) extraction of important nuclear fuel components from HNO_3 solutions, 2) management of Zr and Mo in the process, and 3) selective stripping of Am from the loaded solvent. Comparisons are made between solvents prepared with as-received versus purified HEH[EHP].

Extraction from Nitric Acid

Figure 1 presents the values of the distribution ratio, D , for Am, La, Ce, Pr, Nd, Sm, Eu, and Gd when extracted from HNO_3 solutions into 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in *n*-dodecane (hereafter referred to as the “ALSEP solvent”). Data are presented for measurements made with purified and as-received HEH[EHP], and for measurements made in the forward and reverse directions.

For the forward extractions, the D values obtained for the purified ALSEP solvent are virtually identical to those obtained for the as-received ALSEP solvent. The D values increase with increasing atomic mass for the lanthanide ions. The D_{La} values remain below 1 throughout the HNO_3 range examined (0.5 to 4.5 mol/L), while the D_{Am} values are greater than 1 at $[\text{HNO}_3] > 1.5$ mol/L. Thus, it is possible to separate La from Am during the extraction step.

Forward and reverse extractions should give identical D values; however, significant differences are seen between the D values obtained in the forward and reverse directions. These differences are magnified for ALSEP solvent prepared from the as-received HEH[EHP] versus the purified HEH[EHP]. They are also more pronounced a) for the light lanthanides and b) at the lower end of the HNO_3 concentration range examined. For example, the D_{La} values obtained for the purified ALSEP solvent are slightly higher in the reverse direction, especially at $[\text{HNO}_3] < 2$ mol/L. However, the

D_{La} values are substantially higher when measured in the reverse direction for the as-received ALSEP solvent. Furthermore, under the latter conditions D_{La} decreases with increasing HNO_3 concentration, which is completely opposite the trend seen for D_{La} measured in the forward direction. Similar observations are made for Ce, Pr, and Nd, although the deviations between the forward and reverse extraction data obtained with the purified solvent are less pronounced for Pr and Nd. For the reverse extraction of Sm, Eu, and Gd, there is reasonable agreement between the data for the as-received and purified ALSEP solvents; however, the D values for these elements tend to be higher in the reverse direction than in the forward direction.

These observations might be explained by the presence of kinetically stable complexes between HEH[EHP] and the lighter lanthanide ions. Such complexes should form at lower acid concentrations where deprotonation of the HEH[EHP] molecule is more favorable, which explains why the higher D values are seen at low HNO_3 concentrations in Figure 1b. The presence of HDEHP impurity in the ALSEP solvent would be expected to exacerbate this problem by forming even stronger complexes with lanthanides, which explains the even higher D values seen for the light lanthanides under low HNO_3 conditions in the reverse extraction.

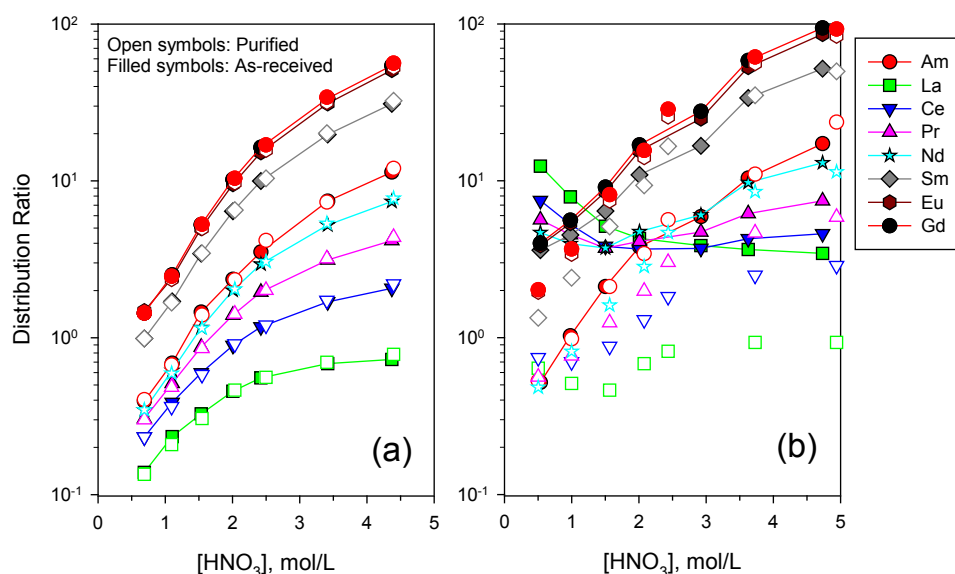


Figure 1. Am, La, Ce, Pr, Nd, Sm, Eu, and Gd distribution ratios as a function of HNO_3 concentration: a) forward extraction and b) reverse extraction.

Zirconium and Molybdenum in ALSEP

Zirconium and Mo are strongly extracted from HNO_3 into the ALSEP solvent.^[10] Two approaches have been established for managing Zr in the process. First, the extraction of Zr can be completely suppressed by adding 50 mmol/L *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA) to the HNO_3 solution. The distribution ratios for the lanthanide elements are little affected by the presence of CDTA. However, one potentially complicating factor introduced by adding CDTA is an apparent dramatic increase in the extraction of Ru. Further work is needed to understand this effect, especially since no such effect was reported in a similar

system employing T2EHDGA and HDEHP as the solvent.^[11] As an alternative, Zr can be removed from the ALSEP solvent after the minor actinides have been stripped (as described below) and after the lanthanides have been stripped with *N,N,N',N'*-tetra(ethyl)diglycolamide. Once these components have been removed from the solvent, Zr can be readily stripped into aqueous oxalic acid.^[10]

Molybdenum must be removed from the loaded ALSEP solvent before conducting the minor actinide stripping step so that it does not contaminate the minor actinide product. This can be accomplished by contacting the loaded solvent with citrate solution. Figure 2a presents the distribution ratios for selected lanthanides and Mo for contact of the loaded ALSEP solvent with 0.2 mol/L citrate at different pH values. Figure 2b presents the distribution ratios for the same elements with variable citrate concentrations at pH ~ 3.3. The data show that there is no advantage in using citrate concentrations > 0.2 mol/L. Indeed, the lanthanide *D* values decrease significantly at higher citrate concentrations. Presumably, Am would behave in the same way, which is undesirable for the Mo scrubbing step. Citrate at 0.2 mol/L should be very effective at scrubbing Mo from the loaded ALSEP solvent, especially above pH 3.3. In the pH range 3.3 to 4.0, the Mo distribution ratios were approximately constant at ~0.17, and the lanthanide distribution values remained high. So a solution consisting of 0.2 mol/L citrate at pH 4 is recommended for scrubbing Mo from the ALSEP solvent.

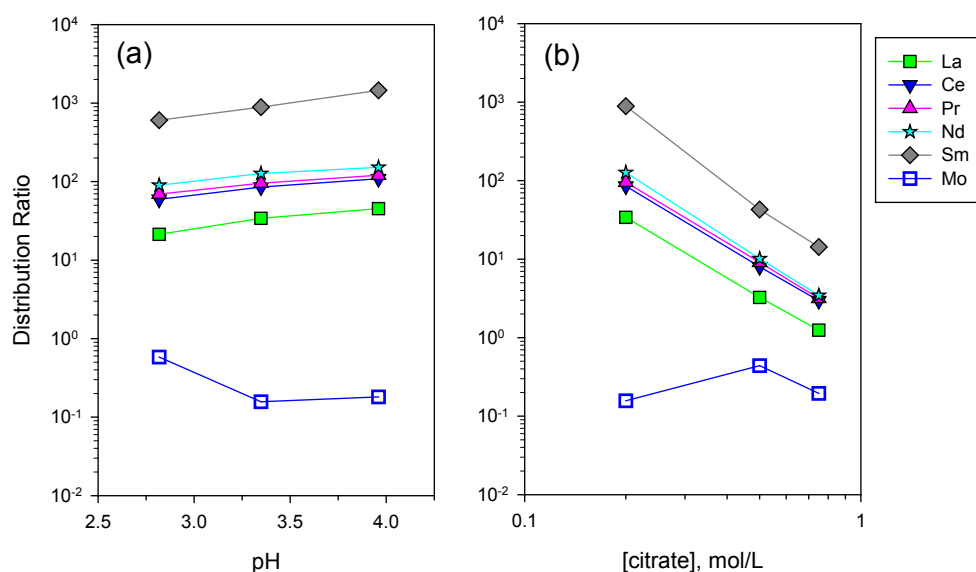


Figure 2. Distribution ratios for various elements as a function of pH for contact of an *n*-dodecane solution of 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] with (a) 0.2 mol/L citrate at various pH conditions and (b) variable concentrations of citrate at pH ~ 3.3.

Minor Actinide Stripping

Selective stripping of the minor actinides from the loaded ALSEP solvent is done in a manner analogous to “reverse TALSPEAK.”^[8] In this approach, the solvent containing both the minor actinides and the trivalent lanthanides is contacted with a carboxylate-buffered aqueous solution containing a polyaminocarboxylate ligand. The amine groups impart a sufficiently soft character to the ligand that it binds the slightly softer

actinide ions in preference to the harder lanthanides. N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) is the polyaminocarboxylate ligand used in the ALSEP system. Citric acid is used as the buffering agent.

Figure 3 presents the D values for Am and selected lanthanide elements as a function of pH when the metal-loaded ALSEP solvent is contacted with 0.125 mol/L HEDTA in 0.2 mol/L citrate buffer. Data are presented for both the as-received (Figure 3a) and the purified (Figure 3b) ALSEP solvents. The data indicate that purifying the solvent has little impact on the minor actinide stripping step. The minimum Ln/Am separation factor is relatively insensitive to the pH in the pH range 2.5 to 4, and they range from about 15 to 20 (defined by D_{Nd}/D_{Am} in this pH range). Furthermore, the dependence of the D values on the pH is much less than in the conventional TALSPEAK process. For example, slopes of the best fit lines through the Am data in Figure 3 are approximately -0.5 , whereas the slopes for analogous TALSPEAK data from the literature are -2 .^[12] This is another advantageous feature of the ALSEP system.

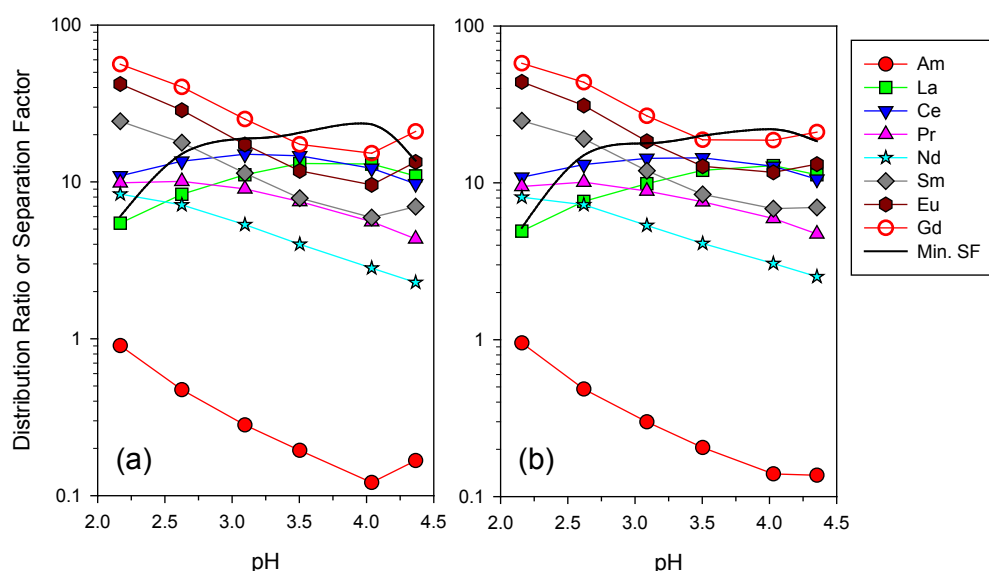


Figure 3. Distribution ratios for various elements as a function of pH for contact of an *n*-dodecane solution of 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] with 0.125 mol/L HEDTA plus 0.2 mol/L citrate: (a) as-received solvent and (b) purified solvent.

References

- Hill, C. Overview of Recent Advances in An(III)/Ln(III) Separation by Solvent Extraction. In *Ion Exchange and Solvent Extraction: A Series of Advances*; Moyer, B. A., Ed. CRC Press: Boca Raton, 2010; Vol. 19, pp 119-193.
- Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. Use of Soft Heterocyclic N-Donor Ligands to Separate Actinides and Lanthanides. *Inorg. Chem.* **2013**, 52, 3414-3428.
- Lumetta, G. J.; Gelis, A. V.; Vandegrift, G. F. Solvent Systems Combining Neutral and Acidic Extractants for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2010**, 29, 287-312.

4. Lumetta, G. J.; Carter, J. C.; Gelis, A. V.; Vandegrift, G. F. Combining octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel. In *Nuclear Energy and the Environment*; Wai, C. M.; Mincher, B. J., Eds; American Chemical Society: Washington, DC, 2010; pp 107-118.
5. Lumetta, G. J.; Neiner, D.; Sinkov, S. I.; Carter, J. C.; Braley, J. C.; Latesky, S. L.; Gelis, A. V.; Vandegrift, G. F. Combining Neutral and Acidic Extractants for Recovering Transuranic Elements from Nuclear Fuel. XIX International Solvent Extraction Conference, Santiago, Chile, Gecamin Ltda, Santiago, Chile: Santiago, Chile, 2011; p Paper No. 68.
6. Lumetta, G. J.; Gelis, A. V.; Braley, J. C.; Carter, J. C.; Pittman, J. W.; Warner, M. G.; Vandegrift, G. F. The TRUSPEAK Concept: Combining CMPO and HDEHP for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2013**, *31*, 223-236.
7. Horwitz, E. P.; Kalina, D. G.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. The TRUEX Process – A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent. *Solvent Extr. Ion Exch.* **1985**, *3*, 75-109.
8. Nilsson, M., Nash, K.L Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process. *Solvent Extr. Ion Exch.* **2007**, *25*, 665-701.
9. Braley, J. C.; Lumetta, G. J.; Carter, J. C. Combining CMPO and HEH[EHP] for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2013**, *31* (6), 567-577.
10. Lumetta, G. J.; Carter, J. C.; Niver, C. M.; Guelis, A. V. Zirconium and Fission Product Management in the ALSEP Process. Global 2013, Salt Lake City, UT, September 29 – October 3, 2013; American Nuclear Society: Salt Lake City, UT, 2013; pp 912-916.
11. Nayak, P. K.; Kumaresan, R.; Venkatesan, K. A.; Rajeswari, S.; Subramaniam, G. G. S.; Antony, M. P.; Vasudeva Rao, P. R. Single-cycle separation of americium (III) from simulated high-level liquid waste using tetra-bis(2-ethylhexyl)diglycolamide and bis(2-ethylhexyl)phosphoric acid solution. *Journal of Environmental Chemical Engineering* **2013**.
12. Svantesson, I.; Hangström, I.; Persson, G.; Liljenzin, J. O. Separation of Americium and Neodymium by Selective Stripping and Subsequent Extraction with HDEHP Using DTPA–Lactic Acid Solution in a Closed Loop. *Radiochemical and Radioanalytical Letters* **1979**, *37*, 215-222.

High LET Radiolytic Degradation of Solvent Extraction Processes for Used Nuclear Fuel

Mikael Nilsson, Jeremy Pearson*

University of California, Irvine, Department of Chemical Engineering and Materials Science, Irvine, CA 92697-2575, USA. Phone: 949-824-2800, Email: nilssonm@uci.edu

Solvent extraction processes commonly undergo degradation and losses in performance due to harsh acidic or caustic conditions and the presence of metal ions which may accelerate or catalyze degradation reactions. In addition to these, solvent extraction processes developed for recycling used nuclear fuel are susceptible to radiation and the reactive molecular products of radiolysis. The nature of radiation type, alpha vs. gamma, or high linear energy transfer (LET) vs. low LET, determines the extent to which individual degradation pathways are followed as well as the overall extent of degradation to the process. The presence of electron scavenging molecules such as oxygen can also influence reaction rates and degradation products produced. In our studies we are building on previous work by other groups and continue to systematically study different contributions to radiation degradation of solvent extraction reagents towards developing a picture of the whole. To study the effects of high LET radiation we apply a novel method utilizing the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. The $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction was applied to compare sensitivity of two extraction reagents used for separation processes for used nuclear fuel TBP (the PUREX process) and CMPO (the TRUEX process). 1M solutions of TBP in n-dodecane and 0.1M solutions of CMPO in n-dodecane were irradiated and the solutions were analyzed for degradation products. Degradation of TBP via this approach was shown to match that from other high LET irradiations of similar systems in the literature. A comparison of alpha versus gamma induced degradation is discussed along with some discussion of the variation in degradation products observed.

Introduction

The increasing potential for adoption of nuclear energy as a replacement for fossil fuels depends largely on the ability to streamline and increase efficiencies of nuclear fuel cycles. At the same time it is beneficial to reduce the toxicity of spent nuclear fuel by partitioning and transmutation of transuranics and long lived fission products. Solvent extraction has been utilized for decades for separation of elements in used nuclear fuel and is used in commercial plants such as La Hague in France or Sellafield in the UK. The PUREX process (or advanced adaptations thereof) is currently the only process used at the industrial scale to recycle usable uranium and plutonium. A multitude of other unique solvent extraction processes such as the TRUEX process are under development at lab and pilot scale for partitioning of used nuclear fuel. Extraction reagents utilized in all of these processes will inevitably be exposed to harsh environments including ionizing radiation, high concentration of acid and possible metal ion catalyzed hydrolysis. Partial destruction of these ligands leads to reduction in process efficiency and selectivity. Candidate ligands must be

screened for susceptibility to these types of attack in order to assess viability for economical application in an extraction process.

In light of this many studies have been performed assessing the impact of gamma radiation on tributyl phosphate (TBP), the extraction reagent utilized in the PUREX process, and these findings have been reported recently in a review by Mincher et al.^[1]

Most radiolysis studies, of both TBP and other extraction reagents, in the past have focused on the degradation due to gamma radiation. Experimentally this is much more readily achieved since the gamma radiation can be radiating from an outside source and the sample need never come into direct contact with the radioactive material. Gamma radiation deposits only small amounts of its energy as it passes through matter and radiolysis product formed may not recombine resulting, in water, in smaller radicals of hydroxide and protons. The used nuclear fuel contains a large number of heavier elements that decay mostly by alpha radiolysis. Compared to gamma radiation the alpha particles deposit all their energy in a very short distance, said to have a large LET (Linear Energy Transfer) value. This causes a much greater degree of recombination of the degradation products formed in the track of the alpha particle and degradation products from alpha radiation may differ slightly from those formed by gamma radiation.

However, due to the short range of alpha particles, radiolysis studies are much more complicated to carry out since no outside source may be used and alpha decaying material must be introduced into the sample studied. This causes problems since most alpha decaying materials are actinides and to achieve high doses isotopes having relatively high specific activity, such as ^{238}Pu and ^{242}Cm or ^{244}Cm , must be used. Introducing this material in a sample makes post irradiation analysis very challenging since few labs have the capability to analyze samples containing large amounts of alpha emitting actinides and the presence of the metal ions themselves may complicate the analysis. Addition of alpha emitting isotopes with very short half-life which would result in a non-radioactive sample within ~ 10 half-lives of the isotope is one way to get around this problem. Recent work carried out by Ekberg et al. [2] utilized ^{211}At with a 7.2h half life as the source of alpha particles. This method has a lot of benefits since the samples can be analyzed as non-radioactive samples once the material has decayed to low levels. Indirect methods that cause alpha radiolysis in samples can be used such as accelerating helium and exposing the sample to a beam of high energy helium ions. This method is useful in that the sample can be analyzed immediately after it has been exposed and has great benefit for kinetics studies. The downside of the method is that the distribution of alpha radiation in a sample may be localized to the surface of the sample being irradiated.

In our previous work we have studied a method to selectively observe the effects of high LET particles, without the addition of alpha emitting metal ions, e.g. plutonium,

via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction.[3-6] The high LET particles created by the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction simulate alpha radiation, shown in figure 1.

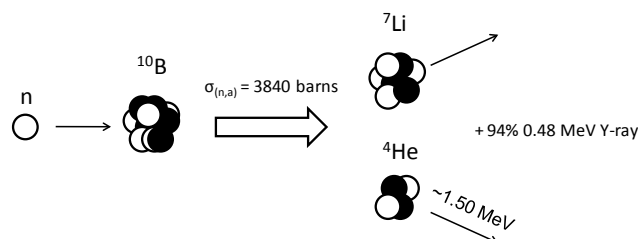


Fig. 1. Neutron induced high LET particle production used in this study.

An organic soluble compound containing boron is added to the organic phase containing the extractant and the sample is exposed to a neutron field which induces the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. As a proof of concept this method was applied to solutions of methyl red in n-dodecane and degradation of methyl red was observed with increasing boron concentration.[3] A more detailed description of this method and verification that the method is consistent over the full range of reactor power necessary for compounds that require higher doses was recently published.[4] Below is a summary of our studies of the high LET degradation of TBP [5] and octylphenyl-N,N-diisobutylcarbamoyl methyl phosphine oxide (CMPO) [6], representative reagents for separation processes of used nuclear fuel.

Experimental Work

Organic solutions studied in this work irradiated in the presence of gamma rays from an external ^{137}Cs source and high LET particles produced from boron activation during exposure to thermal neutrons in the UCI TRIGA reactor.

Solutions of 1M TBP in n-dodecane and 0.1M CMPO in n-dodecane were degassed with nitrogen and irradiated at various distances from the gamma source for varying durations. TBP Solutions were removed and analyzed on an HP 5890 gas chromatograph utilizing an Agilent DB-1301, 30 m, 0.32 mm, 1.00 μm capillary column. Solutions of CMPO were removed and analyzed by high performance liquid chromatography (HPLC) with UV detection at 220 nm, after the method of Elias et al. [7]. Details of the analysis can be found in previous papers from our group for TBP [5] and CMPO [6], respectively.

For high LET irradiations, samples containing various concentrations of bis(pinacolato)diboron were placed in a sample carousel (lazy-susan) next to the core of the UC Irvine 250 kW TRIGA Mark I reactor. Solutions of 1M TBP in n-dodecane and bis(pinacolato)diboron at concentrations of 0-0.15M were degassed with nitrogen and irradiated for 3-10 hours at 250 kW. Solutions of 0.1M CMPO with 0-0.15M bis(pinacolato)diboron were irradiated for 2 hours at 250 kW. The estimated neutron flux in the carousel positions is 8×10^{11} neutrons/cm²/s at 250 kW. Post irradiation samples were removed and analyzed as described above. Samples with 0 M bis(pinacolato)diboron were treated as blanks to estimate the high LET dose, i.e. blanks were exposed to only low LET from the reactor core. The high LET dose was

estimated to be between 0 (for 0 M bis(pinacolato)diboron) up to 213 kGy/hr (for 0.15 M bis(pinacolato)diboron). The low LET dose in the reactor core was estimated to be 40.4 kGy/h at full power (250 kW).

Samples of CMPO irradiated in the reactor was tested for Am extraction. Aliquots of the irradiated organic phase diluted to 0.016 M CMPO (based on initial concentration before irradiation) were contacted with aqueous phases containing trace amounts of ^{243}Am . The Am distribution ratios were analyzed by HPGe measurements.

Results and Discussion

Results for the gamma and high LET radiolysis of TBP are shown in Figure 2. Results for the gamma and high LET induced formation of DBP are shown in Figure 3. Results for the gamma and high LET radiolysis of CMPO are shown in Figure 4. The total high LET dose received by the samples irradiated in the reactor ranged from 500 kGy to 2000 kGy. The background gamma dose from the reactor during the 10 hour irradiation was approximately 400 kGy.

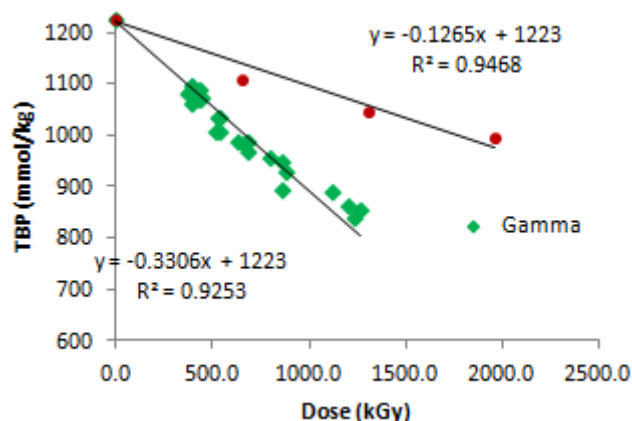


Figure 2. Degradation of 1M TBP/dodecane in the presence of low and high LET radiation.

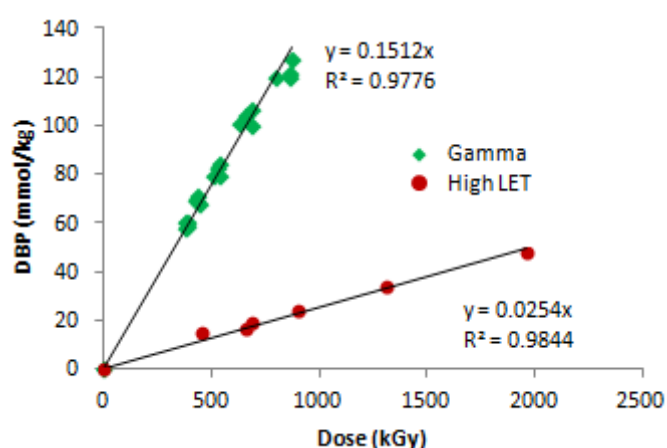


Figure 3. Formation of DBP in the presence of low and high LET radiation (10 hr at 250 kW) of 1M TBP/dodecane.

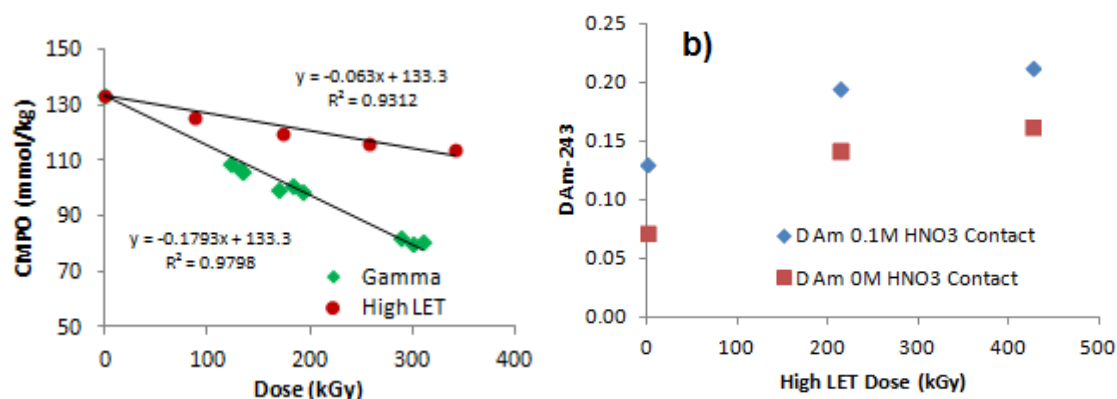


Figure 4. a) Degradation of 0.1M CMPO/dodecane in the presence of gamma and high LET radiation. b) Dose dependence of measured americium distribution ratios for forward extraction for High LET irradiations. Initial CMPO concentration was 0.10 M, however, all solutions were diluted to 0.016 M prior to extractions.

Using the data in these graphs we can derive estimate G-values for the degradation of TBP and formation of DBP and the degradation of CMPO in the presence of both gamma and high LET radiation in the dose and concentration range studied here. These are $-0.33 \mu\text{mol/J}$ and $-0.13 \mu\text{mol/J}$ for TBP in the presence of gamma and high LET respectively and $0.15 \mu\text{mol/J}$ and $0.025 \mu\text{mol/J}$ for DBP in the presence of gamma and high LET respectively. For CMPO degradation the G-values were $-0.18 \mu\text{mol/J}$ and $-0.063 \mu\text{mol/J}$ in the presence of gamma and high LET respectively.

It is interesting to note that the high LET dose to samples containing CMPO result in an elevated extraction of americium.

Previous studies performed with this method evaluated methyl red degradation in the presence of low and high LET radiation and showed a notable difference between the two types of radiation where low LET resulted in larger G-values than high LET.^[3] As can be seen in Figures 2-4 and from the derived G-values, the high LET appears less damaging than the low LET. The exact reason for the difference in low and high LET is still under investigation. However it has been suggested that due to the high LET radiation depositing all energy in a small volume there is less interactions outside the radiation track. Radicals formed in the dense track recombine, possibly to the original molecule, and an apparent reduction in the degradation is observed. Low LET radiation produces radicals that have a lesser chance of recombining and thus react with other molecules outside the track.

Conclusions

Data show a decreased effect of degradation of TBP and CMPO and formation of DBP for high LET radiation vs. gamma radiation. DBP formation constant (G-value) decreases from $0.15 \mu\text{mol/J}$ for gamma to $0.025 \mu\text{mol/J}$ for high LET. CMPO degradation decreases from $0.18 \mu\text{mol/J}$ for gamma to $0.06 \mu\text{mol/J}$ for high LET. Our results for low LET match well with previous work by Egorov et al.[8] Understanding the degradation of extraction reagents due to radiolytic attack is useful for assessing their robustness and modeling industrial and pilot scale processes to increase efficiencies. Continued studies using the method will include details of formation and

degradation constants for high and low LET radiation for various solvent extraction reagents.

Acknowledgements

This project was funded by U.S. Department of Energy through the Nuclear Energy University Program (NEUP) project no. DE-AC07-05ID14517. The authors are grateful for the support of the UC Irvine TRIGA® reactor for irradiations, Dr. George Miller for helpful discussions and Donald Morrow III for providing data for the gamma background dose in the reactor.

References

1. Mincher, B.J.; Modolo, G.; Mezyk, S.P. Review article: The effects of radiation chemistry on solvent extraction: 1. Conditions in acidic solution and a review of TBP radiolysis. *Solvent Extr. Ion Exch.*, 2009, 27(2), 1-25.
2. Ekberg, C., Aneheim, E., Fermvik, A., Skarnemark G., Using ^{211}At as internal alpha radiolysis source allowing for simple detection of radiolysis products. *Rad. Phys. Chem.*, 79(4), 454-456, (2010).
3. Pearson, J.; Jan, O.; Miller, G.E.; Nilsson, M. Studies of high linear energy transfer dosimetry by $^{10}\text{B}(n,\alpha)^7\text{Li}$ reactions in aqueous and organic solvents. *J. Radioanal. Nucl. Chem.*, 2012, 292(2), 719-727.
4. Pearson, J.; Jan, O.; Wariner, A.; Miller, G.E.; Nilsson, M. Development of a method for high LET irradiation of liquid systems. *J. Radioanal. Nucl. Chem.*, 2013, 298(2), 1401-1409.
5. Pearson, J., Nilsson, M. Radiolysis of tributyl phosphate by particles of high linear energy transfer. Accepted for publication, *Solvent Extraction and ion exchange*, 2014.
6. Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S.; Ekberg, C.; Skarnemark, G.; LaVerne, J.A.; Nilsson, M.; Pearson, J.; Schmitt, N.C.; Tillotson, R.D. The radiation chemistry of CMPO: Part 2. Alpha Radiolysis, *J Solvent Extr. Ion Exch.*, 2014, 32(2), 167-178.
7. Elias, G.; Groenewold, G.S.; Mincher, B.J.; Mezyk, S.P. Determination of CMPO using HPLC-UV. *J Chromatography A* 2012, 1243, 47–52.
8. Egorov, G.F.; Tkhorzhnitskii, G.P.; Zilberman, B.Y.; Shmidt, O.V.; Goletskii, N.D. Radiation chemical behavior of tributyl phosphate, dibutyl phosphoric acid, and its zirconium salt in organic solutions and two phase systems. *Radiochemistry*, 2005, 47(4), 392-397.

The radiation chemistry of CMPO

Stephen P. Mezyk,^{1*} Bruce J. Mincher,² M. Nilsson,³ J. Pearson,³ J.A. LaVerne⁴

¹Department of Chemistry and Biochemistry, California State University at Long Beach, 1250 Bellflower Blvd, Long Beach, CA 90840, USA

²Aqueous Separations and Radiochemistry Department, Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415-4107, USA

³Department of Chemical Engineering and Materials Science, University of California Irvine, Irvine, CA 92697-2575, USA

⁴Department of Physics and Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

Summary:

The actinide/lanthanide ligand CMPO (octylphenyl-N,N-diisobutylcarbmoylmethyl phosphine oxide) was subject to gamma irradiation using ⁶⁰Co γ -rays, and alpha-irradiation using a He-ion beam, ²⁴⁴Cm isotopic α -rays, and by He and Li ions created by the n, α reaction of ¹⁰B in a nuclear reactor. Post-irradiation samples were analyzed for the decrease in CMPO concentration, the appearance of degradation products, and the effects on americium solvent extraction. The -G-value for the radiolytic degradation of CMPO was much lower for alpha irradiation as compared to gamma, and was dependent upon the presence of nitric acid and oxygen during irradiation, with both providing protection from radiolytic degradation. The -G-value does not depend on the γ -ray dose rate, or the CMPO concentration. Effects on solvent extraction performance were independent of the change in CMPO concentration, but rather related to the nature of the degradation products. The main CMPO products were identified by ESI-MS, and were different for CMPO irradiation performed in the presence of nitric acid.

Introduction

The compound octylphenyl-N,N-diisobutylcarbmoylmethyl phosphine oxide (CMPO) (Fig. 1) is a strong Lewis base that was designed to partition the trivalent actinides and lanthanides from acidic solutions of high-level nuclear waste. It has also been proposed as a solvent extraction ligand in the treatment and recycling of used nuclear fuel. The irradiation of any solvent extraction ligand

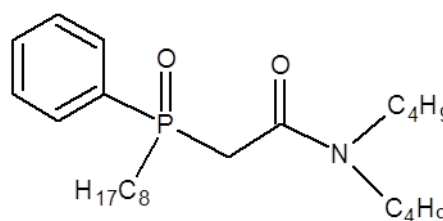
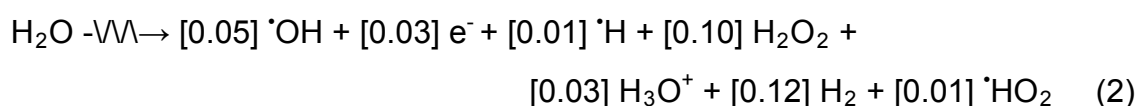
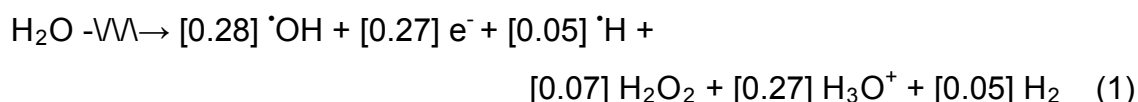


Figure 1. The structure of octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).

in an organic diluent in contact with a radioactive aqueous phase exposes that ligand to numerous radiolytically-produced reactive species. These reactive species are created by the decomposition of water, nitric acid and the organic diluent. Thus, successful deployment of CMPO for fuel cycle applications will depend on its radiolytic stability under these conditions.

Among the major reactive species produced by radiation are the oxidizing $\cdot\text{OH}$, $\cdot\text{NO}_2$, and $\cdot\text{NO}_3$ radicals from water and nitric acid radiolysis, the reducing solvated electron e^-_{sol} and $\cdot\text{H}$ atom, produced by water and organic diluent radiolysis, and various carbon centered radicals produced from the organic diluent.^[1] In contact with dissolved nuclear fuel, CMPO is exposed to both low linear energy transfer (LET) β/γ radiation from fission product decay and high-LET α radiation from actinide decay. The LET of the incident radiation influences the amounts of the reactive species produced during diluent radiolysis.^[2] For example, the yields of the primary reactive species in the radiolysis of water for low-LET electron beam irradiation are shown in Eq. 1,^[3] in comparison to the yields for high-LET radiation shown in Eq. 2:^[4]



These equations present a list of radiolytic products and are not intended to be stoichiometric. The numbers shown in brackets are absolute yields (G-values) given in $\mu\text{mol J}^{-1}$. From these two equations it can be seen that the yields of the products favor increased production of the molecular species such as H_2O_2 and decreased production of the radical species such as $\cdot\text{OH}$ radical as the LET increases. This change is due to the deposition of larger amounts of energy in a small volume along the path of the higher LET radiation, which results in high localized concentrations of radicals, allowing for their recombination into molecular species prior to reaction with the ligands.^[5] Therefore, it might be expected that the $-G_{\text{CMPO}}$ -value and products of CMPO degradation would be different for the two radiation types.

The adverse effects of γ -irradiation on the solvent extraction properties of CMPO-containing solutions have previously been investigated by Simonzadeh et al.,^[6] Logunov et al.,^[7] and Chiarizia and Horwitz.^[8] In contrast, almost no work has been done on the α -radiolysis of CMPO, mainly due to the radiological control difficulties associated with the handling of α -emitters and of analyzing post-irradiation, α -emitter contaminated samples. Only Buchholz et al.^[9] performed α -irradiation of a CMPO-containing solution; however, neither degradation yields nor products analyses were obtained.

Therefore, we have investigated both the γ and α -radiolysis of this compound in dodecane under a variety of conditions, using various steady-state sources. The γ irradiations were performed using a ^{60}Co irradiator, the α irradiations were done by the isotopic α -source ^{244}Cm as well as with a He-ion beam and with He/Li ions generated by the reaction of neutrons with ^{10}B . The effects on $-G_{\text{CMPO}}$ and the solvent extraction performance of these irradiated solutions were compared to degradation products analyses.

Experimental Methods:

Gamma-ray irradiations:

These irradiations were conducted at the Idaho National Laboratory (INL) by ^{60}Co irradiation of 0.1 M CMPO/dodecane solutions, either as neat organic solutions, or as organic solutions in contact with an equal volume of an aqueous phase of varying nitric acid concentration. Samples were irradiated in sealed glass scintillation vials to a series of absorbed doses determined by their duration in the irradiator. An additional series of samples was irradiated with continuous air sparging, using room air delivered by a diaphragm pump through a syringe needle inserted into septum-capped scintillation vials. The INL irradiator was a Nordion GammaCell 220E (Ottawa, Canada) with a center-line sample chamber dose rate of 6.2 kGy h^{-1} at the time of these experiments, as determined by standard decay-corrected Fricke dosimetry.

Isotope α -irradiations: ^{244}Cm

Samples of 0.1 M CMPO/dodecane were α -irradiated in a glovebox using ^{244}Cm at the Idaho National Laboratory, Idaho Falls, ID, USA. Curium-244 decays by emission of a 5.8 MeV α -particle with an 18.1-y half-life. These irradiations were performed by dissolving 0.6 mg of ^{244}Cm in 0.1 M HNO_3 and then contacted with the CMPO/dodecane solution with constant stirring for amounts of time appropriate to deliver the desired absorbed dose. Absorbed doses in J kg^{-1} (Gy) were calculated based on the α -particle energy, the calculated number of decays occurring for the duration of the irradiation, and the solution mass. The dose rate varied from $1.1\text{--}1.4 \text{ kGy h}^{-1}$, depending on the volume irradiated. The irradiations were performed at room temperature in sealed 20 mL scintillation vials with about 10 mL of headspace. The vials were opened intermittently for sampling purposes and thus these samples are considered to have been aerated during the irradiation.

α -irradiations: He-ion beam

He-ion beam irradiations were performed at the University of Notre Dame, IN, USA. Helium ions were produced using a 9 MV FN-Tandem Van de Graaff generator with a 20 keV duoplasmatron source.^[10] The α -particle energy was selected by varying the accelerator terminal voltage to provide sufficient initial particle energy such that after passing through the cell window the energy incident to the sample was 5.0 MeV to simulate the α -particle energies produced by actinide decay. Since penetration of the ions in the solution is low, samples were continuously and vigorously stirred at room temperature to ensure uniform dose deposition to the entire sample and bubbled throughout the irradiation with air or argon to achieve aerated or deaerated conditions, respectively.

α -irradiations: ^{10}B (n, α) ^7Li

In a novel high-LET radiolysis technique reported by Pearson et al.,^[11] He ions were generated by neutron-induced fission of ^{10}B nuclei. The reaction, shown in Eq. 3,

produces He ions with an energy of about 1.4 MeV and Li ions with an energy of about 0.85 MeV. Neutrons were generated using the University of California, Irvine TRIGA® Mark I reactor with the samples irradiated in a sample carousel at a flux of $8.0 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ at 250 kW power for 2 h. Different absorbed doses to these 0.1 M CMPO/dodecane samples were achieved by varying the total boron concentrations to values of 0, 0.03, 0.06, 0.09, 0.12, or 0.15 M using bis(pinacolato)diboron, to generate high-LET dose rates of 0, 43, 86, 129, 171, or 213 kGy hr^{-1} , respectively. Background corrections for gamma (estimated at 40 kGy h^{-1}) and neutron absorbed doses were performed by irradiating CMPO samples that contained no added boron. Alpha dosimetry was performed using the standard Fricke dosimeter, modified by the addition of boric acid.^[12, 13] The temperature of the reactor-irradiated samples did not exceed 31°C.

CMPO analysis by HPLC

The concentration of CMPO in dodecane was determined by high performance liquid chromatography (HPLC) with UV detection at 220 nm, after the method of Elias et al.^[11] Briefly, samples in dodecane were diluted 1:100 with 2-propanol to ~1 mM, then analyzed using a Supelcosil C-18, RP, 25 cm, 4.6 mm x 5 μm column and guard column. The eluent solutions used were either 30 mM 60:40, pH 2.7 phosphate buffer/alcohol mix or 60:40 0.1% formic acid at pH 2.7/alcohol mix, where the alcohol mix was 3.6% 1-octanol in 2-propanol. The flow rate was 1 mL min^{-1} . The column temperature was 50°C, and the run time was 35 min. Acid-contacted samples required separate calibration due to the formation of an equilibrium $\text{CMPO} \cdot \text{HNO}_3$ complex^[13,14] in dodecane that decreased the apparent concentration of CMPO by UV detection. Reported concentrations were the means of triplicate determinations. The relative standard deviation for the method was reported to be < 1%.

Solvent extraction experiments

Irradiated CMPO/dodecane solutions were used in Am solvent extraction experiments. Equal volume, pre-equilibrated, room temperature ($21 \pm 2^\circ\text{C}$) extraction contacts of 1 min duration were performed from ^{243}Am traced 2 M HNO_3 . The irradiated solutions were diluted to nominal 0.016 M CMPO (based on the pre-irradiation concentration of 0.1 M) with fresh dodecane prior to use. Following contact, 1 mL aliquots of each phase were removed for γ -ray counting, with the Am activity determined at 74.7 keV. The loaded organic phase was next stripped with an equal volume of 0.1 M HNO_3 and aliquots of these phases were also removed for γ -counting.

For α -irradiated samples only, a single determination was performed at each absorbed dose due to the small amounts of material available, and the organic phases were not pre-equilibrated prior to extraction to minimize loss of any water-soluble radiolysis products. For radiolysis product-amended samples, the extractions were performed in triplicate with the mean values reported, and triple 1-min pre-equilibration contacts were performed.

Results and Discussion:

Typical data for CMPO loss induced by γ irradiation as measured by HPLC are shown in Figure 2, for α irradiation are shown in Figure 3. These data demonstrate that the loss is condition-dependent, but under both conditions minimal loss is observed for aerated, acidic-contacted solutions. Some minor loss from the reactor data are seen in Figure 3.

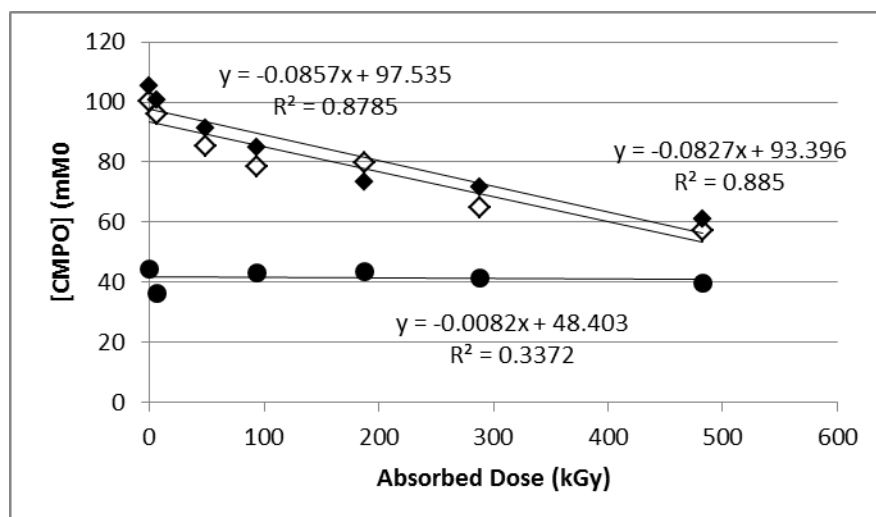


Figure 2. The γ -radiolytic decrease in CMPO concentration for aerated samples in the absence of the aqueous phase (closed diamonds); in contact with an equal volume of 0.1 M HNO₃ (open diamonds); in contact with an equal volume of 2 M HNO₃ (closed circles). Duplicate irradiations for the 2 M acid contacted samples provided an RSD of $\pm 15\%$.

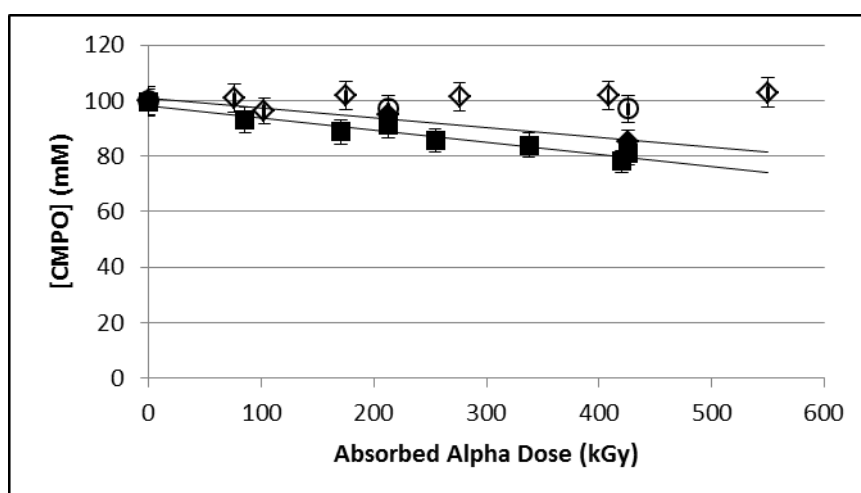


Figure 3. The change in CMPO concentration under various conditions of alpha (high LET) irradiation. Cm irradiation in the presence of 0.1 M HNO₃ (open diamonds); Reactor He/Li irradiation in the presence of 0.1 M HNO₃ (closed diamonds); Normalized reactor He/Li irradiation in the presence of 3 M HNO₃ (open circles); and reactor He/Li irradiation with no aqueous phase (closed boxes). Error bars shown are $\pm 5\%$ in CMPO concentration.

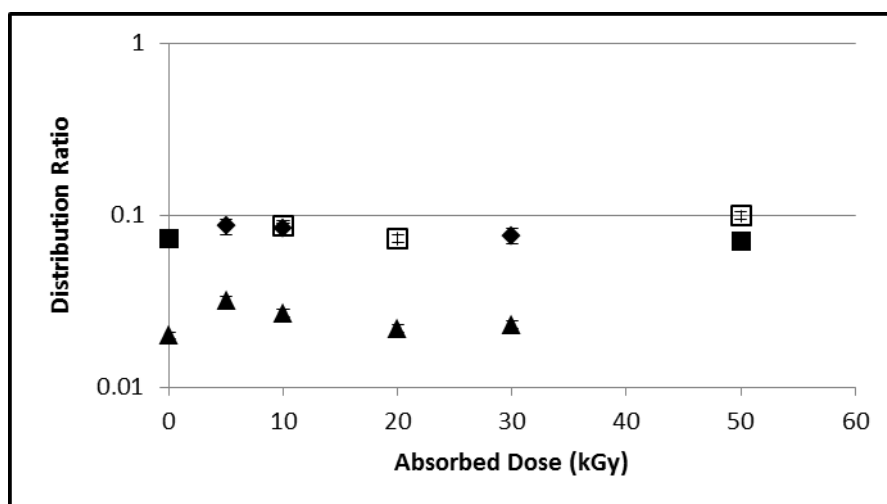


Figure 4. The solvent extraction distribution ratios of Am from 2 M HNO₃, for initially 0.1 M CMPO/dodecane irradiated using the He-ion beam: aerated (closed diamonds); deaerated trial 1 (open boxes); deaerated trial 2 (closed boxes); pre-equilibrated with 3 M HNO₃ (closed triangles). The CMPO concentration was diluted to 0.016 M with fresh dodecane prior to extractions.

In addition, information on solvent extraction and CMPO degradation mechanisms were also measured in this study. Typical solvent extraction data for He ion beam irradiation are shown in Figure 4, demonstrating that minimal dose effects occurred under these conditions, consistent with the loss measurements shown previously. These data, along with other mass spectrometric product identification will be presented.

References:

- Mincher, B.J.; Mezyk, S.P. *Radiochim. Acta* **2009**, 97, 519–534.
- Burns, W.G.; Sims, H.E. *J. Chem. Soc. Faraday Trans.* **1981**, 77, 2803–2813.
- Buxton, G.V.; et. al., *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886.
- LaVerne, J.A. *Radiation Chemical Effects of Heavy Ions*. In: Mozumder, A.; Hatano, Y. **2004**, Marcel Dekker, New York, pp. 403-429.
- Spinks J.W.T.; Woods, R.J. *An Introduction to Radiation Chemistry 3rd Edition*, **1991**, John Wiley and Sons, New York, NY.
- N. Simonzadeh, A.M. Crabtree, G.F. Vandegrift, *Radiolysis and hydrolysis of TRUEX-NPH solvent*. Argonne National Laboratory Report ANL-90/14, July **1992**.
- M.V., Logunov, et. al. *Radiochemistry*, **2006**, 48, 55-61.
- R. Chiarizia, E.P. Horwitz, E.P. *Solvent Extr. Ion Exch.*, **1986**, 4, 677-723.
- B.A., Bucholz, et. al. *Sep. Sci. Technol.*, **1996**, 31, 2231-2243.
- Dhiman, S.; La Verne, J.A. *J. Nuc. Mat.* **2012**, 436, 8-13.
- Pearson, J.; et. al. *J. Radioanal. Nucl. Chem.* **2012**, 292, 719–727.
- Pearson, J.; Jan, O.; Wariner, A.; Miller, G.E.; Nilsson, M. **2013**, *J. Radioanal. Nucl. Chem.* 258, 1401-1409.
- Elias, G.; Groenewold, G.S.; Mincher, B.J.; Mezyk, S.P. *J Chromatography A* **2012**, 1243, 47–52.
- Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S.; Riddle, C.L.; Olson, L.G. **2013**, *Solvent Extr. Ion Exch.* 31, 715-730.

Adsorption Characteristics of Fission Product Elements Constituting High Level Liquid Wastes for Macro-cyclic Resins

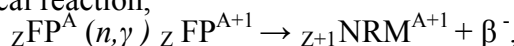
Masaki Ozawa¹, Toshitaka Kaneshiki¹, Thomas Sychra², Masao Nomura¹, Yukiko Ohishi³ and Tatsuya Sakurai³

1] Tokyo Institute of Technology, Research Laboratory for Nuclear Reactors, 2-12-1 Ookayama, Meguro-ku, Tokyo, Japan

2] Slovak University of Technology, Slovak Republic

3] ATOX CO., LTD, Japan

Après ORIENT research program, newly initiated in 2011, will deal with transmutation of radioactive fission product elements to create rare metals / rare earth (RE) elements by (n,γ) reaction with subsequent β⁻ decays in the reactors. We call this reaction as modern alchemical reaction,



target ${}_Z\text{FP}^A$ must be radioactive, and eventually created ${}_{Z+1}\text{NRM}^{A+1}$ should be more valuable, strategic and non or extremely less radioactive than that of the target.

In the context, separation of ${}_Z\text{FP}^A$ from high level liquid wastes (HLLW) for target fabrication, and mutual separation of ${}_Z\text{FP}^A$ and ${}_{Z+1}\text{NRM}^{A+1}$ will be required after the transmutation. Fig.1 shows the resin polymerized in the micro pores of silica carrier, ca. 60μm. Functional crown ether (CE) are Benzo-15-crown-5, Benzo-18-crown-6 and Dibenzo-21-crown-7.

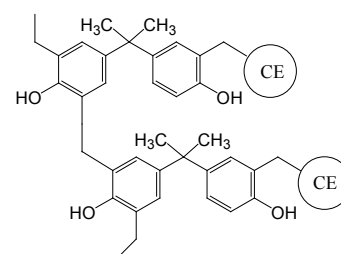


Fig.1 Polyphenol-based Thermosetting Resin

Fig.2 shows the typical adsorption characteristics of the element for Benzo-18-Crown-6 (BC18) -substituted resin in the simulated HLLW / 9M HCl medium. The highest distribution coefficient (K_d) was obtained for bigger divalent cations, Sr²⁺ and Ba²⁺, as expected. Since little affinity and size dependency were observed for mono-valent elements and tri-valent RE elements,

quantitative separation of Ba²⁺ from them are highly expected. As for the adsorption of oxo-anionic MoO₄²⁻ and ReO₄⁻, another mechanism like a co-extraction with the other counter cations might be involved.

The paper will discuss chromatographic column separation behavior of Ba²⁺/Sr²⁺/La³⁺/other elements.

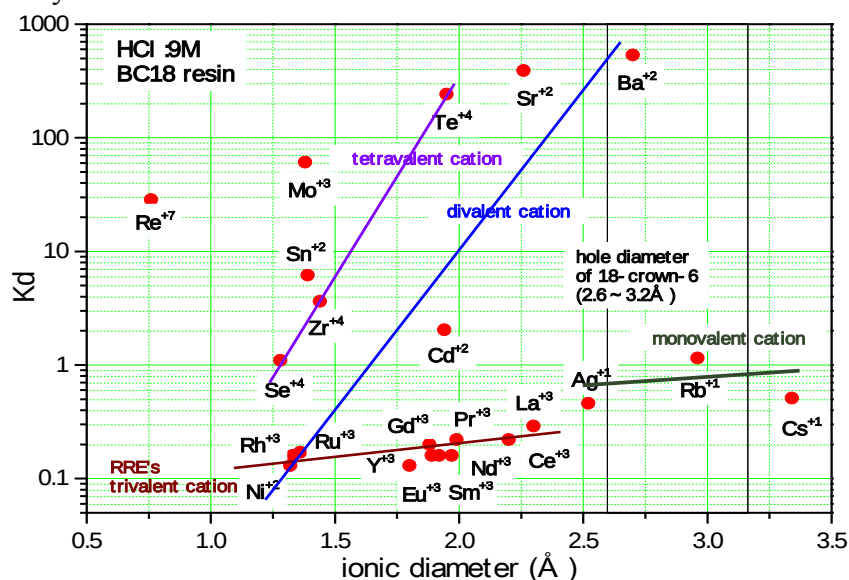


Fig.2 Adsorption of Elements for Benzo-18-Crown-6 (BC18) -substituted Resin; simulated HLLW, 9M HCl medium, ambient temperature

Application related design of liquid-liquid decanters of challenging technical systems

*M. Haneke, Evonik Industries, Marl, Germany; J. Leistner, Evonik Industries,
Darmstadt, Germany; M. Mendorf, Evonik Industries, Marl, Germany*

In chemical industry a reliable design and scale up of the downstream process is essential. In case of liquid-liquid extraction processes many tools are available to design extraction apparatus like columns and mixer-settlers. For all extraction processes it is important to minimize the phase entrainment, particularly to increase the availability and stability for further down streaming, e.g. distillation columns.

Within Evonik the department Process Technology & Engineering designs extraction processes. Therefore a range of tools and standard apparatus are available. Liquid-Liquid decanters are designed along a simplified method, based on sedimentation behaviour in lab trials. For some technical systems this design tool shows several disadvantages, e.g. no direct consideration of coalescence.

In literature¹, several models are described which are based on both, sedimentation and coalescence. The performance of these models has been compared along standard extraction systems (e.g Toluene, Acetone, Water) as well as technical relevant systems with partly wide differences in the design geometry of the resulting decanters.

The speech will demonstrate the effect of technical systems on the design results of different models and how these findings can be used in the industrial daily grind of designing decanters. In the majority of cases in spite of the best way for designing decanters leads inevitably to phase entrainment. Further technologies are shown to minimize entrainment that has been successfully implemented in challenging separation processes, including a strong crud formation.

¹ Henschke, M., 1995: Dimensionierung liegender Flüssig-Flüssig-Abscheider anhand diskontinuierlicher Absetzversuche. VDI-Fortschr.-Ber., Reihe 3, Nr. 379, VDI-Verlag Düsseldorf

Characterization of Liquid-Liquid Mixing Intensities in Static Mixers, Turbulent Pipe Flow and Centrifugal Pumps

Manfred Weber¹

A simple approach is presented to predict droplet diameters for liquid-liquid dispersion in static mixers, turbulent pipe flow and centrifugal pumps. The droplet diameter of the dispersed phase can be estimated from the volume specific mixing intensity. For centrifugal pumps it is shown by a theoretical approach that they can even act in the opposite way and so enhance phase separation.

Introduction

Dispersion of two immiscible liquids in static mixers is well described in literature /1/. But only little data is available about droplet sizes in turbulent pipe flow /2/ and there is even no published data about dispersion in centrifugal pumps.

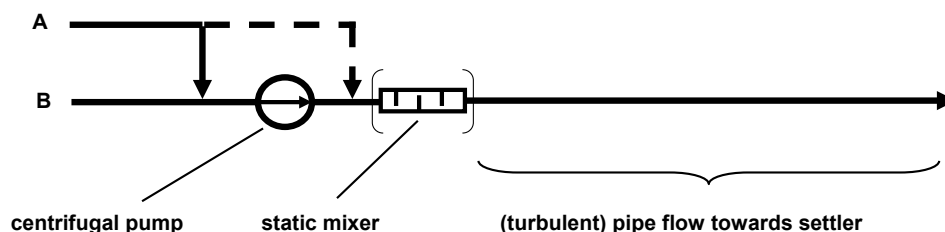


Fig. 1: Arrangement for centrifugal pump, static mixer and turbulent pipe flow

For example, a centrifugal pump can be used for dispersion to even eliminate the static mixer, see Fig. 1. Alternatively the pump can be used for a pre-dispersion prior to the static mixer. In the turbulent pipe flow towards the settler, it is necessary to keep the dispersion at least stable for a subsequent mass transfer. For technical applications it is helpful to have at least *rules of thumb* for predicting mean droplet sizes for these devices.

Mixing intensity in static mixers, turbulent pipe flow and centrifugal pumps

Definition of mixing intensity

Fig. 2 shows the general approach.

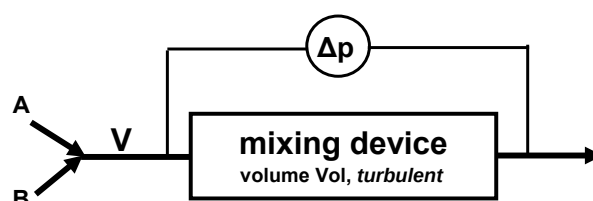


Fig. 2: Definition of mixing intensity

¹ Manfred Weber, INEOS Phenol GmbH, Gladbeck/Germany

Two immiscible liquids A and B are dispersed in a mixing device such as static mixer with a certain volume Vol [m^3]. The total flow is V in [m^3/s]. With the pressure drop Δp in [Pa], the volume specific energy dissipation P / Vol in [W/m^3] can be calculated as being the characteristic *mixing intensity*:

$$P / Vol = \Delta p \cdot V / Vol \quad [W/m^3] .$$

Static mixer

Fig. 3 shows the definition of the mixing volume Vol for a static mixer. In the framework of a capacity increase for a large phenol plant, pilot plant tests for liquid-liquid dispersion were performed using static mixers of sizes DN 25 and DN 50. The criterion $P / Vol = \text{const}$ was successfully used for the scale-up of static mixers in the production unit with sizes between DN 250 and DN 400.

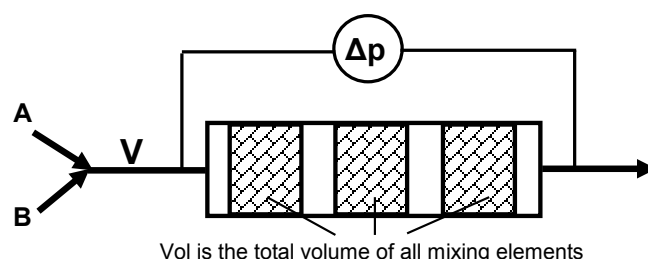


Fig. 3: Defintion of the mixing volume Vol for a static mixer

Fig. 4 shows some calculated droplet diameters d_D for static mixers. $\Delta \rho$ is the density difference between the organic and the aqueous phase and σ is the interfacial tension. From two static mixers, samples were taken and the phase separation was recorded in a tall glass cylinder. From the *standard batch separation profile*, the droplet diameter of the dispersed liquid was calculated. These diameters are marked up as “measured”.

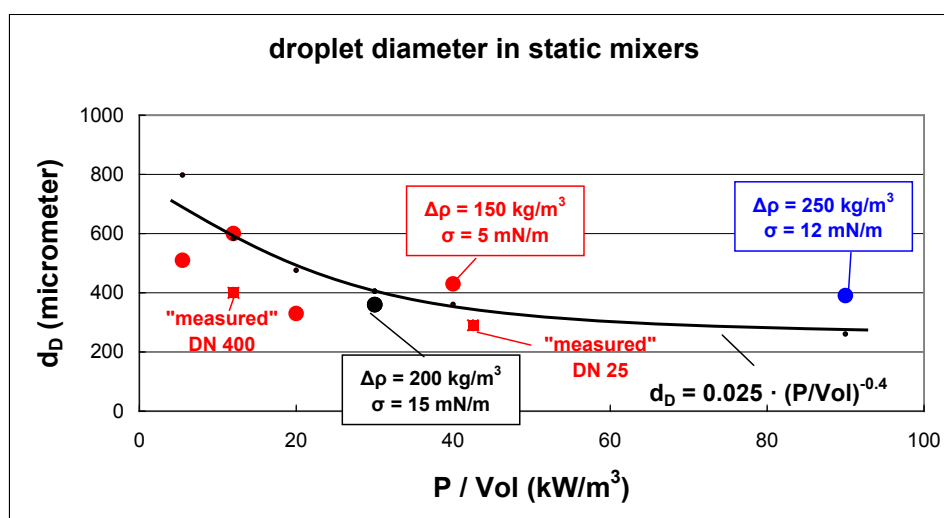


Fig. 4: Droplet diameters in static mixers

With the well-known dependency between the mixing intensity P / Vol and the droplet diameter $d_D \sim (P / \text{Vol})^{-0.4}$, a simple correlation can be evaluated [3]:

$$d_D = 0.025 \cdot (P / \text{Vol})^{-0.4} \quad [\text{m}] .$$

Note that P / Vol is in $[\text{W}/\text{m}^3]$ and d_D in $[\text{m}]$.

Turbulent pipe flow

In the same manner as for static mixers, the mixing intensity for a turbulent pipe flow is calculated from the pressure drop Δp , see Fig. 5. The pressure drop over a pipe length L is

$$\Delta p = \zeta \cdot \rho / 2 \cdot v^2 \cdot L / D$$

with the friction factor ζ of 0.03 and ρ as the mean density of the two-phase flow.

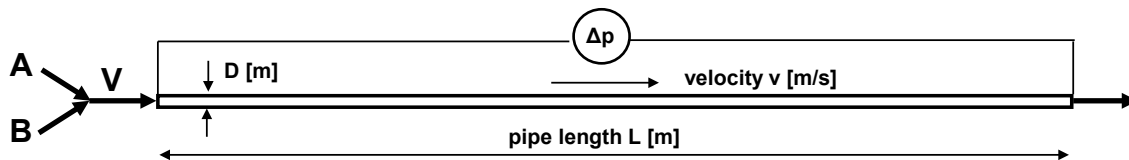


Fig. 5: Turbulent pipe flow

The mixing intensity for the turbulent pipe flow is

$$P / \text{Vol} = \zeta \cdot \rho / 2 \cdot v^3 / D \quad [\text{W}/\text{m}^3] .$$

Fig. 6 shows some calculated droplet diameters for a turbulent pipe flow in a velocity range between 1 and 2 m/s [2].

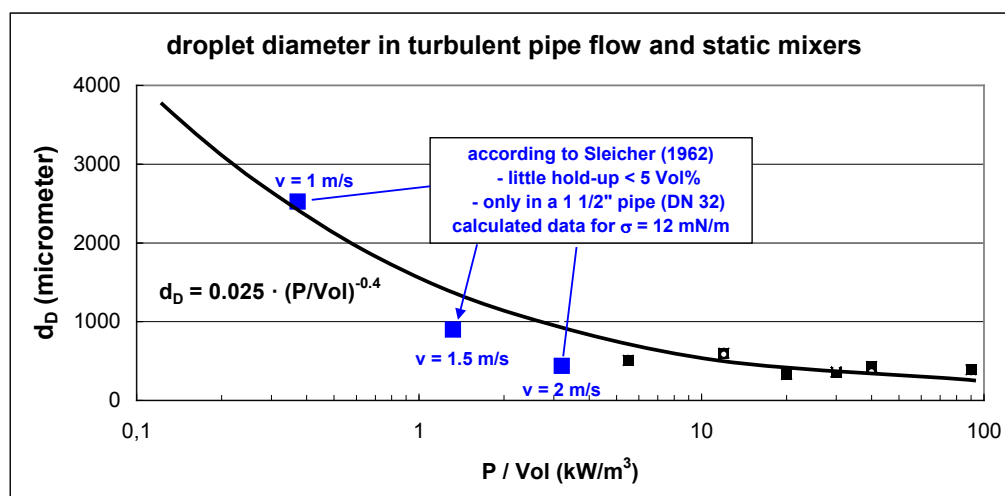


Fig. 6: Droplet size in turbulent pipe flow [2]

Although this seems to fit quite well to the characteristics for the static mixers, great care should be taken since the experiments in /2/ were made in a 1 ½" pipe only. Furthermore, the interfacial tension has a big influence on the calculated droplet diameter.

Centrifugal pumps

More or less no information is available about liquid-liquid dispersion in centrifugal pumps. Experiments indicated that a centrifugal pump can create a liquid-liquid dispersion, but can also act in the opposite way as a coalescing device /4/. This is in accordance with own experience.

At a certain rotation speed [rpm], the centrifugal pump creates a pressure rise Δp_L in the liquid, called the pumping lift, see Fig. 7. This is typically in the range of 75 % of the shaft power. Thus, about 25 % of the power is dissipated because of the highly turbulent flow conditions in the pump. Again, this behaviour can be expressed as a pressure drop Δp , which leads to

$$\Delta p \sim 1/3 \cdot \Delta p_L \quad [\text{Pa}]$$

and to the associated mixing intensity

$$P / \text{Vol} = 1/3 \cdot \Delta p \cdot V / \text{Vol} \quad [\text{W/m}^3] \quad .$$

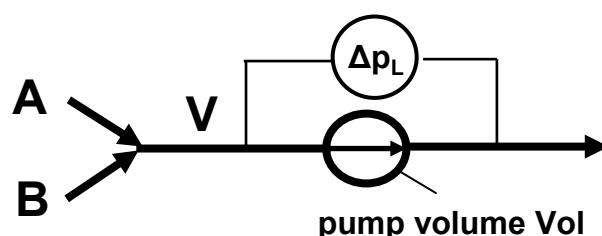


Fig. 7: Centrifugal pump

The question is now whether the flow conditions in the pump will always create a liquid-liquid dispersion, which somehow can be correlated to the mixing intensity, or is it possible that the pump acts more like a coalescer and so would even enhance phase separation of a liquid-liquid dispersion when it enters the pump? This will be checked now in more detail.

A liquid-liquid dispersion (water in oil) is sucked into a frequency driven pump, see Fig. 8. Water droplets with a higher density are dispersed in an organic phase. In the rotating impeller, especially when the liquid-liquid mixture is exiting the impeller, a further dispersion takes place. The resulting droplet diameter again can be correlated with the mixing intensity with $d_D \sim (P / \text{Vol})^{-0.4}$.

In the spiral housing, phase separation can occur due to centrifugal forces. If there is sufficient time for the aqueous droplets to separate to the wall surface, an aqueous phase will be formed and so a liquid-liquid separation can occur.

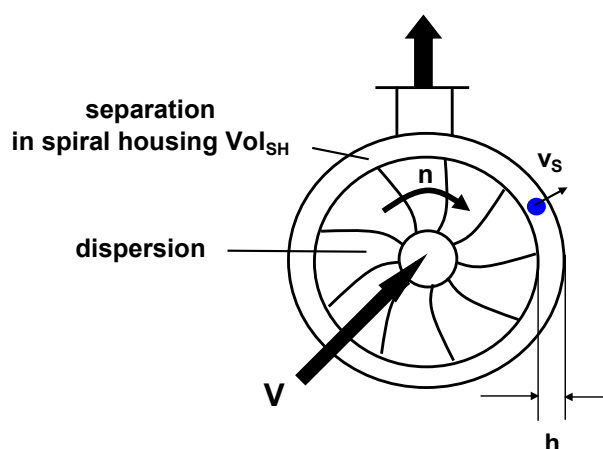


Fig. 8: Model for dispersion versus separation in a centrifugal pump

The separation velocity v_S of a droplet under centrifugal forces is

$$v_S \sim (d_D \cdot z)^{0.5} .$$

The centrifugal acceleration z is correlated to the pump speed according to

$$z \sim n^2 .$$

Furthermore, the following correlations are valid for a centrifugal pump:

$$V \sim n, \Delta p_L \text{ or } \Delta p \sim n^2 \rightarrow P / Vol \sim n^3 \text{ and so } d_D \sim n^{-1.2} .$$

d_D and z can be substituted in the correlation for v_S , what leads to

$$v_S \sim n^{0.4} .$$

The droplet must separate over the distance h , see Fig. 8. This needs a separation time $t_S = h / v_S$, which can now be correlated from the pump speed according to

$$t_S \sim 1 / n^{0.4} \text{ (separation time)} .$$

If t_S is significantly shorter than the mean residence time in the spiral housing, which is $t_{RT} = Vol_{SH} / V$ or

$$t_{RT} \sim 1 / n \text{ (residence time)} ,$$

a phase separation will occur. If t_S is higher than t_{RT} , a phase separation will not occur and the dispersion can even be enhanced.

Fig. 9 shows the result for a technical pump. At lower pump speed, separation is expected. At higher pump speed (> 2300 rpm), a dispersion will occur. This general behaviour of centrifugal pumps correlates to own experience.

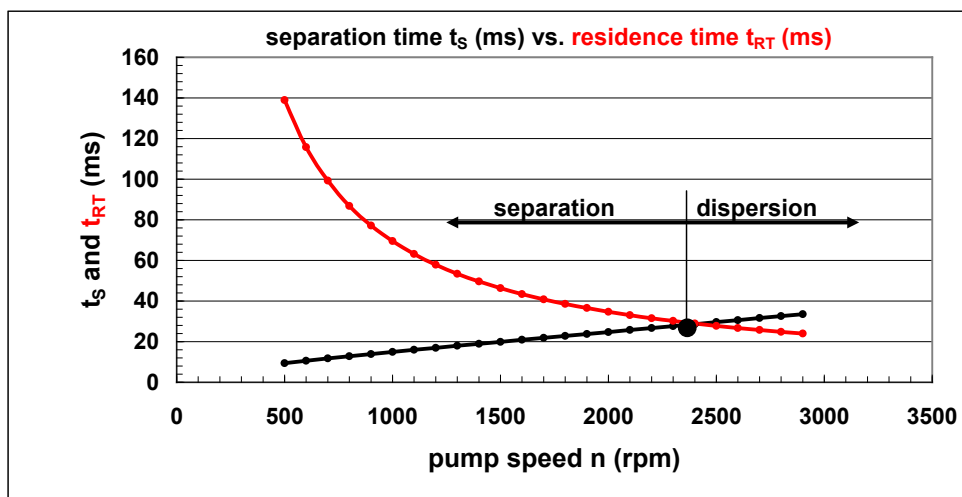


Fig. 9: Separation time vs. residence time in a centrifugal pump (max. $V = 200 \text{ m}^3/\text{h}$, pumping lift 3 bar, w/o with 5 Vol% hold-up, $\Delta\rho = 150 \text{ kg/m}^3$)

At the highest pump speed of 2900 rpm, the mixing intensity P/Vol is around 120 kW/m^3 . The estimated droplet diameter according to

$$d_D = 0.025 \cdot (P / \text{Vol})^{-0.4}$$

gives 230 micrometer. From a *standard batch separation profile* of a sample, a droplet diameter of 200 micrometer can be determined. That is in good correlation to the *rule of thumb*, which was derived from static mixers.

Summary

Based on experience and theoretical investigations, the approach $d_D \sim (P / \text{Vol})^{-0.4}$ is a suitable *rule of thumb* to predict droplet diameters in static mixers, turbulent pipe flow and centrifugal pumps. However, for turbulent pipe flow as well as for centrifugal pumps, experimental data is very limited and more research in this field is worthwhile.

References

- /1/ F. Streiff; *Anwenden statischer Mischer beim In-line-Dispergieren*, Maschinenmarkt, Würzburg, 83 (1977), 17, 289
- /2/ C. A. Sleicher; *Maximum Stable Drop in Turbulent Flow*, A.I.Ch.E. Journal, (1962), No. 4, 471
- /3/ A. Mersmann, H. Großmann; *Dispergieren im flüssigen Zweiphasensystem*, Chem.-Ing.-Tech. 52 (1980), No. 8, 621
- /4/ M. Soika; *Zentrifugalpumpen – mehr als nur Förderaggregate?* TVT Akzente 2007, RWTH Aachen/Germany

Comparison of Model prediction and Industrial Data for a Pulsed Disc and Doughnut Extraction Column

Yong Wang¹, Kathryn A. Mumford¹, Simon Ballestrin², Kathryn H. Smith¹, Teobaldo F. Grabin¹ and Geoff W. Stevens¹

¹Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia.

²Uranium One Australia Pty. Ltd.

Corresponding author email address: gstevens@unimelb.edu.au

Summary

A one dimensional axial dispersion model was used to enable the prediction of the solvent extraction performance of an industrial pulsed disc and doughnut column. Using the industrial column operational parameters, physical properties and column dimensions, the model was able to predict the organic phase outlet concentration, the aqueous phase outlet concentration and overall extraction efficiency to within $\pm 20\%$, $\pm 30\%$ and $\pm 5\%$, respectively.

1. Introduction

Solvent extraction in continuous columns is one of the most important separation processes in chemical engineering. Many different types of agitation and internals have been developed for solvent extraction columns over many years. In particular, the pulsed disc and doughnut column (PDDC) has revealed itself as one of the more interesting counter-current columns for a wide range of solvent extraction applications ^[1] including hydrometallurgical ^[2] and spent nuclear fuel recycling ^[3]. In comparison to mixer-settlers, the design of PDDC is attractive from a safety and economic standpoint, particularly its simplicity of design, less space consumption, and no internal moving parts ^[4].

A number of investigations into the performance of PDDC have been conducted previously. Amongst these Angelov^[5] investigated the pressure drop in a 2.5m height PDDC and Torab studied drop size ^[6], holdup^[7] and mass transfer^[8] in a 74 cm long glass PDDC. Jahya^[1] investigated the effects of operational conditions on the hydrodynamics, axial dispersion coefficient and mass transfer parameters in a 1.0m high PDDC. However, minimal work has been conducted on industrial PDDC columns which range in size from 10 to 30 meters in height.

In this work, a solvent extraction model is used to predict the extraction performance of an industrial scale PDDC utilized for uranium extraction.

2. Uranium Extraction Model

The uranium solvent extraction (USX) model used in this study here based on the material balance equations and axial diffusion model ^[9]. The equations describing

material balances of solute and mass transfer over a differential height, dz is shown in Figure 1 and are presented as follows:

$$E_x \frac{d^2 c_x}{dz^2} - V_x \frac{dc_x}{dz} - k_{ox} a (c_x - c_x^*) = 0 \quad (1)$$

$$E_y \frac{d^2 c_y}{dz^2} + V_y \frac{dc_y}{dz} + k_{ox} a (c_x - c_x^*) = 0 \quad (2)$$

Here E_x and E_y are the axial dispersion coefficients of aqueous phase and organic phase; V_x and V_y are the superficial velocity of aqueous phase and organic phase; k_{ox} is the overall mass transfer coefficient based on the interfacial area between phases per unit tower volume a ; a interfacial area between phases per unit tower volume; c_x is the concentration of solute in aqueous phase; c^* is the concentration in equilibrium with the second phase; z is the distance from feed end.

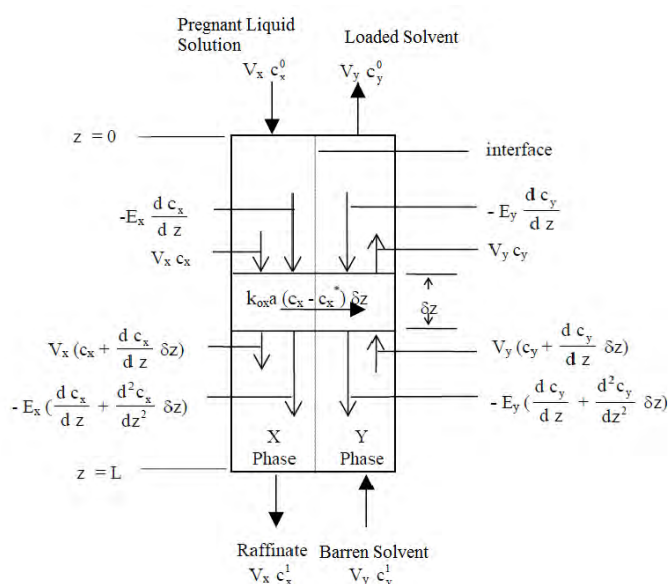


Figure 1. Schematic diagram of continuous contactor with diffusion model

The axial dispersion coefficients, E_x and E_y , are predicted by the empirical correlations which developed from the experimental data using tracer injection technique [2]. The overall mass transfer coefficient, $K_{ox}a$, was calculated from the equation: $K_{ox}a = N_{ox} \cdot V_x / L$. N_{ox} is the number of transfer units and can be determined by the model which developed from pilot plant experimental data [2] and updated by the industrial data. Equilibrium concentration c^* is obtained from the Langmuir extraction equilibrium model.

Assuming negligible axial dispersion of the dispersed phase, equations (1, 2) were solved using excel spread sheet, whose roots are functions of the axial dispersion and mass transfer parameters. Solving these equations, the uranium concentration profile of the aqueous/organic phase and extraction efficiency in the PDDC is obtained.

3. Experimental

The uranium extraction PDDC at Uranium One Australia's Honeymoon mine site (Honeymoon) consists of discs and doughnuts with a diameter of 4.0 m in an

active section of height 18.0 m. The column contacts two immiscible phases, the heavier aqueous phase (Pregnant Liquor Solution (PLS) - aqueous) enters at the top of the column, while the lighter phase (Barren Solvent (BS) - organic) is fed at the bottom of the column. When these immiscible phases come into contact, uranium is transferred from the aqueous to the organic phase by complexation with the extractant. After extraction, the raffinate (aqueous) flows out from the bottom decanter and Loaded Solvent (organic) flows out from the top decanter.

Information regarding the physical properties of the liquid systems has been provided in Table 1.

Table 1. Test system and corresponding physical properties

Physical Property	Phase	Density, ρ (kg/m ³)	Viscosity, μ (Pa.s)	Interfacial tension, γ (mN/m)
Continuous Phase	Organic	822	0.0015	10.4
Dispersed Phase	Aqueous	997.2	0.0019	

In PDDC, a pulsation leg is set in the bottom providing agitation using compressed air thereby aiding mass transport. Amplitude of pulsation is adjusted using air pressure whilst frequency is set by adjusting the rate at which the 4-way valves at the entrance of the pulse leg open and close.

The amplitude and frequency of the pulsation were varied and uranium concentrations in raffinate and loaded solvent were measured via X-ray fluorescence spectrometer (XRF) to understand the impact to PDDC performance and the applicability of the USX model to the industrial system.

4. Results and discussion

4.1 Prediction of the Extraction Performance

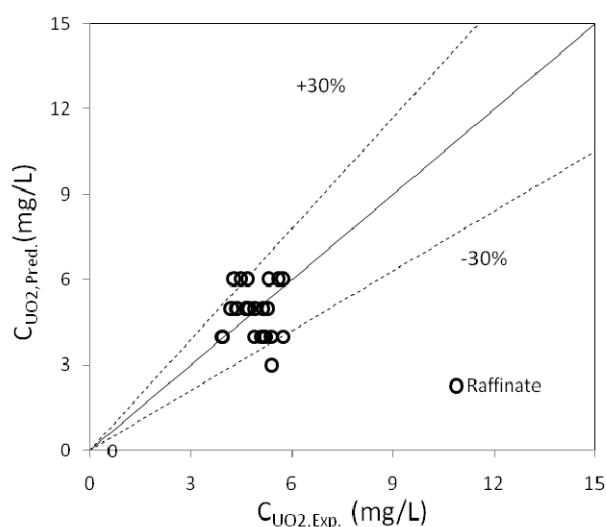


Figure 2. Comparison of experimental data with the USX model developed to predict the uranium concentration in raffinate.

Using the USX model (Eq 1,2), the outlet concentrations of the aqueous and organic phases and the overall extraction efficiency of the extraction column can be predicted from the inlet concentration of the aqueous/organic phase and column operational parameters.

As shown in Figure 2, the actual uranium concentration in raffinate ($[U_3O_8]_{Raff}$) is about 4-6 mg/L whilst the predicted $[U_3O_8]_{Raff}$ by USX model is in the range of 9-42 mg/L. The overall deviation between the plant data and model prediction is less than $\pm 30\%$.

A comparison of the predicted and experimental results for the outlet uranium concentration in Loaded Solvent ($[U_3O_8]_{Loaded}$) is shown in Figure 3. The experimental $[U_3O_8]_{Loaded}$ in PDDC is in the range of 600 -900mg/L, and the predicted $[U_3O_8]_{Loaded}$ by USX model is in the range of 600 -850mg/L. The predicted uranium concentration in the Loaded Solvent compares well to the experimental data (Deviation $< \pm 20\%$).

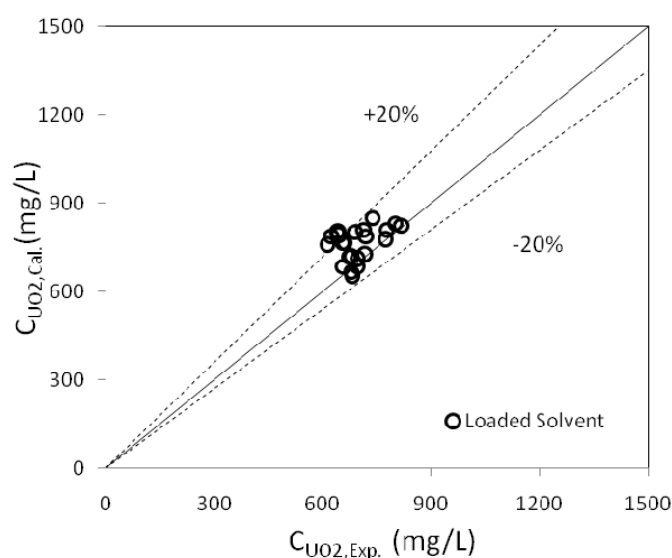


Figure 3. Comparison of experimental data with the USX model developed to predict the uranium concentration in loaded solvent.

The overall uranium extraction efficiency is a very important index of uranium extraction process. It can be calculated from the equation below:

$$E \% = \left(1 - \frac{C_{x,Raff}}{C_{x,PLS}} \right) \times 100\% \quad (3)$$

Here E is the overall uranium extraction efficiency, $C_{x,Raff}$ is the uranium concentration in the raffinate, and $C_{x,PLS}$ is the uranium concentration in the PLS.

The results of calculated uranium extraction efficiency based on equation (3) are shown in Figure 4. It can be seen that the experimental efficiency in PDDC is in the range of 85-91%, and the predicted efficiency is in the range of 85-90%. The USX model can provide a good prediction for the uranium extraction efficiency with the deviation being less than $\pm 5\%$.

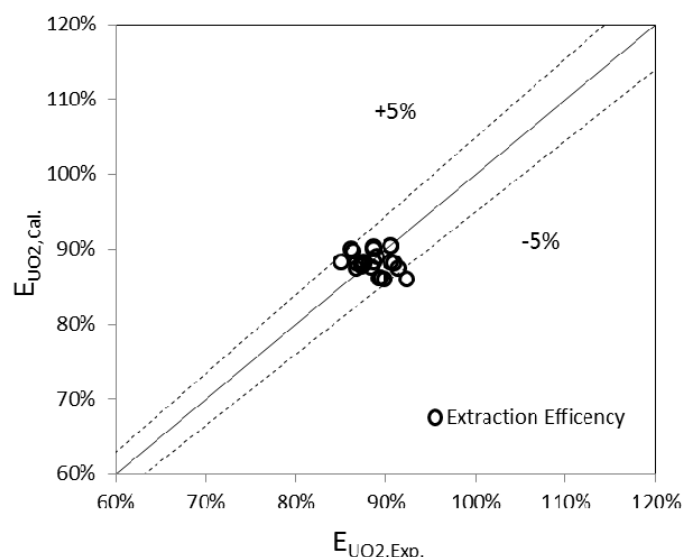


Figure 4. Comparison of experimental data with the USX model developed to predict the extraction efficiency.

5. Conclusions

Based on the mass balance and axial dispersion, a USX model was developed and can be used to predict the uranium extraction performance of the disc and doughnut pulsed columns at Honeymoon. The results show that the outlet uranium concentration in the aqueous and organic phases and the overall extraction efficiency can be predicted well, and the prediction deviation is about $\pm 30\%$, $\pm 20\%$ and $\pm 5\%$. Therefore, the USX model can be used in the uranium extraction simulation, which can ensure the PDDC is working under the optimised conditions.

Acknowledgement

The authors would like to acknowledge the funding provided by Australian Research Council (ARC) for this project and Uranium One Australia for access to plant resources which provided the basis for this study. Also, thank you to the Particulate Fluids Processing Centre (PFPC), a Special Research Centre of the Australian Research Council for the resource provided for this project.

Literature

- [1] A.B.Jahya, G.W.Stevens, H.R.C.Pratt, Pulsed disc and doughnut column performance, *Solv.Ex.Ion Exch.* **2009**, 27(1): 63-82
- [2] A.B.Jahya, Ph.D. thesis, The University of Melbourne, Australia, **2002**.
- [3] G.Angelov, C. Gourdon, A. Line, Simulation of flow hydrodynamics in a pulsed solvent extraction column under turbulent regimes. *Chem. Eng. J.*, **1998**, 71, 1-9.
- [4] R.L.Movsowitz, R.Kleinberger, E.M.Buchalter, Application of Bateman pulse columns for uranium solvent extraction. Bateman Projects Ltd., Israel **1997**.

- [5] G.Angelov, C.Gourdon, Pressure drop in pulsed extraction columns with internals of discs and doughnuts, **2012**, 90,877-883
- [6] M.Torab-Mostaedi, J.Safdari, F.Torabi-Hokmabadi. Prediction of mean drop size in pulsed packed extraction columns, *Iran.J.Chem.Eng.*, **2011**, 8 (4), 3-10
- [7] M.Torab-Mostaedi, H.Jalivand, M.Outokesh. Dispersed phase holdup in a pulsed disc and doughnut extraction column, *Braz.J.Chem.Eng.*, **2011**, 28 (2), 313-323
- [8] M.Torab-Mostaedi, A.Ghaemi, M.Asadollahzadeh, et al. Mass transfer performance in pulsed disc and doughnut extraction columns, *Braz.J.Chem.Eng.*, **2011**, 28(3), 447-456.
- [9] C.A.Sleicher, Axial mixing and extraction efficiency, *AIChE J.* **1959**,5(2),145-149

OSN (Organic Solvent Nanofiltration) – A New Technology for Hybrid Processes with Solvent Extraction

Andrew Boam, Evonik Membrane Extraction Technology Ltd., London, United Kingdom; Axel Kobus, Evonik Industries AG, Marl, Germany; Christian Schnitzer, Evonik Membrane Extraction Technology Ltd., London, United Kingdom; Ines Rocha, Evonik Membrane Extraction Technology Ltd., London, United Kingdom; Velichka Koleva, Evonik Membrane Extraction Technology Ltd., London, United Kingdom; Yuri Bouwhuis, Evonik Membrane Extraction Technology Ltd., London, United Kingdom

Organic solvent nanofiltration (OSN) is an emerging field of membrane technology. To date, the vast majority of liquid-phase industrial membrane separations have been performed in aqueous environments. However, innovations in the last decade have led to a number of membranes being developed and commercialised that are capable of performing molecular separations in a broad range of organic solvents – from polar solvents such as methanol, through polar aprotic solvents such as N,N-dimethylformamide, to apolar solvents such as hexane or toluene. In particular these membranes are designed to operate as nanofiltration membranes, meaning that they are capable of discriminating between species in the 200-1,000 g.mol⁻¹ molecular weight range, and are known as OSN membranes.

Membranes are capable of providing unique separation properties based on their mass transport properties. However, in the majority of cases combining membranes with a more conventional technique, such as solvent extraction, provides a better process solution than either individual technology. For instance, OSN membranes can be used instead of distillation/evaporation to recover solute(s) from the organic solvent phase of an aqueous-organic extraction process. By applying the OSN membrane thermal stress on the solute species is much reduced, and the solvent can be recycled at near-ambient conditions with minimal need for thermal processes.

This paper will provide insight into the use and application of OSN-solvent extraction hybrid process techniques by Evonik MET through case studies and application development – these will include examples in the natural extract field.

Stacked Multi Channel Reactor for Solvent Extraction Process

*Akira Matsuoka^{*1}, Koji Noishiki*

Summary

In this work, the application of a new type micro-channel reactor, called the Stacked Multi Channel Reactor (SMCR), to the solvent extraction process was investigated. The SMCR enables increase of throughput by using a concept of numbering up of the channel. Extraction experiments of phenol in dodecane to water were performed to compare the mass transfer performance of SMCR and mixer-settler. The SMCR achieved equilibrium extraction in ten to one hundred times shorter residence time than that of a conventional mixer-settler type. The organic and aqueous phases were immediately separated after they were flowed out from the SMCR. The advantages regarding mass transfer and phase separation enable a smaller plot area and lower liquid hold-ups in the continuous multi-stage solvent extraction process.

1. Introduction

The micro-channel reactor has attracted attention in recent years due to its high thermal and mass transfer performances arising from operation in a small space. For practical use of the micro-channel in industrial scale operation, the numbering up of channel is necessary to increase throughput. Conventional micro-channel reactors have a Y-shaped or T-shaped junction for fluids mixing. These structures are not suitable to arrange numerous channels efficiently in an apparatus. Consequently, the number of channels per unit volume of an apparatus is low and the throughput is limited. So the application is also limited to low throughput production processes, such as the production of high value added products. A new type of micro-channel reactor is under development, called the Stacked Multi Channel Reactor (SMCR) which is able to increase throughput by using a concept of numbering up of the channel. **Fig.1** shows the schematics of the stacked multi channel reactor. The SMCR consists of plates which have multi-channels on both sides and a through-hole which connects the channels on both sides of the plate. This structure enables efficient arrangement of numerous channels efficiently. Furthermore the number of channels per unit volume of an apparatus can be significantly increased by stacking plates. Each fluid is introduced from each header and distributed to the multi-channels. The SMCR can

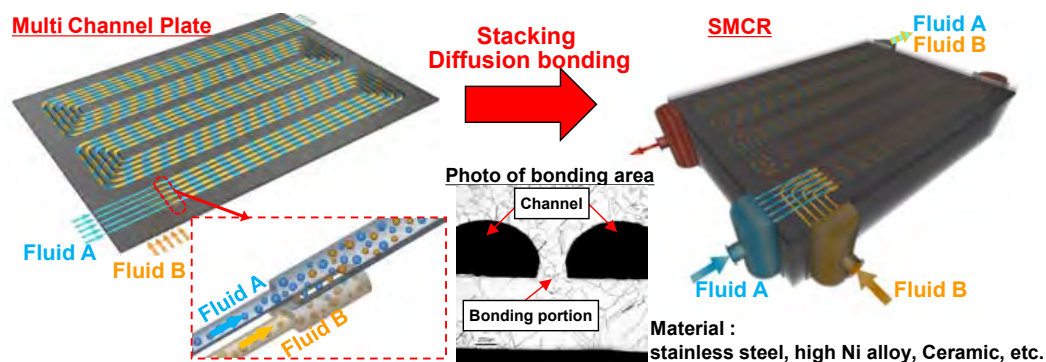


Fig.1 Schematic of stacked multi channel reactor (SMCR)

^{*1} Akira Matsuoka, Kobe Steel, LTD., matsuoka.akira@kobelco.com

be made from various metals and ceramic. By using SMCR, the technology of micro channel can be applied to high throughput processes such as bulk chemical process. In this work, the application of SMCR to the solvent extraction process was investigated.

2. Experimental setup

The experimental apparatus used to investigate the characteristics of mass transfer and phase separation of SMCR for solvent extraction is shown in **Fig.2**. Dodecane with 0.1 wt% phenol and water were used as the organic phase and the aqueous phase, respectively, and the extraction of phenol in dodecane to water was studied. SMCR testing devices which have channels of semicircular cross section and stainless steel circular tubes were used as testing channels. The SMCR testing device consisted of a stainless steel plate fabricated with channels and a cover plate. The circular tube was connected to a Swagelok T-joint of 2.4mm inner diameter as a junction of the two liquids. The transparent testing channels were used to visualize the flow pattern. Double plunger pumps were used to introduce the liquids to testing channels at the same volume flow rates constantly.

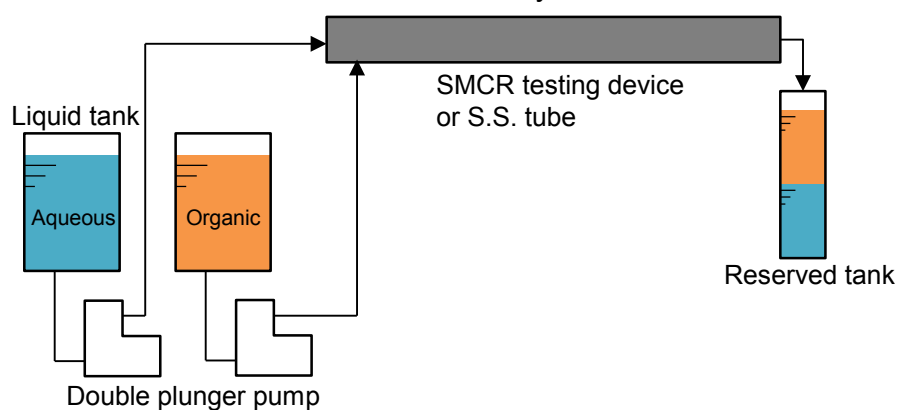


Fig.2 Outline of experimental setup

3. Result and Discussion

3.1 Basic characteristics for solvent extraction

3.1.1 Flow characteristics

Visualization experiments were performed in a circular glass tube (1mm in diameter) and a transparent SMCR testing channel (1mm in radius) which consisted of a stainless steel channel plate and a glass plate. **Fig.3** shows the typical flow patterns at a total flow rate of 4 ml/min. Dodecane and water arrange alternately in the direction of flow direction. This flow pattern is called Taylor flow or slug flow generated when the interfacial tension between the organic and aqueous phase is dominant over viscous force, inertia force and gravity force. The slug flow is also generated in the SMCR testing channel as in the circular channel. The slug flow forms a thin liquid film of continuous phase surrounding the dispersed phase [1,2]. The organic phase is the dispersed phase if the inner wall of the channel is hydrophilic. In this experiment, dodecane is the dispersed phase because the channel materials, glass and stainless steel, are hydrophilic.

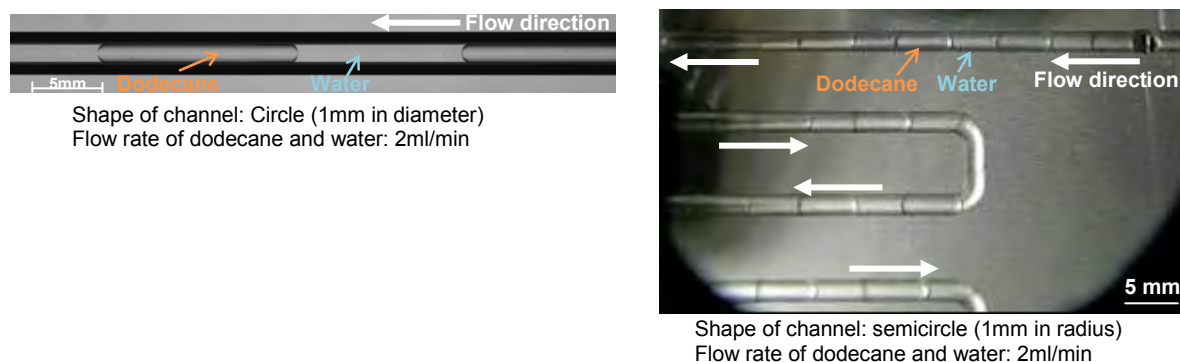


Fig.3 Photographs of two phase flow pattern of dodecane and water in SMCR and glass tube

3.1.2 Mass transfer characteristics

Extraction experiments were carried out to evaluate the mass transfer performance of SMCR. The changing of the phenol concentration in dodecane against residence time was obtained by changing the channel length at a given constant flow rate. The concentrations of phenol in dodecane change according to the following equation:

where K_a is the overall volumetric mass transfer coefficient, C and C^* are phenol concentration in dodecane at a given residence time and extraction equilibrium, respectively. K_a was obtained from the slope of measurement values of phenol concentration for three or four different residence times against residence time. **Fig.4** shows the effect of Reynolds number on K_a for various channels of different shapes and diameters. K_a increases with increasing Reynolds number. This effect is attributed to the convection enhancement by the increment of recirculation flow in the slugs. K_a increases with decreasing hydraulic diameter of channels, D_h regardless of the channel shape. Hydraulic diameter of channels, D_h , are defined

where A is the cross sectional area and L is the wetted perimeter of the cross-section. Decreasing hydraulic diameter causes increasing specific interfacial area and

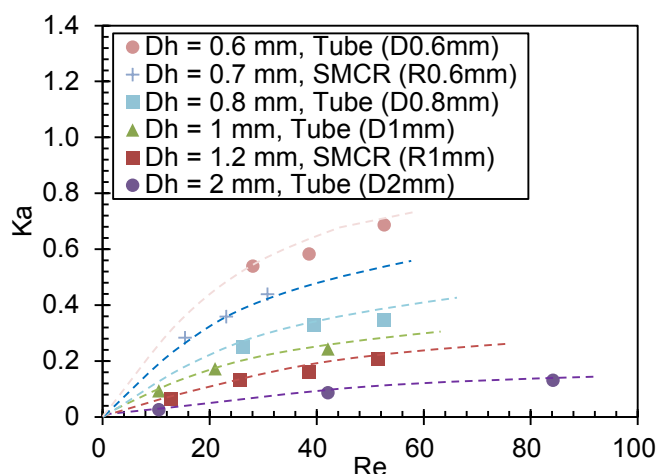


Fig.4 Effect of Reynolds number on overall volumetric mass transfer coefficient

strength of recirculation flow in the slug. Consequently, the mass transfer is enhanced.

3.2 Practical use of micro-channel technology

3.2.1 High throughput by numbering up

To validate the theory that the throughput can be increased by numbering up of channels for SMCR, extraction experiments were carried out using SMCR testing device with different channel number (1 to 25 channels). Experiments using an agitation vessel, in which dodecane with phenol and water, 100ml of each, were poured into a 200ml glass beaker and the water layer was agitated at a given rpm using a magnetic stirrer, were also performed to compare the extraction performances between conventional equipment and SMCR. **Fig.5** shows the change in the equilibrium extraction ratio (=extraction rate, E (%) / equilibrium extraction rate, E^* (%)) against residence time. For the agitation vessel, increased revolution of the agitation shortens the time required for equilibrium extraction; however, revolutions higher than 400rpm resulted in a dispersion of the organic phase in aqueous phase, making separation difficult. It took approximately 100 minutes for extraction using the agitation vessel to reach an equilibrium extraction. SMCR achieved the equilibrium extraction in 1 minute and gave the same extraction performances for different channel numbers. SMCR can decrease the operation time of extraction to 1/100 compared with conventional equipment and increase throughput by increasing the number of channels.

3.2.2 Phase separation characteristics

Experiments for observations of phase separation after extraction operations were performed to compare the phase separation characteristics with SMCR and agitation vessel. Water was used as the aqueous phase, and dodecane with surfactant was used as the organic phase. The surfactant was added to enhance the generation of emulsion between aqueous and organic phase. In the experiment with the agitation

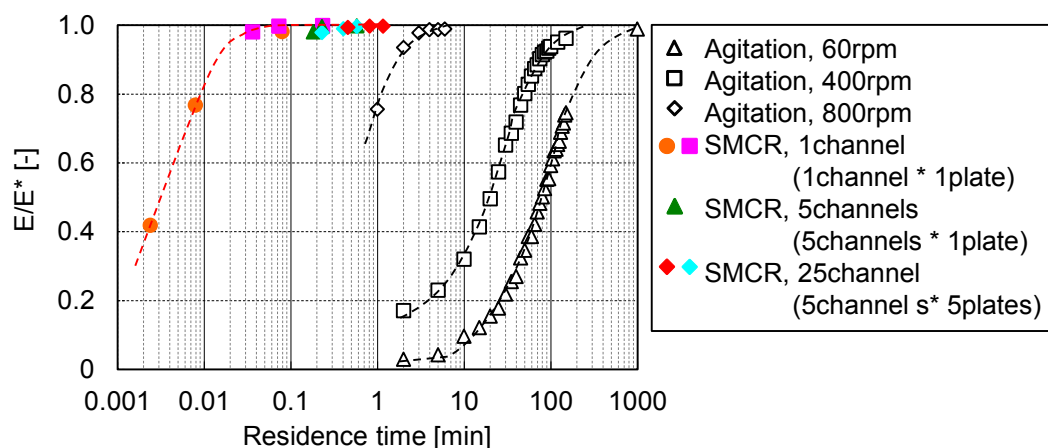


Fig.5 Change in the equilibrium extraction ratio against residence time

vessel, the same volumes of aqueous phase and organic phase were poured into a glass beaker and agitated by turbine at 400rpm for 30 seconds. After the agitation was stopped, the phase condition was observed. For SMCR, the aqueous phase and organic phase were introduced at the same flow rate to SMCR testing device. The Aqueous phase and organic phase were collected at the outlet of SMCR testing device and the phase condition was observed. **Fig. 6** shows photographs of phase separation conditions. In the case of the agitation vessel, the emulsion phase is generated by agitation and the emulsion phase does not disappear within 60 minutes after stopping agitation. On the other hand, the aqueous and organic phases flowing through the SMCR testing device separate completely at the outlet. By using SMCR, the residence time for phase separation is not necessary and continuous multi-stage extraction process can be constructed without a large settler.

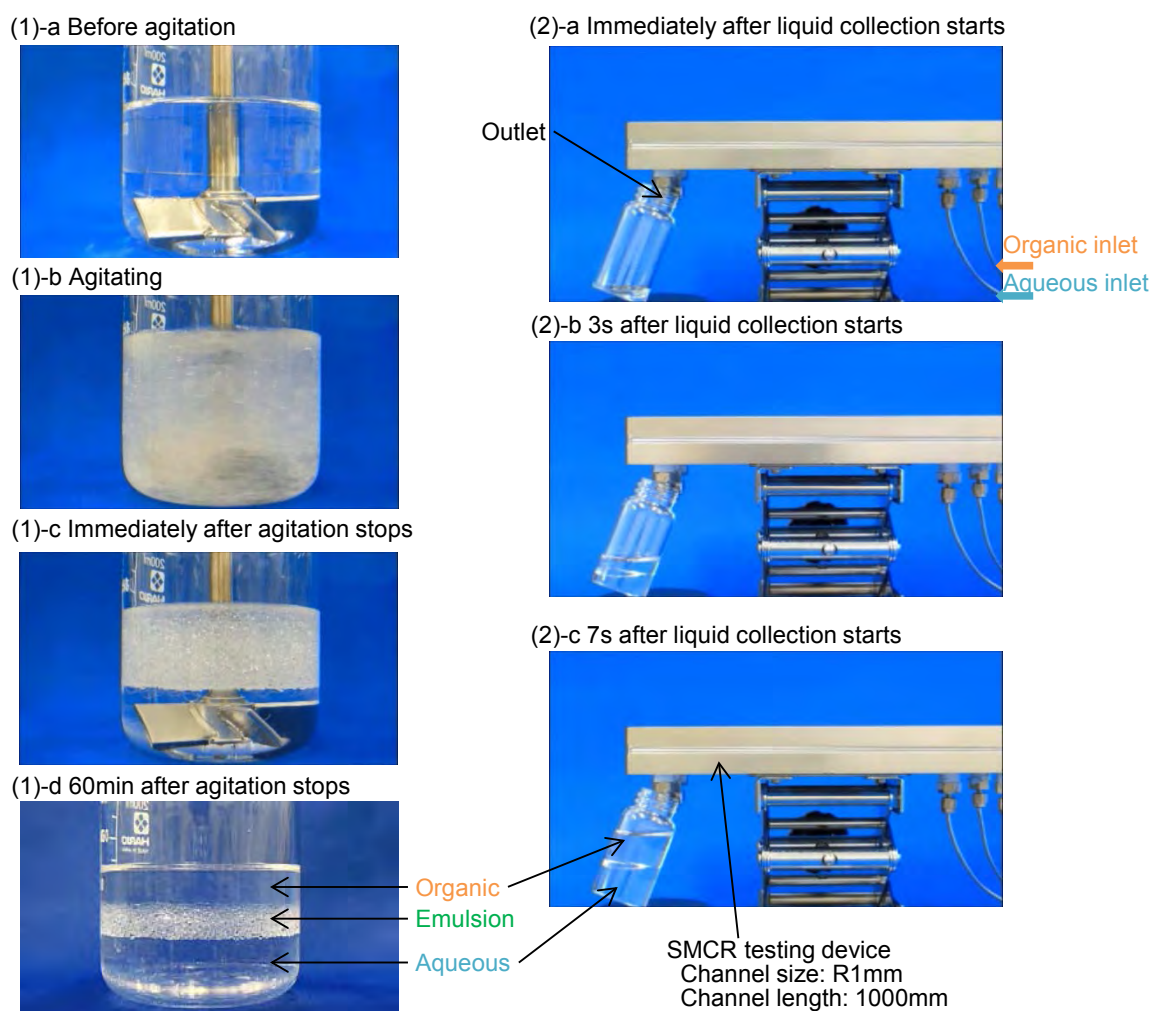


Fig.6 Photographs of phase separation conditions

4. Conclusion

Application of the Stacked Multi-Channel Reactor (SMCR) to the solvent extraction process was investigated. In the channel of the SMCR which has a semi-circular shape in cross-section, the aqueous and organic phases generated slug flow. At the slug flow, high specific interfacial area and recirculation flow give a ten to hundred

times higher mass transfer rate than that of the agitation vessel. It is confirmed that the increasing throughput can be achieved by numbering up the channel. And also, SMCR needs low residence time for phase separation at the outlet. The advantages for mass transfer and phase separation enable a smaller plot area and lower liquid hold-ups in continuous multi-stage solvent extraction process.

References

- [1] Aras Ghaini, Axel Mescher, David W. Agar, Hydrodynamic studies of liquid-liquid slug flows in circular microchannels, *Chem. Eng. Sci.* 66 (2011) 1168-1178.
- [2] Raghvendra Gupta, Sharon S.Y. Leung, Rogerio Manica, David F. Fletcher, Brian S. Haynes, Hydrodynamics of liquid-liquid Taylor flow in microchannels, *Chem. Eng. Sci.* 92 (2013) 180-189.

Troubleshooting at Honeymoon – from problems to success

*Hani Aharon¹, Baruch Grinbaum^{*2}*

ABSTRACT

As in many cases, the technology for the new uranium solvent extraction (SX) plant relied on ideas that were based on theoretical principals. These ideas were initially tested in the laboratory and subsequently scaled up to a pilot plant. Even though the idea itself may be a very good one it is expected that unforeseen parameters will be encountered during full scale plant operation. These parameters hold the potential of upsetting the plant. The goal became to monitor, understand and solve these problems online.

The parameters that needed to be controlled were:

Too high U_3O_8 values in Raffinate and Extraction efficiency below 90%

Organic Entrainment in the Raffinate

Flooding or phase inversion in the column

Crud formation in the Stripping settler

Organic:Aqueous (O:A) Phase Ratio in mixers being too high or low (Mixers not Aqueous continuous)

All the problems were satisfactorily solved and the plan proceed very well.

This article examines the problems, review the causes and the reasons for them and then summarizes how we solved them.

Introduction

The Honeymoon plant for production of uranium was significantly different from other uranium plants. Its high chloride and iron feed concentrations prevented this operation from using the regular solvent of Alamine 336 in aliphatic diluent. Thus, a new solvent was composed [1] and tested in a laboratory as well as in a pilot plant [2], with very good results. Nevertheless past experience indicates that scale up bares the potential of introducing parameters that were not encountered during piloting. These, in turn, can present problems, that may affect the plant's operation. The objective was to monitor, understand and solve these problems online.

The major challenge is to understand which parameter caused the main problems, e.g. elevation of impurities levels within the loaded solvent (LS). This problem can stem from coincidental decrease of solvent flow rate; and may also

¹ Hani Aharon, Tenova Bateman Technologies, Hani.Aharon@tenova.com

^{*2} Baruch Grinbaum, Tenova Bateman Technologies, Baruch.grinbaum@tenova.com

be facilitated by the utilization of incorrect solvent composition. Solving of such a problem calls for a two ways approach, e.g., on the one hand, the solvent composition should be evaluated by laboratory loading tests, and on the other hand the flow rate should be monitored closely.

Once this major hindrance is overcome, other relatively easier process problems may be addressed. This paper elucidates the main problems that were encountered and solved in the Honeymoon plant operation.

Problems & Results

Extraction

The process objective was to extract uranium from a pregnant leach solution (PLS) so that the raffinate U_3O_8 concentration would not exceed 5 ppm. Initially the process performances were on specification. However, deterioration in performance was observed after several weeks of operation where uranium levels in the raffinate have been increased above permissible levels and thus the extraction efficiency was reduced below 90%

A number of potential causes were evaluated. These included: solvent composition; extraction pH; Organic:Aqueous (O:A) phase ratio; operation temperature and pulsation intensity.

Solvent Composition

A mixture of four different substances composed this unique solvent: DEHPA is the uranium extractant [1]; Alamine 336 depresses iron extraction[1]; TBP utilized as a modifier to prevent a third phase formation [1]; and aliphatic oil is used as a diluent.

Based of the pilot plant [2], the solvent's composition was set: 2% Alamine 336, 2% DEHPA and 3% TBP in Shellsol 2046 as diluent. The O:A phase ration was set as 0.05. As described above initial results were most satisfactory. Nevertheless, a couple of weeks after start up, due to reduction in uranium feed concentration, the extraction capacity of the solvent was higher than the amount of uranium in the PLS. This resulted in significant co-extraction of iron, and production of a contaminated loaded solvent. This problem was solved by 50% reduction of the active ingredient in the solvent. Thus, the new concentrations were 1% Alamine 336, 1% DEHPA and 1.5% TBP.

This amendment to the solvent proved itself, until the uranium levels in the PLS rose again. Now the new solvent was ill-equipped to extract the uranium, and elevated uranium concentration in the raffinate ensued.

The solution was to fabricate a solvent containing of 1% Alamine 336 and 1.5% TBP. As DEHPA is the U extractant, its concentration will be 1% initially and would gradually increase over time to a maximum of 2% [2].

The use of this procedure yielded satisfactory results, and thus the following protocol was set:

A barren solvent (BS) sample was removed from the process and evaluated periodically. These tests composed of both loading experiments (by contacting it with the PLS) as well as analytical analysis. The results were used to determine the required increase in DEHPA concentration as described. TBP was added in cases where a third phase started to materialize.

Extraction pH

Uranium extraction is highly dependent on the pH. For that purpose it is vital to ensure pH 1.9-2.2 in the PLS. In the extraction stage the BS returning from the stripping stage, and the PLS are introduced to the Bateman Pulsed Column (BPC) in a counter current mode. Due to the fact that the stripping is being carried out using soda ash (Na_2CO_3) the BS has a basic pH. It is essential to ensure sufficient concentration of acid in the PLS in order to keep the extraction pH within the expectable parameters. In case the pH is lower than specified, either Na_2CO_3 amount in the Strip Solution is reduced or additional acid is inserted to the PLS.

Only after the solvent component and the pH control were successfully solved, we could treat the less crucial operations problems, as follows:

O:A phase ratio

Naturally, O:A ratio will directly influence the amount of uranium extracted. In cases the O:A ratio is too low, only part of the uranium will be extracted the residual amount will leave the process in the raffinate. The solution is to increase the O:A ratio by increasing the solvent flow as much as can be allowed and if the flow rate is still too high then decrease the PLS flow rate. It is vital to ensure that the barren solvent tanks do not run empty

The Effect of Temperature

It is assumed that the temperature of the PLS would have a significant influence on the extraction. At lower temperatures, the rate of extraction is lower. Moreover, low temperature increases the viscosity of the solvent in the column, which leads to formation of emulsion. Emulsion in turn causes organic losses to the raffinate and an aqueous entrainment in the loaded solvent overflow of the column.

Initial concern was that during ambient temperatures drop, a flux reduction will be necessary. Such a reduction will undermine the desired plant capacity. However, it was found during operation that extraction efficiency and capacity were not affected by ambient temperature changes. Evaluation of the occasional increase in organic entrainment in the raffinate stream is ongoing. The reason may be related to increased phase separation times due to lower temperature.

It is quite likely that the relatively low design flux and high residence time are both ample enough to off-set the influence of temperature on extraction performance.

Pulsation Intensity

If the pulsation intensity applied to the column is too low then the contact time and the hold-up of the column will be too low (<10% for both) as well, because the mixing is not good enough. The hold-up should be increased by increasing the pulsation pressure. This must be done gradually and in small steps (3-5 kPag), to avoid overshoot. If this does not help, because the pulsation frequency mechanism is at the maximum flux reduction has to be performed in order to give more time to achieve the phase dispersion in the plant.

As can be seen from the above description, when the problems are mixing of the phases, a step by step solution is required. This is done in order to achieve the correct aqueous droplet dispersion in a continuous organic phase.

Scrubbing

After the scrubbing stage, it was observed that, the purified LS had high concentration of iron, indicating poor scrubbing. Impurity levels are influenced by two factors: the composition of the BS, and the composition of the scrub solution. As the composition of the BS was optimized in the extraction stage, this was not adjusted further, leaving the optimization of the scrub solution as the only factor to be handled. It was known that sodium metabisulfite (SMBS) in lower pH values is a good scrubbing agent. Nevertheless, elevated amount of this substance will scrub out uranium from the LS. Therefore, the exact amount that is introduced into the scrubbing stage needs to be optimized.

Stripping

As previously discussed the stripping agent is Na_2CO_3 . The exact amount of soda ash needed for this stage is determined stoichiometrically by the Uranium concentration in the purified solvent. In order to ensure on spec product pH profile has to be monitored and corrected. . Thus, changes to pH values were performed by controlling the soda ash flow rate e.g., too acidic solution resulted in increment of the flow rate.

Raffinate Organic Entrainment

Organic losses through entrainment are, for the large part, govern by couple of factors:

- Lower decanters interface level, where the set point is 65-55% of the decanter height. In cases the interface level is dropped to 20% or below organic losses are expected.
- Pulsation intensity – reduction of this intensity reduces the breakeage of the organic droplets, and thus reduces the entrainment. Notwithstanding that, such a reduction has negative effect on the mass transfer in the extraction process as described above.
- Flux trough the column – as a rule the higher the flux the higher the entrainment. However reduction of flux will hinder uranium production.

Crud Formation

Crud is one of the most challenging problems with any SX operation. Crud may be formed in the contactor and will be accumulated in the interface. If this is not resolved, constant removal of crud has to be done. For the current operation there are two places where such a problem can occur. The first is the extraction column where elevation of the pH in the PLS above 1.9-2.2 will result in crud formation. This additionally emphasizes the need to closely monitor this pH levels. Nevertheless, periodically checks to see if crud has formed are in order. In cases that crud did form it has to be drained out. The second contactor that may be susceptible to crud formation is the stripping settler. As the pH is much higher in the settler crud may be formed due to the presence of precipitates, namely iron. This problem is normally resolved by correct scrubbing procedure. In addition to precipitants, air bubbles in the mixer tank may facilitate crud formation. Prevention of air suction through the pump mixer will solve this problem. This is accomplished by good level control on the organic feed to the mixer.

Conclusions

The Honeymoon uranium operation uses a novel approach for the production of U_3O_8 . This is a challenging process, and couple of hiccups presented themselves during plant startup. These obstacles have been tackled in a two way approach, where several issues were dealt with in parallel. This approach proved successful and all operation problems have been resolved. After startup, a troubleshooting guide was formulated [3]. As a result and all production was on spec, where the target of selectively of uranium separation from the PLS has been met.

References

1. Lancaster, B., "Honeymoon Project" (confidential report)
2. Grinbaum B, Coleman E., Buchalter, E., "Pilot test work at the Uranium One Honeymoon site", Ref. No. 13182/1 (internal confidential report),
3. Aharon, H., "Honeymoon Project SX – Trouble shooting Guide", Ref. No. 13224 (internal confidential report)

Mooresboro Zinc Project: First Solvent Extraction Plant in the World to Produce Zinc Entirely from Recycling

*Gustavo Díaz¹, *Emilio Pecharromán¹, Sergio Sanguilinda¹,*

John Pusateri², Anthony Staley²

Using recycled materials as feedstock to zinc production plants has become commonplace, with obvious environmental and economical advantages. Most of these recycled materials come from the industry of galvanized steel, such as the zinc oxides generated in Waelz kilns processing Electric Arc Furnace dusts.

Addition of recycled materials to Roasting-Leaching-Electrowinning (RLE) plants is limited, due to the presence of halogens and other impurities that impair electrowinning of zinc and cannot be removed by conventional purification processes. This limitation is overcome by properly applying purification by solvent extraction, which is a very effective barrier against impurities.

Técnicas Reunidas' Modified ZINCEXTM Process consists in coupling Leaching, Solvent Extraction and Electrowinning steps, producing zinc metal either from primary ore or from a wide range of recycled materials. Indeed, Waelz oxide is regarded as an ideal feedstock for the process.

Modified ZINCEXTM technology has known several milestones from its development: Skorpion Zinc refinery in Namibia was the first plant to produce zinc from primary ore by SX purification. Afterwards, this technology has been applied in two medium-sized facilities devoted to recycling secondaries, but attached to conventional existing RLE plants: Akita Zinc in Japan and Portovesme in Italy.

Finally, the expected start-up of the Mooresboro Project (NC USA) by Horsehead Corporation, at early 2014 brings in a new greenfield plant, fully devoted to the recycle of Waelz Oxides and other secondaries by SX purification, with a nameplate capacity of 140.000 mt/y of SHG zinc ingots, the first in the world of its kind. This new approach and the current status of the project are presented in this paper.

* Corresponding author, e-mail: epecharroman@trsa.es

¹ Técnicas Reunidas S.A. Madrid. Spain.

² Horsehead Corporation. Pittsburgh PA, USA.

Introduction. Limitations for Zinc Recycling.

Production of zinc from recycled materials currently represents approximately 2.9 million tons per year, most commonly from steel scrap treated in Electric Arc Furnaces (EAF)^[1]. EAF dust is processed in rotary kilns (Waelz kilns), to render a very fine dust (Waelz oxide) with approximately 60% zinc. Minor components of Waelz oxides are lead, iron, calcium, chloride, and other metals. This Waelz oxide is the most usual feedstock for zinc recycling facilities, but it has also become common to add it along with zinc ore concentrates (sulfides) in primary production facilities.

Approximately 90% of the installed capacity of zinc nowadays is based in electrowinning (EW). The conventional technology is based in the “RLE” scheme: Roasting of the sulfide to oxide, Leaching of the oxide to produce a zinc solution, and Electrowinning of zinc from the solution to produce metallic zinc plates. The solution to electrolytic cells needs to undergo a purification to guarantee final product quality and prevent inefficiency in electrical power usage. A number of harmful impurities have to be removed from the zinc solution^[2]. Cementation with metallic zinc dust, with different additives and process arrangements, is used for removal of copper, cadmium, nickel and cobalt^[3].

Conventional purification methods are not conceived for removal of other impurities, as halogens or alkaline elements, which are present in Waelz oxides. In electrowinning, chloride causes anode corrosion, and fluoride makes zinc stick to the cathodes, so both impurities are strictly limited. The only way to control them is to bleed a sufficient amount of electrolyte. This is why, in conventional RLE plants, there is a practical limit to the feeding of Waelz oxides, approximately 15% of total feedstock^[4].

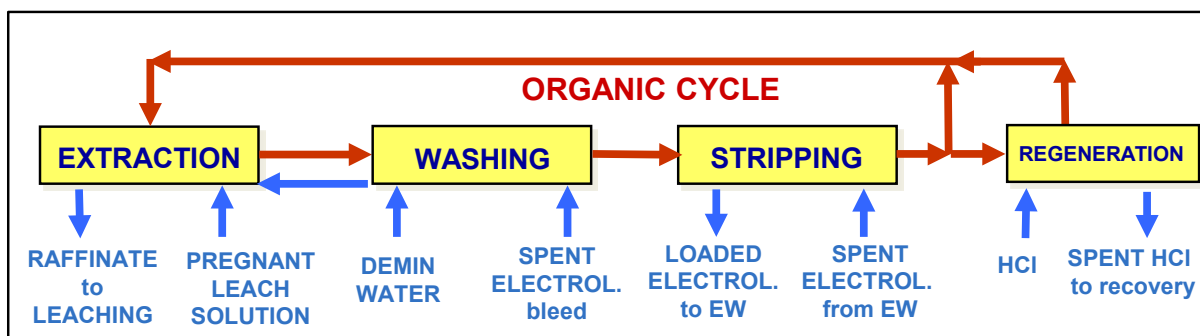
Alternatively, Waelz oxide can be turned into zinc oxide, or into metallic zinc by methods other than electrowinning. For instance, Horsehead’s Monaca plant, in Pennsylvania, employs an electrothermic reduction of zinc oxide with coke, to produce zinc vapour and finally metallic zinc slabs.

Solvent Extraction. The MZP process.

Solvent extraction (SX) is a technical alternative to conventional purification, although not specifically focused on recycled materials. SX allows a selective transfer of zinc between organic and aqueous phases, it purifies and concentrates the zinc solutions, yielding loaded electrolyte to EW. Physically, the aqueous circuits remain separate, and SX becomes an effective barrier for impurities.

Técnicas Reunidas S.A. developed the ZINCEXTM process in the seventies, aiming to integrate zinc SX and EW. Its two early implementations^{[5][6]} treated leaching liquors from pyrite-roasting drosses. In the nineties, the Modified Zincex Process (MZPTM) simplified the flowsheet in a unique organic circuit containing three main stages: Extraction, Washing and Stripping.

The extractant employed is di-2ethyl-hexyl phosphoric acid (D₂EHPA), which is a major product of chemical industry, with guaranteed supply and stable pricing. The organic phase is completed with a diluent selected among available commercial products. No further additive or reagent is needed in the formulation.



MZP™ Solvent Extraction Conceptual Diagram

The activity of D₂EHPA is highly dependent on pH conditions, and it will inevitably co-extract other metals. The arrangement of washing stages minimizes the transfer of impurities to the stripping stages. They combine the effect of physical scrubbing (to remove aqueous droplets in the organic phase) with a chemical washing, using the bleed of spent electrolyte from EW to displace the metals extracted by the D₂EHPA.

Stripping is performed with adjusted spent electrolyte from EW. Organic phase entrainment into the electrolyte must be carefully removed, to prevent contamination in the cellhouse. Activated carbon columns are used for this purpose.

SX is completed with ancillary units for collection and treatment of solids, removal of iron from organic (Regeneration), and recovery of the hydrochloric acid (HCl).

MZP™ Industrial References

MZP™ was conceived as an alternative to conventional RLE processes, with flexibility to accept different raw materials, either primary or recycled. Investment and operating cost of a MZP plant comprising Leaching, SX and EW would be attractive compared with a conventional RLE plant^[7]. Nevertheless the feature that facilitated introduction of MZP in the industry was the ability to deal with “difficult” materials.

The first industrial implementation of MZP was Skorpion Zinc, in Rosh Pinah (Namibia), by Anglo American. The ore, mainly complex silicates and carbonates^{[8][9]} was regarded as untreatable by conventional methods. After a decade of successful operation, it is getting prepared for the depletion of the ore body and the shift to conventional concentrates, and SX will remain as the purification unit.

The following two implementations have been medium-sized plants for recycling of zinc materials (Waelz oxides and similar), attached to bigger conventional RLE plants: Akita Zinc Recycling in Japan^[10], and Glencore’s Portovesme in Italy^[11]. In both cases, the electrowinning is common with the RLE plant, and stripping in SX is performed with the spent electrolyte from a conventional process.

Currently underway, the Mooresboro project, driven by Horsehead Corporation in USA, is the first implementation of MZPTM technology in a greenfield project devoted exclusively to recycled materials. The feed is mostly Waelz oxides, but the plant is prepared to admit a range of zinc secondaries, included metallic and oxide materials.

The following information is valid as of early March 2014, date of delivery of this article.

The Mooresboro Project

Horsehead Corporation is the largest zinc producer in the United States and the leading manufacturer of value-added zinc products. EAF dust is processed in Waelz kilns plants strategically located to collect the raw material: Barnwell SC, Calumet IL, Palmerton PA, and Rockwood TN. Waelz oxide is currently treated in the electrothermic smelter in Monaca plant, which has been the world's largest facility of recycled zinc. After production moves to the new Mooresboro plant, in North Carolina, the outdated facilities at Monaca will be idled.

The Mooresboro project is a strategic move for Horsehead, since the majority of the company's revenue will be relying on the success of this project. The move from Monaca to Mooresboro, involving the transfer of resources and personnel, will be quick due to the limited availability of Waelz oxide. Monaca will continue production only a few weeks after Mooresboro starts, so considerable strain is put in achieving a swift and eventless start-up. Once in full operation, it will be producing with a nameplate capacity of 140,000 mt/y, including Special High Grade (SHG) and specialty products for USA domestic market^[12].



Location of Horsehead's Waelz Kilns, old Monaca Plant and new Mooresboro plant.

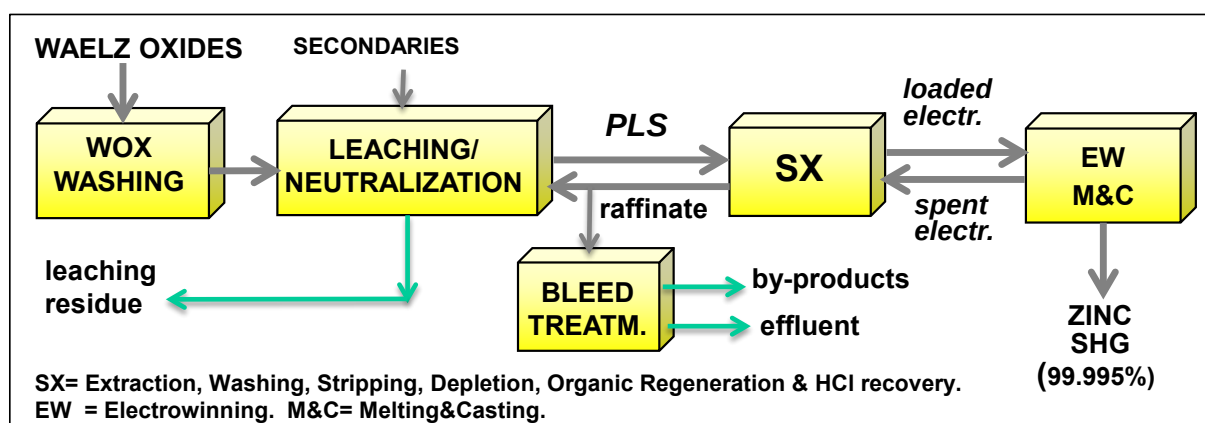
The Mooresboro Process

Waelz oxides are received by railcar and washed for removal of soluble salts. The novelty relies in the fact that a deep removal of salts is not strictly required for MZP, so the washing can be performed with an intermediate process stream instead of fresh water. This results in a considerable optimization of water consumption in the plant.

Waelz oxide is a very favourable feed solid, the leaching reaction is quick, thanks to the small particle size, and besides, the “weight loss” (ratio of feed mass versus residue) is between 80% and 90%. The amount of residue is much smaller than at plants treating zinc ore. Waelz oxide is submitted to atmospheric acid leaching and neutralization in cascade, followed by solid-liquid separation, yielding a neutral pregnant leach solution (PLS) with 30 g/l zinc. The leaching cascade can also be fed with a certain proportion of partially metallic zinc skimmings or other materials, in a “high acidity” stage.

SX follows a pattern consisting in three stages of Extraction, three of Washing, two of Stripping and one of Depletion. The latter one, dedicated to additional recovery of zinc from bleed liquors, makes the difference with the arrangements at Skorpion and Akita.

Organic is regenerated with diluted hydrochloric acid to prevent iron build-up. The recovery of HCl is performed by evaporation and condensation of the water-HCl mixture, leaving the impurities in a liquid bleed.



Simplified Block Diagram of Mooresboro Plant

Water balance and purge of impurities is attained by a bleed of zinc raffinate in the Leaching-SX circuit. This bleed is submitted to a series of treatments, to maximize the recovery of zinc, to recover commercial by-products, and to obtain a clean effluent for disposal.

The plant aims to achieve an overall recovery higher than 98% zinc from the Waelz oxide source, with zinc losses mainly in the Leaching-Neutralization residue. Marketable by-products from the plant are cadmium cement and gypsum. Moreover, in the near future, a facility to recover lead and silver will be started, following a process developed by Técnicas Reunidas^[13].

The electrowinning cellhouse and melting & casting facilities are designed and built under license from Asturiana de Zinc S.A, owned by Glencore-Xstrata.

Commissioning and Start-up

Construction commenced in the 3rd quarter of 2011 and continued through the 1st quarter of 2014. Commissioning activities started in December 2013, and as of March 1st, the commissioning is progressing.



Aerial view of Mooresboro Plant (November 2013)

The organic phase is prepared on-site by circulating the diluent along the SX stages and main organic tank, then continuously adding D₂EHPA reagent. A number of tanks of these organics must be supplied and loaded in a brief time to totalize the 4000 m³ of organic inventory in the plant. On the other side, the initial acidity for stripping zinc must be added as pure sulfuric acid diluted on a continuous flow of demin water to reach a sulfate molarity similar to the electrolyte. This initial acidic solution is stored in the electrolyte tank farm located between the SX unit and the cellhouse.

The four main areas in the plant must be set to work in a nearly simultaneous time frame. In a tightly interconnected flowsheet, the SX unit is in the center, depending on the outcomes from Leaching-Neutralization and EW which, at the same time, depend on SX outcomes. Before start-up, several closed-circuits are run: Leaching-Neutralization with acidic water; Extraction with organic phase and neutral water; Stripping with organic phase and acidic solution on demin water. Then, when the feed of solid Waelz Oxide starts, the closed circuits are opened and the connection of the units should be rapid.

To ensure a smooth start-up of SX, the main points of concern are the presence of solids (that would cause formation of cruds), and the control of iron. Thus, leaching-neutralization unit must ensure an optimal removal of solids (by means of polishing sand filters) and very effective pH control to prevent iron in PLS.

Another concern is the control of organic entrainment from SX to electrowinning, by means of activated carbon columns. The quality of the electrolyte is expected to allow a smooth start-up of the Electrowinning cells. The circuit between the Stripping unit at SX and Electrowinning can only be closed once the cellhouse is working. The concentration of zinc in this closed circuit will rise progressively until the nominal concentrations are reached. This moment marks the production of first zinc.

Immediately after, the ancillary units for regeneration of organic with hydrochloric acid will be started-up, to prevent iron build-up during the production ramp-up.

Once in operation, the Mooresboro plant is expected to become a benchmark in zinc processing technology. It will be the most important milestone in the history of Horsehead Corporation, and the most complete implementation of Técnicas Reunidas' MZP™ process.

References

- [1] International Lead and Zinc Study Group 2013. "Lead and Zinc Statistics", retrieved from www.ilzsg.org
- [2] J. Gnoinski, K.C. Sole, D.R. Swart, R.F. Maluleke, G. Díaz & F. Sánchez. "Highlights and Hurdles in Zinc Production by Solvent Extraction: The First Four Years at Skorpion Zinc". Proceedings ISEC (2008) Tucson, Arizona, USA.
- [3] Roderick J. Sinclair. "The Extractive metallurgy of Zinc". The Australasian Institute of Mining and Metallurgy Spectrum Series Vol. Num. 13 – 2005.
- [4] G. Díaz, C. Frías, C. Onoberhie, F. Sánchez, D. Martín. "Improving Zinc Smelter profitability. Is Secondary Zinc the Solution? Use ZINCEX™ Solvent Extraction". International Symposium on Lead & Zinc Processing (2010). Vancouver, Canada.
- [5] E.D. Nogueira, J.M. Regife, P.M. Blythe. "ZINCEX, the development of a secondary zinc process" *Chemistry and Industry*, 19 (January 1980) Cashew Chemistry.
- [6] E.D. Nogueira, J.M. Regife, M.P. Viegas. "Design Features and Operating Experience of the Quimigal ZINCEX Plant" *111th Annual Meeting* Dallas TX (1982), 59
- [7] C. Frías, G. Díaz, D. Martín, F. Sánchez, C. Onoberhie. "Highly Efficient and Low Cost Zinc Electrolyte Purification Using ZINCEX™ Solvent Extraction". Proceedings EMC (2011).
- [8] J.M. Musadaidzwa and E.I. Tshiningayamwe. "Skorpion Zinc solvent extraction: the upset conditions" *Journal of the Southern African Institute of Mining and Metallurgy*. 109: 691-695. (2009)
- [9] H.F. Fuls, J. Kruger, and P. van Grenen. "Water reduction at Skorpion Zinc and the impact on the environment" *SAIMM Base Metals Conference (2009)*. 307-322.
- [10] C. Frías, G. Díaz, D. Martín, F. Sánchez. "Implementation of First ZINCEX Commercial Plant Treating Zinc Oxides Secondaries". Proceedings EMC (2009)
- [11] G. Díaz, A.B. Mejías, D. Martín, F. Cubeddu. "ZINCEX Technology, Recent Industrial operations". Proceedings Hydrometallurgy (2014).
- [12] "Analysts day 5-7-2013" presentation, retrieved at www.horsehead.net
- [13] C. Frías, J. Palma, M.A. García, & G. Díaz, G. "Recovery of precious metals from metallurgical residues by applying the PLINT process". Montreal, Canada. *32nd Annual Hydrometallurgy Meeting, Chloride Metallurgy*. (October 2002)
- [14] J. Ruetten, C. Frías, G. Díaz, D. Martín, F. Sánchez. "Processing EADF Dust through Waelz Kiln and ZINCEX™ Solvent Extraction: the Optimum Solution". Proceedings EMC (2011)
- [15] J. Ruetten. "Different Ways of Using Waelz Oxide-Overview and Evaluation". Proceedings Lead-Zinc Conference (2010)
- [16] C. David, S. Engelbrecht, D. Díaz, F. Sánchez, A.B. Mejías. "Skorpion Zinc: Lessons learnt in the Operation of the Modified ZINCEX™ Solvent Extraction Process". Proceedings ISEC (2011) Santiago, Chile.
- [17] S. Moats, W.J. Cashwell, A. Staley. "A review of the Modified ZINCEX® Process from Skorpion to Horsehead" (2014).

State of the Art of Solvent Extraction and Electrowinning Design.

Lee W John¹ and Graeme M Miller²

Abstract

Solvent Extraction and Electrowinning design has evolved over the last 5 decades and a brief history of novel designs that have come and gone and the reasons some fundamentals have remained are discussed.

State of the Art designs are discussed that involve mixer settler arrangements with piping that is re-configurable to suit any changes in processing requirements and or chemistry as an operation expands.

Minimalist designs, which have a reduced degree of instrumentation and are designed for self regulation have evolved from multiple implementations in Africa. Such State of the Art designs include elements to minimise the chance of an SX fire and the preservation of other assets nearby in the event of a fire.

Considering that the EW product in a SXEW operation is the most critical output, quality issues due to antagonistic relationship between SX and EW processes are discussed on a practical and chemical level. Design and operating solutions to overcome such are discussed with the incorporation of best practice on mixer settler arrangements, inherent process control and fire risk minimisation.

Background

Commercial Solvent Extraction (SX) facility design has evolved over the past five decades with a number of types of mixer settler and column arrangements tried and tested in pilot and commercial operations. Some fundamentals have however not changed and are often not properly addressed or even considered in some commercial operations, leading to high risk installations, possible catastrophic failure and or fire.

Fundamentals that are often poorly addressed in SX design include:

- Plant layout in-order to minimise piping and electrical routes and for simpler operability and lower CAPEX;
- Inter-stage piping and unit layout;
- Design for re-configuration of the units should the chemistry or flows require such;
- Design for operability issues in commercial plants – extreme organic or aqueous flows needed to change mixer continuity;
- Material selection, earthing, piping, instrumentation and civils;
- The positioning of SX plants relative to other SX plants, process plant and buildings that would be damaged or involved in the event of a SX fire;
- Fire hazards created by static electricity generated via the flow of organic (especially in plastic pipes);

¹ Lee W John, DRA Mineral Projects, South Africa, Lee.John@DRAGlobal.com

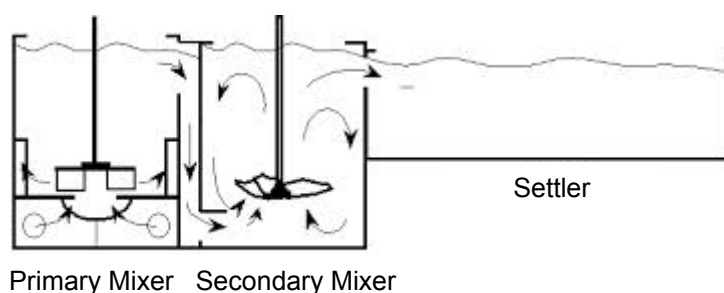
² Graeme M Millier, Miller Metallurgical Services, Australia, gmiller@milliermet.com

- Contamination and organic degradation from oxidation reaction(s) in the closed electrolyte circuit as a result of high Eh generated in Electrowinning (EW) circuit;
- Crud removal access and crud handling facilities;

Commercial Electrowinning (EW) design has changed to a lesser degree than SX design over the same period although there have been small progressive improvements. An understanding of the interactions that EW has with SX under certain conditions has resulted in more specific operating and design criteria to maintain a healthy synergistic relationship between the two.

Mixer Settler Designs

The 'conventional' mixer settler design has gone full circle and now is fundamentally the same as used in uranium plants in the 1950's albeit with many improvements. Novel designs such as Krebs settlers, external organic depth control and pulsed columns have come and gone. After 50 years of innovation, the conventional mixer settler design is the most commonly implemented in the minerals industry today.

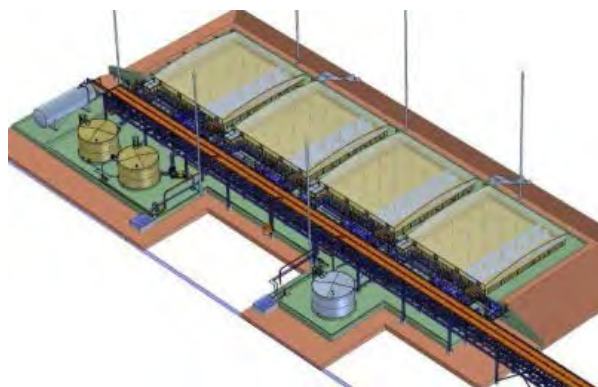


Mt Cuthbert (Aust.) SXEW 2E+1S head to tail

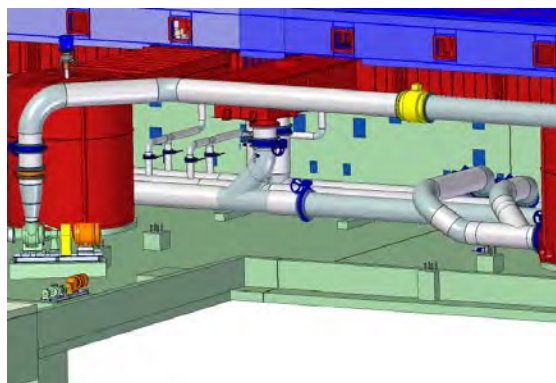


MIM (Aust.) 2E1+S Krebs head to head

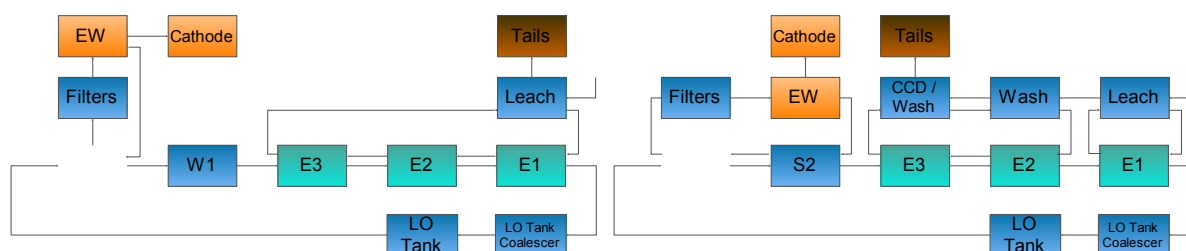
The traditional head to tail arrangements have been reconfigured with some smart piping and nozzle designs so that the mixers are all the same side resulting in considerable operability improvements as well as a reduction in electrical and piping reticulation. The result is a reduced footprint and a reduced CAPEX of the plants. Reverse Flow and the MMS SideFeed™ mixer settlers are now the most commonly used head to head arrangement. Better layouts with these arrangements facilitate reconfiguration of the units to suit any revised duty.



A 3E+1S SX design head to head



Piping detail with on-line bypassing



An initial 3E+1W+1S configuration converted to a 3E+2S or 2E+1PE+2S configuration



The multi-nozzle discharge of the MMS SideFeed™ settler allows neat piping in a head to head layout

The most recent installations of the MMS designed mixer settlers in Australia and Africa now incorporate piping designs to include the flexibility to change the duty of a mixer settler unit should the need arise. These installations are reconfigurable so that mixer settler units can be changed, from or to; Strip (S), Wash (W) or Extract (E).

Being originally designed to be reconfigurable allows changes in piping that avoid the delays and costs associated with shutdowns for hot work (welding).

Such piping also allows a mixer settler unit to be converted easily and without the need for hot work, from a series unit to a parallel unit. In addition to these improvements, the modern mixer settler units have superior flow distribution from the mixer into the settler. Advanced picket fence designs minimise turbulence and achieve better aqueous organic separation with lower entrainments.

Other modern head to tail arrangements are provided by Outotec. These installations are generally very compact and difficult to operate and sample. The use of higher unit settler flow rates has resulted in an increase in organic depth to limit the space velocity. The increased inventory costs are significant in the overall CAPEX profile.

Columns

Uranium, phosphate and nickel SX are the only major metal recovery SX operations where pulsed columns have competed with mixer settlers. The extraction kinetics of ion exchange extractants commonly used for uranium recovery are faster than those of the chelating oxime extractants used for copper recovery. This has meant that while column contactors are not considered for copper SX operations, they have been installed for the extraction stages in a limited number of uranium operations. For uranium SX there is no technical imperative for the use of columns.

While columns have been used for the extraction stages of uranium SX plants, they have not to date been used in the stripping and scrubbing stages. There are examples where the use of columns in pilot plant stripping and scrubbing operations has been met with difficulties due to the requirement of stage by stage pH control (3). As a result the scrubbing and stripping activities of base metals processes are all conducted in mixer settlers.

Materials of Construction

Settler fabrications over the years have ranged from fiber reinforced plastics (FRP) lined concrete, anchored polyethylene (PE) lined concrete, full FRP and full stainless steel in no particular order. The choice between full stainless steel and full FRP has usually been one of price although chloride or fluoride content of acid process liquors has also affected selection. Major teething problems have regularly been experienced in projects where a transition of different materials occurs; for example where stainless steel mixers transition into FRP lined concrete settler.

Composite materials and transitions suffer from differential rates of thermal expansion causing leaks and cracks. Anchored PE lined concrete has been successful in Chile but few other places. Compatible materials include polyvinyl chloride (PVC) nozzle's and piping in FRP tanks. Full stainless steel fabrications do not have this issue and have proven to be far more robust than FRP units.

Fire Prevention and Containment

Fire risks management in SX plants have justifiably been scrutinised due to the number and severity of such fires during the last fifteen years. Poor layout and or selection of piping material have resulted in several major SX fires around the world. Two of these being at Olympic dam, where they were found to be the result of minimal compliance with the standards for control of static electricity (5).

The diluent used in copper SX typically has a high flash point and thus copper SX plants could be classified as non-hazardous areas. From a general survey by Miller (5), over 50% of copper SX plants were found to be unclassified or unrated for electrical apparatus fire initiation. Many of the advances made in the understanding and minimisation of fire risks in copper SX are directly transferrable to other SX plants including:

- The use of fire plume analysis to position other assets outside the fire affected zone from an SX fire and should be applied to all new SX plants.
- Understanding and implementing the standards on static electricity generation and relaxation. The conductivity of uranium SX organic is two to three orders of magnitude higher than copper SX organic. This means that in theory the static electricity codes could be applied; but the risk of a static accumulation is in any case much lower.
- Application of the appropriate hazardous area rating codes. With the use of isodecanol, other alcohols or other modifiers, in an SX plant the effective flash point is often lowered and the plant must be hazardous rated appropriately.
- Attention to the detailed design of the mixer settlers and other elements to eliminate the generation of aerosols that could lower the effective flash point even further.

Crud prevention and treatment

The acid leach processes commonly used in uranium, copper and other base metal leaching can dissolve significant amounts of silica from the ore. Along with suspended solids (SS), dissolved SiO_2 concentrations in the resulting PLS can range from a few hundred ppm up to several thousand ppm.

For this reason alone, SX circuits are best equipped with PLS clarification and silica removal circuits which should always be conservative in design to cope with plant upsets (No one has complained yet that the PLS feeding an SX plant is too low in silica and suspended solids ...or that the crud processing plant is not being utilised fully!).

Crud and organic recovered from Electrowinning (EW) cells should under no circumstance be returned to crud processing or the SX. The extractant has most likely been oxidised and chemically altered in the EW cell, and will only serve to create issues of crud, reduced chemical capacity of the SX organic and slow phase disengagement issues. Such organic must be disposed of.

Antagonistic Reactions in SXEW

Permanganate degradation of SX extractants occurs by a now well understood mechanism as follows (4):

- Manganese in the PLS is transferred by entrainment (or more often silica based floating crud) into the electrolyte;
- Contamination with traces of other extractants such as Cyanex 272 will chemically transfer Mn;
- Mn^{2+} is oxidized to Mn^{7+} in the EW operation;
- The Mn^{7+} returns in the spent electrolyte sent to the SX strip and oxidizes the organic, forming surface active polar products;
- The oxidized organic has lower chemical capacity and slower phase separation times leading to more entrainment of the PLS in the organic and thus to the electrolyte;
- The higher entrainment of manganese in the electrolyte gives a faster degradation of the SX organic finally leading to a catastrophic collapse of the SX operation due to less than one percent degradation of the organic.

Prevention of permanganate degradation of the extractant is relatively easy and has been covered previously (4, 6).

Contamination from other SX extractant(s) used at the same location.

A significant example of this is that experienced at the Olympic Dam Operation which has a sequential Cu SX and U SX circuit. The problem was chloride transfer into the EW; resulting in pitting corrosion of the stainless steel cathodes which causes the copper sticking and not being easily stripped from the cathode (2).

The eventual culprit was found to be the U SX reagent that was entrained in the raffinate in such quantities that it was returning to the copper PLS via the leach and CCD circuit. In the Cu SX, the trace of U SX extractant was transferring the chloride to the EW electrolyte with disastrous consequences for the stainless steel cathodes.

The cause of the high losses was not purely entrainment but physical transfer during start and stop transients. The column extraction system released much of the contactor organic contents to the raffinate tank on shut down; due to poorly sealing aqueous discharge valves.

Conclusions

Design improvements to the conventional mixer settler including: flow distribution, picket fence designs based on CFD modelling, smart piping layouts combined with extensive practical experience have resulted in numerous operating improvements such as higher unit capacities and lower reagent losses. These refined conventional mixer settler designs have proved to be the best all round performers for a wide range of SX duties in the minerals industry. State of the art SX plant design allows for both reconfiguration and flexibility as well as fire risk minimisation.

Crud management must start at the front end with conservative designs for the maximum possible removal of suspended solids and dissolved silica. Crud processing is part and parcel of any commercial SX operation and should always be well catered for.

SX designs need to cater for the prevention of all possible sources of contamination; and such designs also need to be conservative. Prevention of SX cross contamination may involve diluent washing or activated carbon processing of raffinate prior to the next SX stage.

EW design and commissioning needs to be mindful of the relationship EW has with SX and steps need to be taken to ensure an ongoing healthy synergy, especially for Eh control of the spent electrolyte.

New SX extractants and associated technologies will develop over the coming years, but prior to successful commercialisation, the SX system should be verified against, and designed for, the many lessons already learnt in SX operation over the past five decades.

References

1. Balakrishnan N, *Review of GRP design codes and manufacturing practices*, in ALTA 2010 Nickel/Cobalt/Copper Conference.
2. Dudley, D., Lawson, B. & Wilson D. (2003) *Hydrometallurgical Operations at Olympic Dam*. ALTA Copper Conference 2003, ALTA Metallurgical Services, Perth.
3. Grinbaum B.; *Direct SX of Uranium from Low-grade Leach Solutions*, in E.K. Lam, J.W. Eowson, E. Ozberk, "The future is U", Uranium2010, vol. 1, pp. 717-723, CIM, Saskatoon (2010).
4. Miller, G. M., Readett, D. J. & Hutchinson, P. (1997) *Experience in Operating the Girilambone Copper Circuit in changing Chemical Environments*. Minerals Engineering, Vol 10, No5, pp 467-481.
5. Miller, G. M., *SX Fires – Their Initiation and Propagation*, in ALTA SX Fire Protection Summit, Perth, May 2005.
6. Miller, G., Readett, D. & Hutchinson, P. (1996) *Entrainment Coalescing in Copper SX Circuits*. ISEC '96, Vol II, pp 795-800.
7. Nofal, P., Allen, S., Hosking, P. & Showell, T. (2001) *Gypsum control at Bulong the final hurdle?* ALTA Ni-Co Conference 2001, ALTA Metallurgical Services, Perth.

Recovery of phenol from catalytic pyrolysis bio-oil – an industrial perspective

Katarina Babić¹, Barthel Engendahl¹, Tom van Houtem¹, Johan Tinge¹, Rudy Parton¹

¹ DSM Chemtech Center, P.O.Box 18, 6160 MD Geleen, The Netherlands

Summary

Within the scope of the BioBoost project (EU FP7, no. 282873), we investigate the feasibility of recovering valuable components, such as phenol, from bio-oils on an industrial scale. An economical bulk chemical process can be built if the starting material (pyrolysis oil) is available at sufficient quantities at a competitive price and at high enough concentration of the desired chemical, ideally higher than 2 wt.%. It is a continuous process with few extraction steps required to produce an end product of reasonable purity. Since the bio-oil contains a myriad of components, to reduce its complexity it is envisaged to first remove the polar components by extracting them with water. The phenol-rich raffinate will then be subjected to another extraction step to recover phenol. The bio-oil remaining after the extraction of phenol is a very convenient feedstock for further upgrading to fuels in a conventional refinery.

In this research we evaluated hydro-thermal carbonization (HTC), fast pyrolysis (FP) and catalytic pyrolysis (CP) oil. Due to the sufficiently high phenol concentration and acceptable viscosity, the CP oil proved to be a good feedstock. The HTC yielded aqueous streams with very low phenol concentration and was thus not investigated further.

Processing bio-oils is a challenge due to their high viscosity. FP bio-oils do not flow at room temperature, whereas CP oils are still viscous (200-350 mPas) but processable. After extraction of smaller polar compounds, the bio-oil becomes even more viscous. Viscosity decreases with increasing temperature. At 40°C it is already largely reduced.

The aqueous extraction step was efficient in reducing the complexity of the CP bio-oil. Acetic acid distributes favorably to the aqueous phase, whereas phenol and cresol remain mainly in the oil phase.

Introduction

The BioBoost project (EU FP7, no. 282873) aims to pave the way towards decentralized conversion of residual biomass and wastes as feedstock to intermediate energy carriers. These are further processed into transportation fuels, chemicals and used for the generation of electricity and heat. The biomass is converted by fast pyrolysis (FP), catalytic pyrolysis (CP) or hydrothermal carbonization (HTC) to produce bio-oil. All three biomass conversion processes are based on thermal degradation. HTC uses dilute aqueous acid solutions at low temperatures (250°C) and long residence times (4-24 h). Pyrolysis is performed at much higher temperatures (500°C) and short residence times (0.5-2 s), without (FP) or with catalyst (CP). Of interest to the project is phenol, present in the bio-oil and a precursor for many industrial chemicals. In this work we investigate the feasibility of extracting phenol from pyrolysed biomass on an industrial scale.

Renewable phenol for the chemical industry

Phenol has a worldwide production capacity of 11000 kta (1). Its uses in chemical industry are manifold. 37% of all the phenol produced is processed further to bisphenol-A, used in high grade polycarbonates and epoxy-resins. Further 31% is used in the production of phenol-formaldehyde resins. The third largest demand is the production of caprolactam which captures 8% of the world's production or about 728 kta in 2010 (1). The current price of phenol at the European contract market is 1500 €/t, making it a value added product, worth isolating from biomass (2). DSM is one of the world leaders in caprolactam, thus to produce sustainable caprolactam we are interested in this renewable resource.

Phenol is a bulk product, so the market rules for bulk products play an important role in any consideration for a process to isolate phenol. After *quality*, the most important factor in bulk chemicals is the *selling price*. If the price of the phenol from renewable resources, such as phenol extracted from pyrolysis oils, is not competitive, a market introduction will be extremely difficult due to the very low return on investment that can be achieved. To achieve a reasonable cost-price for phenol, a recovery process needs to be cost effective in fixed costs, variable costs and capital investments.

The *size of the production* is a very important factor for both capital investment and fixed costs. The labor costs per unit produced decrease with an increasing number of units produced per worker). The size of the installed equipment follows the “square-cube-law”, i.e. while the volume of a vessel increases by the power of three its surface increases with the power of two (3). In conclusion, a larger plant can operate at lower unit production costs than a small plant.

The capital investments are also determined by *the complexity of the process*. The lower the number of process steps, the lower the capital investments required for building and commissioning of each separate unit.

An important factor in the variable costs is *the operating mode of the plant*. A chemical plant can operate in either batch or continuous mode. For bulk chemical processes only the continuous mode is relevant, as the batch mode is more labor intensive and it requires larger equipment to produce the same value (4). Also, since the production volume is large, the E-factor (tons of product/ tons of waste) has to be $\gg 1$, otherwise the disposal of waste will be more expensive than the product itself (5).

Finally, to achieve a feasible large scale production, the feed material for an extraction process needs to contain a *sufficient concentration of the desired product*. From our experience a concentration no smaller than 2 wt.% is required. For example, a 10 kta plant requires a supply of bio-oil containing 2 wt.% of phenol of 500 kta. Having in mind that current phenol production plants are rather of the size of 300 kta, it becomes obvious that low starting concentrations are not desirable. Moreover, low concentrations result in general in high capital investments and high energy costs.

In conclusion, an economical bulk chemical process can be built if the starting material (pyrolysis oil) is available at sufficient quantities at a competitive price and at high enough concentration of the desired chemical. Ideally, it is a continuous process with one to maximum three extraction steps required to produce an end product of reasonable purity which can be further purified via distillation or crystallization. Furthermore, the extraction solvents must be either completely recoverable or a valuable product in downstream processing of either the raffinate or the extract. The process does not produce by-products that have to be disposed, but rather used in another process. The waste products that will inevitably be produced are of such nature that can be easily disposed of.

Recovery of phenol from bio-oils

Besides phenol, bio-oil contains a myriad of other polar components such as acids, aldehydes and others. In order to reduce its complexity the more polar components can be extracted in the first step using water (6), (7). The phenol-rich raffinate will then be subjected to another extraction step in order to recover phenol. The bio-oil remaining after the extraction of phenol is a very convenient feedstock for further upgrading to fuels in a conventional refinery (Figure 1).

In this research we evaluated FP and CP bio-oils. The hydrothermal carbonization yielded aqueous streams with very low phenol concentration to result in an industrially feasible process and was thus not investigated further.

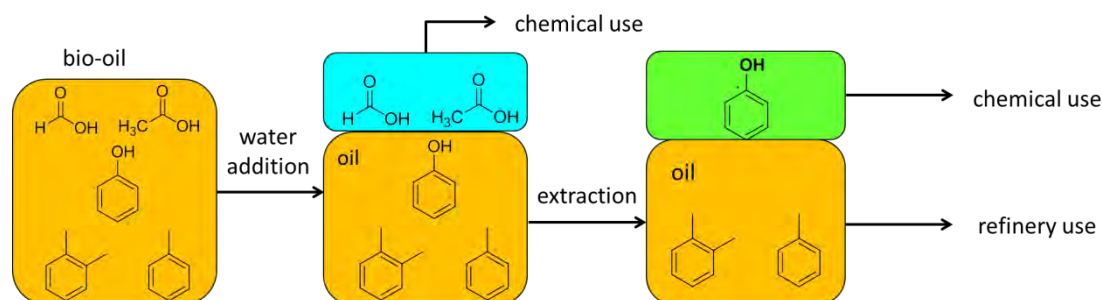


Figure 1. Extraction scheme concept

Experimental

Materials

For this study, the FP bio-oil was supplied by the KIT Institute, Karlsruhe, Germany and CP bio-oil by CERTH Institute, Thessaloniki, Greece. The quantification of the bio-oil samples was performed by the below described GC method. The chemicals used in the analytical procedure were purchased from Aldrich and used as received.

Experimental procedure

A pre-determined amount of bio-oil (0.6 mg, 2.5 g or 10.1 g) was placed in a stoppered vial together with a pre-determined amount of water (0.5 mg, 1.2 g, 10.2 g, respectively). The solutions were stirred with a magnetic stirrer (speed 400 rpm) for 6 hours in order to reach equilibrium and then left overnight to settle so that the complete phase separation can be achieved. The experiment was performed at room temperature. After settling, the samples of each phase were taken and analyzed to determine the concentration of phenols and acids.

Analytical procedure

The equivalent of 10-30 mg of the organic sample is dissolved in a 1 ml pyridine and derivatized with 100 mg N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and injected to the GC. The sufficient quantity of the MSTFA was determined by the presence of its peak in the chromatogram. The equivalent of 10-30 mg of the aqueous sample is dissolved in a 1 ml pyridine and directly injected into the GC. The organic acids were analyzed using the derivatization method with 10 mg sample dissolved in 1 ml pyridine whereby 250 mg MSTFA is added. The GC analysis is performed using CP-Sil 8 column (30m×0.25mm×0.25mm). The oven was kept 1 min at 40°C and then the temperature was increased with a rate of 10°C/min to 300°C.

Data processing

The mass of the phenol extracted into the aqueous phase was obtained from the GC analysis, whereas the remaining mass of phenol in the bio-oil rich phase was calculated by mass balance (Eq.1).

$$m_{i, \text{ raff}} = m_{i, \text{ f}} - m_{i, \text{ extr}} \quad (1)$$

Distribution ratio is defined as a weight fraction of a component *i* in aqueous phase over the weight fraction of a component *i* in organic phase (Eq.2).

$$D_i = x_{i, \text{ aq}} / x_{i, \text{ org}} \quad (2)$$

Loss is defined as the mass of a component *i* extracted with water over the mass of the same component *i* in the bio-oil feed (Eq.3).

$$L_i = m_{i, \text{ aq}} / m_{i, \text{ f}} \quad (3)$$

Results and discussion

Characterization of bio-oils

The factor determining the feasibility of the phenol recovery process from bio-oil is its concentration. Table 1 presents the concentrations of phenol and acetic acid in the bio-oil samples, obtained using different catalyst or process conditions. The other phenolic components may also be interesting for recovery yet an additional step would be required to convert them to phenol. Acetic acid is measured as the main unwanted impurity in bio-oil, together with other carboxylic acids present in smaller quantities. From the presented composition, we concluded that CP oil is a better source of phenols than FP oil. The fast pyrolysis is optimized to maximize the yield of transportation fuel components rather than chemicals, whereas the catalytic pyrolysis can more easily be tuned for increased concentration of chemicals through the choice of a catalyst.

Table 1. Concentration of relevant components in the pyrolysis oils

Type of oil	Sample	Concentration, wt.%		
		phenol	cresol	acetic acid
Catalytic pyrolysis oil	CP1	2.8	1.5	4.0
	CP2	1.8	n.a.	8.5
	CP3	3.0	n.a.	5.5
Fast pyrolysis oil	FP1	0.49	n.a.	7.1
	FP2	0.46	n.a.	6.4

In large scale processing, it is important to know the bio-oil's physical characteristics, such as density and viscosity which determine the ease of operation and pose certain constraints. As can be seen from Table 2, bio-oil is rather viscous and thus difficult to process. Different CP bio-oils have different viscosities, but all are in the same range (200-300 mPas). As a comparison, the viscosity of a typical Middle East crude oil at 20°C ranges from 0.1 to 77 mPas (8), depending on composition. Additionally, the extraction of chemicals caused a further increase in viscosity. The remaining non-aqueous bio-oil (raffinate) turned into a sticky solid making further processing almost impossible and is undesired for an industrial extraction process. CP bio-oil was more processable than FP bio-oil due to its lower viscosity. FP bio-oil proved to be extremely viscous and at lower temperatures viscosity measurements were impossible.

However, the characteristic of viscosity is that it exponentially decreases with the temperature increase. Thus the viscosities of the CP bio-oils also decrease to processable values already at 40°C. This is important to take into account for the overall process design and its heat integration. However, exposing bio-oil to temperatures higher than 40°C is less desirable as at higher temperatures the risk of oil degradation, due to for instance polymerization of smaller molecules, is increased. The viscosity of FP bio-oil at 60°C is still rather high.

Extraction of phenol and acetic acid

Bio-oil used in this work is a viscous and difficult to process liquid. It tends to adhere to the glass wall of the experimental vessel resulting in difficult mixing and phase separation. It was therefore very difficult to perform a reproducible experiment (Table 3). Nevertheless, the mass balance check between measured and calculated values shows deviations up to a maximum of 5.8%, which we considered acceptable for the preliminary experiments. However, the quantification of acetic acid is not so accurate and the results should be taken only as indications rather than absolute values.

Table 2. Densities and viscosities of the various pyrolysis oil before and after extraction with water

Sample	Temperature (°C)	Before extraction		After extraction	
		Density (g/cm ³)	Viscosity (mPas)	Density (g/cm ³)	Viscosity (mPas)
CP1	20	1.122	294	1.125	743
	40	1.105	56.4	1.109	108
	60	1.090	19.0	1.092	28.7
CP2	20	1.155	326	1.137	624
	40	1.138	65.7	1.121	92
	60	1.121	21.1	n.a.	n.a.
CP3	20	1.135	217.5	n.a.	n.a.
	40	1.119	42.1	n.a.	n.a.
	60	1.102	14.7	n.a.	n.a.
FP1	40	not measurable		n.a.	n.a.
	60	1.155	240-245	n.a.	n.a.

Two groups of experiments were performed to assess the aqueous extraction step. In the initial experiments, performed with small quantities of feed, only phenol was quantified (Table 3), whereas in subsequent experiments, with somewhat larger amounts of feed (to improve the reproducibility), also cresol and acetic acid were quantified (Table 4). The obtained distribution ratios of phenol are in agreement in both sets of experiments. The low value of distribution ratio is in this case very desirable as it minimizes the losses of phenol in this step. As expected, losses are higher for higher W/O ratios. Cresol, due to the presence of a methyl group, exhibits even lower distribution towards aqueous phase, and subsequently lower losses. The obtained results are similar to those reported by Vitasari et al. (6) for guaiacol and syringol, although phenol exhibits somewhat lower distribution ratios and yields. Compared with the results reported by Fele-Žilnik and Jazbinšek (7), we obtained consistently lower values for the distribution ratios of phenol. For instance, at a W/O ratio of 0.8 they report distribution ratio of about 0.2, whereas we obtained values of about 0.07 to 0.09. In their case, however, there was no difference between phenol and guaiacol and syringol. With the decrease of W/O ratio, Fele-Žilnik and Jazbinšek (7) observe the increase in distribution ratio of phenol towards water. Since the variation in our results falls within the error of the analytical method we cannot confirm this trend. It is likely that the differences between literature values as well as our own, stem from the different origin, and thus composition, of the bio-oil feedstock (6).

Table 3. Extraction of phenol from CP1 bio-oil

E x p N o	W/O ratio	Phenol mass			Loss	Mass balan- ce check	Phenol concentration		Distribu- tion ratio
		initial	extrac- ted	in raffinate			in extract	in raffi- nate	
		µg	µg	µg			wt. %	wt. %	
1	0.83	12.8	0.86	12.6	6.7	5.5	0.17	1.98	0.087
2	0.83	12.8	0.73	12.2	5.7	1.4	0.15	2.00	0.073
3	0.82	12.8	0.69	12.7	5.4	5.4	0.14	1.97	0.070

Acetic acid being the most polar component, as expected, distributes preferentially to the aqueous phase. In this case, the loss is desirable, as removal of acids reduces the complexity of bio-oil, enabling the efficient subsequent recovery of phenols. The distribution ratios calculated from our experiments are not very accurate, though the

obtained values are rather similar to those obtained by Vitasari et al. (6). They report distributions in the range of 2 to 2.7, whereas our values are in the range of 2.2 to 3.9. Similarly to phenols, they also observe different values of acetic acid distribution ratios for bio-oils of different origin.

Table 4. Extraction of phenol, cresol and acetic acid from CP1 bio-oil

E x p e r i m e n t N o	Compo- nent	W/O ratio	Mass			Loss	Mass balan- ce check	Concentration		Distri- bution ratio
			initial	extrac- ted	in raffi- nate			in ex- tract	in raffi- nate	
			mg	mg	mg	%	%	wt. %	wt. %	wt. %/ wt. %
1	Phenol	0.49	68.0	2.5	67.2	3.7	2.6	0.23	2.57	0.089
	Cresol		36.7	0.5	36.1	1.3	0.4	0.04	1.38	0.031
	Acetic acid		98.1	51.7	56.6	52.7	10	4.65	2.16	2.2
2	Phenol	0.47	69.5	2.8	67.2	4.1	0.8	0.23	2.57	0.089
	Cresol		37.6	0.5	36.1	1.4	2.5	0.04	1.38	0.029
	Acetic acid		100.3	54.0	56.6	53.8	10	4.47	1.33	3.4
3	Phenol	1.0	280.8	24.1	273.0	8.5	5.8	0.23	2.76	0.083
	Cresol		151.7	5.3	149.6	3.5	2.1	0.05	1.51	0.033
	Acetic acid		405.02	356.3	85.4	88.0	9.1	3.40	0.86	3.9

Conclusions

An economically feasible bulk process for the recovery of phenol from a bio-oil can be developed if the pyrolysis oil contains about 2 wt.% or more of phenol. In this respect, the CP bio-oil proved to be a good feedstock.

Processing bio-oils is a challenge due to their high viscosity. The viscosity differs between bio-oils. FP bio-oils do not flow at lower temperatures, whereas CP bio-oils were still viscous (200-350 mPas) but processable. After extraction of smaller polar compounds, the bio-oil becomes even more viscous. Viscosity decreases with increasing temperature. At 40°C it is already largely reduced (about 40-70 mPas for the crude bio-oil; 90-110 mPas for the extracted ones).

The aqueous extraction step was efficient in reducing the complexity of the CP bio-oil. Acetic acid distributes favorably to the aqueous phase with distribution ratios of about 3. Phenol is largely retained in the bio-oil phase, with the distribution ratio of about 0.085. The maximum observed losses to water are 8.5 % of the initial phenol mass. Cresol exhibits even lower affinity towards the aqueous phase.

References

1. Weber, M., Weber, M. and Kleine-Boyman, M. Phenol. *Ullmans Encyclopedia of Industrial Chemistry*. Weinheim : Wiley-CVH Verlag GmbH, 2012, pp. 503-519.
2. <http://www.dewittworld.com>. [Online] 2013. [Cited: March 17, 2013.]
3. Moore, F. 2, 1959, Quarterly Journal of Economics, Vol. 73, pp. 232-245.
4. Arpe, H-J. *Industrielle Organische Chemie: Bedeutende Vor- und Zwischenprodukte*. Weinheim : Wiley-VCH Verlag GmbH, 2007.
5. Sheldon, R. A. 2007, Green Chem. , Vol. 9, pp. 1273-1283.
6. Vitasari, C., Meindersma, G.W. and Haan, A.B de. 2011, Biores. Techn., Vol. 102, pp. 7204-7210.
7. Fele-Žilnik, Lj. and Jazbinšek, A. 2012, Sep. Pur. Techn., Vol. 86, pp. 157-170.
8. Hemmati-Sarapardeh, A., Shokrollahi, A., Tatar, A., Gharagheizi, F., Mohammadi, A.H., Naseri, A. 2014, Fuel, Vol. 116, pp. 39-48.

Copper Solvent Extraction Plant Commissioning

Mark F. Vancas, Tenova Bateman Technologies, Tucson, Arizona, USA

Summary

This discussion will give examples of what activities need to be considered when commissioning a copper solvent extraction plant. Also an example detailed description of how a typical single step in the process may be accomplished. Commissioning is largely about how all the various activities are coordinated and how one may interact with or be dependent upon another.

An example of one type of visual aid is given to assist even inexperienced commissioning team members with comprehension of the overall task and to initiate them into the realm of looking beyond their specific task to determine how their actions affect others and vice versa.

What is Commissioning?

Commissioning is basically checking of all components of a processing plant before the plant is actually placed in operation with the feed material and the expectation of producing the desired product.

Use of actual process fluids is necessary to fully check individual sections of the plant but, not until all sections have been checked with process fluids and deemed acceptable to operate in continuous mode can commissioning be called complete. If done properly the transition to production will be as simple (in the case of copper SX-EW) as adding extractant to the circuit and waiting to energize the rectifier.

Note that Electrowinning (EW) was included in the Solvent Extraction (SX) plant commissioning. In actuality the Leaching circuit could have been included as well because all three of these circuits must be in operation at the same time for any one of them to operate properly. They simply cannot be separated. For the sake of this discussion, the leaching circuit has been considered to be in operation on a recirculation basis and therefore sufficient Pregnant Leach Solution (PLS) readily available as needed.

What plant components need to be commissioned?

A typical commissioning list of components might look like the following:

- *PLS Pumps*
- *SX Feed Pond*
- *SX Feed Pond O'Flow*
- *Raffinate Pond*
- *Leach Solution Pumps*

For this example, these items were considered complete

Commissioning list of components con't.

- SX Feed Line
- Extraction Mixer-Settlers
- SX Raffinate line from Extraction Settlers to Raffinate Pond
- Stripping Mixer-Settler
- Wash Mixer-Settler
- Loaded Organic Tank
- Electrolyte Filter Feed Tank
- Electrolyte Filters and associated equipment
- Filter Backwash Tank
- Filtered Electrolyte Tank
- Electrolyte Recirculation Tank
- Spent Electrolyte Tank
- Crud Handling System
- Drainage systems and sump pumps
- Fire hydrant network
- Fire Suppression (foam or fog) system
- Sulfuric Acid tank
- Sulfuric Acid supply network
- Diluent storage Tank
- Holding Tank
- EW Heat Exchanger
- EW cells
- EW crane
- EW rectifier
- EW cathode stripping machine
- EW ventilation system

Note: This is a list only; no specific order is indicated or inferred as each project will have a different order.

The preceding list can get quite long depending on how much detail is desired. Normally a “Commissioning Plan” is created which explains in detail how each of the above line items is to be tested. These individual plans (often called “modules”) will look something like the following:

1.1.1 COPPER EXTRACTION MODULE 301

P & ID No's. 240-B-DH-001

240-B-DH-002

Objective

To test and prepare for operation the copper extraction circuit consisting of.

- the copper SX feed pond 240-TK-411
- the copper SX gravity feed line 240-PPC-401
- The copper extraction mixer-settlers and the associated agitators. 240-TK-401-403

Pre-requisites

Other modules that must be operational before this module can be fully tested include.

- PLS Pumps and fire water supply/distribution (Module 006)
- Instrument air (Module 001)
- Potable water supply/distribution (Module 004)

Procedure

Inspect the copper SX feed Pond (240-TK-411) to insure that no construction debris has been left in the pond or the gravity siphon line to the SX Plant.

Fill the pond with solution. The source of the solution can be water or, if available, the PLS. The tank will need to be completely full to supply sufficient volume to fill the mixers and settlers unless the mixers and settlers have been left full after leak testing by the construction crew.

Inspect all of the copper extraction mixer-settler units to insure that no construction debris has been left in the tanks or settlers. The false bottoms of each primary mixing tank also need to be inspected (this is best done before the mixing impeller has been installed).

The copper extraction system will be operated with water or PLS from the Copper SX Feed Pond, through the three extraction stages and set to recycle within each mixer-settler unit. Ensure the main valving is set for this operation.

For the Feed Line check the following:

Open the SX Feed Line (240-PPC-401) valves (including the manual valve immediately in front of the primary mixer). If the automatic flow control valve (FCV-40002) and flow indicator (FIC-40002) are functional, they can be used as needed.

Once the line has filled with water as much as possible by gravity, fill the first stage primary and secondary mixing tanks with water. After all the air in the line has been expelled into the primary mixing tank, the flow rate at FV-40002 can be increased.

When the primary mixer is completely full, start the agitator. When the secondary mixer is full, start the secondary mixer. During this time, the settler will be filling. Check the Primary Mixer amp draw and note along with the other information requested.

Adjust the level control column to minimise the volume in the settler while still allowing water to flow into and fill the organic launder.

Close the organic discharge valves on all the stages of extraction.

Adjust the level control column discharge valve to maintain a steady level within the column and allow the water to flow into the primary mixer of the second stage of extraction.

As the second stage mixers are filled, start the second stage agitators and adjust the discharge valves. This procedure should be repeated for all of the extraction stages.

When the water begins to overflow the last extraction stage, the raffinate should discharge should be closed and the recycle lines opened so that the water recycles within each mixer-settler unit. The water can then be circulated continuously until all systems have been tested and approved.

Open the organic advance valves on extraction stages to allow flow through the lines and into the primary mixer of the preceding stage. Keep the organic advance valve on the first stage closed.

Continue to operate the entire circulation system while the other systems are commissioned.

Inspect the entire circulation system and correct any leaks detected.

Check the operation of each of the level elements in each of the settlers. Observe and note the levels indicated and check the alarms are initiated by temporarily closing each settler overflow. Note the observed results.

Note: Within this module, other modules that must be complete prior are indicated. These “other” modules will always include items pertaining to safety. Also included will be documentation that basic safety and operational checks have been performed prior. Do not proceed with any new module until all the documentation has been verified and checked. After each module is identified and detailed, the commissioning team can formulate a plan as to which modules depend on others and which modules can be done independently and in parallel with the others. Experienced operators, having done this before, carry around in their heads a general scheme of things so they do not need a written “recipe”.

The schedule that becomes the commissioning plan can take many shapes but most frequently is shown in the form of a Gantt Chart with activities on one axis and time on the other. The duration of each activity is shown and the relative block of time is indicated by where on the calendar each activity block resides. This system has certainly worked for many projects and will certainly work for many more. Remember the preferences that individuals may have for equally valid methods. This is another case where preferences apply. I favor using the Critical Path Method (CPM) I learned in the army and I am willing to bet that the “general scheme of things” that experienced operators carry around in their heads is actually CPM based. Experienced operators just “know” what comes first, second, etc. and approximately how long each stage will take. For me CPM offers a visual picture of how things fit together to which a first timer can relate. A CPM diagram however cannot be created by someone that has never actually performed the tasks involved.

A typical critical path diagram for a Simplified 2E1S Commissioning might look something like the drawing on the last page.

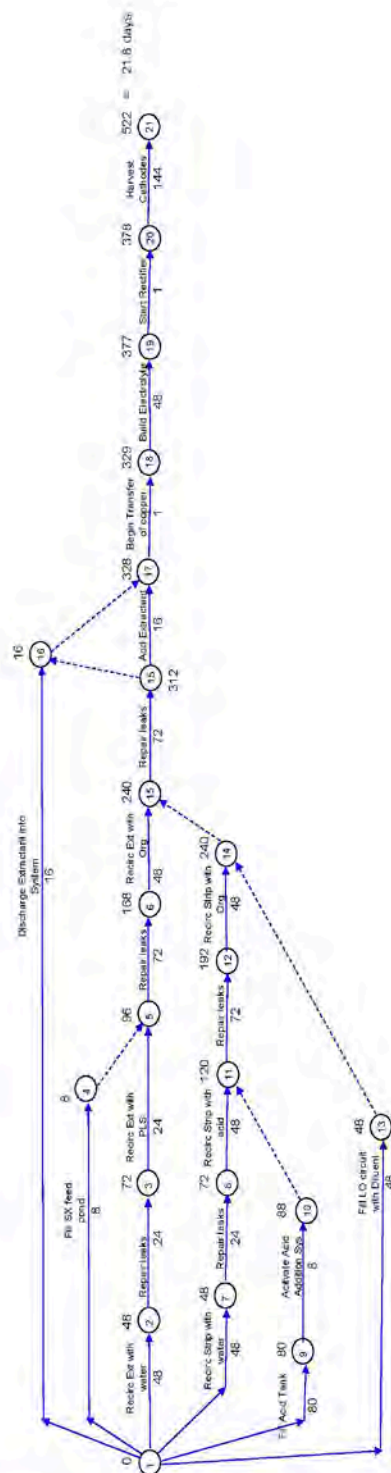
So, in a glance, one can look at a critical path diagram and readily see the interdependencies of the various tasks and also which tasks must stay on schedule and which tasks have plenty of float time available and therefore are not critical activities. At this point one can report to management that commissioning (in this case) will require a certain number of days provided nothing unexpected occurs. If this time does not fit with the expectations of management then management will need to make decisions that will allow certain steps to be sped up. A good example would be to work the repairmen on a 24 h basis. The basis here was an 8 h work day.

Note that beginning at node 17 the electrowinning circuit needs to be operable because once the extractant is added and copper begins to be transferred, there needs to be an outlet for that copper. This is a simplified CPM diagram; a more accurate one would have much more detail and would show the development of the electrowinning circuit in parallel with a dependency connector attaching to the SX node 17 indicating that the extractant cannot be added before the EW circuit is complete.

Conclusion:

Hopefully the foregoing discussion has emphasized the need to approach commissioning of a copper solvent extraction plant in an organized and formal manner, that experienced people must be involved, and that a clear visual depiction of the overall process is important for all parties to easily comprehend all the interdependencies that exist. Hopefully the foregoing has also reinforced the fact that commissioning of a solvent extraction plant is dependent on the commissioning of the leaching circuit as well as the electrowinning circuit.

Simplified 2E1S Commissioning
Critical Path Diagram



Gold and palladium adsorption from leached electronic scrap using ordered mesoporous carbon nanoscaffolds

*Peter Zalupski*¹ and Rocklan McDowell*

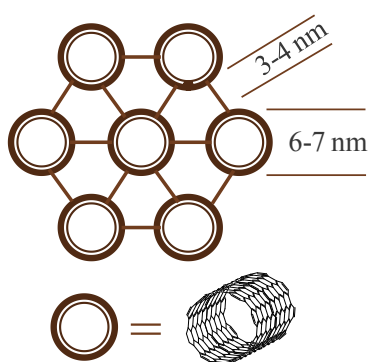
Ordered mesoporous carbon (OMC) nanoscaffolds are engineered agglomerates of carbon nanotubes held together by small carbon nanofibers with uniform pore sizes, high pore volume, and high channel permeability. These materials exhibit very high affinity for the adsorption of gold from aqueous acidic mixtures. The efficiency of gold recovery is comparable to those typically accomplished using biopolymer-based adsorbents. The adsorption efficiency for other precious metals such as palladium and platinum is lower. Studies on the precious metal (Au, Pd) adsorption on OMC materials from actual liquors of leached electronics is presented. Adsorption properties is compared for several different sorbents used for the recovery of precious metals. The leach liquor compositions for three different types of electronic scrap materials (personal computer board, cell phone and tv input/output board) is presented. The sorption efficiencies for Au(III), Pd(II), together with the competing Sn(IV), from such leach mixtures is compared for the investigated adsorbents.

Introduction

Escalating accumulation of electronic scrap materials is, amongst many, a byproduct of an unprecedented growth in technological advancements of modern world. The Environmental Protection Agency estimated that United States discarded 3 million tons of obsolete electronics in 2007, of which 86.4% was not recycled, ending up in landfills. [1] Global growth of e-waste has reached 40 million tons per year, according to the approximations from United Nations University. [2] The growing mountains of “e-waste” have progressively over the last several decades given some momentum to issues of environmental management and resource sustainability.

Recent report by Hagelüken provides a mass balance summary for various categories of electronics, illustrating the value of these materials, and the importance of recycling. [3] For instance, a metric ton of PC circuit boards contains roughly 250 g of gold, some 278 times greater content than that of typical gold ore. [3] Numerous statistics may be provided to support the recovery of valuable metals from used electronics. Besides obvious health benefits to public (especially in China and Africa – common e-waste dump sites for developed nations), economic argument appears straight-forward. Hagelüken reports that a value of common electronics is dominated by precious metals (PMs) and copper. For example, PMs account for 93% of the price for a cell phone, whereas copper hikes up the price of a DVD player by 36%. [3] To maintain the current rate of technological expansion it is perhaps necessary to consider the recovery of metals present at lowest abundance on our planet (Rh, Ru, Pd, Te, Re, Os, Ir, Pt, Au).

This communication adds to a broad spectrum of literature information targeting the recovery of those precious metals present in high concentrations in electronic scrap (Au, Pd). Specifically, studies on the recovery of gold and palladium using mesoporous carbon nanoscaffolds will be discussed. Ordered mesoporous carbon (OMC) materials are engineered agglomerates of carbon nanotubes held together by small carbon nanofibers with uniform pore sizes, high pore volume, and high channel permeability. [4] Their carbonaceous nature indicates that physico-chemical properties of OMC materials are similar to activated carbons. However, their structural architecture adds space, allowing for excellent channel accessibility and wettability in aqueous mixtures. [4] The diameters of typical pores of mesoporous materials range between 2 and 50 nanometers. The schematic drawing on the left



illustrates a simplified cross-sectional representation of possible architecture, where each circle corresponds to one carbon nanotube. The depth dimension represents the length of the mesoporous structure, which commonly measures several micrometers. Such mesoporous assembly may span ~100 channels, i.e. carbon nanotubes of 6-7 nanometer diameters, interlocked into hexagonal unit cells by carbon nanofibers to create wide 3-4 nanometer channel voids.

[5] In contrast, activated carbons are microporous, i.e. their pore sizes typically span the low Angstrom dimensions (5 – 20 Å). Parajuli et. al., when investigating gold adsorption on biopolymer gels, argued that limited space afforded by highly microporous activated carbon channels prevents the agglomeration of adsorbed gold particles, and, subsequently, reduces the adsorption capacity of gold. [6] In contrast, the mesoporosity of gels investigated by Parajuli afforded more opportunity for gold coagulation. Accordingly, similar adsorption differences for gold should be observed when mesoporous carbon is compared with activated carbon.

This study compares the adsorption efficiencies of Au(III) and Pd(II) for a spectrum of carbon-based porous materials, attempting to indicate which adsorbent is most efficient when equilibrated with harsh acidic environment of aqua regia leacheates of three types of circuit boards: cell phone, personal computer and tv output card. Aqueous compositions of leacheates of those materials will be presented, and factors influencing the differences in the adsorption of the investigated metal ions on five carbonaceous platforms will be discussed. The adsorbents analyzed in this work are: 1) mesoporous carbon, 2) activated carbon, 3) N-aminoguanidine modified grape skin tannin gel, 4) cross-linked cellulose gel, 5) mesoporous carbon impregnated with 2-mercaptobenzothiazole.

Experimental

All chemicals and reagents used in this study were of analytical grade and were utilized without further purification. Fresh aqua regia solutions were prepared prior to circuit board leaching using concentrated hydrochloric acid and nitric acid (Aldrich, *TraceSELECT*). The motherboard from an IBM T20 ThinkPad personal computer, a signal input board from Emerson LCD TV, and all the inside parts of a Motorola RAZR cell phone were leached. Electronic scrap was chopped, weighed and treated with aqua regia, introducing single pieces into the solution and waiting until vigorous exothermic reaction subsides. For cell phone leach, 31.8 g of scrap was introduced into 64 mL of aqua regia, dissolving 9.0 g of total mass. For PC board, 208.3 g of scrap was leached with 416 mL of aqua regia, dissolving 49.3 g of total mass. For TV output board, 235.4 g of scrap was submerged in 471 mL of aqua regia, dissolving 80.4 g of total mass. All leach mixtures were left soaking overnight to complete the dissolution process. All solutions were filtered using Acrodisc PVDF 0.2 μm filters (Pall Life Sciences, USA). The leachate mixtures were diluted (9.5 mL of leach to 25.0 mL) using 0.1 M HCl to reduce total concentration of hydrogen ions approximately to 5 M prior to all adsorption tests.

Mesoporous carbon (CMK-3) was purchased from ACS Material (USA). Activated charcoal, DARCO, 100 mesh, was purchased from Aldrich. N-aminoguanidine modified tannin gel was prepared according to the procedure by Gurung et. al., substituting persimmon tannin with grape skin tannin powder. [7] Cross-linked cellulose gel was prepared following the recipe by Pangen et. al. [8] Impregnation of CMK-3 with 2-mercaptobenzothiazole (Aldrich) followed the procedure by Zakharchenko, modified to prepare a 50 % w/w inorganic-organic hybrid.[9]

Metal ion adsorption properties were investigated in a static, batch contact mode. In all sorption experiments 30 mg of adsorbent was equilibrated with 10 mL of diluted leach solution. All experiments were conducted at room temperature (22 ± 2 °C), vigorously shaken for 18 hours using a Glas-Col multitube mixer. The suspensions were filtered after equilibration. All adsorption experiments were performed in triplicate, and each solution was sampled in triplicate. Leachate mixtures before and after contact with adsorbent materials were characterized for Au, Ag, Pd, Pt, Fe, Sn, Cu, Zn, Al, Ni, Cd, Pb and Hg using an ELAN 6000 Inductively Coupled Plasma with Mass Spectrometer (ICP-MS, Perkin Elmer). Reproducible measurements of metal content in aqua regia leachate mixtures required the presence of at least 10 % HCl v/v. Terbium internal standard proved most suitable in such analyses. The adsorption percentage is reported according to the equation 1, where C_i and C_e correspond to the concentration of a metal ion before and after equilibration with an adsorbent, respectively.

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Results and Discussion

Aqueous compositions of actual leacheates of cell phone, PC, and TV board scrap are compared in Table 1. The overall amounts of dissolved metals vary greatly due to different sample sizes, i.e. weights of scrap material used in three aqua regia dissolutions. However, when the amounts of liberated metals are considered in proportion to the total weights of used scrap (assuming their complete dissolution) their content agrees well with the general composition breakdown in electronics, as reported by Hagelüken. [3] Overall, good mass recoveries were accomplished. Bulk

Table 1. Composition of aqua regia mixtures after e-scrap leaching process. Total mass (mg) indicates the amount of metal dissolved in a known volume of leach solution (64 mL for cell phone, 416 mL for PC, 471 mL for TV). Mass basis composition (ppm or %) represents metal's mass fraction in studied e-scrap.

	cell phone		PC board		TV board	
	mg in leach	ppm or % [#]	mg in leach	ppm or %	mg in leach	ppm or %
Au	10.3 ± 0.7	325 ± 23	80 ± 2	386 ± 8	1.5 ± 0.4	6 ± 2
Pd	1.4 ± 0.1	43 ± 3	22 ± 1	106 ± 4	0.5 ± 0.2	2.1 ± 0.8
Ag	2.6 ± 0.5	82 ± 16	81 ± 10	391 ± 48	29 ± 1	124 ± 6
Pt	1.1 ± 0.1	35 ± 3	0.56 ± 0.01	2.7 ± 0.1	-	-
Cd	-	-	0.1 ± 0.01	0.50 ± 0.03	0.1 ± 0.02	0.41 ± 0.08
Hg	-	-	5.2 ± 1.5	25 ± 7	0.04 ± 0.01	0.19 ± 0.03
Fe	4570 ± 194	14.4 ± 0.6	8032 ± 356	3.9 ± 0.2	51482 ± 2042	21.9 ± 0.9
Sn	922 ± 20	2.9 ± 0.1	8498 ± 47	4.08 ± 0.02	6613 ± 242	2.8 ± 0.1
Al	98 ± 12	0.31 ± 0.04	4327 ± 261	2.1 ± 0.1	2464 ± 84	1.05 ± 0.04
Cu	4169 ± 415	13.1 ± 1.3	29299 ± 1765	14.1 ± 0.8	3526 ± 414	1.5 ± 0.2
Ni	420 ± 25	1.3 ± 0.1	2426 ± 61	1.20 ± 0.03	82 ± 2	0.04 ± 0.01
Zn	615 ± 31	1.9 ± 0.1	795 ± 133	0.4 ± 0.1	9033 ± 175	3.8 ± 0.1
Pb	1548 ± 50	0.74 ± 0.02	55 ± 5	0.17 ± 0.02	1.4 ± 0.1	< 0.01
[M] _t	170 ± 11 g/L		133 ± 7 g/L		156 ± 6 g/L	

[#]ppm for Au, Pd, Ag, Pt, Cd, Hg

% for Fe, Sn, Al, Cu, Ni, Zn, Pb

of the scrap material corresponds to plastics and glass, with metals ranging roughly between 20-40% of mass. Some distinct features of individual e-scrap sources (ex: high iron content in TV board, high tin content in PC board, low precious metal presence in TV board) are also apparent. Some findings, however, are in contrast to data provided by Hagelüken, most notably cell phone leach containing higher amount of lead, relative to PC and TV scrap. It is important here to indicate that the

compositions of leach mixtures are based on individual scrap pieces, which naturally may vary appreciably.

Table 2 summarizes the adsorption efficiencies for metals showing significant uptake (% uptake > 3 σ) from three studied e-scrap leach mixtures on five adsorbent materials. Adsorption of gold, palladium and tin are observed for all investigated adsorbents. Also, significant adsorption (6-11%) of iron from TV scrap leacheates (presumably due to its very high content) was observed on all adsorbent materials.

Table 2. Gold, palladium and tin adsorption efficiencies from aqua regia leached cell phone, PC and TV board scrap on mesoporous carbon, activated charcoal, tannin gel, cellulose gel and mesoporous carbon impregnated with 2-mercaptobenzothiazole.

	Cell phone			PC board			TV board		
adsorbent	Au(III)	Pd(II)	Sn(IV)	Au(III)	Pd(II)	Sn(IV)	Au(III)	Pd(II)	Sn(IV)
CMK-3	99 $\pm$ 5	25 $\pm$ 1	3.8 $\pm$ 0.1	99 $\pm$ 11	8 $\pm$ 1	0.9 $\pm$ 0.1	96 $\pm$ 2	29 $\pm$ 4	6.2 $\pm$ 0.2
charcoal	99 $\pm$ 7	35 $\pm$ 1	3.0 $\pm$ 0.1	99 $\pm$ 7	17 $\pm$ 1	3.3 $\pm$ 0.1	99 $\pm$ 2	29 $\pm$ 2	6.1 $\pm$ 0.1
tannin	73 $\pm$ 14	36 $\pm$ 1	4.5 $\pm$ 0.1	30 $\pm$ 1	37 $\pm$ 2	1.0 $\pm$ 0.1	16 $\pm$ 1	6 $\pm$ 1	3.4 $\pm$ 0.1
cellulose	99 $\pm$ 7	-	1.6 $\pm$ 0.1	18 $\pm$ 1	32 $\pm$ 3	3.1 $\pm$ 0.1	4 $\pm$ 1	9 $\pm$ 1	3.0 $\pm$ 0.1
CMK/MBT	99 $\pm$ 12	92 $\pm$ 3	4.0 $\pm$ 0.1	96 $\pm$ 4	80 $\pm$ 3	2.4 $\pm$ 0.1	98 $\pm$ 2	72 $\pm$ 3	4.0 $\pm$ 0.1

The adsorption of Au(III) is nearly quantitative from each type of leach environment for mesoporous (CMK-3) and microporous (charcoal) carbons. In contrast, the efficiency of gold adsorption on biopolymer-based sorbents varies on the composition of leach solutions. It appears that the presence of tin and iron in the mixtures competes with the adsorption of gold to solid surfaces. The tannin and cellulose gels adsorb most of Au(III) from cell phone leach solution, where the gold-to-tin proportion is highest of the three investigated mixtures. This efficiency is greatly reduced for PC and TV board leacheates, where high tin content (PC) and high iron content (TV) are present. At the same time, the adsorption of Pd(II) appears steady throughout the study, and only increases for CMK/MBT hybrid, which was specifically functionalized to enhance the uptake of this metal ion. It follows that the adsorption of competing tin and iron chloroanionic species inhibits the adsorption-reduction mechanism of gold uptake on biopolymer-based materials. The adsorption of gold typically follows this mechanism, and results in the agglomeration of gold particles on carbon-rich surfaces. [8] As a result, adsorption capacities for Au(III), relative to Pd(II) and Pt(IV), may in some cases be order of magnitude greater. [10] Higher palladium uptake, relative to gold, was observed in our studies for tannin and cellulose gels, suggesting that the formation of metallic gold is obstructed on those surfaces. X-ray diffraction and scanning electron microscopy studies are planned in our laboratories to investigate this anomaly in more detail.

Our preliminary conclusions from this applied work on the comparison of adsorbent materials must focus on the very similar uptake performance observed for mesoporous and microporous carbons. The adsorption properties for Au(III), Pd(II), Sn(IV), and Fe(III) are statistically the same for both carbon materials, and only the additional soft-bonding functionalization (CMK/MBT) enhances the palladium adsorption features of such materials. No apparent advantages of using mesoporous carbons over traditional activated carbon could be found. Nonetheless, the utilization of any type of carbonaceous material to separate precious metals dissolved in aqueous acidic leachates of electronic scrap appears to require a follow-on differentiation from tin, and (depending on the type of e-scrap) iron.

Acknowledgements

This research was supported by Idaho National Laboratory Director's Research and Development program.

References

1. *Electronics Waste Management in the United States*; EPA530-R-08-009; U.S. Environmental Protection Agency: Washington DC, 2008.
2. *Recycling: From E-Waste to Resources*; DTI/1192/PA; United Nations Environment Programme & United Nations University: 2009.
3. Hagelucken, C. In *Improving metal returns and eco-efficiency in electronics recycling*, IEEE International Symposium on Electronics and the Environment, San Francisco, 2006.
4. Ryoo, R., Joo, S., Kruk, M., Jaroniec, M., *Adv. Mater.* **2001**, *13*, 677-681.
5. Ji, X., Lee, K.T., Nazar, L.F., *Nat. Mater.* **2009**, *8*, 500-506.
6. Parajuli, D., Adhikari, C.R., Kuriyama, M., Kawakita, H., Ohto, K., Inoue, K., Funaoka, M., *Ind. Eng. Chem. Res.* **2006**, *45*, 8-14.
7. Gurung, M., Adhikari, B.B., Morisada, S., Kawakita, H., Ohto, K., Inoue, K., Alam, S., *Bioresour. Technol.* **2013**, *129*, 108-117.
8. Pangen, B., Paudyal, H., Abe, M., Inoue, K., Kawakita, H., Ohto, K., Adhikari, B.B., Alam, S., *Green Chemistry* **2012**, *14*, 1917-1927.
9. Zakharchenko, E., Mokhodoeva, O., Malikov, D., Molochnikova, N., Kulyako, Y., Myasoedova, G., *Procedia Chemistry* **2012**, *7*, 268-274.
10. Parajuli, D., Khunathai, K., Adhikari, C.R., Inoue, K., Ohto, K., Kawakita, H., Funaoka, M., Hirota, K., *Mat. Eng.* **2009**, *22*, 1173-1178.

Molecular and supramolecular speciation in organic extractant solutions: influence of the metal concentration on extraction efficiency

*Laurence Berthon^{*1}, Yannick Meridiano, Julie Muller, Ross Ellis², Mark Antonio, Thomas Zemb³ and Philippe Guilbaud*

Summary

In order to better understand the mechanisms involved in the extraction process, molecular and supramolecular speciation studies have been performed in the organic phases composed of a DMDOHEMA diluted in an alkane. Combining molecular dynamic simulations with experimental investigations (by UV-visible, EXAFS and FTIR spectroscopies, Vapour Pressure Osmometry and Small Angle X-Ray Scattering) provide a new understanding of the structural evolution of the organic solution driven by Eu(III) extraction that could account for the non-classical extractive behaviors. Extraction occurs initially by direct coordination of the Eu(III) ion to the O-donor ligands available in the organic phase (nitrate, water and DMDOHEMA). This seeds the formation of reverse micelles of malonamides. At increasing Eu(III) concentrations, the reverse micelle clusters attract each other to form larger polynuclear Eu(III) aggregates with metal cation bridged by nitrate. These pre-organized hydrophilic domains, provide improved Eu(III) solvation environments that drive the observed extractive properties.

Introduction

In the framework of nuclear waste reprocessing, the French 'commissariat à l'énergie atomique et aux énergies alternatives' (CEA) develops liquid-liquid extraction processes. Solvent extraction systems based on malonamide extractant DMDOHEMA (N,N'-dimethyl-N,N'-dioctyl hexylethoxymalonamide, in alkane are used in several processes (DIAMEX, DIAMEX-SANEX, EXAM process) to extract actinides and lanthanides from aqueous solutions.^{1, 2} In order to better understand the mechanisms involved in such extraction process, comprehensive studies are needed to gain a better representation of the species distribution. The properties of the solvent extraction system have traditionally been understood from concepts rooted in coordination chemistry. However, it is now well established that, the organic phases involved in such processes are not molecular solutions of extractants but, rather, structured solutions.^{3, 4}

The main objective of this study is to characterize the species in DMDOHEMA-alkane solutions when increasing the lanthanides concentration and explain the variation of extraction properties by combining experimental measurements with Molecular Dynamics (MD) simulations. The nature of the complexes in the organic phase was

* Corresponding Author,

¹ CEA Marcoule, Nuclear Energy Division, Radiochemistry and Processes Department, Separation Process Modelling and Chemistry Section, laboratory of interactions Ligands-Actinides. F- 30207 Bagnols-sur-Cèze (France) E-mail: laurence.berthon@cea.fr

² Argonne National Laboratory, Chemical Sciences and Engineering Division, Argonne, IL, 60439 (USA)

³ Institut de Chimie Séparative de Marcoule, UMR5257 CEA/CNRS/UM2/ENSCM, 30207 Bagnols-sur-Cèze (France)

investigated by complementary techniques (UV-visible, EXAFS and FTIR spectroscopies) and the supramolecular speciation was performed by Vapor Pressure Osmometry (VPO) analysis and Small Angle X Ray scattering (SAXS).

Results

Liquid-liquid extraction

Extraction of increasing concentrations of europium from the LiNO_3 aqueous phase by malonamides in n-heptane is investigated. The solutions compositions are reported in table 1. The extraction efficiency (europium distribution ratios) increases with the increase of Eu(III) concentration in the organic phase (Figure 1). This behavior is surprising and is not explainable by referring to the simple extraction mechanism by solvation as traditionally proposed for lanthanides extraction by malonamides (MA).^{5, 6} Indeed, a decrease in the 'free' malonamide concentration is expected when more Eu(III) are extracted and, consequentially, a decrease of the distribution ratio should be observed as the system approaches saturation.

In order to understand the surprising variation of Eu(III) distribution ratio, molecular and supramolecular speciation studies were performed in the organic phases.

Table 1: Column 2-5: Solute concentrations in aqueous (aq) and organic (org) samples after Eu(III) extraction from LiNO_3 aqueous solution by 0.5 M DMDOHEMA in n-heptane. The LiNO_3 concentration was adjusted in order to keep the water activity in the aqueous phase constant ($a_{\text{H}_2\text{O}} \approx 0.87$). Column 6: europium distribution ratio. Columns 7-10: Summary of the parameters used in the interpretation of the SAXS data (figure 3b) using Baxter's model for hard sticky spheres (N: Aggregation number (exclusive monomers), [mono]: monomer concentration, R_p : polar core radius, $U/k_B T$: inter-micellar interaction potential).

sample#	$[\text{LiNO}_3]_{\text{aq}}$ (mol/L)	$[\text{Eu}]_{\text{aq}}$ (mol/L)	$[\text{Eu}]_{\text{org}}$ (mol/L)	$[\text{H}_2\text{O}]_{\text{org}}$ (mol/L)	D_{Eu}	N	[mono] (M)	R_p (Å)	$U/k_B T$
1	2.93	0	0	0.062	0	4	0.21	5.8	-0.511
2	2.93	0.0066	0.0025	0.063	0.38	4	0.21	5.8	-0.606
3	2.83	0.037	0.0148	0.07	0.4	4	0.185	5.9	-1.229
4	2.76	0.0711	0.0307	0.076	0.43	4.5	0.13	6.2	-1.504
5	2.67	0.1391	0.0645	0.16	0.46	5	0.08	6.9	-1.764
6	2.37	0.2981	0.1034	0.221	0.35	5.8	0.02	7.2	-1.969
7	2.34	0.2855	0.1259	0.246	0.44	6.5	0.005	7.6	-2.037

Molecular characterisation

First, the immediate coordination environment around lanthanides as a function of mole ratio between extractant and metal in the organic phase was investigated by visible absorption spectroscopy (Figure 2a). Neodymium was chosen for this study because Nd (III) optical transitions between 500 and 900 nm are particularly sensitive

to the metal coordination environment.⁷ The spectra are quite similar, suggesting that little or no change in immediate coordination environment occurs in organic phase as the concentration of extracted Ln(III) cations increase. To supplement this investigation, EXAFS measurements were performed for organic phases containing Eu(III) cations. The Fourier transforms (FTs) of the EXAFS data (figure 2b) show that the positions of the main peaks do not change significantly with Eu(III) concentration, indicating as for Nd(III) extraction that the immediate environment around the Eu(III) center remains similar.

Fourier transform infra-red (FT-IR) spectroscopy from the 0.5 M DMDOHEMA solution before and after Eu(III) extraction confirmed, as expected, the coordination of the amide function to Eu(III) through its oxygen donor, and the presence of coordinated nitrate in organic solutions. Varying the europium concentration induces only changes in the intensity of peaks though no additional shift is observed.

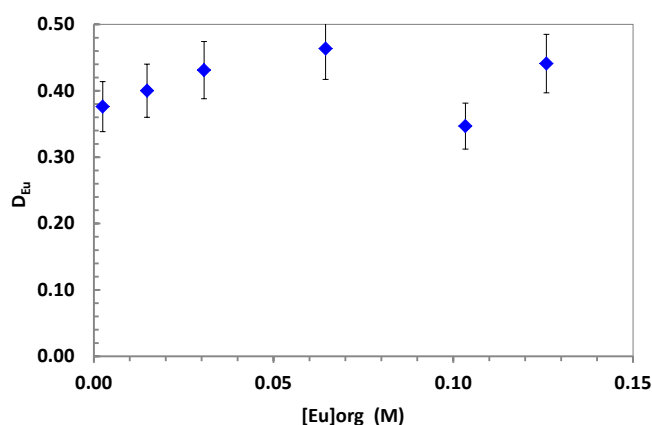


Figure 1: Variation of europium distribution ratio (D_{Eu}) as a function of organic phase Eu(III) concentration. Extraction conditions: organic phase: 0.5 M DMDOHEMA in *n*-heptane, aqueous phase europium nitrate in $LiNO_3$ aqueous phase (solute concentrations are reported in table1).

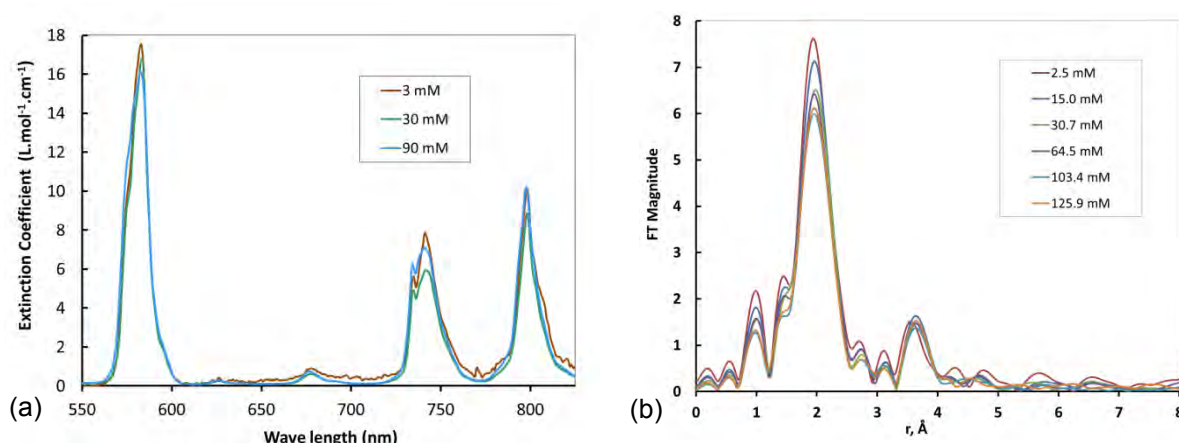


Figure 2: (a) UV-vis spectra from organic (0.6M DMDOHEMA in *n*-heptane) solutions of increasing Nd(III) concentrations produced by solvent extraction of Nd(III) from 3 M $LiNO_3$.

(b) Fourier transforms of the EXAFS data from organic (0.5 M DMDOHEMA in *n*-heptane) solutions of increasing Eu(III) concentration generated in the solvent extraction experiment.

Supramolecular organization

Vapor pressure osmometry (VPO) was used to estimate the average total aggregation number of the organic phase with increasing concentrations of extracted Eu(III) (Figure 3a). The average DMDOHEMA aggregation number n (taking into account monomers), increased from just under 2 to about 7 at very high concentrations of Eu(III). Without metal ion, 0.5 M DMDOHEMA in *n*-heptane solution is composed of 0.21 M of monomer and 0.072 M of tetramers.³ The introduction of Eu(III) seeds the formation of aggregates so that the proportion of monomers steadily decreases resulting in an increase in total average aggregation number, n .

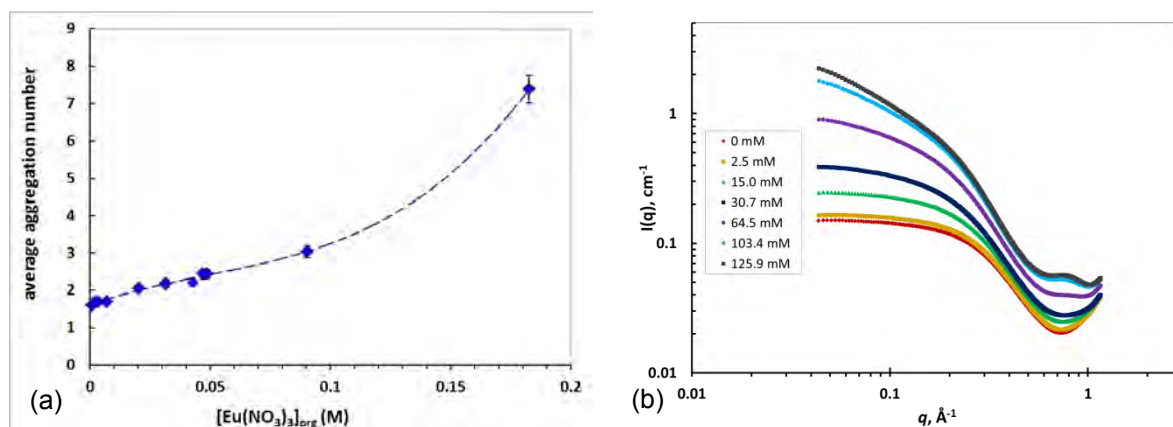


Figure 3: (a) VPO average aggregation number, n , for solutions of increasing Eu(III) concentrations produced by solvent extraction of Eu(III) from ca. 3 M $LiNO_3$ into 0.5 M DMDOHEMA in *n*-heptane. (b) SAXS data collected from 0.5M DMDOHEMA in *n*-heptane organic phases generated in the solvent extraction experiment containing up to 125.9 mM Eu(III).

To probe the supramolecular aggregate structures, small-angle X-ray scattering (SAXS) experiments were performed (figure 3b). The shapes of the curves are typical for particle scattering. These data were interpreted using the Baxter model for hard sticky spheres as described in [4] and the modelling parameters are presented in Table 1. The solution becomes more structured as Eu(III) is extracted, manifest in a significant decrease in monomer concentration. Aggregates also become larger with average aggregation numbers N (exclusive of monomers) increasing from 4 to 6.5 confirming the VPO results.

Molecular Dynamics simulations

To complete the experimental approach, molecular dynamics (MD) simulations were conducted. The systems were simulated at low (0.015 M) and high (0.126 M) Eu(III) concentrations. The number of Eu^{3+} , NO_3^- , *n*-heptane, H_2O and DMDOHEMA molecules included in each of the two simulated solutions were determined, after extraction of Eu(III), from the experimental organic solutions element analyses.

The aggregating behaviour was investigated by statistical analyses of the entire systems (Figure 4a and 4b). At low concentration, Eu(III) has a limited influence on

the extractants organization, which are distributed in small and polydispersed aggregates (as suggested by the VPO and SAXS data). At higher concentrations, the DMDOHEMA and water molecules are drawn around the Eu(III) clusters, with much less independent extractant monomers distributed in the available space. This is consistent with the Baxter model interpretation of the SAXS data that shows Eu(III) to trigger the formation of more defined aggregates and hence decrease monomer concentration in equilibrium with the aggregates.

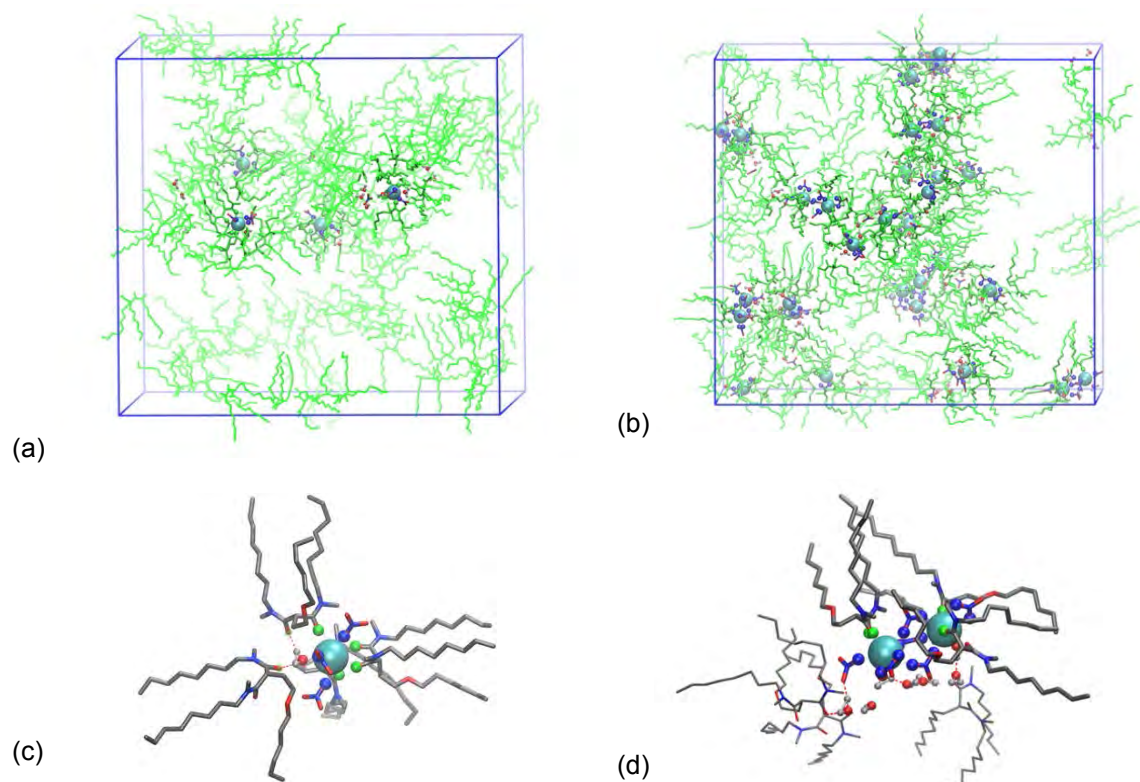


Figure 4: Snapshots of the MD simulation boxes at low (a) and high (b) Eu(III) concentrations corresponding to the composition of samples N°3 and 7 respectively. Figures a and b are from the snapshot without the n-heptane solvent. DMDOHEMA is shown in green, nitrate in red/blue, water in red/white and Eu(III) as large cyan spheres. Illustrative examples of Eu(III) – DMDOHEMA complexes isolated from MD simulation (snap-shots) for dilute (c) and concentrated (d) europium systems.

The average Eu(III) coordination environment in relation to the other hydrophilic solutes was then calculated from radial distribution functions (RDFs) centered on Eu(III) for both solutions. At low Eu(III) concentration (Figure 4c), an average of three DMDOHEMA molecules coordinate the Eu(III) cation (two through bidentate mode and one through monodentate mode). 2.8 nitrate molecules (0.7 bidentate and 2.1 monodentate) are coordinated in the cation inner-sphere, and 0.2 nitrate molecules are in the cation second sphere (at 5 Å away from Eu(III)). Less than one (0.8) water molecule is bounded directly to Eu(III), which is in agreement with the experimental TRLIFS result⁴ and shows that the majority of the water that is co-extracted into the organic phase with Eu(III) is not directly involved in metal coordination. At high Eu(III)

concentration, changes in the cation inner-sphere are relatively minor and therefore, consistent with the experimental EXAFS and UV-visible data. The major differences occur in the coordination outer-sphere, where the most prominent structural change is indicated by (i) the presence of a significant peak attributable to a Eu..Eu correlation on the RDF (between 5 and 6.4 Å,) and (ii) the increase of bound nitrate above the number 3 (which is required to form neutral mono-nuclear $\text{Eu}(\text{NO}_3)_3$ complexes). This is a result of the formation of binuclear clusters of Eu(III) bridged by nitrate ions, as shown in Figure 4d. The high Eu(III) concentration also results in a decrease of the average number of malonamides per cation.

Conclusion

Combining the MD simulation with the experimental investigation provide a new understanding of the structural evolution within organic solutions driven by Eu(III) extraction that could account for the non-classical extractive behaviors. Extraction occurs initially by direct coordination of the Eu(III) ion to the O-donor ligands available in the organic phase (nitrate, water and DMDOHEMA). This seeds the formation of reverse micelles of malonamides. As the Eu(III) concentrations, the solution become more structured. The aggregates attract each other to form larger polynuclear Eu(III) aggregates with metal centers bridged by nitrate. These pre-organized hydrophilic domains, provide improved Eu(III) solvation environments and drive the observed extractive properties.

References

1. C. Madic, M. Lecomte, P. Baron and B. Boullis, *Separation of Long-Lived Radionuclides from High Active Nuclear Waste*, *Comptes Rendus Physique*, 2002, **3**, 797-811.
2. C. Poinssot, C. Rostaing, P. Baron, D. Warin and B. Boullis, *Main Results of the French Program on Partitioning of Minor Actinides, a Significant Improvement Towards Nuclear Waste Reduction*, *Procedia Chemistry*, 2012, **7**, 358-366.
3. Y. Meridiano, L. Berthon, X. Crozes, C. Sorel, P. Dannus, M. R. Antonio, R. Chiarizia and T. Zemb, *Aggregation in Organic Solutions of Malonamides: Consequences for Water Extraction*, *Solvent Extr. Ion Exch.*, 2009, **27**, 607-637.
4. R. J. Ellis, Y. Meridiano, R. Chiarizia, L. Berthon, J. Muller, L. Couston and M. R. Antonio, *Periodic Behavior of Lanthanide Coordination within Reverse Micelles*, *Chemistry-a European Journal*, 2013, **19**, 2663-2675.
5. C. Musikas and H. Hubert, *Extraction by N,N'-Tetraalkylmalonamides. II. Extraction of Metallic Ions*, *Solvent Extr. Ion Exch.*, 1987, **5**, 877-893.
6. M. C. Charbonnel, J. L. Flandin, S. Giroux, M. T. Presson, C. Madic and J. P. Morel, in *Extraction of Ln(III) and Am(III) from Nitrate Media by Malonamides and Polydentate N-Bearing Ligands*, eds. K. C. Sole, P. M. Cole, J. S. Preston and D. J. Robinson, South African Institute of Mining and Metallurgy, Marshalltown, South Africa, 2002, vol. 2, pp. 1154-1160.
7. M. P. Jensen, R. Chiarizia and V. Urban, *Investigation of the Aggregation of the Neodymium Complexes of Dialkylphosphoric, -Oxothiophosphinic, and -Dithiophosphinic Acids in Toluene*, *Solvent Extraction and Ion Exchange*, 2001, **19**, 865-884.

Process for the selective membrane-based solvent extraction recovery and enrichment of Pt, Pd and Rh from spent catalyst leaching solutions

D.J. van der Westhuizen^a, E. Bringas^b, I. Ortiz^b and H.M. Krieg^a

^aFocus Area: Chemical Resource Beneficiation, North-West University, Private Bag X6001, Potchefstroom 2531, South Africa

^bUniversidad de Cantabria. Dpto. Ingeniería Química y Química Inorgánica. ETSIIyT. Avda. de los Castros, s/n -39005 Santander, Spain.

Membrane based solvent extraction (MBSX) is a combined process of solvent extraction performed in membrane contactors. These contacting devices can be used in various solvent extraction applications and allow two liquid phases to have direct contact with each other, for mass transfer between the two liquid phases, without dispersing one phase into the other. In this study, the foregoing approach for the extraction and separation of platinum, palladium and rhodium, was achieved by making a water-in-oil emulsion of the organic solvent and the aqueous stripping liquor prior to the extraction process. During the process, the platinum group metals (PGMs) were transferred from the aqueous phase (shell side) by the organic extractant through the fiber pores, via the continuous organic phase to the water droplets in the emulsion (lumen side). Subsequently, the emulsion was segregated to recover the PGMs in the aqueous solution and the organic solvent was recycled.

This approach lead to a simultaneous extraction and stripping of the selected PGMs, which would lead to a reduction in plant size. This technique differs markedly from techniques employing conventional mixer-settlers offering a number of important advantages over such conventional dispersed phase contactors, including; (i) the absence of undesirable emulsions and third-phases which can form when the extractant material and the feed aqueous solution are traditionally contacted which could lead to poor phase separation resulting in erroneous mass balances; (ii) flooding at high flow rates is avoided; (iii) unloading at low flow rates is prevented; (iv) density differences between fluids is no longer required; and (v) high interfacial areas are achieved. Furthermore, in mixer-settlers, the contact area formed on the surface of the water-in-oil droplets varies considerably depending on numerous factors. In contrast to this, the available surface area that is created by the membrane pores in a membrane contactor remains constant and known. Furthermore, membrane contactors can achieve higher efficiencies with significantly larger contact areas (x 500). A further advantage is that linear scale-up is achieved thereby facilitating scale-up procedures across a range of various commercial available membrane contactors of different sizes varying from 100 L/h to 100 000L/h. When considering these advantages, it can be expected that this technique will increase the sustainability and profit of the secondary resource PGM separation and recovery in the South Africa's hydrometallurgical industries from spent catalytic converters, while reducing the ecological footprint of the process.

Recovery of Platinum(IV) and Palladium(II) from Complex Hydrochloric Acid Matrices by a Thiodiglycolamide Derivative

*A.P. Paiva^{*1}, G.I. Carvalho¹, M.C. Costa², A.M.R. Costa³, C.A. Nogueira⁴*

Summary

The solvent extraction performance of *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) towards Pt(IV) and Pd(II) in HCl solutions has recently been published. It was shown that these two platinum-group metals (PGMs) are efficiently extracted from 8 M HCl aqueous phases, being subsequently separated by sequential strippings: 1 M HCl allows Pt(IV) recovery, whereas Pd(II) is only back-extracted by thiourea in HCl. In this work, selectivity tests were carried out to evaluate the performance of DMDCHTDGA towards the recovery of both PGMs, from 8 M HCl aqueous phases, when in presence of Rh(III), Fe(III), Ni(II), Zn(II), Al(III), Ce(III) and Zr(IV), simulating the leaching solutions that may result from the hydrometallurgical treatment of spent automobile catalytic converters. It was generally observed that the additional metal ions do not affect the recovery of Pd(II) and Pt(IV) by DMDCHTDGA. Fe(III), Zn(II) and Zr(IV) are co-extracted with Pt(IV) and Pd(II); Fe(III) and Zn(II) were efficiently scrubbed with water, whereas Zr(IV) was removed by an acidified aqueous solution. Inversely, Ni(II) is not extracted, and Rh(III) and Ce(III) appear only traceably in the loaded organic phase. Al(III) is a concern, as it is appreciably extracted, and none of the tested back-extraction solutions was able to strip it.

Introduction

Platinum, palladium and related rare metals are nowadays considered critical raw materials. In fact, platinum-group metals (PGMs) are not abundant in the Earth's crust, and the maintainance of their supply is a concern, mainly because PGMs technological applications have been progressively increasing in last years and are hardly replaceable – in electronics, fuel cells, and in automobile and industrial catalysts, to mention only a few [1]. Furthermore, PGMs large utilization in areas such as jewelry and health should not be forgotten as well. All these reasons justify an extensive investigation on new and modified hydrometallurgical processes to attain PGMs separation and / or concentration from complex industrial leaches or effluents [2], and the versatility of solvent extraction to contribute for such objectives is widely recognized [3].

The solvent extraction systems that are industrially used to recover Pt(IV) and Pd(II) from chloride leaching solutions of primary sources usually involve tertiary amines, ammonium salts and neutral organophosphorus compounds, as well as alkyl sulfides, hydroxyoximes and 8-hydroxyquinolines for Pd(II) [3]. These extractants are generally not so adequate to treat leaching solutions coming from the recycling of secondary sources, as these latter traditionally have more complex and specific compositions. Therefore, the investment on the finding of new types of extractant

^{*1} CQB, DQB-FCUL, Universidade de Lisboa, 1749-016 Lisbon, Portugal. E-mail: appaiva@fc.ul.pt

² CCMAR, DQF-FCT, Universidade do Algarve, 8005-139 Faro, Portugal

³ CIQA, DQF-FCT, Universidade do Algarve, 8005-139 Faro, Portugal

⁴ LNEG, 1649-038 Lisbon, Portugal

molecules, which may show a more versatile behavior in terms of selectivity and kinetics, for instance, is presently rather active.

Considering the novel extractant molecules that have recently been proposed for Pt(IV) and Pd(II) recovery from chloride aqueous phases, extractants bearing nitrogen and / or sulfur atoms are the most popular. Compounds of the amide-type, e.g., malonamide for Pt(IV) [4-6], diglycolamide and thiodiglycolamide for Pt(IV) and Pd(II) [7,8], and sulfide-containing monoamides [9], a dithioether [10], pyridinecarboxamides [11] and fatty imidazolines [12] for Pd(II) have been reported.

In sequence of the investigation revealing the adequacy of *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) to simultaneously recover Pt(IV) and Pd(II) from 8 M HCl solutions [8], this work describes and discusses the behavior of DMDCHTDGA towards the two PGMs when Rh(III) and other rare and contaminating metals coexist in the aqueous solutions. The chosen metals were Fe(III), Al(III), Ni(II), Zn(II), Ce(III) and Zr(IV), and the objective was to roughly simulate the composition of a leaching solution obtained from the hydrometallurgical treatment of a spent automobile catalytic converter.

Experimental

The synthesis of DMDCHTDGA was carried out as previously reported [8]. Its overall purity, determined by liquid chromatography coupled with mass spectroscopy (LC-MS), is above 85%. 0.05M DMDCHTDGA solutions in 1,2-dichloroethane (1,2-DCE) were used as organic phase.

For the preparation of the feed aqueous phases, atomic absorption spectroscopy standards of Pt(IV), Pd(II), Rh(III), Ce(III) and Zr(IV), and chloride salts of Fe(III), Al(III), Ni(II) and Zn(II) were arranged. Several 8 M HCl aqueous media were prepared, always containing Pt(IV) and Pd(II), and bearing different combinations of the other metals, with a maximum of five. All metal ion concentrations were of about 100 mg/L, with the exception of Fe(III) and Al(III), both with 500 mg/L. Distilled water, 1 M HCl, and 0.1 M thiourea in 1 M HCl were used as stripping agents.

General extraction and stripping experiments were performed at room temperature through contact of equal volumes of the organic and aqueous phases ($A/O = 1$) for 30 minutes, by mechanical shaking, adopting a rotation speed between 900 and 1000 rpm. This contact time is enough to reach equilibrium conditions [8]. After separation of the two phases, the aqueous and organic extracts were always filtrated, to minimize mutual entrainments.

All the metal ion contents in the aqueous solutions, before and after extraction, were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Horiba Jobin-Yvon, Ultima). Metal concentrations in organic phases were found by mass balance. The coefficient of variance calculated for the extraction and stripping results presented in this article is about $\pm 5\%$.

For some of the experiments described in sequence, the involved DMDCHTDGA samples were not fresh, they had already been used for Pt(IV) extraction. This recycling procedure has been systematically adopted throughout the study, as it was found that DMDCHTDGA is robust and stable, its loading capacity is rather elevated [8], and its general extraction performance is not affected by incomplete Pt(IV) stripping. That is the reason why some of the determined Pt(IV) concentrations are untypically high, but those occurrences do not invalidate the information picked up from the extraction profiles obtained.

Results and Discussion

Pt(IV) and Pd(II) binary mixture

A 8 M HCl solution containing 100 mg/L Pt(IV) and Pd(II) was equilibrated with a 0.05 M DMDCHTDGA solution in 1,2-DCE, and the loaded organic phase was then sequentially contacted with 1 M HCl and 0.1 M thiourea in 1 M HCl, under the adopted general experimental conditions. The results obtained are displayed in Figure 1.

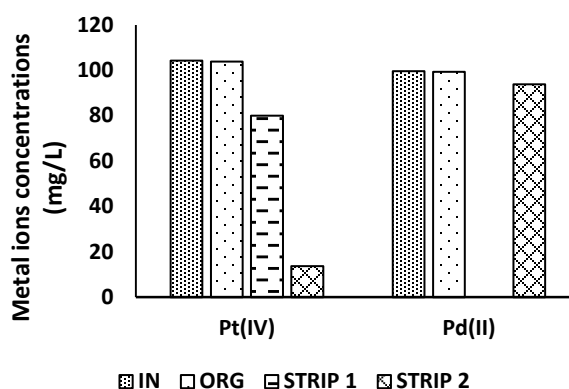


Figure 1 - Pt(IV) and Pd(II) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl - STRIP 2). Standard deviations: $\pm 5\%$.

It can be observed that DMDCHTDGA extracts Pt(IV) and Pd(II) almost quantitatively. The 1 M HCl solution strips 80 mg/L (77%) of Pt(IV), and Pd(II) stays in the organic phase. The thiourea solution efficiently re-extracts Pd(II) (94%), but about 14 mg/L of Pt(IV) are also co-stripped. A second contact of the organic phase with a new portion of thiourea solution did not release the Pt(IV) and Pd(II) contents still remaining in the organic medium after the first contact.

Ternary mixtures

The solvent extraction performance of DMDCHTDGA was evaluated for four aqueous solutions containing one more metal - Rh(III), Ce(III), Al(III) or Zr(IV) - in addition to Pt(IV) and Pd(II), under the usual set of experimental conditions. Neither Rh(III) nor Ce(III) were appreciably extracted by DMDCHTDGA – only about 7 mg/L of both metals were extracted. None of these metals was detected in any stripping solution. The solvent extraction behavior towards Pt(IV) and Pd(II) was not affected.

Regarding the influence of Zr(IV), it was found that this metal ion is also efficiently extracted by DMDCHTDGA, but completely stripped by 1 M HCl – Figure 2. Hence, Pt(IV) and Zr(IV) co-exist in the 1 M HCl stripping solution.

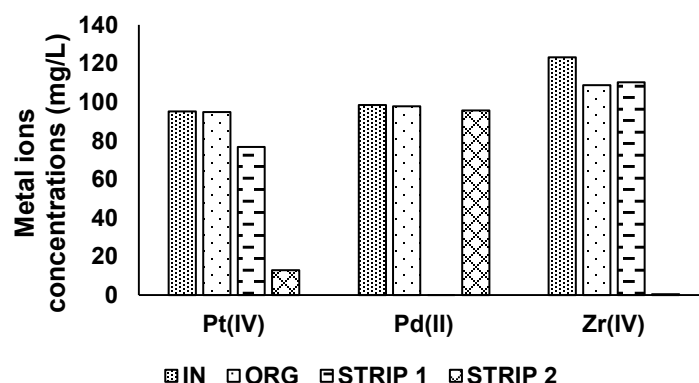


Figure 2 - Pt(IV), Pd(II) and Zr(IV) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations: $\pm 5\%$.

When in presence of 500 mg/L Al(III), DMDCHTDGA was able to transfer approximately 90 mg/L of this metal to the organic phase, about the same concentration as those of the PGMs – Figure 3. Al(III) was not detected in any of the stripping solutions. As the performance towards Pt(IV) and Pd(II) remains the same, it can be anticipated that the problem caused by the co-extraction of Al(III) may be solved if a suitable stripping agent, to be applied at the end of the solvent extraction scheme, is found.

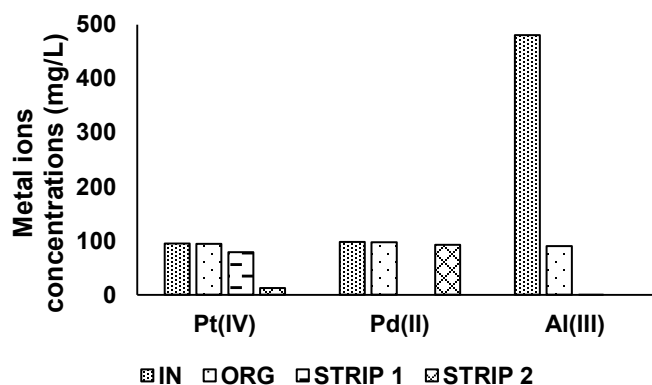


Figure 3 - Pt(IV), Pd(II) and Al(III) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations: $\pm 5\%$.

Complex mixtures with four and five metals

The solvent extraction performance of DMDCHTDGA was checked with a few complex mixtures containing four and five metals simultaneously. For instance, the results obtained for a mixture containing Pt(IV), Pd(II), Rh(III) and Fe(III) can be observed in Figure 4. For this case, and in the expectation that Fe(III), if extracted, could be scrubbed with water, the loaded organic phase was firstly contacted with

water, before the stripping stages. The DMDCHTDGA sample used was recycled, which explains why more Pt(IV) than expected appears in water and in stripping solutions.

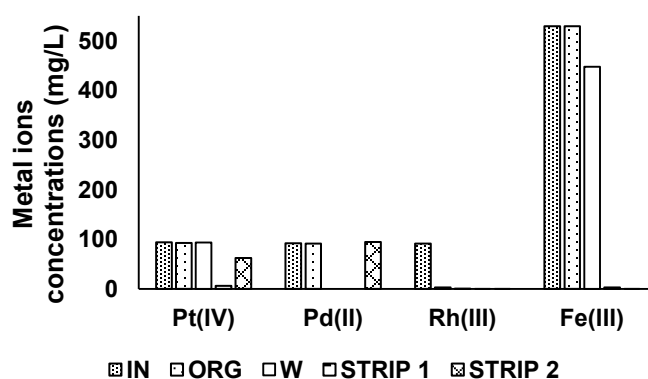


Figure 4 - Pt(IV), Pd(II), Rh(III) and Fe(III) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), scrubbing water (W) and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations: $\pm 5\%$.

It can be observed that the majority of Fe(III) is effectively scrubbed with water. The solvent extraction behavior of DMDCHTDGA for the PGMs remains unchanged. Water is also a good releasing agent for Pt(IV).

A final example of the DMDCHTDGA solvent extraction performance towards complex metal ion mixtures can be observed in Figure 5, where Pt(IV), Pd(II), Rh(III), Ni(II) and Zn(II) coexist in the 8 M HCl solution. The scrubbing step with water was also carried out, and again the DMDCHTDGA sample was overloaded with Pt(IV).

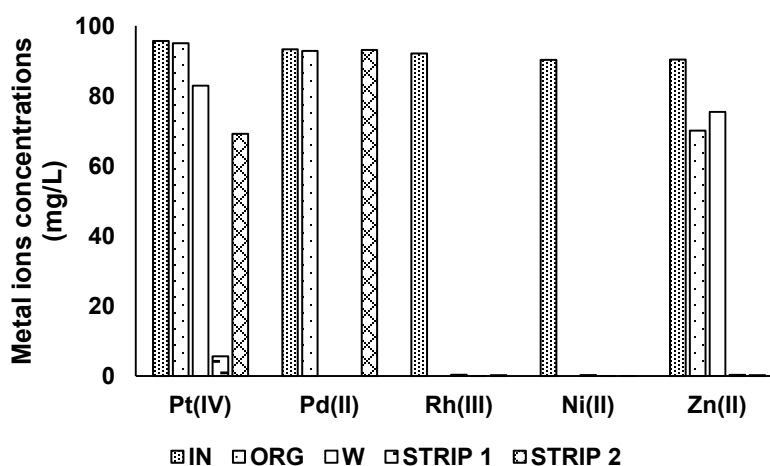


Figure 5 - Pt(IV), Pd(II), Rh(III), Ni(II) and Zn(II) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), scrubbing water (W) and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations: $\pm 5\%$.

It can be seen that the performance towards Pt(IV) and Pd(II) is similar as before, Rh(III) and Ni(II) are not extracted, and Zn(II) is completely removed in the water scrubbing stage.

Conclusions

N,N'-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA), dissolved in 1,2-dichloroethane, proved to be a skilful extractant to recover Pt(IV) and Pd(II) from complex 8 M HCl solutions, somehow simulating the composition of leaches obtained from the hydrometallurgical recycling of spent automobile catalytic converters. Zn(II), Fe(III) and Zr(IV) were co-extracted with Pt(IV) and Pd(II); the former two were easily removed by a water scrubbing, and Zr(IV) was released by 1 M HCl (water was not tested for Zr(IV) removal). Ni(II), Rh(III) and Ce(III) were practically not extracted. Al(III) was extracted in an amount similar to Pt(IV) and Pd(II), and its stripping by any of the agents tested was unsuccessful. The finding of a suitable Al(III) stripping agent, to be applied after Pt(IV) and Pd(II) recovery, may solve this poisoning problem of DMDCHTDGA. The solvent extraction performance shown by DMDCHTDGA for Pt(IV) and Pd(II), always unchanged for all the conditions tested, is remarkable.

Acknowledgements

The financial support for this work has been kindly provided by FCT, “Fundação para a Ciência e a Tecnologia” (Lisbon, Portugal) under the project PTDC/QUI-QUI/109970/2009, including the investigation grant offered to G. I. Carvalho.

References

1. Saurat, M., Bringezu, S. *J. Ind. Ecol.* **2008**, *12*, 754–767.
2. Hagelüken, C. *Chim. Oggi* **2006**, *24*(2) suppl., 14–17.
3. Cox, M., in *Principles and Applications of Solvent Extraction*, 2nd Ed.; Rydberg, J., Musikas, C., Choppin, G.R., Eds.; Marcel Dekker Inc.: New York, 2004.
4. Malik P., Paiva, A.P. *Solv. Extr. Ion Exch.* **2009**, *27*, 36–49.
5. Malik P., Paiva, A.P. *Solv. Extr. Ion Exch.* **2010**, *28*, 49–72.
6. Costa, M.C., Assunção, A., Costa, A. M. R., Nogueira, C., Paiva, A.P. *Solv. Extr. Ion Exch.* **2013**, *31*, 12–23.
7. Narita, H., Tanaka, M., Morisaku, K. *Proc. ISEC 2005*, Beijing, China, Conf. Proc. Ed. Dep., ed.; 2005, pp. 227–232.
8. Paiva A.P., Carvalho, G.I., Costa, M.C., Costa, A.M.R., Nogueira C. *Solv. Extr. Ion Exch.* **2014**, *32*, 78-94.
9. Narita, H., Tamura, K., Tanaka, M. *US Patent 2009178513-A1*, July 2009.
10. Traeger, J., König, J., Städtke, A., Holdt, H.-J. *Hydromet.* **2012**, *127-128*, 30–38.
11. Szczepanska, I., Borowiak-Resterna, A., Wisniewski, M. *Hydromet.* **2003**, *68*, 159-170.
12. Anpilogova, G.R.; Bondareva, S.O.; Khisamutdinov, R.A.; Murinov, Yu.I. *Solv. Extr. Ion Exch.* **2014**, *32*, 206-220.

Probing the outer coordination sphere to define the mode of action of unusually strong and selective metal extractants.

Peter A Tasker¹, Emma Carter², Ian A Fallis², Ross S Forgan¹, Ross J. Gordon¹, Mary R. Healy¹, Jason B. Love¹, Carole A Morrison¹, Damien M Murphy²

The inter-ligand hydrogen bonding in copper(II) complexes of phenolic oxime extractants has been investigated by a combination of continuous wave electron paramagnetic resonance (CW-EPR), electron nuclear double resonance (ENDOR) and computational methods. The changes in structure resulting from the incorporation of a hydrogen bond acceptor *ortho* to the phenolic oxygen atom that are revealed by the magnetic resonance techniques mirror those found in DFT calculations and are consistent with ligand-ligand secondary bonding in the outer coordination sphere being important in defining the strength and selectivity of metal solvent extractants.

Introduction

Hydrogen bonding between ligands is an important feature in coordination chemistry, often contributing to the thermodynamic and kinetic stability of complexes in systems as diverse as antibiotics, gravimetric reagents and metal extraction.¹ The low polarity of water-immiscible liquids used in commercial solvent extraction processes favours the retention or the formation of hydrogen bonds between extractant molecules. Well known examples (Figure 1) include the formation of (a) 8-membered chelate rings by D2EHPA,² (b) “tridentate” assemblies between α -hydroxyoximes (L) and carboxylic acids, in the remarkable synergistic extraction of nickel as $[\text{Ni}(\text{L}.\text{RCO}_2)_2]$,³ and (c) “macrocyclic” copper complexes of phenolic oxime extractants.⁴

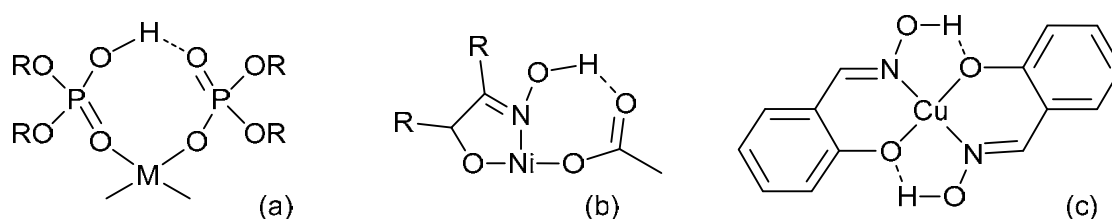


Figure 1: The H-bonding in (a) the 8-membered pseudo-chelates formed² by D2EHPA ($R = 2$ -ethylhexyl), (b) the “tridentate” assembly of α -hydroxyoxime ($R = n$ -propyl) and benzoic acid³ in their nickel(II) complex and (c) the pseudomacrocyclic copper(II) complexes formed by phenolic oximes.⁴

Inter-ligand hydrogen bonding in the phenolic oxime complexes makes a significant contribution to their stability and the introduction of H-bond acceptors in the 3-position, *ortho* to the phenol group (see Figure 2), can be used to “buttress” H-bonding, further strengthening extraction.⁵ For the series shown in Figure 2 the Cu-distribution ratio varies by more than two orders of magnitude on changing the 3-X substituent from a bromo to a *t*-butyl group. The extent to which this depends on H-bond buttressing by the substituent, the acidity of the extractant or to the strength of the bonds formed with the extracted copper ion has been analysed⁵ and is considered in more detail for a related series of phenolic pyrazole extractants in another paper in this conference.⁶

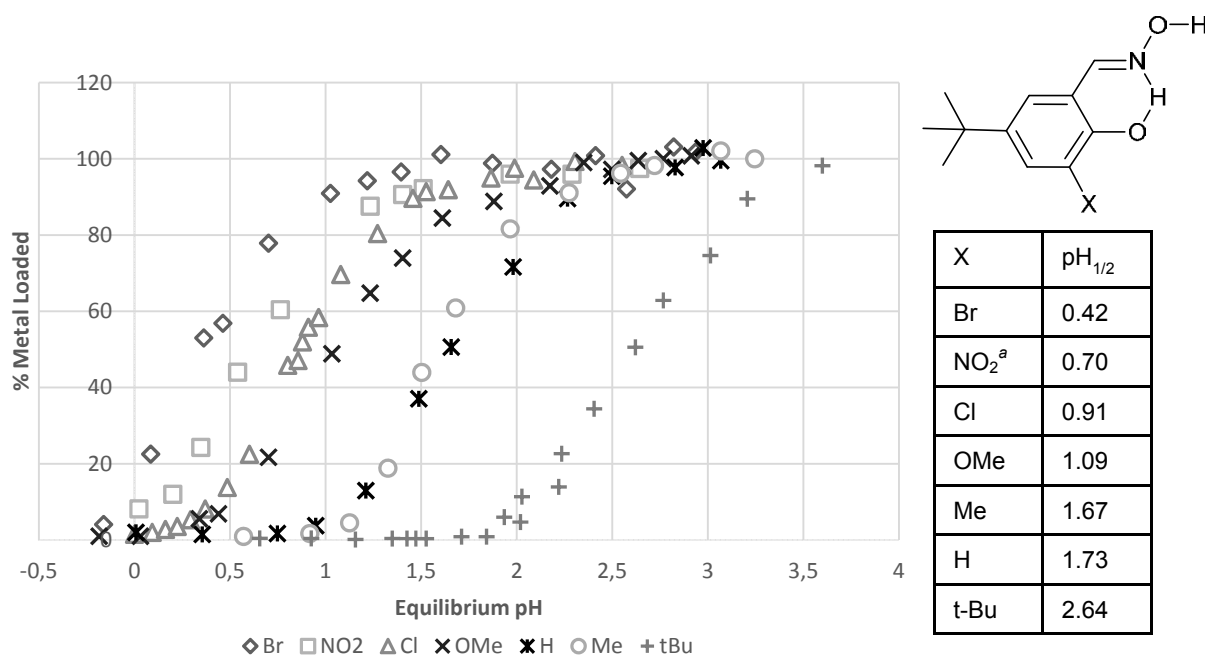


Figure 2: Cu(II) loading⁵ by 0.01 M CHCl₃ solutions of 3-X-5-t-Bu-salicylaldoximes from 0.01 M aqueous CuSO₄. ^aThis has a branched nonyl, rather than t-butyl, group in the 5-position.

Structural information on the regions of the copper complexes that form the inter-ligand H-bonds is necessary to understand the origins of the buttressing effects but has been difficult to obtain. The precision with which H-atoms can be located in transition metal complexes by X-ray methods is limited, and also in the solid state the Cu-atoms have a propensity to form weak bonds to donor atoms in neighbouring molecules which in turn influence the Cu-O and Cu-N bond lengths in the cavity of the molecule and change the inter-ligand contact distances.^{4b} The paramagnetism of Cu(II) provides opportunities for applying EPR techniques to define structures in frozen solution and in this paper we explore the combined use of computational methods, continuous wave (CW) electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) to visualise the hydrogen atoms in the outer coordination sphere using the compounds shown in Figure 3.

Results and Discussion

X-band CW-EPR spectra were recorded at 140K on a Bruker EMX spectrometer operating at 100 kHz field modulation, 10 mW microwave power using an ER 4119HS cavity. Q-band CW EPR and ENDOR spectra were recorded on a Bruker ESP 300E series spectrometer equipped with an ESP360 DICE ENDOR unit operating at 12.5 kHz field modulation in a Q-band ENDOR cavity (Bruker ER 5106 QT-E). The ENDOR spectra were obtained using 8dB RF power from an ENI A-300 RF amplifier and 50 or 200 kHz RF modulation depth and 1mW microwave power. Q-band EPR spectra were recorded at 50K, while the Q-band ENDOR measurements were performed at 10K. Spectral simulations were performed using the EasySpin toolbox in Matlab developed at ETH Zurich.⁷ Density functional theory (DFT) calculations used the Gaussian '09 program.⁸ Full structural optimizations

were carried out with the H-DFT method B3LYP/LANL2DZ for the $[\text{Cu}(\mathbf{1})_2]$ and $[\text{Cu}(\mathbf{2})_2]$ complexes where ^tBu groups were replaced by CH_3 .

An EPR and ENDOR investigation of the closely related $[\text{Cu}(\text{sal})_2]$ complex (Figure 3) substituted into a $[\text{Ni}(\text{sal})_2]$ single crystal, was previously been reported by Schweiger *et al.*⁹ The principal values of the Cu **g** and **A** tensor, given in Table 1, were used as a starting point for the simulations of the X- and Q-band EPR spectra (not shown for brevity). The agreement between the single crystal data⁹ and the frozen solution data is excellent; a small difference occurs in the A_z ($A_{\parallel}$) component of the $^{63,65}\text{Cu}$ hyperfine splitting and this is likely due to the solvent environment in $[\text{Cu}(\mathbf{1})_2]$ and $[\text{Cu}(\mathbf{2})_2]$ compared to the solid state $[\text{Ni}(\text{sal})_2]$ matrix. The spin Hamiltonian parameters are consistent with a system possessing square planar symmetry with a $d_{x^2-y^2}$ ground state.¹⁰ Interestingly, the A_z ($A_{\parallel}$) splitting of $[\text{Cu}(\mathbf{2})_2]$ (620 MHz) is smaller than in $[\text{Cu}(\mathbf{1})_2]$ (640 MHz), indicating that, despite being a potential hydrogen bond donor, the peripheral $-\text{N}(\text{C}_6\text{H}_{13})_2$ group influences the spin density on Cu^{2+} .

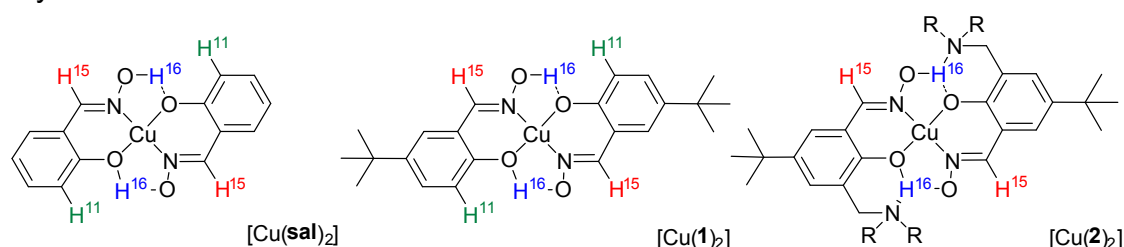


Figure 3: Copper complexes used in this study. The labelling of H^{11} , H^{15} and H^{16} for analysis of spectra and DFT calculations corresponds to that used by Schweiger *et al.*⁹. For $[\text{Cu}(\mathbf{2})_2]$ $\text{R} = \text{C}_6\text{H}_{13}$.

The Q band ^1H ENDOR spectra for $[\text{Cu}(\mathbf{1})_2]$ and $[\text{Cu}(\mathbf{2})_2]$ spectra, recorded over a range of magnetic field positions from 10800G to 12000G, are dominated by hyperfine couplings from two strongly coupled protons: the methine H^{15} and the oxime H^{16} shown in Figure 3 which are the protons closest to the Cu^{2+} centre. The ^1H ENDOR spectra of $[\text{Cu}(\mathbf{1})_2]$ are shown in Figure 4, together with the computer simulations, and the resulting principal values of the hyperfine tensors for both $[\text{Cu}(\mathbf{1})_2]$ and $[\text{Cu}(\mathbf{2})_2]$ are listed in Table 2. The methine protons (H^{15}) are dominated by a large isotropic coupling of $a_{\text{iso}} = 10.42$ MHz (based on the tensor [13.2, 9.35, 8.7 MHz]) for $[\text{Cu}(\mathbf{1})_2]$ and $a_{\text{iso}} = 10.23$ MHz (based on [12.7, 9.3, 8.7 MHz]) for $[\text{Cu}(\mathbf{2})_2]$. The lower a_{iso} value in $[\text{Cu}(\mathbf{2})_2]$ indicates a smaller unpaired spin density in the $1s$ orbital of H^{15} . In addition to these small differences in the isotropic hyperfine, the dipolar components of the hyperfine tensors ($A_{\parallel}$) were also found to be different; 2.78 and 2.47 MHz respectively for $[\text{Cu}(\mathbf{1})]$ and $[\text{Cu}(\mathbf{2})]$. These dipolar terms can be analysed using a simple point-dipole approximation¹¹ so that the resulting $\text{Cu}\cdots\text{H}^{15}$ distances were calculated as 3.97 and 4.13 Å respectively. This indicates that the $-\text{N}(\text{C}_6\text{H}_{13})_2$ group influences the properties of the complexes, in this case by increasing the $\text{Cu}\cdots\text{H}^{15}$ distance and simultaneously decreasing the Fermi contact term (a_{iso}) in $[\text{Cu}(\mathbf{2})_2]$.

	^a <i>g_x</i>	<i>g_y</i>	<i>g_z</i>	^{b,c} <i>A_x</i>	<i>A_y</i>	<i>A_z</i>	ref
[Cu(sal) ₂]	2.056	2.039	2.203	-109	-111	-609	10
[Cu(1)]	2.056	2.039	2.20	-109	-111	-640	
[Cu(2)]	2.050	2.039	2.20	-109	-111	-620	

Table 1. The *g* and *A^{Cu}* spin Hamiltonian parameters for [Cu(sal)₂], [Cu(1)₂] and [Cu(2)₂]. The [Cu(1)₂] and [Cu(2)₂] samples were recorded in 1:1 toluene:dichloromethane solutions. ^a ± 0.002, ^b All hyperfine values are given in units of MHz, ^c ± 3 MHz.

It is important to note that the hyperfine tensor for this H¹⁵ imine proton in [Cu(1)₂] is similar to that reported for [Cu(sal)₂], confirming that the small changes reported in Table 2 by modification of the ligand in [Cu(2)₂] are meaningful.

		^{a,b} <i>A₁</i>	<i>A₂</i>	<i>A₃</i>	<i>a_{iso}</i>	<i>A_{dip}</i>	<i>R / Å</i>	Ref
[Cu(sal) ₂] _{sc}	H ¹⁵	13.0	9.15	8.48	10.21	2.79	3.97	10
	H ¹⁶	6.60	-0.87	-5.97	-0.08	6.68	2.94	10
[Cu(1) ₂] _{ply}	H ¹⁵	13.2	9.35	8.7	10.42	2.78	3.97	
	H ¹⁶	6.90	-1.25	-5.87	-0.07	6.97	2.92	
[Cu(2) ₂] _{ply}	H ¹⁵	12.7	9.3	8.7	10.23	2.47	4.13	
	H ¹⁶	6.90	-1.25	-4.0	0.55	3.65	3.01	

Table 2: ¹H principal hyperfine values in MHz for [Cu(sal)₂], [Cu(1)₂] and [Cu(2)₂]. sc = single crystal; ply = frozen toluene/dichloromethane solution; ^a ± 0.05 MHz, ^b *g*/*A* axes are co-incident (*α, β, γ* = 0).

Only two components of the hyperfine for the oxime proton (H¹⁶), are clearly visible in the ENDOR spectra (the experimental equivalents of *A₁* and *A₃*, labelled * in Figure 4). The reported principal values of this H¹⁶ proton in [Cu(sal)₂] were [6.60, -0.87, -5.97 MHz] with *a_{iso}* = -0.08 MHz and Cu...H¹⁶ = 2.94 Å. Using the reported values as a guide, the best fit ENDOR simulations revealed the values of the hyperfine tensors for H¹⁶ in [Cu(1)₂] and [Cu(2)₂] as listed in Table 2. The larger *a_{iso}* value for [Cu(2)₂] indicates a higher unpaired spin density on this H¹⁶ proton, whilst the smaller dipolar *A_{||}* value indicates a longer Cu...H¹⁶ distance of 3.01 Å compared to 2.92 Å in [Cu(1)₂]. The longer Cu...H¹⁶ distance in [Cu(2)₂] is consistent with the buttressing aminomethyl nitrogen atom “pulling” the H¹⁶ proton away from the centre of the complex and DFT calculations (Figure 5) predict a similar trend (2.96 c.f. 2.60 Å). The concomitant weakening of the H¹⁶...phenolate hydrogen bond enhances the charge density and hence donor strength of the latter, leading to a shorter Cu-O bond, a longer Cu-N bond and an increase in the Cu...H¹¹ distance. The weakening of the H-bond to the phenolate in [Cu(2)₂] is reflected by natural bond orders (63 vs 8 kJ/mol) and the stronger interaction with the amino nitrogen atom (91 kJ/mol).

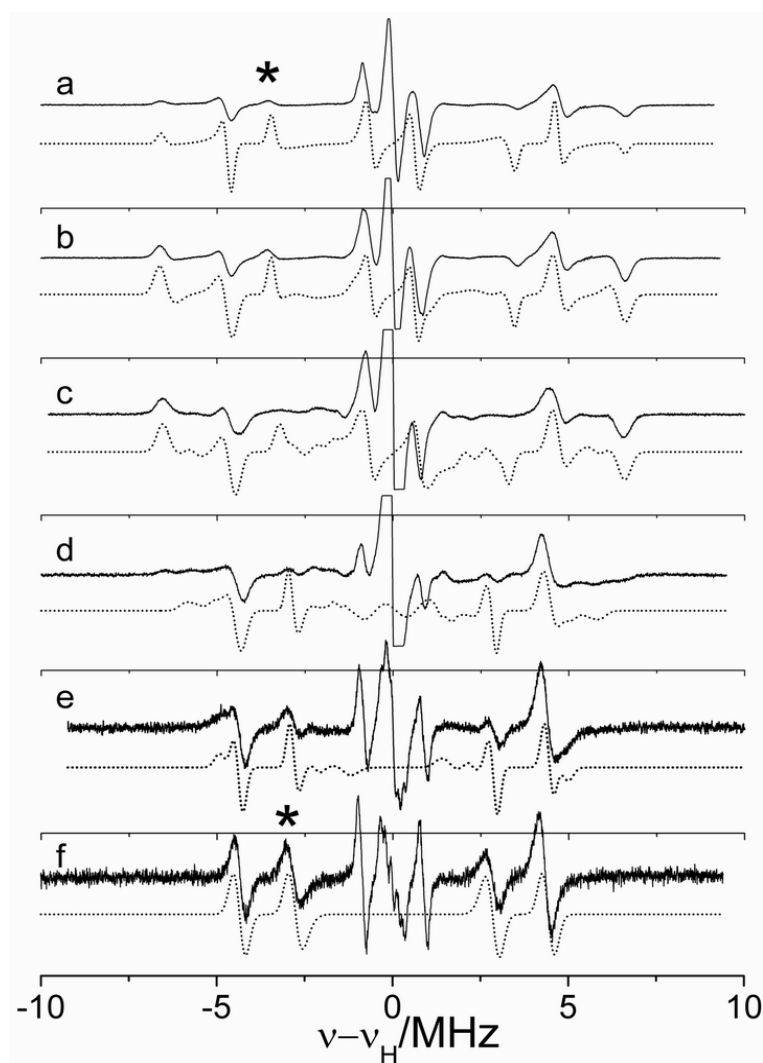
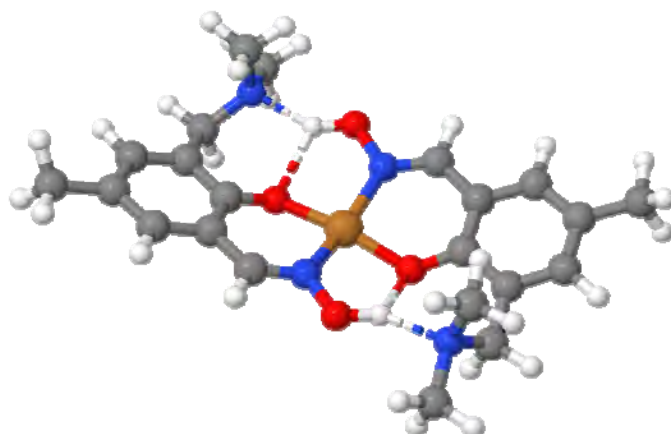


Figure 4: Q-band ^1H ENDOR spectra for $[\text{Cu}(\mathbf{1})_2]$ recorded at the field positions a) 12001, b) 11955, c) 11818, d) 11441, e) 11029 and f) 10824 Gauss. Two peaks arising from the oxime proton (H^{16}) are marked with an asterisk (the remaining A_2 component of this hyperfine is unresolved). Corresponding simulations are shown at each field position with dotted lines.

Care is needed in interpreting the origins of the small differences in lengths/strengths of these secondary bonding interactions. The buttressing group in $[\text{Cu}(\mathbf{2})_2]$ is different from those studied previously (Figure 2) in which the H-bond acceptor lies in the coordination plane.⁵

	$[\text{Cu}(\mathbf{1})_2]$	$[\text{Cu}(\mathbf{2})_2]$	$[\text{Cu}(\mathbf{2})_2]^\#$
$\text{O}\cdots\text{H}^{16}$	1.70	2.17	2.12
$\text{N}\cdots\text{H}^{16}$	-	1.75	1.76

Figure 5: Energy-minimised structures of $[\text{Cu}(\mathbf{2})_2]$ showing the displacement of the amino methyl groups to the same side of the complex plane and a small tetrahedral distortion of the $\text{N}_2\text{O}_2^{2-}$ donor set. [#]A slightly higher energy form (+3.8 kJ/mol) has a more nearly planar conformation but very similar H-bond lengths.



The tetrahedral geometry of the amino-methyl atoms allows the nitrogen to make a nearer to ideal OH...N contact (1.75 Å) to the oxime by lying out of the plane (Figure 5) and appears to induce a small tetrahedral distortion of the CuO₂N₂ unit. It is clear from the lengths included in Figure 5 that the dominant interaction of the oxime H-atom is with the buttressing group rather than the phenolate oxygen.

Conclusions

An analysis of the ENDOR data and DFT calculations indicates that the incorporation of an aminomethyl group *ortho* to the oxygen atom in phenolic oximes has a major effect on the hydrogen bonding in the *outer* coordination sphere of copper complexes which in turn influences their properties and the structure and bonding in its *inner* coordination sphere. This buttressing effect is greater than has been observed⁵ with other *ortho* substituents. The combination of ENDOR and computational methods could prove useful in understanding the mode of action of extractants of other paramagnetic metals, particularly when this depends on the formation of outer sphere assemblies involving modifiers or synergistic combinations of reagents.

References

1. J. A. Hamilton, M. N. Sabesan, and L. K. Steinrauf, *J. Am. Chem. Soc.*, 1981, **103**, 5880–5885; L. E. Godycki, and R. E. Rundle, *Acta Cryst.*, 1953, 6, 487-495; J. R. Turkington, P. J. Bailey, J. B. Love, A. M. Wilson, and P. A. Tasker, *Feature Article, Chemical Communications*, 2013, **49**, 1891-1899.
2. M. J. Nicol, C. A. Fleming, J. S. Preston, *Comprehensive Coordination Chemistry* 1987, 6, 779
3. K. R. Barnard *et al*, 19th ISEC, Santiago, Chile, 2011, Proceedings p161, Gecamin, Chile, 2011
4. (a) J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, USA, 1993; (b) A.G. Smith, P.A. Tasker and D.J.White, *Coordination Chemistry Reviews*, 2003, 241, 61-85.
5. R. S. Forgan, *et al*, *Inorg. Chem.*, 2011, **50**, 4515–22.
6. M. R. Healy, V. A. Cocalia, E. D. Doidge, A. J. Fischmann, J. B. Love, C. A. Morrison, J. W. Roebuck, T. Sassi, P. A. Tasker
7. S. Stoll and A. Schweiger, *J. Magn. Reson.* 2006, **178**, 42-55.
8. D. J. Frisch, *et al*, *Inc., Wallingford CT*, 2009.
9. A. Schweiger, *Struct. Bonding (Berlin)*, 1982, **51**, 1 and refs therein.
10. J. R. Pilbrow, *Transition Ion Electron Paramagnetic Resonance*, Oxford Science Publications, Oxford, 1990.
11. D. Attanasio, *J. Phys. Chem.*, 1986, **90**, 4952-4957.

AN INNOVATIVE MIXING TECHNOLOGY TO IMPROVE PHASE SEPARATION IN RECOVERY AND PURIFICATION OF CARBOXYLIC ACIDS BY SOLVENT EXTRACTION

*Nadav Dobrin^{*1}, Oded Lerner², Roman Sheinman³*

Summary

There is a growing interest in the recovery of carboxylic acids from fermentation broths. Reactive extraction of carboxylic acids using amines is a known effective separation method. Applying this extraction process by using conventional mixing systems of a standard agitator in a baffled stirred tank results in long phase separation times, thus the use of extraction by amines has not been widely used.

New mixing technology for faster and more complete separation of liquid phases in solvent extraction was developed and has been successfully implemented at the production scale in hydrometallurgy processes and plants. The mixing system generates an optimal turbulent energy distribution for efficient coalescence of the smallest droplets onto the surface of large and medium size droplets of the dispersed phase.

Several carboxylic acids systems were tested at laboratory and pilot scale. It was found that in comparison to systems with standard mixing separation times of the phases were significantly reduced and that clear separated phases were obtained.

Introduction

Purification of carboxylic acids by amines

With an increase in demand for materials from renewable feedstocks, the recovery of organic acids from dilute solutions resulting from fermentation processes has become of interest. Economics of the process, however, depends on the development of an effective recovery method for the organic acids from the broth.

Solvent extraction processes as a promising recovery technique have been proposed as an alternative to conventional lime-sulfuric recovery process, and many solvents have been tested for such recovery [1]. Reactive extraction of carboxylic acids using amines was shown to be an effective separation method in the 70's. An example of a well-known commercial application of liquid-liquid extraction in bioprocessing is the Baniel process for the recovery of citric acid from fermentation broth with tertiary amine extractants [2].

Amines – carboxylic acids systems typically have low interfacial tension (<3 mN/m). Those systems easily form small droplets (<50 µm), resulting in incomplete separation and in extreme cases stable emulsion.

^{*1}Nadav Dobrin, Tenova Bateman Technologies, Nadav.dobrin@tenova.com

² Oded Lerner, Tenova Bateman Technologies

³ Roman Sheinman, Turbulent Technologies Ltd.

Innovative mixing technology

Tenova Bateman Technologies, together with Turbulent Technologies Ltd. (TT), have developed a new technology that ensures faster and more complete separation of liquids in solvent extraction plants by means of optimization of the mixing regime in auxiliary mixing tanks. This mixing technology is based upon a combination of Kolmogorov's theory of the local isotropic turbulence, DLVO theory, which describes physical chemistry of interfaces [3] and TT own proprietary know-how. For each mixing unit the energy distribution is optimized for efficient coalescence of the smallest droplets onto the surface of large and medium size droplets of the disperse phase. This reduces the amount of small droplets in the emulsion with a narrower droplet size distribution, improving both the speed and the efficiency of phase separation. Generation of optimal turbulence conditions is based on a mathematical model of drop breaking and coalescence in turbulent flows developed during Turbulent Technologies' systematic research.

The novel system has been shown to work in practice at industrial scale in hydrometallurgical solvent extraction applications. In particular, the system has been shown very effective for decreasing organic entrainment in mixer-settler separated aqueous phase leaving the settler [4].

A new area of application of the technology is the liquid-liquid systems with very low interface tension. These systems are highly sensitive to energy dissipation in the proximity of blades of conventional mixing impellers – hydrofoils and turbines. The value of energy dissipation in the proximity of blades of these types of impeller blades is usually two orders of magnitude higher than in the bulk [5]. For such liquid systems the TT mixing systems are especially suitable, due to their ability to prevent the generation of tiny droplets, by precise control of the turbulence intensity at every point in the stirred vessel. The mixing optimization provides a distribution of turbulent energy of high intensity in the whole volume of the vessel with a relatively low ratio of maximum to average values of energy dissipation rates, i.e. the turbulence is relatively uniform throughout the tank. The mathematical model of TT mixing has made it possible to design custom mixing systems at any desired scale for each specific application. The model is used to design an optimal mixer for the specific turbulence conditions required for a given geometry, rather than simply scaling equipment to the dimensions of the tank.

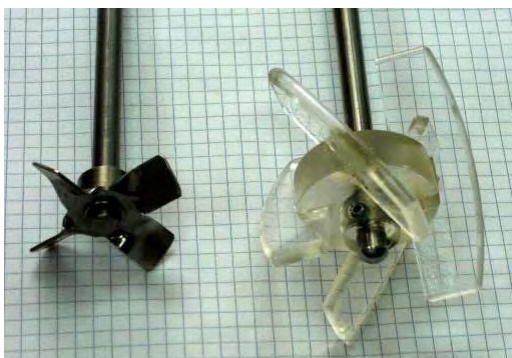


Figure 1 – a schematic picture of standard impeller vs. TT impeller

Influence of turbulent technology on phase separation

Citric acid system

The amine-citric acid system was tested at the laboratory scale for both extraction and back-extraction processes.

The mixing was performed with TT agitator. Two additional mixers were used for comparison: hydrofoil mixer of 70 mm diameter and Saw-tooth mixer of 50 mm. The total volume of fluids and Organic: Aqueous phase ratio were maintained at 1200 mL and 3:1 respectively. The vessel diameter was 125 mm. The TT mixer speed was kept constant in all tests at 300 RPM and mixing times were selected for ensuring complete mixing. The results are described in Table 1:

Table 1 – Citric acid laboratory scale results

System	Aq. phase	Org. phase	Stirring	25°C		50°C	
				Separation time [sec]	Opacity (*)	Separation time [sec]	Opacity
Extraction	Feed solution 300 mL	Loaded amine solvent 900 mL	TT, 300 RPM	300-400	1	50-80	2
			Hydrofoil, 800 RPM	1200-1500	0	80-100	0 org. 1 aq.
			Saw-tooth, 1800 RPM	Stable emulsion	0	90 - 100	1
Back – extraction	Water 300 mL	Barren amine solvent 900 ML	TT, 300 RPM	150-180	1	60-90	2
			Hydrofoil, 800 RPM	900-1200	0	150	1 org. 2 aq.
			Saw-tooth, 1800 RPM	Stable emulsion	0	120	0

(*) opacity code: 0-opaque; 1-limited transparency; 2- transparent solutions

Acetic acid system

Extraction of acetic acid from sugar hydrolyzate stream was tested at the laboratory scale and in a continuous pilot plant as described in Tables 2 and 3. The laboratory mixing system is described in the citric acid section above.

Table 2 – Acetic acid laboratory scale results

System	Aq. phase	Org. phase	Phase ratio O:A [v/v]	Stirring	60°C		comments
					Separation time [sec]	Opacity(*)	
Ext.	Hydrolyzate	Loaded amine solvent	0.5:1	TT(**), 250 RPM	<30	1 org. 1 aq.	minor haze in aq. after 5 minutes
				Pitch blade(***), 600 RPM	30	1 org. 0 aq.	Aq. was turbid even after 10 minutes

(*) opacity code: 0-opaque; 1-limited transparency; 2- transparent solutions



Figure 2 - (**) TT agitator – transparent aqueous (***) pitch blade stirrer – turbid aqueous

The continuous pilot scale tests were performed in the following system:

Mixer: diameter =150 mm, 3 L volume.

Settler: width = 160mm, length = 320 mm, 20 L volume.

TT agitator was compared to a turbine pump mixer.

Table 3 – Acetic acid continuous pilot results

System	Aq. phase	Aq. recycle	Org. phase	Phase ratio O:A [v/v]	Stirring	60°C	
						Separation	Entrainments O in A [%v/v]
Extraction	Hydrolyzate, 6.8 L/h	17.2 L/h	Barren amine solvent, 12 L/h	0.5:1	TT, 100 RPM	Clear interface	0.05
					Turbine pump mixer, 500 RPM	Stable emulsion	

Analysis of results

The laboratory scale tests show that in both carboxylic acids systems the introduction of the turbulent technology agitator decreased the separation time and the separation was more complete, i.e. fluids were more transparent.

The continuous pilot results emphasize the findings of the laboratory: stable emulsions in the settler were observed when a turbine pump mixer was used, while the separation in the settler using the turbulent technology mixer was reasonable, making the amine solvent extraction process feasible.

These results indicate that in an industrial installation a turbulent technology mixer can improve dramatically the phase separation of emulsifying systems characterized by low interfacial tension. The improvement in separation is positively affecting both operational costs and capital costs. Operational costs by reduction in organic entrainments (solvent loss) and aqueous entrainment (less impurities washing required from the loaded solvent). Capital costs as a smaller settler size is required and by elimination of the need for an after-settler (required in cases of high entrainments). In some cases, using this novel turbulent mixer can even eliminate the need of extractive centrifuges.

Conclusions

The new mixing technology has been shown to be effective for the carboxylic acids recovery and purification processes and at an industrial scale can be coupled with reasonably-sized settlers to make gravity separation feasible.

References

1. Kertes A.S., King C.J. (1986). Extraction chemistry of fermentation product carboxylic acids. *Biotechnol Bioeng*, 28, 269-282.
2. Baniel A.M., Blumberg R., Hadju K. (1980). U.S. Patent 4,275,234.
3. Braginsky L.N., Kokotov Y.V. (1993). Influence of turbulence and viscosities on the kinetics of drop breaking. *Journal of Dispersion Science and Technology*, 14(3), 373-394.
4. Morgan J., Ostberg N., Sheinman R., Braginsky L., Kokotov Y., Vancas M. (2013). Homogenous turbulent mixing for reducing entrainment in copper SX, Copper 2013-Cobre 2013, Santiago, Chile.
5. Harnby N., Edwards M.F., Nienow, A.W. (1992). *Mixing in the process industries*, 2nd ed. Butterworth-Hinemann.

API recovery from pharmaceutical waste streams by continuous countercurrent extraction

*Svetlana Ignatova¹, Peter Hewitson¹, Ian A. Sutherland¹, Philip Wood²,
Nathalie Douillet³, Chris Thickitt³, David Johns³, Keith Freebairn³*

¹Brunel Institute for Bioengineering, Brunel University, Uxbridge, UB8 3PH, UK

²Dynamic Extractions Ltd, Plymouth Road, Slough SL1 4LP, UK

*³GlaxoSmithKline, Pharmaceuticals R&D Facility, Gunnels Wood Road,
Stevenage SG1 2NY, UK*

When new projects are scaled up from the research and development stage into manufacturing, recovery or disposal of waste streams becomes more and more important to minimise cost and reduce both the environmental and safety impact. Modern telescopic synthesis techniques and their follow-on purification processes are not always efficient enough to prevent loss of active pharmaceutical ingredients (API) in the waste stream. There are technologies available by which components of such streams can be disposed of, treated or recovered.

The drive towards greener processes, process economics, technology availability, and legislation, all play a part in the selection of the best available technology for waste stream processing. One such technology is Continuous Counter-current Extraction (CCCE) in a fluctuating g-field which is being evaluated as new cost effective continuous platform technology, initially as part of a 3 year Technology Strategy Board High Value Manufacturing initiative entitled “Scalable Technology for the Extraction of Pharmaceuticals”. This was an industry led collaborative project involving end-users, GSK and Pfizer, a technology supply company, Dynamic Extractions Ltd, and Brunel University all actively working together to improve process efficiency and reduce both cost and waste.

This CCCE method development for waste steam purification has been done at the analytical scale with subsequent scale up to the preparative 1L instrument. This demonstrated the potential of the technology for the recovery of APIs from complex waste streams in both batch and continuous processing modes. The direct scalability of the dynamic extraction process enables optimization work at the laboratory scale to be transferred directly to the 18L pilot scale instrument. Different scenarios of throughput/purity/yield will be presented demonstrating the flexibility of the technology to purify the target compound at the required trial grade and avoiding expensive clean up processes. This process is therefore capable of reducing the environmental impact of pharmaceutical waste streams.

RECOVERY OF VALUABLE PRODUCTS FROM BIOMASS USING A KARR® COLUMN

Donald J. Glatz and Wendy L. Parker, Koch Modular Process Systems LLC, Paramus, New Jersey, USA

ABSTRACT

Designing a liquid-liquid extraction (LLE) column for the extraction of valuable chemical from biomass requires a column that is efficient and can handle systems with high tendency to emulsify. In this work, LLE data is generated in the pilot plant using a 25 mm diameter KARR® Column for two systems; a fermentation broth and algae broth. Both of these processes had demonstrated a high tendency to emulsify and were unsuccessfully tested in other LLE equipment. The KARR® Column worked very well for both systems and sufficient data was generated for scale-up and design of production size column. This work confirms that the KARR® Column is an excellent choice for many biomass extraction processes.

INTRODUCTION

In recent years there has been a large emphasis on generating chemicals from renewable resources via such processes as fermentation and algae growth. Liquid-liquid extraction (LLE) is an ideal first step recovery of these chemicals because many boil higher than water making distillation energy intensive and expensive. However, these systems tend to have low partition coefficients for acceptable organic solvents and they also have a high tendency towards emulsification. Thus, an extraction column is required that can offer both high efficiency while minimizing the tendency to emulsify. The KARR® Column has been proven to offer both. The reciprocating plate stack generates the required agitation to maximize mass transfer. Also, the uniform shear action of the plates has been proven to be superior to mixing with rotating internals for systems with low density difference and low interfacial tension [1]. This paper demonstrates the effectiveness of the KARR® Column when other LLE devices were proven to be ineffective. The success of the KARR® Column is demonstrated in pilot plant testing for two applications; a fermentation process and an algae broth.

EXPERIMENTAL

All pilot plant tests are performed using a 25 mm diameter KARR® Column with glass shell and 316SS internals (Figure 1). Variable speed pumps with manual adjustment are used for the feed and solvent streams. Heat exchangers control the inlet temperatures. The interface is manually controlled using a variable speed bottoms pump, and the light phase is allowed to leave the column by overflow. The glass shell column allows visual observation of the phase behavior (droplet formation, dispersed phase hold-up, coalescence, interface behavior, etc.). It also allows an experienced engineer to assess the column performance and systematically “tweak” the process conditions to obtain optimal performance.

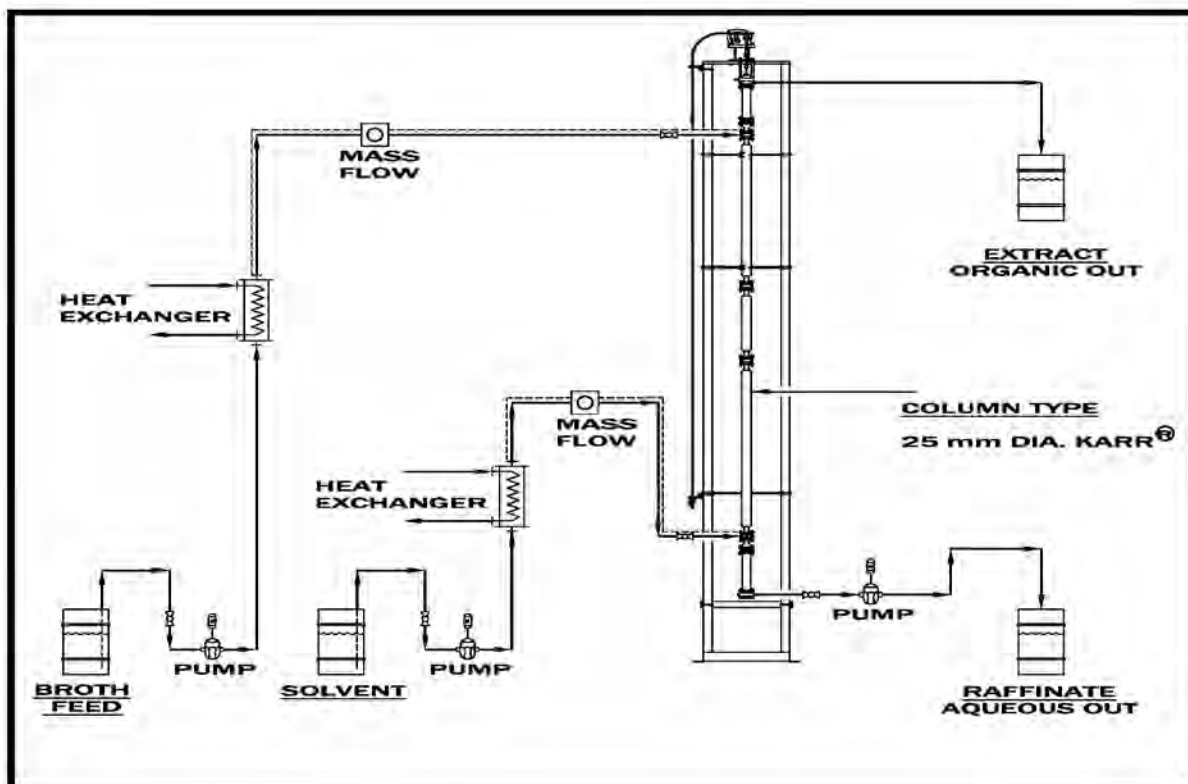


Figure 1. Pilot KARR® Column Set-up for testing broth extraction

The test procedure follows:

- For start-up each day, the column is filled with the continuous phase. Once full, the agitator is turned on at a low speed and the dispersed phase is also added.
- Inlet flows are adjusted to the desired rates and the interface level controlled by adjusting the bottoms take-off pump as required.
- The agitator speed is adjusted to the specified rate.
- The test supervisor specifies the conditions for each run. Feed and solvent rates are confirmed on a regular basis. The temperature is adjusted as required using the heat exchangers for the feed and solvent streams. At the completion of the run, raffinate and extract flow rates are measured and samples of each phase taken for analyses.
- During start-up each day, a total of 5 column turnovers are performed before the initial samples are taken. A column turnover is defined as the total column volume divided by the combined flow of feed and solvents. After the first run, and following adjustments of the variables, a total of 3 turnovers are performed before additional sampling.

The authors use step-by-step optimization during pilot plant testing [2]. This method requires experience and immediate access to analytical equipment for all samples. Initial operating conditions are set based upon an understanding of the physical and chemical properties, equilibrium data, visual observation of the phase behavior, and experience. During the initial runs, the agitation speed is incrementally increased until flooding is achieved. Based upon the results from the initial series of runs, variables are adjusted and evaluated at several levels. These included the column height, capacity, and solvent to feed ratio. The results are

continuously monitored and used to determine the operating conditions for the next set of runs. Testing continues until the desired results are achieved. Data from the runs producing optimal performance are used for empirical scale-up to the production column using proven design correlations.

RESULTS AND DISCUSSION

Application 1 – fermentation broth

This application involved the extraction of carboxylic acids from an aqueous fermentation broth generated in a cellulosic ethanol process. Ethyl acetate (EA) was the selected solvent. The desired outcome was >95% acetic acid recovery and solvent to feed ratio (S/F) ≤ 1.7 . Initial attempts to test this process in a rotating disc contacting column (RDC) proved to be unsuccessful due to emulsification in the column. Subsequently, the process was tested in a 25 mm diameter KARR® Column. The KARR® Column demonstrated excellent operability, generating fine dispersion of the solvent phase. Results from pilot runs are shown in Table 1. A review of the data shows; (1) a solvent to feed ratio of 1.5 was acceptable, (2) > 98% acetic acid extraction at 40-45 °C and a plate stack height of 3660 mm, and (3) successful operation at a capacity of 26.5 – 28.5 m³/m²hr.

RUN #	Plate Stack Ht. (feet)	Capacity GPH/ft ²	Temp. C	S/F Ratio	Agitation SPM	Acid Recovery %
1	12	700	23	1.7	30	95.0
2	12	700	23	1.7	40	97.5
3	12	700	23	1.7	50	Flooded
4	8	700	23	1.7	30	93.3
5	8	700	23	1.7	40	Flooded
6	10	700	23	1.7	30	96.3
7	12	650	23	1.5	30	96.5
8	12	500	23	1.5	40	97.6
9	12	700	23	1.5	30	94.3
10	12	650	45	1.5	30	98.3
11	12	650	45	1.5	50	98.7
12	12	650	45	1.5	60	Flooded

Table 1. Pilot plant data for fermentation broth extraction in 25 mm diameter KARR® Column

Application 2 – algae broth

This application involved the extraction of an organic product from an aqueous broth generated in an algae pond using an alkane solvent (proprietary). Initial attempts by the end user to develop the LLE process step in a batch mix-decant mode of operation were reported to be

difficult. The system demonstrated a high tendency to emulsify and phase separate was slow and inefficient. Subsequently the process was tested in a 25 mm diameter KARR® Column. The reciprocating action of the perforated plates allowed for solvent dispersion in the broth as well as phase separation resulting in a controllable interface at the top of the column. Results from pilot runs are shown in Table 2. A review of the data shows; (1) a design capacity of 19.7 m³/m²hr is optimal, (2) > 97% product recovery can be achieved with S/F as low as 0.5, and (3) the full plate stack height of 3660 mm was required to maximize the product recovery.

RUN #	Plate Stack Ht. (feet)	Capacity GPH/ft ²	Temp. C	S/F Ratio	Agitation SPM	Oil Recovery %
1	12	500	65	1.0	30	88.3
2	12	500	65	1.0	50	97.8
3	12	500	65	1.0	75	Flooded
4	12	500	65	2.0	30	96.3
5	12	500	65	2.0	75	Flooded
6	12	500	65	1.0	50	98.4
7	8	500	65	2.0	50	93.1
8	8	500	65	1.0	50	90.8
9	12	700	65	1.0	50	85.1
10	12	900	65	1.0	40	Flooded
11	12	500	65	0.8	50	98.2
12	12	500	65	0.5	50	97.6

Table 2. Pilot plant data for algae broth extraction in 25 mm diameter KARR® Column.

CONCLUSIONS

The KARR® Column proved to be an excellent column for extraction in the two processes tested; acetic acid extraction from fermentation broth, and oil product extraction from algae broth. Whereas an RDC column failed for the fermentation process and batch mix-decant was ineffective for the algae broth, the KARR® Column worked effectively for both applications. This is an important finding because developing bio-based processes often require solvent extraction for recovery of chemicals produced in these processes.

REFERENCES

1. R. Cusack, and P. Frameaux, "A Fresh Look at Liquid-Liquid Extraction, Inside the Extractor", Chemical Engineering, March 1991
2. R. Cusack, and D. Glatz, "Apply Liquid-Liquid Extraction to Today's Problems", Chemical Engineering, July 1996

A new approach to coil-planet centrifuges for extraction and phase separation in downstream processing

Peter Scherübel¹⁾, Andreas Pfennig¹⁾

¹⁾*TU Graz, Institute of Chemical Engineering and Environmental Technology*

Biotechnological production routes attain increasing importance these days. To make them competitive in comparison to bulk processes which are commonly based on fossil raw materials it is essential to design efficient and economical downstream processes. A good option to isolate the target compound from fermentation broths is liquid-liquid extraction. The challenge of downstream processing using extraction is often related to the high viscosity of the phases as well as hindered coalescence resulting from solid particles e.g. bacteria cell fragments in two-phase systems. To enhance extraction efficiency and settling time which is a very important criterion for economical downstream processes coil-planet centrifuges are capable appliances. The main objective of the research is to enhance a counter-current chromatograph designed as coil-planet centrifuge. While the current field of application uses coil-planet centrifuges with one mobile and one stationary phase the new approach realizes the continuous flow of both phases to enable counter-current extraction processes with a large number of theoretical stages. Further the tube routing is enhanced to reduce attrition and increase lifetime of the rotating tubes. In addition the mathematical description of the location-depending centrifugal field gives information about the settling and mixing zones in the coil. In the presentation the new design of the apparatus the mathematical description and experimental results will be shown.

Poster Programme

Determination of PCDD/Fs and dioxin-like PCBs in the Ambient Air of the cement industry in Sour El Ghoulane suburban atmosphere, Algiers, using the CALUX bioassay and the sensitive H1L7.5c1 mouse hepatoma cell line

Khedidji S^{1,2*}, Croes K³, Yassaa N^{1,4}, Ladj R⁵, Elskens M³, Baeyens W³

¹L'université Akli Mohand Oulhadj, Rue Drissi Yahia BP10000, Bouira, Algeria;

²Laboratoire d'analyse Organique Fonctionnelle, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El-Alia Bab-Ezzouar, 16111, Algiers, Algeria;

³Vrije Universiteit Brussel, Department of Analytical and Environmental Chemistry (ANCH), Pleinlaan 2, 1050 Brussels, Belgium ;

⁴Centre de développement des Energies Renouvelables (CDER) EPST, BP 62, Route de l'observatoire, Bouzaréah, Algiers, Algeria ;

⁵Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (CRAPC), BP 248, Alger RP, 16004, Algiers, Algeria

Since the CALUX (Chemically Activated Luciferase gene eXpression) bioassay is a fast and inexpensive tool for the throughput analysis of dioxin-like compounds in a large number of samples and requires only small sample volumes.

In this study, a new method for the analysis of PCDD/Fs and dioxin-like PCBs in Ambient air of the cement industry in Sour El Ghoulane suburban atmosphere at a sampling point from March 2013 to April 2013. with the CALUX bioassay was developed, optimized and validated. The method consists of 4 steps: sampling, extraction, clean up and bioassay analysis.

To avoid the use of large amounts of toxic solvents, new techniques were used for filtration and extraction. During sampling, the airborne particulate matter was enriched onto PTFE filters by using a two medium volume samplers with or without a size-selective inlet for PM₁₀ and TSP were used and each sampling period lasted approximately 24 h. and an Accelerated Solvent Extractor (ASE) was used instead of the traditional Soxhlet extraction. After sampling and extraction the extract, clean up was done using a multi-layer silica gel column coupled to a carbon column. The PCDD/F and PCB fractions were finally analyzed with the H1L7.5c1 mouse hepatoma cell lines. The 24 h average concentrations of PCDD/F and PCB of Sour El Ghoulane suburban atmosphere were found in the range 4.76–165.76 CALUX BEQ pg/m³ and 28.63–800.14 CALUX BEQ pg/m³, respectively, in the sampling period. The limit of quantification was 1.4 CALUX BEQ pg/m³ for the PCBs and 5.6 CALUX BEQ pg/m³ for the PCDD/Fs, when using the new sensitive H1L7.5c1 cell line.

References:

1. Khedidji S, Ladj R, Yassaa N. (2013); *Environ Sci Pollut Res.* 10-1007: s11356-012-1430-y
2. Van Langenhove K, Croes K, Denison M S, Elskens M, Baeyens W. (2011); *Talanta.* 85: 2039-2046
3. Ladj R, Yassaa N, Balducci K, Cecinato A, Meklai B Y. (2009); *Atmospheric Research.* 92: 258-269

Transport of Pd(II) and Au(III) through redox-active bulk liquid membranes and the simultaneous formation of gold micro- and nanoparticles

María Guadalupe Sánchez-Loredo^{*1}, Manfred Grote²

Summary

Three S-decyldithizone derivatives were used as carriers for the uphill transport of Pd(II) through a bulk liquid membrane. Factors such as strip reagent (thiourea and sodium thiocyanate), ligand and thiocyanate concentration, and the presence of other precious metals, influence the Pd(II) transport. Under optimum conditions, the amount of Pd(II) transported across the liquid membrane is almost quantitative after 48 h. Permeation of gold by means of the ortho-carboxyl substituted S-decyldithizone derivative was also studied, where partial precipitation of the gold and oxidation of the extractant were observed in the feed phase. Gold was recovered as fine particles from the loaded carrier by reduction using a sodium borohydride solution, and at the same time, the extractant was reduced and fully regenerated.

Introduction

Bulk liquid membranes (BLMs), with the donor and acceptor phases separated by an immiscible membrane phase, and supported liquid membrane (SLM) systems, with the organic phase contained in the pores of a porous polymeric membrane, are attractive for the simultaneous enrichment and isolation of analytes [1-4].

The extraction properties towards precious and base metal ions of ortho- and meta-monocarboxyl-substituted derivatives of S-decyldithizone (D-oC, ortho, and D-mC, meta, Figure 1), and the unsubstituted parent compound (D-H), dissolved in p-xylene and chloroform, were previously reported [5,6]. Towards Pd(II), the dithizones act via chelation. Stripping was achieved by acidic thiourea solution or thiocyanate ions.

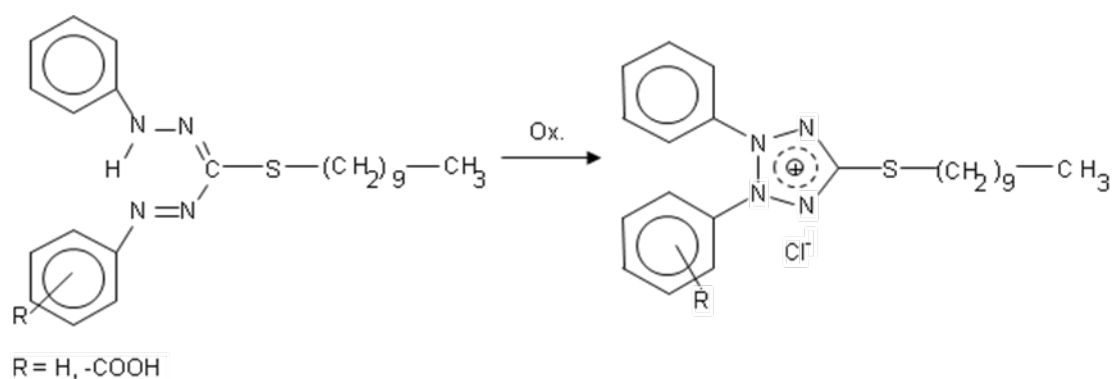


Figure 1. Redox-active S-decyl-dithizones (H, D-H; o-COOH, D-oC; m-COOH, D-mC) and their corresponding oxidation products.

1

^{*} Instituto de Metalurgia/Facultad de Ingeniería, Universidad Autónoma de San Luis Potosí, Sierra Leona 550, San Luis Potosí, México, (52)4448356371, msanchez@uaslp.mx

2

Department Chemie, Universität Paderborn, Paderborn, Germany

However, if Au(III) is present during liquid-liquid extraction in the Pd(II)-source phase, the ligands oxidise [5,7], and the formation of the ion-pairing cationic tetrazolium salts drastically affects the extraction ability by increasing coextraction of accompanying metal ions, particularly Pt(IV) and Os(IV).

In this work, the three derivatives D-H, D-oC and D-mC, were used as carriers for the uphill transport of Pd(II) through a bulk liquid membrane. And, based on the reducing ability of the reagents, a simple and efficient preparative membrane system for producing gold micro- and nanoparticles was obtained by applying an alkaline borohydride solution as stripping agent.

Experimental

All chemicals used were of reagent grade quality. The organic diluent, p-xylene, analytical reagent grade, was supplied by Merck, Darmstadt. Stock solutions of noble metals were prepared from the sodium salts of the individual chloro complexes (Degussa AG). The standard solutions of noble metals were prepared from commercial stock solutions (Spex Industries Inc.). Deionized water was used.

The transport experiments were carried out at room temperature. Two cylindrical glass cells holding a glass tube separating the two aqueous phases (Figure 2) were used. A small cell was used for Pd(II) and Au(III) transfer, and a bigger cell in experiments using a feed solution containing Pd(II), Pt(IV), Os(IV), Ir(IV), Rh(III) and Ru(III). The p-xylene solution containing the alkylated dithizones was located at the upper part of both aqueous phases and bridged them. The outer aqueous phase (source or feed phase) contained palladium chloride (0.5 mmol/L in 0.1 M HCl). The inner aqueous phase (receiving or strip phase) contained the strip reagent: thiourea (5 %w/w in 0.1 M HCl) or sodium thiocyanate (0.5 or 1 M). In case of Au(III) transfer, the receiving phase contained NaBH₄ (0.1 M in 0.1 M NaOH), which acted also as a reducing agent for the transported metal and the oxidized extractant. The cell was glass-covered to minimize evaporation and the three phases were stirred. Samples of both aqueous phases were analyzed for metal content by DCP-atomic emission using a spectrometer "Spectraspan 7" (Thermo Jarrell Ash). The detailed experimental conditions about the cells used are included in Table 1.

The morphology and size were observed by scanning electron microscope (SEM). SEM examinations and EDS analysis (energy-dispersive X-ray spectrometry) were carried out at the University of San Luis Potosí, using an XL-30 SEM (Philips, Netherlands), and a DX-4I (EDAX). Prior to SEM examination, the gold powders were washed with distilled water and acetone.

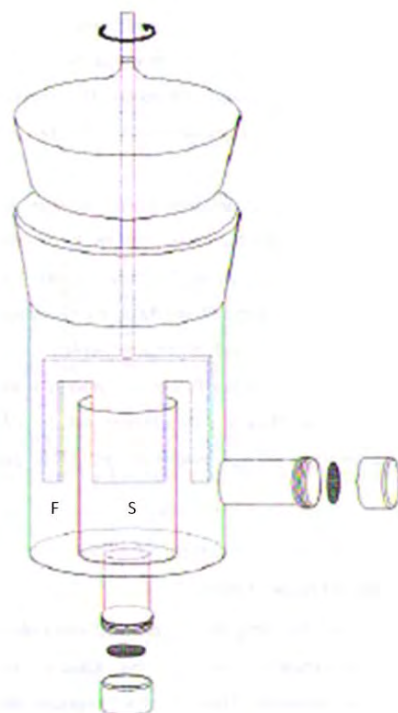


Figure 2. Liquid membrane apparatus (F: feed phase; S: strip phase).

Table 1. Liquid membrane cells used in permeation experiments

	Feed phase, mL	Strip phase, mL	Membrane, mL	Stirring speed, s ⁻¹
Small cell	32	25	20	60
Big cell	75	50	30	80

Results and discussion

Pd(II)-permeation experiments using thiourea as strip reagent showed a rapid decrease of metal concentration in the feed phase for the first 24 h, followed by an increase in Pd(II) content in this phase after a certain amount of time (Figure 3). This can be related to the notorious transport of thiourea to the feed phase, making this reagent unsuitable for the membrane experiments.

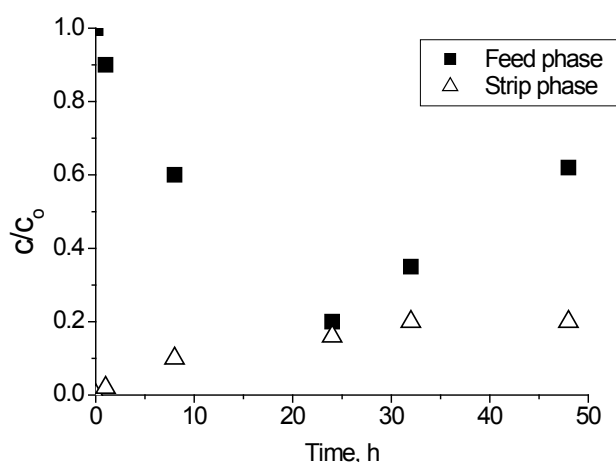


Figure 3. Transfer of Pd(II) vs. time in receiving (Δ) and source ($\blacksquare$) phases. The feed phase contains 0.5 mmol/L Pd(II) in 0.1 M HCl, the membrane phase 2 mmol/L D-oC in *p*-xylene, and the receiving phase 5 %w/w thiourea in 0.1 M HCl.

The Figure 4 shows the Pd(II) permeation results for the three different dithizone derivatives. Compared to the non acidic parent compound D-H, the extraction of

Pd(II) is enhanced in the case of the carboxyl-derivatives. Considering the influence of the position of the acidic group on permeation, the presence of the carboxyl group on the meta-position increases slightly the extraction and stripping rates of the metal. As already reported in [5], several reasons may be responsible for the higher effectiveness of the carboxyl-substituted dithizones. Due to the lower $pK_{(COOH)}$ -values, the carboxylic groups dissociate easier in contact with aqueous acidic feed solutions than the nitrogen-bonded hydrogen of the dithizone skeleton, and besides, the hydrophilicity of the formed ionic species is higher.

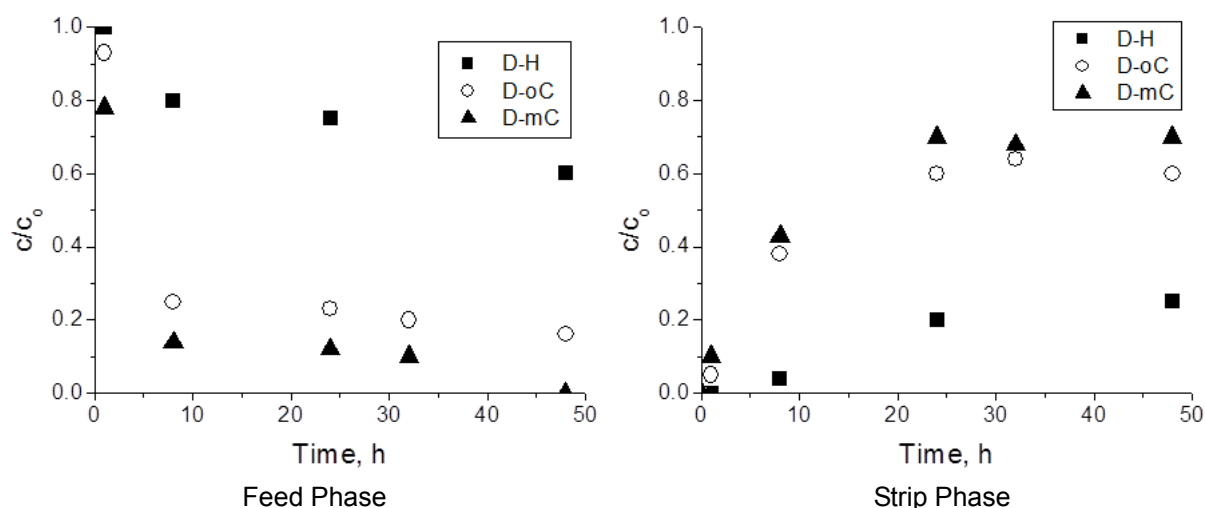


Figure 4. Transfer of Pd(II) vs. time for three different carriers when the feed phase contains 0.5 mmol/L Pd(II) in 0.1 M HCl, the membrane phase 1 mmol/L extractant in *p*-xylene, and the receiving phase 0.5 M NaSCN.

The effect of extractant concentration in the membrane phase on the transport efficiency was studied (Figure 5). The results revealed that the permeation efficiency strongly increases with the increase in concentration for D-oC, decreasing for the meta-substituted derivative. From the results, only D-oC was selected for further studies.

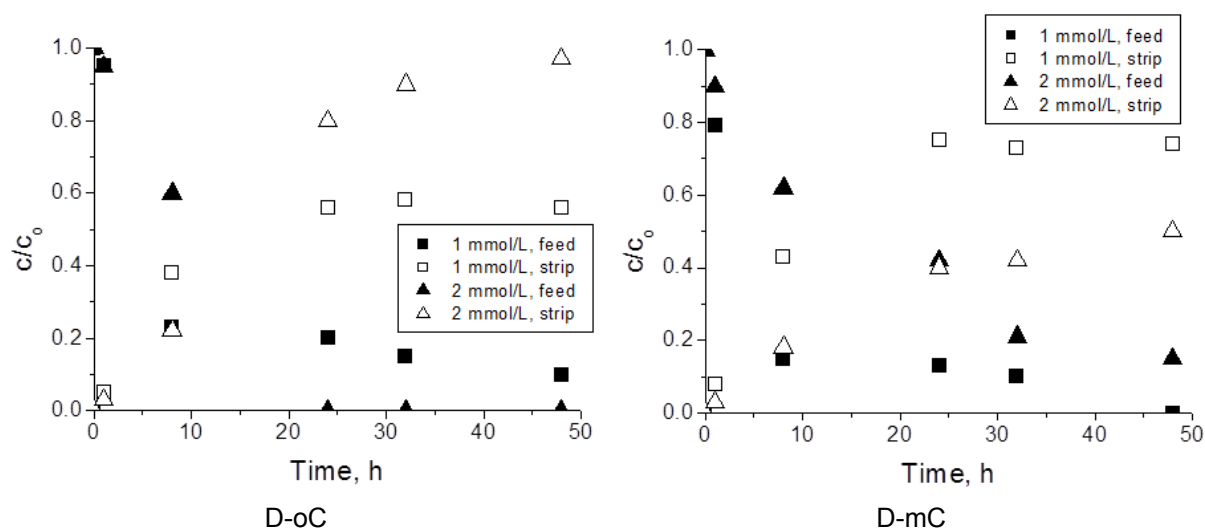


Figure 5. Transfer of Pd(II) vs. time for two different dithizone derivatives. The feed phase contains 0.5 mmol/L Pd(II) in 0.1 M HCl, the membrane phase 1 or 2 mmol/L extractant in *p*-xylene, and the receiving phase 0.5 M NaSCN.

Permeation experiments using two different NaSCN concentrations in the strip phase were carried out. A higher thiocyanate concentration promotes the rapid permeation of Pd(II) during the first hours, but the permeation is not longer affected by the concentration of the strip reagent after 24 h. The increased transport of thiocyanate to the feed phase was also observed when using the 1 mol/L solution.

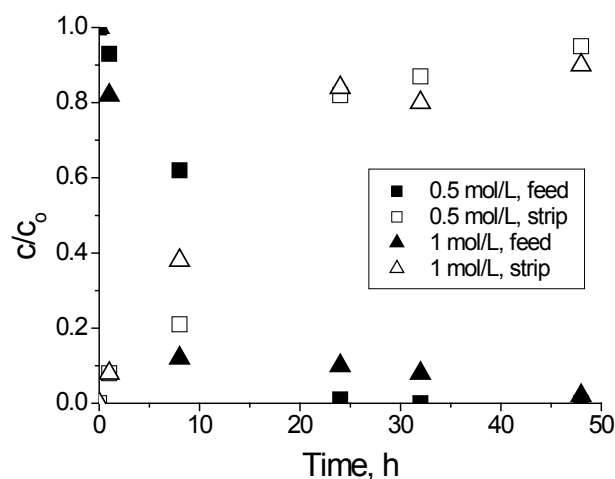


Figure 6. Effect of thiocyanate ions concentration (0.5 and 1 mol/L) on the transfer of Pd(II) for the carrier D-oC (2 mmol/L in *p*-xylene).

For permeation experiments using a feed phase containing Pd(II), Pt(IV), Os(IV), Ir(IV), Ru(III) and Rh(III) (0.5 mmol/L each in 0.1 M HCl), the percentage of Pd(II) extraction remains the same, but the transport to the strip phase decreases. Again, as observed during the liquid-liquid extraction experiments [5], compared to Pt(IV) and the other platinum metals, the extractability of Os(IV) is more pronounced (15% compared to 8.7% Pt(IV)), but the metal remains in the membrane phase.

Table 2. Transfer of precious metals using a bulk liquid membrane after 48 h when the feed phase contains 0.5 mmol/L metal in 0.1 M HCl, the membrane phase 2 mmol/L D-oC in *p*-xylene, and the receiving phase 0.5 M NaSCN.

	Ir(IV)	Pt(IV)	Os(IV)	Ru(III)	Rh(III)	Pd(II)
Extraction, %	7.9	8.7	15.2	10.8	11.2	99.6
Stripping, %	0.8	0.6	2.1	0.39	0.3	43.9

The preparation of fine gold particles from metal-loaded S-decyldithizonates by reduction was already shown to be feasible [7], although some particles agglomeration was observed. In order to obtain finer and dispersed particles, the use of this liquid membrane assembly containing the extractant D-oC as carrier was proposed. Figure 7 shows SE micrographs of the gold particles obtained in the feed phase due to the extractant oxidation (promoted by Au(III)), and in the receiving phase by stripping the extracted gold from the carrier solution with sodium borohydride in alkaline solution. SEM examination revealed the powders to consist mostly of amorphous particles. The microparticles (i.d. 1-20 μm) were formed by the partial oxidation of the dithizone in the feed phase, and the nanoparticles (i.d. < 500 nm) in the reducing stripping phase.

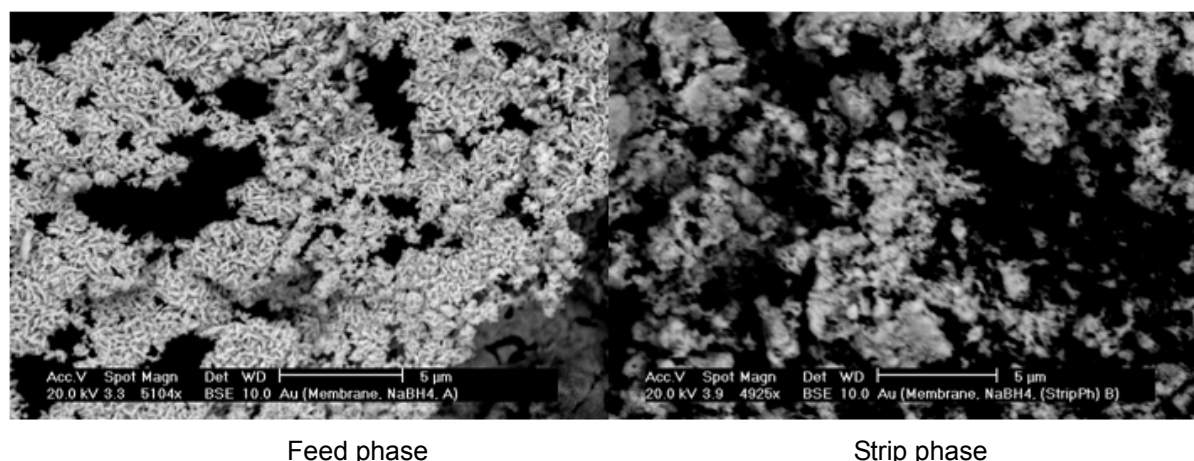


Figure 7. SEM of gold particles precipitated during permeation using sodium borohydride solutions as strip media in a bulk liquid membrane. Left, particles deposited in the feed cell, and right, in the strip phase.

Conclusions

S-decyldithizone derivatives were used as carriers for the uphill transport of Pd(II) through a bulk liquid membrane. Factors such as strip reagent (thiourea and sodium thiocyanate), ligand and thiocyanate concentration influence the metal transport. In absence of other metals, and using thiocyanate ions as stripping reagent in the receiving aqueous phase, the transport of palladium across the membrane was almost quantitative. In presence of other precious metals (Ir(IV), Os(IV), Ru(III), Rh(III), Pt(IV)), the membrane system shows some selectivity for Pd(II) but with lower transport efficiency. By replacement of Pd(II) by Au(III), and the metal complexing receiving phase for an alkaline sodium borohydride solution, a simple system for recovering gold as fine particles was obtained.

Acknowledgements

Maria G. Sánchez-Loredo is grateful to the Deutscher Akademischer Austauschdienst (Germany) and to the Fondo de Apoyo a la Investigación (UASLP, México) for financial support. The assistance of Rodica Knaup of the University of Paderborn in performing careful analytical work is gratefully acknowledged.

References

1. A. Safavi, E. Shams, *J. Membrane Sci.* 144, 1998, 37-43.
2. M. Grote, B. Haciosmanoglu, J. Nolte, Proceedings of the International Solvent Extraction Conference, ISEC 2002, Cape Town, South Africa; Ed.: K. C. Sole, M. Cole, J. S. Preston and D. J. Robinson, Chris van Rensburg Publications (Pty) Ltd, South Africa; Vol. 1, 607-613.
3. P. Ajwani, L. Lokwani, U. Sharma, *Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci.*, 2012, 82(2), 91-95
4. M. Ma, B. Chen, X.-B. Luo, H. Tan, D.-Sh. He, Q.-J. Xie, Sh.-Z. Yao, *J. Membrane Sci.* 234, 2004, 101-109.
5. M.G. Sanchez-Loredo, M. Grote, *Solvent Extr. Ion Exch.*, 18(1), 2000, 55-76.
6. R. Jiménez Cataño, I.H. Salazar Gómez, M.G. Sánchez Loredo, *Hydromet.*, 80, 2005, 203-210.
7. M.G. Sánchez-Loredo, A. Robledo-Cabrera, M. Grote, *Mat. Chem. Phys.*, 76, 2002, 279-284.

The extraction of Co(II) with Cyanex272 in a neutral micellar system

*Faxin Xiao^{1, 2}, Yong Wang¹, Xiaoni Shen², Geoff W. Stevens¹, Jilska M. Perera^{*1}*

¹Particulate Fluids Processing Centre, Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria, 3010, Australia

²School of Materials Science & Engineering, Henan University of Science & Technology, Luo Yang, 471023, China

Summary

The rate of extraction of metals by complexing agents solubilised in microheterogeneous systems is of interest in both fundamental and applied studies [1]. The transparency of micellar systems, makes possible the use of conventional techniques such as spectroscopy and stopped flow to study the kinetics of metal complexation [2]. Such studies can contribute to the knowledge of reactions mechanisms of metal complexation. They also enable the study of the effect of additives on the rate of complex formation [3], which is of value in many practical applications. The aim of this study is to determine the extraction reaction mechanism for Co(II) by the extractant Cyanex272 (bis 2,4,4-trimethylpentyl phosphinic acid) and to develop a model to obtain the rate constants associated with the process.

The rate of complexation between Co(II) and Cyanex272 in a neutral micelle system, Teric G₁₂A₈, (octa-ethyleneglycol mono-n-dodecyl ether) was monitored using a combination of stopped flow and UV-visible spectrophotometry. A two-step mechanism was found to fit the experimental data and reaction rate constants for the forward and reverse reactions were obtained.

INTRODUCTION

Solvent extraction is an important separation processes in the hydrometallurgical industry. It has been widely used to purify a range of metals including cobalt, copper and nickel. In some cases the operation is limited by the rate of metal extraction [4]. Micellar solutions can be considered as pseudo-biphasic systems in order to investigate the kinetics and mechanisms of metal ion complexation/extraction by hydrophobic chelating extractants [5]. Micelle extraction offers the advantage of not having an organic phase, which reduces the impact of the process on the environment and it can be used in some cases to elucidate the mechanisms involved in the extraction of metals with particular chelating agents [6]. The aim of this study is to determine the extraction reaction mechanism for Co(II) by the extractant Cyanex272 (bis 2,4,4-trimethylpentyl phosphinic acid) and to develop a model to predict the rate constants associated with the process.

EXPERIMENTAL SECTION

Chemicals

Cyanex272 (bis 2,4,4-trimethylpentyl phosphinic acid) was supplied by Cytec (USA) and used without further purification. Teric G₁₂A₈, poly-dispersed octa-ethylene glycol mono-n-dodecyl ether, average mol. wt. 559, was supplied by the Huntsman Corporation Australia Pty. Ltd. All other reagents (AR grade) were used as supplied:

cobalt chloride hexahydrate, hydrochloric acid, ethanol and sodium hydroxide. All aqueous solutions were prepared with MilliQ® water.

Measurement of Extraction Equilibrium Constant

The equilibrium constant of cobalt extraction by Cyanex272 in the micellar system was determined at 20°C by monitoring the wavelength of maximum absorbance of the Co(II)/Cyanex272 complex at 633 nm (molar extinction coefficient: $327 \text{ M}^{-1}\text{cm}^{-1}$), while varying the pH. The pH was adjusted by the addition of small amounts of concentrated sodium hydroxide or hydrochloric acid. Once the pH stabilized, samples were taken and the UV-visible spectrum measured using a Cary 1E UV-Visible spectrophotometer and 1 cm path length quartz cuvettes.

Kinetic Measurements

A RX2000 rapid kinetics spectrometer accessory (Applied Photophysics, UK) was used to perform the kinetic experiments. A reference scan was made and then solutions of Co(II) and Cyanex272/Terpic $G_{12}A_8$ at known pH were mixed in the reaction syringes and the absorbance spectra recorded with an Agilent 8453 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Stoichiometry of Co(II)-Cyanex272 in micellar solution

Solutions with different metal molar fraction (metal/ (metal and ligand)) in 0.1M Terpic $G_{12}A_8$ were prepared. The total concentration of metal and ligand was kept constant at 0.01M. The curves of Co-Cyanex272 concentration varying with the metal molar fractions are shown in Fig.1.

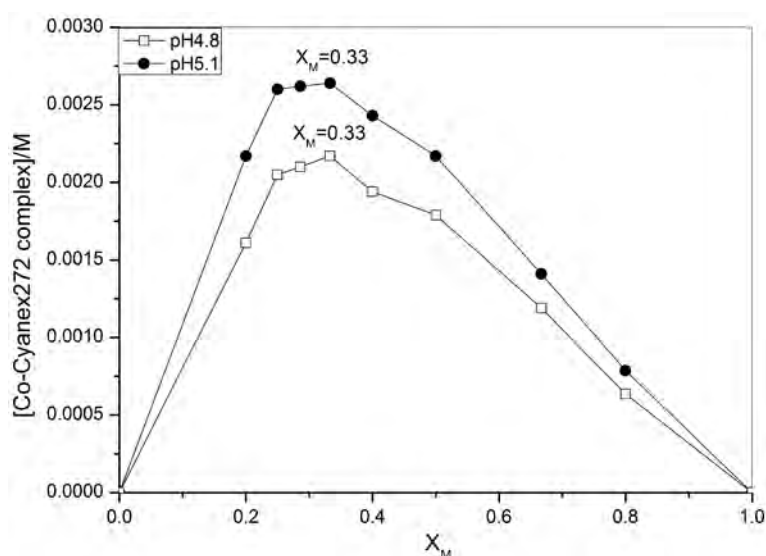


Figure 1. [Co-Cyanex272] versus molar fraction of cobalt (X_M) in 0.1M Terpic $G_{12}A_8$ micellar solution.

It can be seen from Fig.1 that the concentration of Co-Cyanex272 reaches the maximum at the metal molar fraction of 0.33, which indicates the extraction species may be represented as CoR_2 (where HR denotes the protonated form of Cyanex-272) in the micellar solution.

Determination of equilibrium constant

Based on the results above, the overall reaction of Co^{2+} ions with Cyanex272 (HR) can be described as follows:



the equilibrium constant K_{ex} is defined by Eq. (2):

$$K_{\text{ex}} = \frac{[\text{CoR}_2][\text{H}^+]^2}{[\text{Co}^{2+}][\text{HR}]^2} \quad (2)$$

Since the total concentration of cobalt and extractant in the system is known, (Eqs. (3) and (4), respectively), then at a given pH it is possible to solve the three simultaneous equations and obtain the concentration of all the species involved [7].

$$[\text{Co}]_{\text{T}} = [\text{Co}^{2+}] + [\text{CoR}_2] \quad (3)$$

$$[\text{HR}]_{\text{T}} = [\text{HR}] + 2[\text{CoR}_2] \quad (4)$$

where $[\text{Co}]_{\text{T}}$ is the total cobalt concentration within the system and $[\text{HR}]_{\text{T}}$ is the total extractant concentration within the system. Substituting Eqs. (3) and (4) into (2), the cubic Eq. (5) is obtained.

$$4[\text{CoR}_2]^3 - (4[\text{HR}]_{\text{T}} + 4[\text{Co}]_{\text{T}})[\text{CoR}_2]^2 + \left([\text{HR}]_{\text{T}}^2 + 4[\text{Co}]_{\text{T}} + \frac{[\text{H}^+]^2}{K_{\text{ex}}} \right) [\text{CoR}_2] - [\text{Co}]_{\text{T}}[\text{HR}]_{\text{T}}^2 = 0 \quad (5)$$

Eq. (5) can be solved numerically for a given K_{ex} , $[\text{H}^+]$, $[\text{Co}]_{\text{T}}$ and $[\text{HR}]_{\text{T}}$ to calculate the concentration of complex, $[\text{CoR}_2]$, under those conditions. For this study, the software MATLAB was used to solve the cubic equation. The variation in the concentration of the Co^{2+} /Cyanex272 complex with pH measured experimentally is shown in Fig. 2, for two sets of conditions. The experimental data was fitted using Eq. (5). A value of $K_{\text{ex}} = 4.4 \times 10^{-6}$ was found to provide the best fit for all the data. The lines in Fig. 2 show the calculated CoR_2 concentration using $K_{\text{ex}} = 4.4 \times 10^{-6}$ and Eq. (5). The K_{ex} for the Co(II)/Cyanex272 system has been reported to be approximately $6.0\text{--}6.8 \times 10^{-8}$ in hexane and toluene [8-10]. No published values of the equilibrium constant of Co^{2+} extraction by Cyanex272 in a micelle phase could be found for comparison.

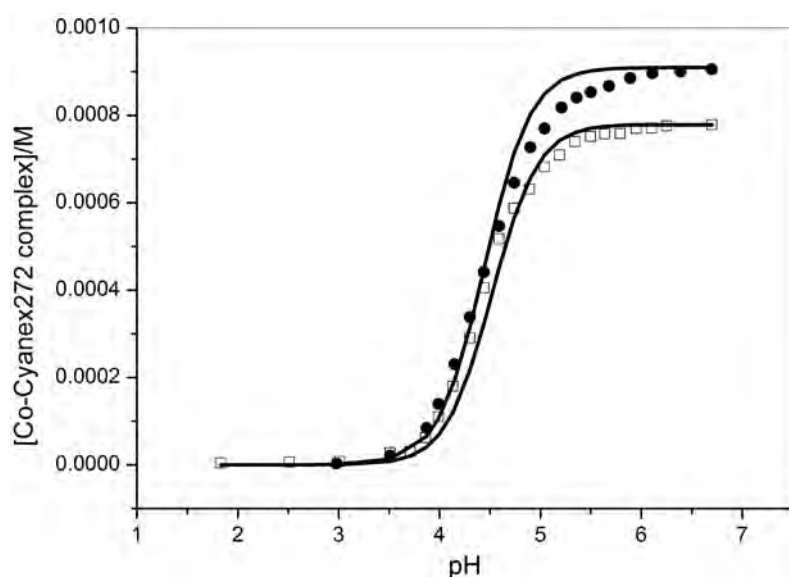
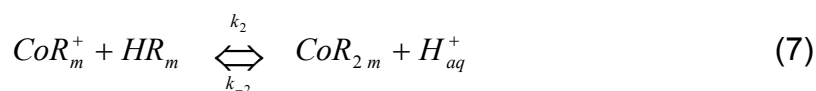
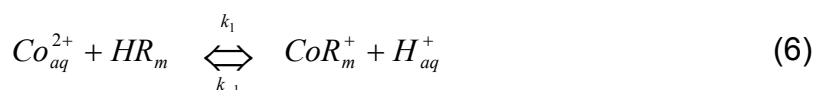


Figure 2. Cobalt/Cyanex272 extraction isotherm in micellar phase, experimental (symbols) and fitted (lines) with $K_{ex}=4.4 \times 10^{-6}$; micellar phase 0.1M Teric $G_{12}A_8$, ((•) and (—)), 0.018M Cyanex272 and 0.00091M $CoCl_2$; ((□) and (—)) 0.02M Cyanex272 and 0.00078M $CoCl_2$.

Kinetics of Co(II) Extraction by Cyanex272

The extraction of Co(II) by Cyanex272 in micellar solution was monitored using the stopped flow technique. In summary, this involved tracking the absorbance at 633 nm (molar extinction coefficient: $327 \text{ M}^{-1}\text{cm}^{-1}$), at discrete time intervals, from an initial introduction of two solutions containing known concentrations of the reactants into the syringes. The experiment was repeated several times with varying initial concentrations of Co(II) and Cyanex272.

Assuming the cobalt extraction by Cyanex272 in micellar solution proceeds as follows:



where k_1 ($\text{M}^{-1} \text{s}^{-1}$) and k_2 ($\text{M}^{-1} \text{s}^{-1}$) are the forward rate constants, and k_{-1} ($\text{M}^{-1} \text{s}^{-1}$) and k_{-2} ($\text{M}^{-1} \text{s}^{-1}$) are the back rate constants. Equations (8)-(11) give the rate equation for the formation of intermediate and complex.

$$\frac{d[Co^{2+}]_{aq}}{dt} = k_{-1}[CoR^+]_m[H^+]_{aq} - k_1[Co^{2+}]_{aq}[HR]_m \quad (8)$$

$$\frac{d[HR]_m}{dt} = k_{-1}[CoR^+]_m[H^+]_{aq} - k_1[Co^{2+}]_{aq}[HR]_m + k_{-2}[CoR_2]_m[H^+]_{aq} - k_2[CoR^+]_m[HR]_m \quad (9)$$

$$\frac{d[CoR^+]_m}{dt} = k_1[Co^{2+}]_{aq}[HR]_m - k_{-1}[CoR^+]_m[H^+]_{aq} + k_{-2}[CoR_2]_m[H^+]_{aq} - k_2[CoR^+]_m[HR]_m \quad (10)$$

$$\frac{d[CoR_2]_m}{dt} = k_2[CoR^+]_m[HR]_m - k_{-2}[CoR_2]_m[H^+]_{aq} \quad (11)$$

The results of the modelling of kinetic data using the MATLAB program are shown in Figures 3-4.

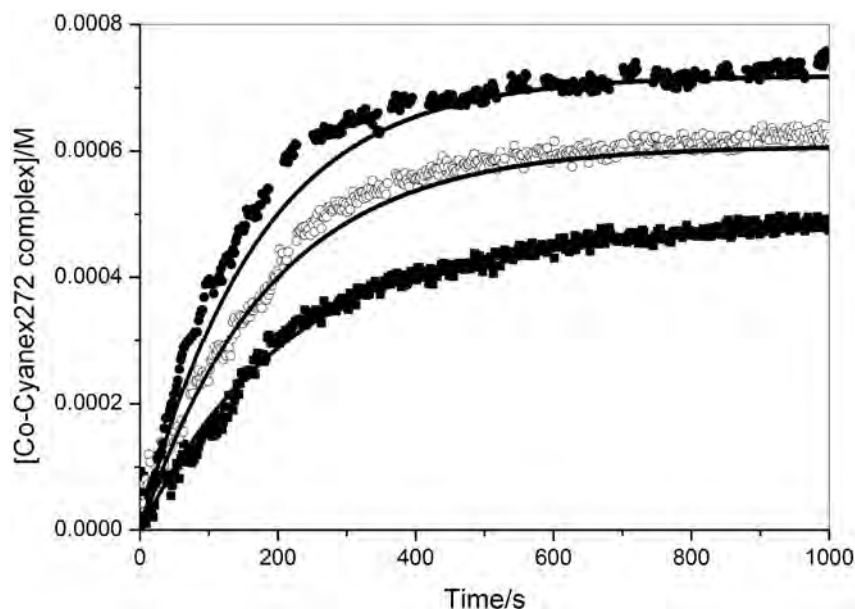


Figure 3. Effect of Co^{2+} concentration on the Co-Cyanex272 extraction kinetics in 0.1M Teric $G_{12}A_8$. Initial concentrations: $[Cyanex272] = 0.008\text{ M}$; $pH = 5.0$; (■) $[Co^{2+}] = 0.001\text{ M}$, (○) $[Co^{2+}] = 0.0015\text{ M}$, (●) $[Co^{2+}] = 0.002\text{ M}$; (—) Theoretical curve for $k_1 = 0.32\text{ M}^{-1}\text{s}^{-1}$, $k_{-1} = 17000\text{ M}^{-1}\text{s}^{-1}$, $k_2 = 220\text{ M}^{-1}\text{s}^{-1}$ and $k_{-2} = 960\text{ M}^{-1}\text{s}^{-1}$.

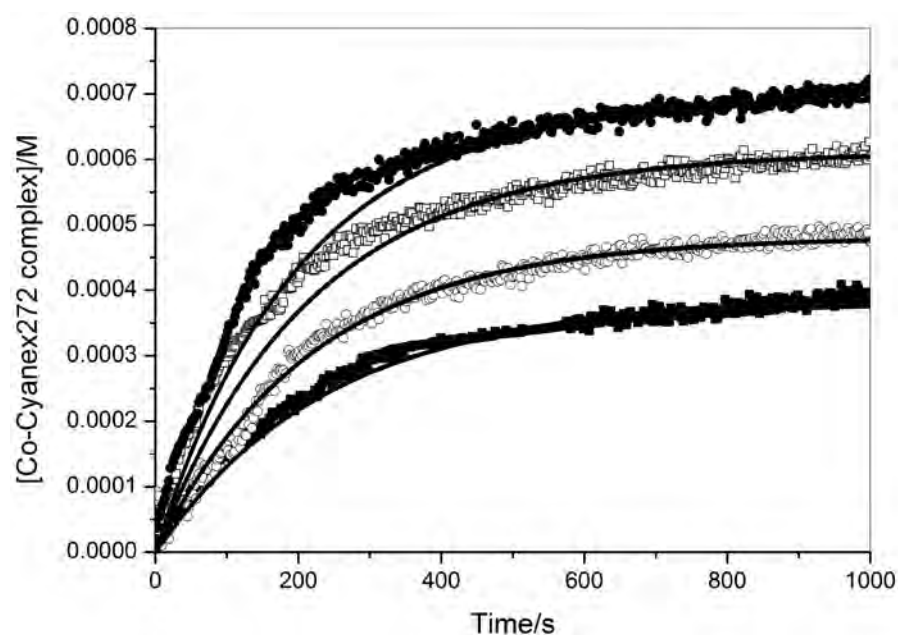


Figure 4. Effect of Cyanex272 concentration on the Co-Cyanex272 extraction kinetics in 0.1M Teric $G_{12}A_8$. Initial concentrations: $[Co^{2+}] = 0.001M$; $pH = 5.0$; (■) $[HL] = 0.006 M$, (□) $[HL] = 0.008 M$, (○) $[HL] = 0.010 M$, (●) $[HL] = 0.012$; (–) Theoretical curve for $k_1 = 0.32 M^{-1}s^{-1}$, $k_{-1} = 17000 M^{-1}s^{-1}$, $k_2 = 220 M^{-1}s^{-1}$ and $k_{-2} = 960 M^{-1}s^{-1}$.

It can be seen from Figs. 3 and 4, that for the reaction rate constants, i.e., $k_1 = 0.32 M^{-1}s^{-1}$, $k_{-1} = 17000 M^{-1}s^{-1}$, $k_2 = 220 M^{-1}s^{-1}$ and $k_{-2} = 960 M^{-1}s^{-1}$, obtained by the MATLAB program, the theoretical curves provide a close fit to the experimentally obtained data for a range of conditions.

CONCLUSIONS

The Co(II)/Cyanex272 extraction reaction kinetics in a non-ionic micellar phase were investigated. The proposed two-step mechanism was found to describe the experimental data over a range of conditions. The forward and reverse reaction rate constants were successfully determined with a program written using the MATLAB software.

ACKNOWLEDGEMENTS

Support from the Australian Research Council and the Particulate Fluids Processing Centre is gratefully acknowledged. We would also like to acknowledge the National Natural Scientific Foundation of China (50904023) and the support from the International Joint Research Laboratory for Advanced Nonferrous Metals of Henan, China.

REFERENCES

- [1] C. Tondre, M. Hebrant and M. Perdicakis, J. Bessiere, *Langmuir*, **1997**, 13, 1446.
- [2] G. W. Stevens, J. M. Perera and F. Grieser, *Curr. Opinion in Coll. & Interface Sci.*, **1997**, 2, 629.
- [3] D. B. Warren, F. Grieser, J. M. Perera and G. W. Stevens, *Colloid & Surfaces A*, **2004**, 243, 127.
- [4] A. Hokura, J. M. Perera, F. Grieser and G. W. Stevens, *Solvent Extr. Ion Exch.*, **1998**, 16, 619.
- [5] R. Cierpiszewski, M. Hebrant, J. Szymanowski, and C. Tondre, *J. Chem. Soc., Faraday Trans.*, **1996**, 92, 249.
- [6] X. Fu, G.W. Stevens, J.M. Perera, Y. Pan, Z.Hu and D. Wang, *Solvent Extr. Ion Exch.*, **1998**, 16, 1111.
- [7] D. B. Warren, G.Dyson, F. Grieser, J.M. Perera, G.W. Stevens and M.A. Rizzacasa, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2003**, 227, 49.
- [8] I. Van de Voorde, L. Pinoy, E. Courtijn, and F. Verpoort, *Solvent Extr. Ion Exch.*, **2006**, 24, 893.
- [9] P.R. Danesi, L.R. Yinger, C. Cianetti, and P. G. Rickert, *Solvent Extr. Ion Exch.*, **1984**, 2, 781.
- [10] P.R. Danesi, L.R. Yinger, G. Mason, L. Kaplan, E. P. Horwitz and H. Diamond, *Solvent Extr. Ion Exch.*, **1985**, 3, 435.

Optimizing crude oil separations – a study of turbulence and composition influence on the drop size distribution of crude oil in sea water

S. Maaß, SOPAT GmbH, Berlin, Germany; sebastian.maass@sopatec.com

The optimum utilization of existing resources, transportation of oil and natural gas over longer and longer distances and the efficient exploration of difficult crude oil deposits are key factors for the oil and gas industry. As the large amounts of feed water are used for the fast exploration a fast and efficient separation process of the liquid/liquid dispersion is necessary for energy friendly transportation costs. The dispersion is thermodynamically unstable, meaning that given time, the droplets will separate out to form two bulk liquid phases. The drop size distribution plays the key factor in those separation processes. Many efforts have been made to measure the size of liquid dispersed droplets. The techniques can be divided into those that require a sample to be withdrawn from the vessel (or pipe) and those that take the measurement in situ. For deep sea analyzes only in-situ methods can be considered as they size the drops under the crucial surrounding conditions.

Large numbers of investigations into droplet size distributions (or simply d_{32}) have focused on extremely dilute dispersions, where it is assumed that coalescence can be eliminated. As this applications are with low practical application, a measurement technology for high concentrations is necessary.

Application in petroleum industry may be somewhat additionally challenging compared to chemical, pharmaceutical, and food manufacturing as the optical conditions of the oil streams are much more complex then specialty and fine chemicals. Also the variation of fluid physical properties and process conditions is stronger.

The understanding, prediction and control of the drop size in crude oil applications is extremely challenging. A detailed understanding of the opposed phenomena of drop breakage and coalescence is necessary for a successful mathematical modelling. A further difficulty handling such dispersed systems is the possible danger of a phase inversion (PI). Does this phenomenon occur spontaneously during a process, it can have fatal consequences for product and equipment [1]. Opposed, it can be used for a more controlled handling of the described applications. Therefore also a deeper understanding and modelling of this phenomenon is desirable.

A turbulent liquid/liquid system using original North sea crude oils and sea water was investigated. The operation parameters dispersed phase fraction, turbulence intensity and surfactant concentration have been varied systematically. The transient drop sizes as the instable behaviour of the water and organic phase have been observed using an in-situ microscope [2]. The drop size was measured using a fully automated image analysis tool [3].

[1] Nienow, A. W., Adv. Colloid Interface Sci. 2004, 108, 95-103.

[2] Maaß, S., Wollny, S., Voigt, A., Kraume, M., Exp. Fluids 2011, 50, 259-269.

[3] Maaß, S., Rojahn, J., Hänsch, R., Kraume, M., Comput. Chem. Eng. 2012, 45: 27-37.

Extraction of Succinic Acid by Aqueous Two Phase System (ATPS) using Ionic Liquid and Salts

*Aulia Indah Pratiwi, Michiaki Matsumoto ^{*1}, and Kazuo Kondo
Doshisha University, Kyoto, Japan*

Summary

Succinic acid is considered as the basis of many important intermediate and speciality chemicals for consumer product industries. Recently, production of succinic acid by the fermentation was taken an growing interest. Therefore it is important to develop an efficient and economic separation from the fermentation broth. In this research, we investigated the extraction of succinic acid by aqueous two phase system (ATPS) using imidazolium-based ionic liquids (BmimBr, HmimBr, and OmimBr) in the presence of phosphate salts such as K_2HPO_4 and K_3PO_4 . The partition coefficients of succinic acid in ionic liquid/ K_3PO_4 -ATPS decreased with increasing salt concentration. The maximum extent was found to be 91.4 % using 40 g- K_3PO_4 /100 mL-solution and HmimBr.

Introduction

Succinic acid as one of bio-based compound has been one of important biomolecules due to its wide application in industries such as pharmacy, food and textiles. Nowadays, instead of using petrochemical-based materials, production of succinic acid using fermentation was focused. Therefore, many studies on separation technique of succinic acid from fermentation broth have been reported in order to find efficient and economic recovery processes.

ATPS are usually formed as a result of mutual incompatibility of two-polymers or one polymer and one salt above certain concentration. The advantages of ATPS are high selectivity, easy to scale-up, having continuous mode and low energy consumption. In the recent times, ionic liquids (ILs) and salts were used in ATPS instead of polymer system (Li, 2010).

ILs, which were known as green solvents, were well-developed because their unique properties such as negligible vapor pressure, non-flammability, thermal and chemical stability, and strong solubilization power (Freire, 2012).

In IL-based ATPS, salting-out effect of salts was found to be important for formation of two-phase beside their hydrophobicity and electrostatic interaction (Pei, 2009). Claudio *et al.* (2011) also showed that the pH of solution containing inorganic salts was determining factor to cause liquid-liquid phase separation.

Although there are a number of reports of IL-based ATPS in the literature, ATPS for separating succinic acid have not been reported. In this study, we investigated the optimum condition for extraction of succinic acid such as IL, salt, and their amount.

^{*1} M. Matsumoto, Doshisha University (E-mail address: mmatsumo@mail.doshisha.ac.jp)

Experimental

Materials

The ILs-based ATPS studied in this work were conducted by using 3 different imidazolium ILs and phosphate salts. The ionic liquids used in this research were 1-butyl-3-methylimidazolium bromide, [BmimBr]; 1-hexyl-3-methylimidazolium bromide, [HmimBr]; and 1-octyl-3-methylimidazolium bromide, [OmimBr]. Salts used were KH_2PO_4 , K_2HPO_4 , and K_3PO_4 which were purchased from Wako Pure Chemical Industries, Ltd. Japan. Succinic acid was from Nacalai Tesque, Inc. Kyoto, Japan. All chemical were used without further purification.

Methods

Phase diagrams. Determination of binodal curves was prepared by turbidimetric titration at room temperature. A few grams of concentrated salt aqueous solution were weighed into an Erlenmeyer flask. Thus a solution of known concentration of IL was added drop by drop and then mixed. The solution is clear at first, but after a certain amount of IL is added, one further drop makes the mixture turbid and separate into two phases. The mass of mixture is noted and the composition of the two phase system is determined. The addition of a few drops of water makes the mixture clear again, and the above procedure is repeated to obtain sufficient data to construct the phase diagram.

Extraction. At first 5 mL of succinic acid solution of 5 g/L was added into flask tube and followed by adding salt at various amount. All components were mixed until mixtures form clear solution. After that, 1 g of IL were added to the mixture and mixed. Furthermore the flask tube was put into thermo-mixer for 12 hours to get well separation between aqueous phase and IL phase at 298 K. Before and after extraction process, the succinic acid concentration in the aqueous phase was determined by HPLC, volumes of both phases were measured by graduated tube, and the water contents in IL phase were determined by Karl-Fisher method. The extraction of succinic acid were calculated by equation (1),

$$E\% = \frac{V_{IL} \cdot C_{IL}}{V_a^0 \cdot C_a^0} \cdot 100\% \quad (1)$$

where V_{IL} and V_a^0 are the volume of ionic liquid phase (upper phase) and initial volume of aqueous phase (lower phase) respectively. C_{IL} and C_a^0 are the concentration of succinic acid in ionic liquid phase and aqueous phase, respectively.

Results and discussion

Phase diagrams

As one of the major components in IL-based ATPS, the effect of inorganic salts on the phase separation was investigated. When using kosmotropic ions such as HPO_4^{2-} and PO_4^{3-} , the aqueous two phases were formed. While using H_2PO_4^- , which is the border of kosmotropic and chaotropic ions, the phase separation was not observed. Li (2010) reported that the kosmotropic ions are beneficial to ATPS formation because the interactions between these anions and water molecules are stronger than those between water molecules. The interaction between water and chaotropic ion is weaker than those of kosmotropic ions which make ionic liquids hard to dissolve in water. Figure 1 shows the bimodal curves of ionic liquids and phosphate salts. From Figure 1, it can be seen that HmimBr has the strongest-phase forming ability because of less amount of salts and ILs to form two-phase system. Although these results did not follow the order of hydrophobicity of ILs, these results agree with results that have been observed by other researcher when using imidazolium based ILs (Chun, 2001; Pei, 2009). These trends suggest us to use HmimBr as IL to form ATPS with salts for further studies.

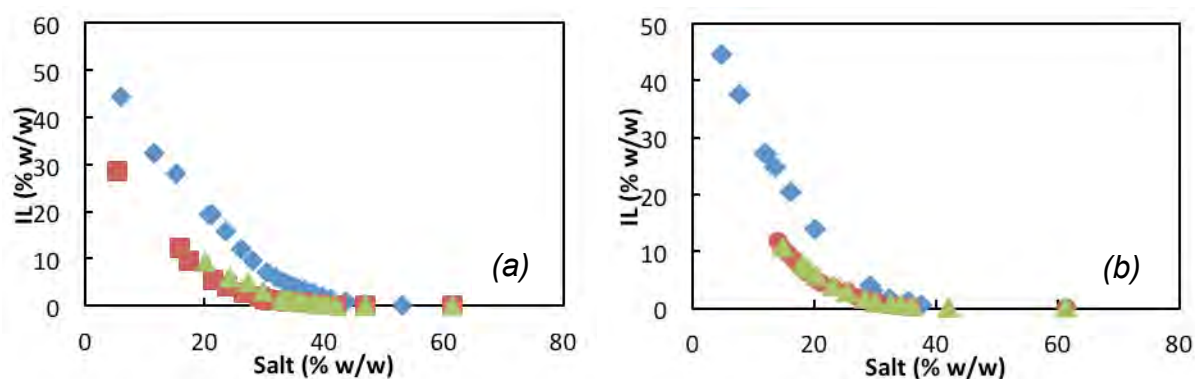


Figure 1. Binodal curves imidazolium-based ILs with K_2HPO_4 salt (a), with K_3PO_4 salt (b); BmimBr ($\blacklozenge$), HmimBr ($\blacksquare$), OmimBr ($\blacktriangle$).

The Gibbs' energy of hydration, ΔG_{hyd} , was known to have the significant impact to the two-phase forming capacity. The smaller values of ΔG_{hyd} , the easier to form two-phase by adding salts. ΔG_{hyd} values of PO_4^{3-} and HPO_4^{2-} were -2765 and -1125 kJ/mol, respectively (Marcus, 1991). Figure 2 shows that K_3PO_4 has better salting-out ability than K_2HPO_4 .

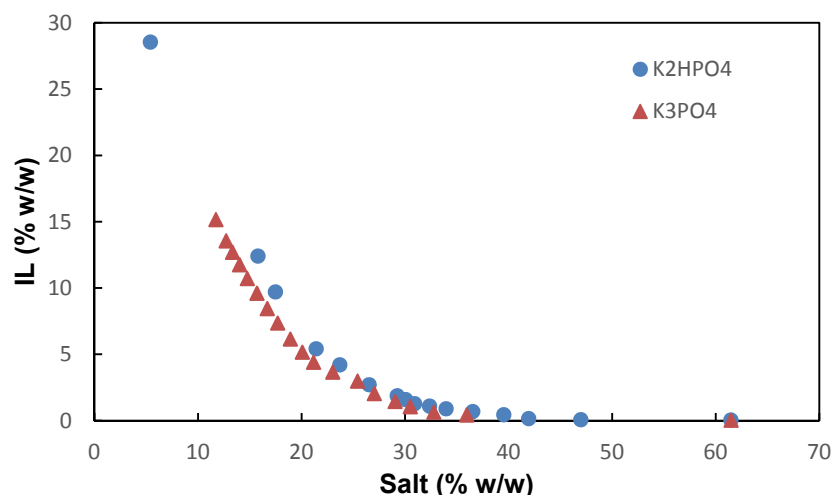


Figure 2. Binodal curves HmimBr IL with K_2HPO_4 and K_3PO_4 salt.

Extraction of succinic acid

We used HmimBr as IL and K_3PO_4 as salt in order to separate succinic acid from aqueous phase. Table 1 shows the extraction extent of succinic acid, concentration of succinic acid and water contents in the IL phase. Extraction of succinic acid by ATPS gave higher value than supported ionic liquid membrane (SILM) and polymer inclusion membrane (PIM) methods (Pratiwi, 2013; 2014). From Table 1, succinic acid concentration and the water contents in the upper phase decreased with increasing the salt concentration. This result suggests that succinic acid accompanying water is considered to move to the upper phase because of the high affinity of between succinic acid and water. Succinic acid concentration in the upper phase was 2.8 times that in the initial concentration at 40 g- K_3PO_4 /100mL. In that case, almost quantitative recovery and enrichment of succinic acid was achieved.

Table 1. Extraction of succinic acid by ATPS-HmimBr IL

K_3PO_4 (g/100 mL)	E (%)	C_{IL} (g/L)	Water contents (%)
40	91.1	14.2	35.9
60	56.8	10.7	30.4
80	41.5	9.1	23.7
100	33.8	6.9	17.8

References

- Chun, S., S.V. Dzyuba, R.A. Bartsch. 2001. Influence of structural variation in room temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by crown ether. *Anal. Chem.*, 73, 3737-3741.
- Claudio, A.F.M., A.M. Ferreira, S. Shahriari, M.G. Freire, and J.A.P. Coutinho. Critical assessment of the formation of ionic-liquid-based aqueous two-phase systems in acidic media. 2011. *J. Phys. Chem. B*, 115, 11145–11153.

- Freire, M.G., A.F.M. Claudio, J.M.M. Araujo, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, and L.P.N. Rebelo. 2012. Aqueous biphasic systems: A boost about by using ionic liquids. *Chem. Soc. Rev.*, 41, 4966-4995
- Li, Z., Y. Pei, H. Wang, J. Fan, and J. Wang. 2010. Ionic liquid-based aqueous two-phase systems and their applications in green separation processes. *Trends in Anal. Chem.*, 29, 1336-1346.
- Marcus, Y. 1991. Thermodynamics of solvation of ions. Part 5. –Gibbs free energy of hydration at 298.15 K. *J. Chem Soc. Faraday Trans.*, 87, 2995-2999.
- Pei, Y., J. Wang, K. Wu, X. Xuan, and X. Lu. 2009. Ionic liquid-based aqueous two-phase extraction of selected proteins. *Separ. Purif. Technol.*, 64, 288-295.
- Pratiwi, A.I., M. Matsumoto, K. Kondo. 2013. Permeation of succinic acid through supported ionic liquid membranes. *J. Chem. Eng. Japan*, 46, 383-388.
- Pratiwi, A.I., M. Matsumoto, K. Kondo. 2014. Permeation of succinic acid through polymer inclusion membranes containing ionic liquid. *J. Chem. Eng. Japan* in press.

Reactive extraction of aminoacids - selective separation

Alexandra Cristina Blaga¹, Dan Cascaval¹, Lenuta Kloetzer¹, Alexandra Carlescu¹,
Anca-Irina Galaction²

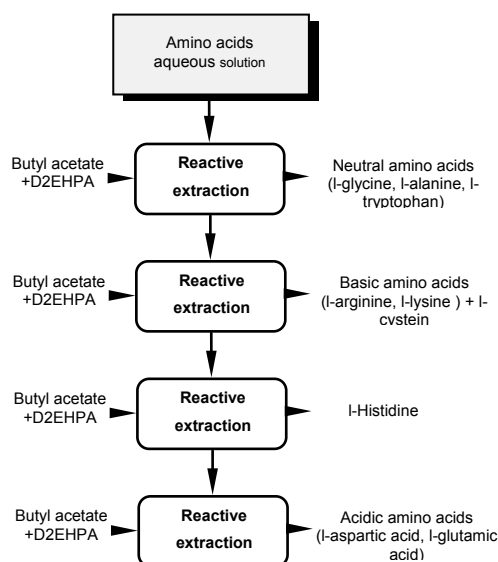
¹"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Dept. of Organic, Biochemical and Food Engineering, D. Mangeron 73, 700050 Iasi, Romania

²"Gr. T. Popa" University of Medicine and Pharmacy of Iasi, Faculty of Medical Bioengineering, Dept. of Biomedical Science, M. Kogalniceanu 9-13, 700454 Iasi, Romania

As the application of biotechnology has progressed much in recent years, demands for more sophisticated separation methods have increased. Consequently, the interest in developing the techniques that can improve the selectivity and the yield of downstream processes for the separation and purification of amino acids increased significantly in the last decades.

The liquid-liquid extraction of amino acids (dissociated at any pH-value of the aqueous solutions) is possible only by using the reactive extraction technique, mainly with extractants of organophosphoric acid derivatives, high molecular weight amines, and crown-ethers. In this study the separation of nine amino acids of acidic character (l-aspartic acid, l-glutamic acid), basic character (l-histidine, l-lysine, l-arginine) and neutral character (l-glycine, l-tryptophan, l-cysteine, l-alanine) by reactive extraction with di-(2-ethylhexyl)phosphoric acid (D2EHPA) is analysed.

The study on separation of amino acids by reactive extraction indicated that it is possible to selectively extract amino acids from fermentation broth or protein hydrolysates. The reactive extraction of amino acids with D2EHPA is possible only if the amino acids exist in aqueous solution in their cationic forms (pH of aqueous phase below the isoelectric point).



Using the reactive extraction technique, the total separation of the following amino acids groups has been performed: neutral amino acids at pH 5–5.5, basic amino acids and l-cysteine at pH 4–4.5, l-histidine at pH 3–3.5, and acidic amino acids at pH 2–2.5. Due to the rather low extraction degrees of each group of amino acids at the required pH-values for selective separation, for total recovery of the considered amino acids a multistage extraction is required.

STUDY OF SEPARATION OF ZIRCONIUM AND HAFNIUM BY SOLVENT EXTRACTION FROM NITRIC LIQUOR – PART 1

Janúbia Cristina B. S. Amaral¹, Carlos Antônio de Moraes²

^{1,2}Centro de Desenvolvimento da Tecnologia Nuclear, CDNT/CNEN, Belo Horizonte, Brazil, jcbasa@cdtn.br; cmorais@cdtn.br

ABSTRACT

The Separation of zirconium and hafnium from nitric liquor with acid extractants (DEHPA, IONQUEST[®]801 and CYANEX[®]272) and with solvating extractants (TBP, CYANEX[®]923 and a mixture of TBP and CYANEX[®]923) was investigated. Aqueous phase solutions prepared from the liquor generated by the dissolution of the product of the zircon alkaline fusion were used. The content of Zr and Hf in these solutions was around 20g.L⁻¹ and 0.4 g.L⁻¹ respectively. The content of NO₃⁻ varied between 3 and 12 mol.L⁻¹ while the acidity content varied from 1 to 12 mol.L⁻¹ H⁺. The experiments were conducted to determine the extraction coefficient and separation factor of the Zr/Hf pair. The effect of the acidity of the liquor, extractants concentration, nitrate concentration and aqueous/organic relationship has been investigated. In the acid extractant experiments, a high extraction of the metals was observed even at high acidities, however, with no selectivity for DEHPA and IONQUEST[®]801 but with some selectivity for CYANEX[®]272. The use of CYANEX[®]272 in the separation of Zr and Hf was unfeasible due to the metal stripping difficulties. Among the extractants investigated, TBP showed the best performance in the separation of Zr/Hf. The extracted zirconium and hafnium in the TBP organic phase was efficiently stripped using water as the stripping agent. The best results were obtained with an acidity of 7.0 mol.L⁻¹ H⁺ and nitrate concentration around 8.0 mol.L⁻¹ NO₃⁻.

KEYWORDS: Zirconium extraction, Hafnium extraction, Zircon, Zirconium and Hafnium separation

INTRODUCTION

Zirconium is an element which presents a large number of uses in modern technology. Properties of zirconium such as its transparency to thermal neutrons has made it a good construction material in nuclear reactors. Amongst the applications of zirconium alloys, its use in the nuclear field as the structural material for nuclear fuel shielding must be emphasized. Hafnium is found in combination with natural zirconium compounds and does not exist as a free element in nature. It is a good absorber of neutrons, leading to its use as a moderator in control rods in nuclear reactors (HABASHI, 1977) (SHARIATI e YAMINI, 2006).

The main source of zirconium, its compounds and alloys is the zircon mineral (zirconium silicate). Due to lanthanide contraction, zirconium and hafnium are similar in chemistry and are found together in nature (SHARIATI e YAMINI, 2006) (PERALTA-ZAMORA e MARINS, 1999) (ABBASPOUR e BARAMAKEH, 2002). The presence of hafnium, in nuclear energy, is a potential problem since hafnium is an absorber of thermal neutrons, and the zirconium alloys for nuclear use cannot present this characteristic. In this case, the content of hafnium in the zirconium concentrate should be lower than 100 ppm. The zirconium and hafnium separation is a difficult task (HABASHI, 1977) (ABDEL-REHIM, 2005). The present work demonstrates studies about zirconium and hafnium separation from nitric liquor using the solvent extraction technique.

EXPERIMENTAL

Methodology

The solvent extraction experiments were performed in a 150 ml beaker with equal volumes in the aqueous and organic phases. It was shaken for about 15 min at a temperature of 25° C. The contact between the phases was carried out through mechanical agitation using IKA agitators model RW 20.n at 600 rpm. After contact the aqueous/organic mixture was transferred to a separation funnel where the phases were separated and sent for analysis. The Zr and Hf were determined by Energy Dispersive X-ray Fluorescence Spectrometry - EDXRF (Shimadzu - EDX 720). The nitrate was determined through molecular absorption spectrophotometry in the ultraviolet region (302 nm) using a spectrophotometer UV visible (Varian - Cary 50 conc). The acidity of the aqueous phase was determined by potentiometry using pH meter (Digimed - DM 22).

The aqueous solutions used were prepared from the liquors obtained from the solubilization of the product of the alkaline fusion of zircon. The solubilization of the zircon fusion product was carried out with nitric acid (HNO₃). The pH and the nitrate concentrations of the solution were adjusted by adding nitric acid (HNO₃) and nitrate sodium (NaNO₃) according to the medium and acidity of the experiment. The chemical characterization with the main constituents of the liquors used in the solvent extraction experiments is presented in Table 1.

Table 1 Chemical characterization of Zr and Hf liquors used in the solvent extraction experiments

Sample	Species (g/L)						
	Zr ⁴⁺	Hf ⁴⁺	^a NO ₃ ⁻	SO ₄ ²⁻	Fe ³⁺	Ti ⁴⁺	Si ⁴⁺
Zr-Hf Zirconite	20.5	0.4	-	0.8	0.6	0.2	2.8

^a The [NO₃⁻] varied according to experiment

The extractant agents used in this study were: DEHPA (di-2-etihexil phosphoric acid) and IONQUEST®801 (2-ethylhexyl phosphonic acid) manufactured by Albright and Wilson Americas and supplied by Pecos Brazil Ltda.; CYANEX®272 (bis (2,2,4-trimethylpentyl) monotiofosfínico) manufactured by Albright and Wilson Americas and supplied by Cytec of Brazil Ltda.; TBP (tributyl phosphate) manufactured by Riedel-de Haen (Hannover, Germany); CYANEX 923 (a mixture of oxides alquilfosfinas) by Cytec Canada – INC. The extractant solutions were prepared at specified concentrations diluted in dodecane.

RESULTS AND DISCUSSION

Acid extractants

The FIG. 1 and TAB. 2 show the results using the acid extractants all at a concentration of 1.5mol/L.

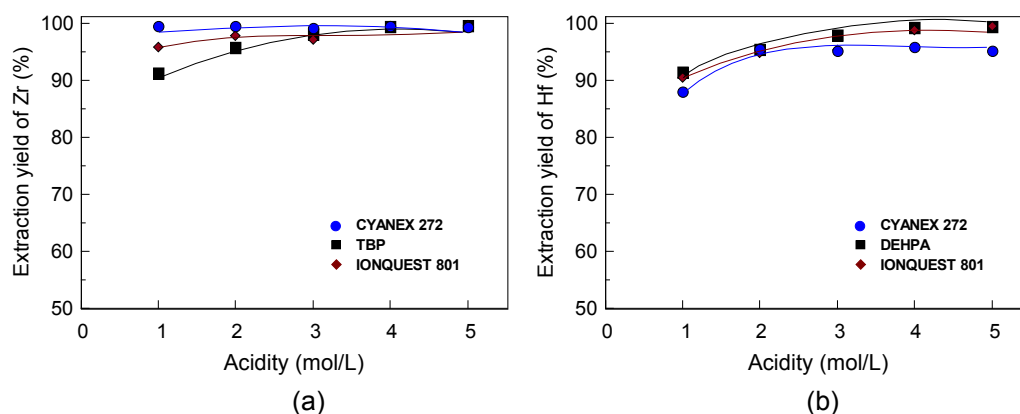


Figure 1 Efficiency in the extraction of Zr (a) and Hf (b) for the acid extractants

Table 1 Separation factor of Zr/Hf for the acid extractants

H^+ (mol/L)	Separation factor (SF)		
	DEHPA	IONQUEST 801	CYANEX 272
1.0	1.0	1.4	22
2.0	1.1	1.2	26
3.0	1.1	1.6	23
4.0	1.3	1.9	25
5.0	1.3	1.5	25

All acid extractants investigated showed a high performance in the extraction for all acidities, however the selectivity was not satisfactory. The best separation factors were obtained for Cyanex 272, but with high Hf extraction - more than 90%. The high percentage of extraction obtained indicates the difficulty of stripping metals from the organic phase. This fact combined with low separation factor led to the conclusion that this class of extractants are not the most suitable for the separation of Zr/Hf metals.

Solvation extractants

Table 3 and FIG. 2 show the results of experiments using solvation extractants at a concentration of 1.5mol/L. For CYANEX 923, the extraction yield of the metals in low acidity is higher, when compared to TBP. In acidity greater than 3.0mol/L, the CYANEX 923 presents an extraction yield over 90% for Zr, but the selectivity is lower than that observed for TBP. For TBP, the extraction percentage and the separation factor significantly increase for values greater than 7.0 mol/L of H^+ .

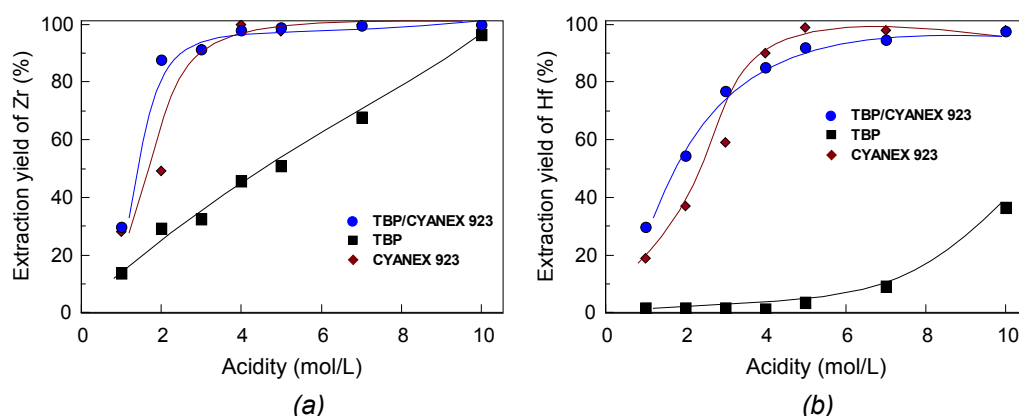


Figure 2 Efficiency in the extraction of Zr (a) and Hf (b) for the solvation extractants

Table 2 Separation factor for Zr/Hf for solvation extractants

H ⁺ (mol/L)	Separation factor (SF)		
	TBP	CYANEX 923	TBP/CYANEX 923
1.0	0.7	1.7	3.5
2.0	1.6	4.4	13
3.0	3.5	10	8.6
4.0	4.7	5.9	8.5
5.0	13	13	6.7
7.0	51	25	14
10	51	15	15

Extraction of Zr and Hf varying the concentration of TBP

Table 4 and FIG. 3 present the yields of extraction and separation factors obtained in the experiments varying the TBP concentration used as extractant. In these experiments the remaining acidity of 7.9mol/L, and the concentration of nitrate in 9.8mol/L. During the experiments using solutions containing TBP concentrations of 1.0, 1.5 and 2.0mol/L, the formation of the third phase was observed, but not when using TBP concentrations of 2.5mol/L and 3.0mol/L. The good experimental results associated with the TBP concentration of 2.5mol/L led to the continuation of the work using TBP as extractant at that same concentration.

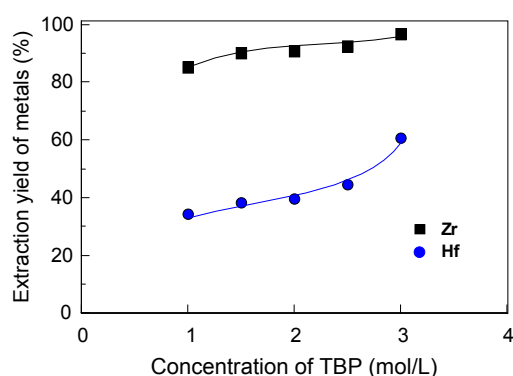


Table 3 Separation factor of Zr/Hf with variation of TBP concentration

TBP (mol/L)	Separatio n factor (SF)	Final concentration in the aqueous (mol/L)	
		H ⁺	NO ₃ ⁻
1.0	11	5.6	3.4
1.5	15	6.5	5.8
2.0	15	5.8	5.2
2.5	15	4.3	6.0
3.0	19	4.2	4.9

Figure 3 Efficiency on the extraction of Zr and Hf with variation the concentration of TBP

Extraction of Zr and Hf with TBP at 2.5mol/L varying the relative phase A/O

Extraction experiments varying the aqueous/organic (A/O phase) relationship were conducted, with TBP concentration of 2.5mol/L, and the results are shown in FIG. 4 and Table 5. In these experiments, the acidity remained at 7.9mol/L and the nitrate concentration at 9.8mol/L.

When using the A/O relationship of 1/1, 2/1 and 3/1 the third phase was formed and when relationships 2/1 and 3/1 were used, in particular, the separation was difficult. In all other cases there was good separation and no third phase. The best separation factors were obtained when using the A/O ratio of 1/3, 1/2 and 1/1, 5.

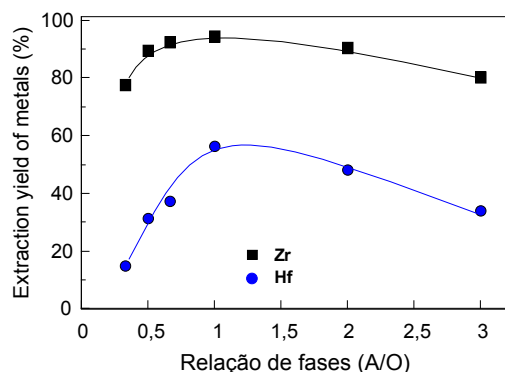


Figure 4 Efficiency on the extraction of Zr and Hf with variation of the A/O relationship phase

Table 4 Separation factor of the Zr/Hf with variation of the A/O relationship phase

A/O	Separation factor (SF)	Final concentration in the aqueous (mol/L)	
		H ⁺	NO ₃ ⁻
1/3	19.6	3.2	3.3
1/2	19.2	4.9	4.4
1/1.5	21.3	5.3	5.3
1/1	13.8	5.8	5.8
2/1	10.4	6.7	6.7
3/1	8.1	7.4	7.3

Stripping

Were performed stripping experiments in organic generated from the tests showed that the best extraction yields. The stripping test was performed using sulfuric acid (H₂SO₄) in concentrations of 1, 2, and 4mol/L and water in all the organic solutions. The organic solutions used in the stripping were: I) organic generates in experiments with Cyanex 272 in concentrations 1.5mol/L and feeds at 2 and 4mol/l of acidity; II) organic generates in experiments with TBP 3.0mol/L and feed acidity of 7.0mol/L; III) organic generates in experiments mixing TBP and Cyanex - 272 and feed acidity of 1 , 2 and 4mol/L.

Stripping using all concentrations of sulphuric acid was performed, (1.0mol/L, 2.0mol/L and 4.0mol/L) and only pure water was used, and the organic solutions used were the ones generated in the extraction experiments using a TBP concentration of 3.0mol/L and feed acidity of 7.0mol/L. In other experiments, stripping of the organic phases did not occur at any concentration of sulphuric acid or when using water.

Distribution Curve – Extraction

The extraction isotherm (equilibrium curve) and the McCabe-Thiele diagram were traced, aiming to determine the theoretical number of stages, and the necessary liquid/solvent volumetric relationship for the achievement of continuous experiments (BARBOSA, EL-NOGER, *et al.*, 1982) (RITCEY e ASHBROOK, 1984). The TBP concentration in the solvent was 2.5 mol/L. The isotherm extraction/McCabe-Thiele diagram for the zirconium is shown in FIG. 5.

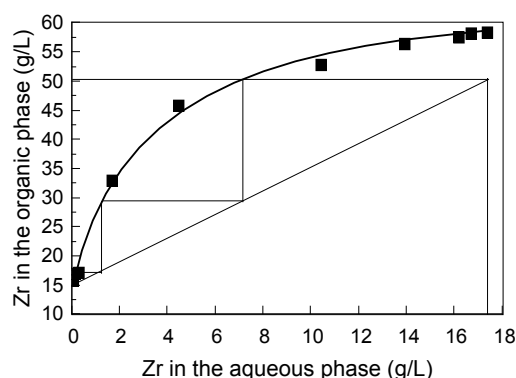


Figure 5 Extraction Isotherm of zirconium / McCabe-Thiele diagram for the solvent containing 2.5 mol/L TBP concentration

According to the results, (McCabe-Thiele diagram), maintaining a volumetric feed/solvent ratio through 3 to 4 stages of mixers/decanter is required to ensure a safe zirconium raffinate. Under these conditions it is possible to get a loaded with a solvent content of approximately 58g/L zirconium.

CONCLUSION

The cationic extractants investigated were not suitable for the separation of Zr and Hf metals. CYANEX 272 showed separation factors ranging from 22 to 25 but with high extraction of Hf (greater than 95%). For Solvation extractants the best results were obtained using 2,5mol/L of TBP at an acidity of 7.0mol/L when using the relation A/O relationship of 1/5. According to the McCabe-Thiele Diagram 3 to 4 extraction stages would be needed for organic loaded with approximately 58g/L of Zr.

BIBLIOGRAFIA

ABBASPOUR, A.; BARAMAKEH, L. Simultaneous Determination of Zirconium and Molybdenum by First-Derivate Spectrophotometry. **Anal. Sci.**, 18, 2002. 1127-1130.

ABDEL-REHIM, A. M. A New Technique for Extracting Zirconium form Egyptian Zircon concentrate. **Int. J. Miner. Process.**, 76, 2005. 234-243.

BARBOSA, J. P. et al. **HIDROMETALURGIA - Associação Brasileira de Metais**. São Paulo: ÉDILE serviços gráficos e editora LTDA, 1982.

HABASHI, F. **Handbook of Extractive Metallurgy**. Québec: Wiley-VCH, v. III, 1977.

PERALTA-ZAMORA, P.; MARINS, J. W. Anomalies in the spectrophotometric and extractive behaviour of zirconium and hafnium evidence of a synergistic effect. **Talanta**, 49, 1999. 937-941.

RITCEY, G. M.; ASHBROOK, A. W. **SOLVENT EXTRACTION Principles and Applications to Process Metallurgy Part I**. Amsterdam: ELSEVIER SCIENCE PUBLISHERS B.V., v. I, 1984. 361 p.

SHARIATI, S.; YAMINI, Y. Cloud point extraction and simultaneous determination of zirconium and hafnium using ICP-OES. **Journal of Colloid and Interface Science**, 2006. 419-425.

Multistage extraction as a method of dicarboxylic acids removal from glycerol bioconversion fermentation broths

Agnieszka Krzyzkowska, Dominika Bednarska, Magdalena Regel-Rosocka,

Maciej Wiśniewski

Poznan University of Technology, Institute of Chemical Technology and Engineering,

Pl. M. Skłodowskiej-Curie 5, 60-965 Poznan, Poland

In the light of growing biodiesel production management of by-products from biorefineries, e.g. glycerol, becomes a vital problem for global economy. Only in Europe biodiesel production (as an additive to engine fuels) amounted to 3.18 mln t in 2005. What is more, almost 100 kg of raw glycerol is obtained for each 1 t of fatty acid esters produced in a biorefinery. As a consequence of raw glycerol overproduction in the world its price has been significantly reduced. Thus, bioconversion of glycerol to compounds that are important industrial substrates has become recently widely investigated. The resulting fermentation broth must be further processed to separate various groups of chemical compounds.

The aim of the work is to apply multistage extraction with basic (TOA, Aliquat 336) and solvating extractants (Cyanex 923) to recover carboxylic acids, mainly succinic or fumaric, from fermentation broth. Some experiments on model solutions indicate that reactive extraction is an efficient technique to recover the organic acids from diluted aqueous solutions and separate them from polyols and other fermentation products. It is important to choose proper extractant concentration in the organic phase, volume ratio and stripping solution to develop a favourable process.

This research was supported by the project „Biotechnological conversion of glycerol to polyols and dicarboxylic acids,” implemented within the Operational Programme-Innovative Economy, 2007- 2013, co-financed by the European Union. POIG.01.01.02-00-074/09.

Drop Formation at a Nozzle Hole in a Plate for Quiescent Continuous Phase

Nirvik Sen[#]; K.K.Singh; S. Mukhopadhyay; K.T.Shenoy; S.K.Ghosh

Chemical Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA-400085

[#]Corresponding Author: nirvik@barc.gov.in

Abstract

The paper presents results of numerical simulations aimed at studying phenomenon of drop formation at a single nozzle hole in a plate. Two-dimensional numerical simulations have been carried out using phase field algorithm for interface tracking. Validation of the numerical model has been done using the experimental data reported in literature. Effects of velocity, geometry and physical properties of the phases on the drop formation process i.e. height of drop detachment, time of drop detachment, equivalent drop diameter and aspect ratio have been studied. Based on simulation results a correlation to predict drop size is presented.

1. Introduction

Formation of drops at nozzle plates is a very important phenomenon encountered in plate extraction columns. Nozzle plates are required specially when the phase which wets the material of construction of the plate needs to be dispersed. Significant work has been carried out on drop formation process but most of it is restricted to drop formation on nozzles submerged in a pool of an immiscible liquid (Harkins and Brown, 1919; Hayworth and Treybal, 1950; Rao et al., 1966; Scheele and Meister, 1968a). Studies on drop formation at a nozzle hole in a plate are relatively few. Soleymani et al. (2008) studied hydrodynamics of drop formation at a hole in a plate. They studied two types of hole-plain and nozzle hole. In the present study phase field method, as available in a commercial solver (COMSOL Multiphysics 3.5a), has been used. A sieve plate with a single nozzle hole is considered. Effects of hole diameter, height of nozzle protrusion, velocity and physical properties on drop formation process have been studied. A correlation with equivalent drop diameter as the dependent variable is obtained using the results from the numerical simulations.

2. Computational approach

Computational approach used for numerical simulations involve coupled solution of Navier-Stokes equations and a partial differential equation for a phase field variable. The two-phase flow dynamics is captured using Cahn-Hilliard equation. The equation tracks a diffuse interface separating the immiscible phases. Details have been omitted for brevity (Singh et al., 2013). The typical 2D computational domain used in the simulation and the mesh is shown in Fig.1. The column having diameter 23 mm and height 38 mm is initially filled with continuous phase, and the dispersed phase is fed upward to the column through a single nozzle hole. The plate thickness is taken as 3 mm. The geometry used in the simulation is same as used by Soleymani et al., 2008.

3. Validation

The numerical technique used to simulate drop formation was validated using data available in literature for water-Exxol D80 system (Soleymani et al., 2008). The hole velocity of the dispersed phase is varied within the range of 3-21 cm/sec. Figs.3-4 show the comparison of the experimental data with the results obtained from simulations. As can be seen, the match between the simulated and the experimental results are very good for time and height of drop detachment and reasonably good for equivalent drop diameter.

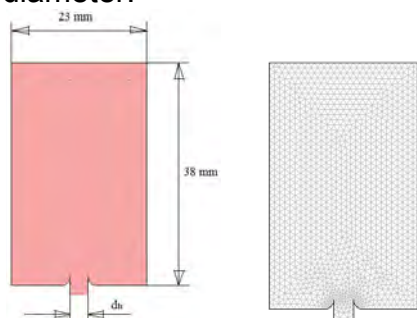


Figure 1: Computational domain

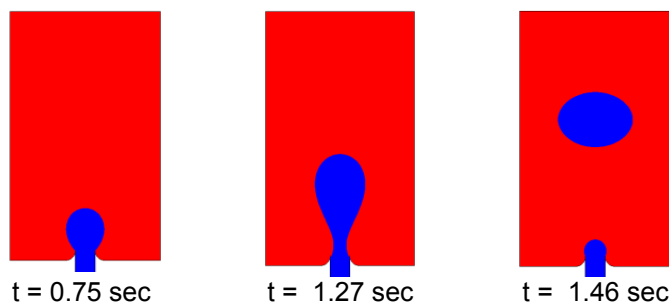


Figure 2: Visualization of drop formation phenomenon

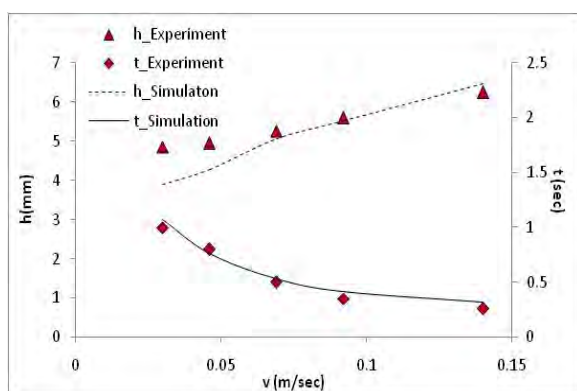


Figure 3: Validation for drop detachment height and drop detachment time

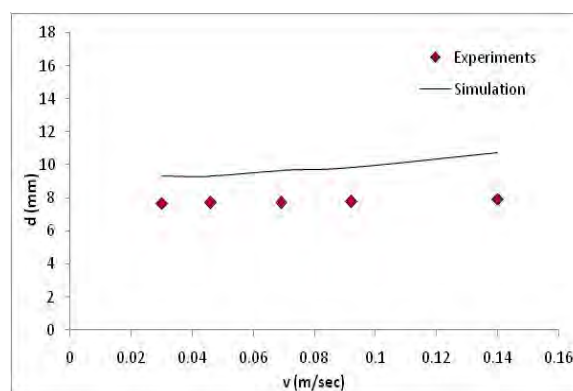


Figure 4: Validation for equivalent drop diameter

4. Results and discussion

4.1 Details of parametric studies

After validating the computational approach, parametric studies were done to study the effects of dispersed phase density, ρ_D (simulations carried out for 398, 597, 716, **793** and 875 kg/m³), contact angle, θ (simulations carried out for 0.98, 1.47, **1.96**, 2.2 and 2.45 radians), interfacial tension, σ (simulations carried out for 27, 40.5, **54**, 67.5, and 81 mN/m), hole velocity, v (simulations carried out for **3**, 4.6, 6.9, 9.2, and 10.7 cm/sec), height of nozzle protrusion, h_c (simulations carried out for 0.5, 1, **1.5**, 2, 2.25 mm), and hole diameter, d_h (simulations carried out for 2, **3**, and 4 mm) on the process of drop formation. The values highlighted in bold font represent the base values. When variation of one parameter was seen the other parameters were kept constant at their respective base values. Dependent variables tracked in the present study are drop detachment height (h), drop detachment time (t), equivalent drop diameter (d) and aspect ratio at the instant drop detachment.

4.2 Effect of hole velocity

Fig.5-6 show drop detachment height and drop diameter increase with increase in hole velocity whereas drop detachment time and aspect ratio decrease with hole velocity. Increase in hole velocity increases inertial force which is a disruptive force and hence increase in hole velocity should promote drop detachment leading to lower drop detachment and diameter. However it is reported (Scheele and Meister, 1968) that during the necking period of drop formation more and more amount of dispersed phase moves into the emerging drop with increasing velocity which increases drop volume. Hence net effect of increase in hole velocity is an increase in drop diameter. Also higher velocities tend to drag the interface in the direction of the velocity thereby increasing the drop detachment height.

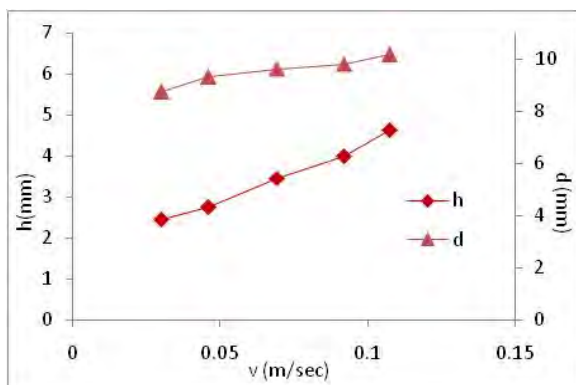


Figure 5: Effect of hole velocity on height of drop detachment and equivalent drop diameter

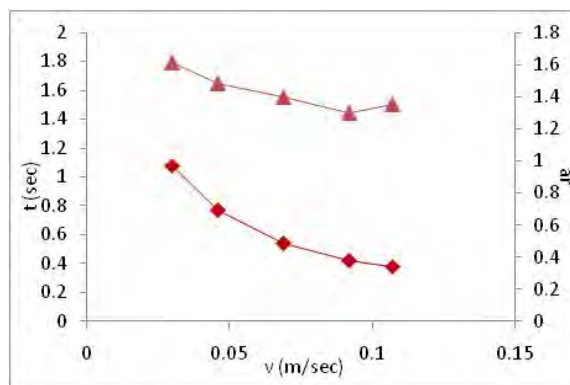


Figure 6: Effect of hole velocity on time of drop detachment and aspect ratio

4.2 Effect of interfacial tension: Fig.7-8 show equivalent drop diameter, drop detachment time and aspect ratio increase whereas drop detachment height decreases marginally by increase in interfacial tension. Interfacial tension is a restraining force and tries to prevent generation of new area. The breakup point therefore shifts closer to the bulk phase and equivalent drop diameter is larger as drop detachment is delayed. Aspect ratio is found to increase marginally with increase in interfacial tension.

4.3 Effect of contact angle: Fig.9-10 show equivalent drop diameter, drop detachment time and drop detachment height decreases with increase in contact angle. A larger contact angle means the plate is less wetted by the dispersed phase. Hence an increase in contact angle reduces the restraining forces which will lead to faster drop detachment, smaller drop detachment height and smaller drop diameter.

4.4 Effect of density of dispersed phase: Fig.11-12 show equivalent drop diameter, drop detachment time and drop detachment height increases with increase in dispersed phase density. Higher the dispersed phase density, less will be the density difference and less will be the disruptive force. This leads to late drop detachment and consequent increase in drop detachment height, drop detachment time and drop diameter.

4.5 Effect of viscosity of dispersed phase: Simulations were carried out to study the effect of dispersed phase viscosity also. The results showed that the effect of viscosity

of the dispersed phase on the drop formation process is hardly any. The equivalent drop diameter did not change with change in dispersed phase viscosity.

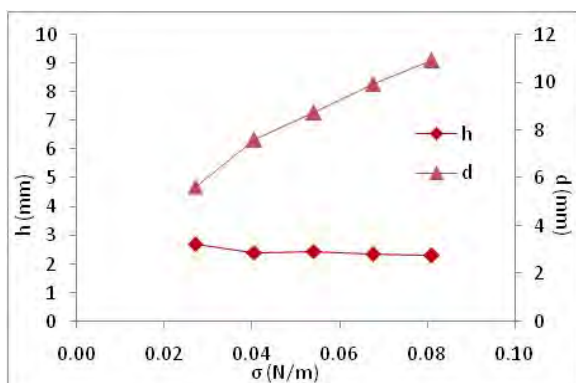


Figure 7: Effect of interfacial tension on height of drop detachment and equivalent drop diameter

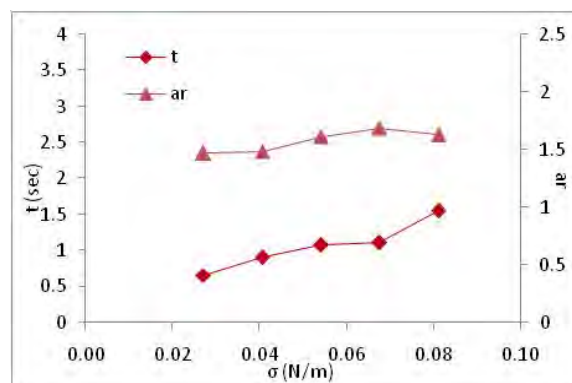


Figure 8: Effect of interfacial tension on time of drop detachment and aspect ratio

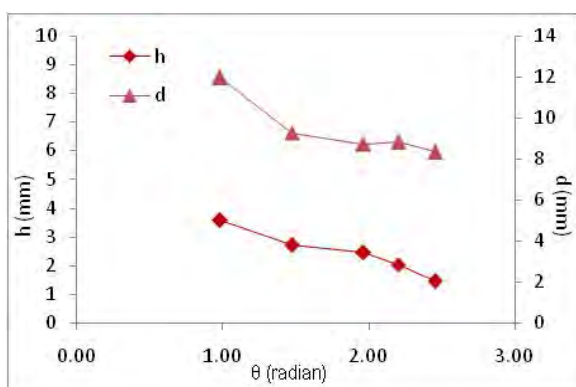


Figure 9: Effect of contact angle on height of drop detachment and equivalent drop diameter

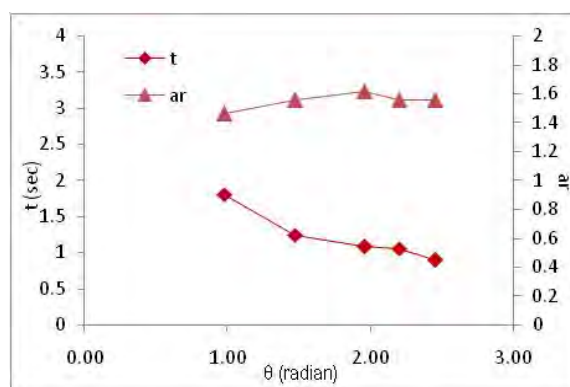


Figure 10: Effect of contact angle on time of drop detachment and aspect ratio

4.6 Effect of hole diameter: Fig.13-14 show equivalent drop diameter, drop detachment time and drop detachment height increase with increase in hole diameter. This is attributed to the fact that at constant hole velocity as hole diameter is increased more will be the accumulation of the dispersed phase leading to larger drop volumes.

4.7 Effect of height of nozzle protrusion: Fig.15-16 show equivalent drop diameter, drop detachment height and drop detachment time decreases with increase in nozzle hole protrusion height whereas aspect ratio decreases. Increase in nozzle protrusion height reduces spread of the dispersed phase on the plate thus reducing restraining force leading to early drop detachment and smaller drops.

5. Correlation for equivalent drop diameter

The results obtained from parametric studies were used to arrive at a correlation that can be used to predict the drop diameter for a given set of physical properties, flow rate, nozzle hole protrusion height, and hole size. LABFit (Silva and Silva, 1999) has been used to obtain the correlation. The correlation is given by Eq.(1).

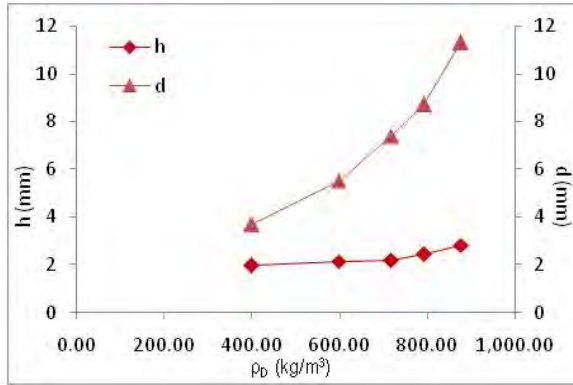


Figure 11: Effect of dispersed phase density on drop detachment height and equivalent drop diameter

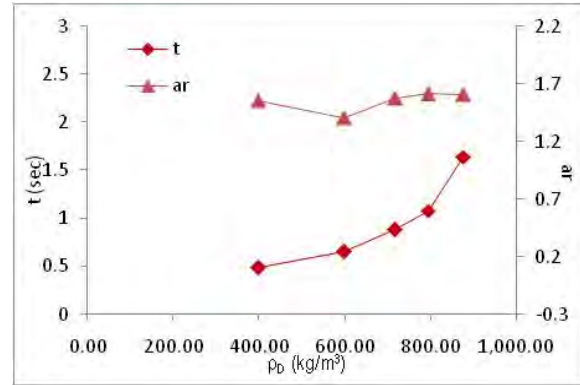


Figure 12: Effect of dispersed phase density on drop detachment time and aspect ratio

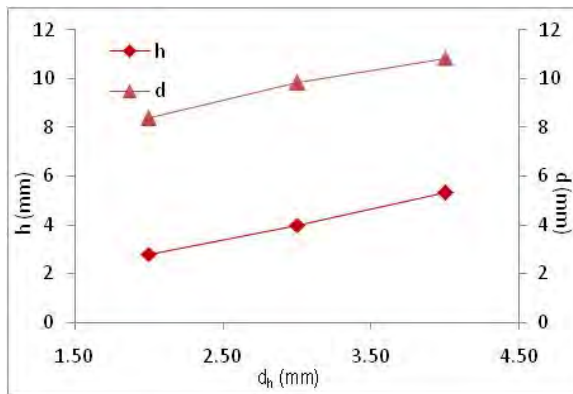


Figure 13: Effect of hole diameter on height of drop detachment and equivalent drop diameter

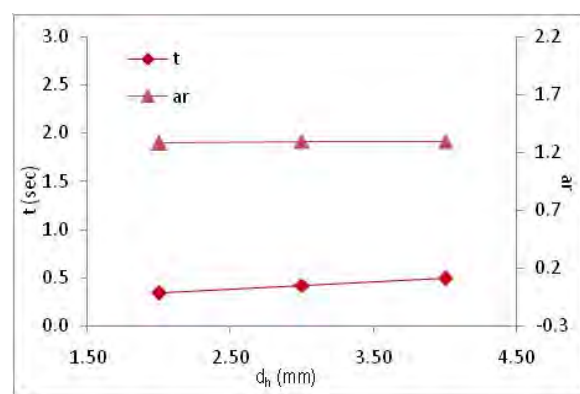


Figure 14: Effect of hole diameter on time of drop detachment and aspect ratio

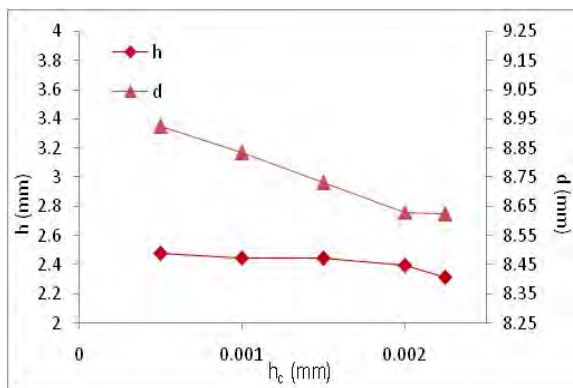


Figure 15: Effect of nozzle protrusion height on drop detachment height and equivalent drop diameter

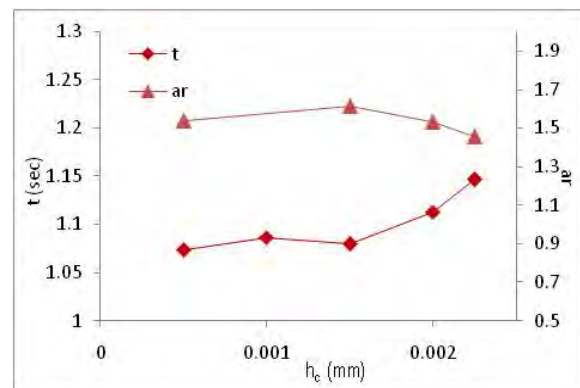


Figure 16: Effect of nozzle protrusion height on drop detachment time and aspect ratio

$$\frac{dE\ddot{o}^{0.42}}{d_h} = 2.0784 Fr^{(0.039851 + 0.09223 \ln(\theta(h_c / d_h)))} \quad (1)$$

where $\theta = (\rho_C - \rho_D) g d_h^2 / \sigma$ and $Fr = v^2 / (g d_h)$. A reasonably good fit was obtained with average error being 6.33%. A sensitivity analysis reveals how sensitive is drop diameter

to changes in different parameters studied. Within the ranges of parameters studied, dispersed phase density influences drop diameter to the greatest extent followed by interfacial tension, contact angle, hole diameter, hole velocity and finally height of the nozzle protrusion.

6. Conclusion

A model to capture drop formation process at a nozzle hole in a sieve plate is developed and validated using reported experimental data. Parametric studies are carried out to quantify to study the effect of different parameters on drop formation phenomenon. It is seen that that the dispersed phase density has the largest influence on drop diameter where as that of height of the nozzle protrusion is the least. A correlation for drop diameter is reported to provide a firsthand estimate of drop diameter of the drops produced at a nozzle hole in a plate.

Nomenclature

ar	aspect ratio of drop at detachment [-]
d	equivalent drop diameter [L]
d_h	hole diameter [L]
E_{tv}	E t v s number [-]
F_r	Froude number [-]
h	height of drop detachment [L]
h_c	height of nozzle protrusion [L]
t	time of drop detachment [T]
v	velocity of the dispersed phase at the hole [LT^{-1}]
<i>Greek letters</i>	
μ	viscosity [$ML^{-1}T^{-1}$]
ρ	density [ML^{-3}]
σ	interfacial tension [MT^{-2}]
θ	contact angle [-]

Reference

- Harkins, W.D., Brown, F.E., The determination of surface tension (free surface energy), and the weight of falling drop: The surface tension of water and benzene by capillary height method, J. Am. Chem. Soc., 41 (1919), 499.
- Rao, E.V.L.N., Kumar, R., Kuloor, N., Drop formation studies in liquid-liquid systems, Chem. Eng. Sci., 21 (1966), 867.
- Scheele, G.F., Meister, B.J., Drop formation at low velocities in liquid-liquid systems: Part I. Prediction of drop volume, AIChE J., 14(1) (1968), 9-15.
- Silva, Wilton, P., Cleide, M.D.P.S., LAB Fit Curve Fitting Software (Nonlinear Regression and Treatment of Data Program), V 7.2.47(1999-2010).
- Singh KK, Shenoy KT, Rao H, Ghosh SK. (2013). Numerical simulation of liquid-liquid two-phase flow at microfluidic junctions. International Journal of Microscale and Nanoscale Thermal and Fluid Transport Phenomena, 4(3-4), 269-282.
- Soleymani, A., Laari, A., Turunen, I., Simulation of drop formation in a single hole in solvent extraction using the volume-of-fluid method, Chem. Engg. Res. Des., 86 (2008), 731-738.

Modelling Approach to Estimate Droplet Interaction Parameters

*Hanin B. Jildeh^{*1}, Menwer Attarakih², Hans-Jörg Bart^{*1}*

Summary

Droplet interaction parameters (breakage, coalescence) are dependent on the system physicochemical properties, column type and geometry, and sometimes on operating conditions. This presents a parameter estimation challenge and limits the benefits of the estimated parameters. To resolve this issue, a coupled experimental and modelling approach is utilized. In this approach, single and swarm droplet experiment results were used under varying liquid-liquid test systems, extraction column geometry and operating conditions. As a modelling approach to this relatively complex problem, the population balance equation is used. As a validation approach of the correlated models, scale-up column simulations were used to validate the modelling approach and the estimated droplet interaction parameters.

Keywords: Interaction parameters, Population balance, Extraction columns

Introduction

Liquid-liquid extraction process is widely used in mining, petroleum, chemical and biochemical industries. Mixer settlers are often used in the extraction field if high residence times with low number of stages are required. Otherwise, extraction columns are favored, if the extraction process requires a higher throughput with high number of stages [1]. With the aim of control, design, optimization and to assure safe and stable operation of extraction process, a substitute for the pilot plant experiments with computer simulation is desirable. These simulations should be able to adapt and recognize the change in droplet internal state (rigid, circulation, oscillation) and in addition the solute mass transfer between phases along the column height and with time. The state-of-the-art is to use the droplet population balance model, which reflects the information of droplet transport, interactions and mass transfer in multiphase flow with time [2].

The population balance simulation is powerful in prediction, with dependence on column internals, droplet velocity (slowing factor) and droplet interactions. In the published literature, different models and correlations were used to predict these droplet interactions. Depending on column geometry, physical properties and operating conditions, different parameters were estimated for the same model [3]. This is because, each researcher calibrates a certain model only for a defined specific case (test system, geometry, operating condition), which reduces the range of model validity when a new process design is needed. Therefore, an alternative approach is proposed to approach this problem. The goal is to have models and parameters that are relatively insensitive to the column geometry, which is essential for extraction column design. For estimating the required parameters, a modelling

^{*1} Chair of Separation Science and Technology, Centre of Mathematical and Computational Modelling, TU Kaiserslautern, 67653 Kaiserslautern, Germany

² University of Jordan, Department of Chemical Engineering, 11942 Amman, Jordan

approach is proposed based on population balances and the available single and column experimental data.

Mathematical and Numerical Modelling

Droplet Population Balance

Now a days, the population balance model for liquid-liquid extraction columns accounts for all important phenomena, which take place in the extraction process. It tracks the changes in the droplet size distribution as the droplets rise along the column height; droplet breaks up or coalesces with the other surrounding droplets and describes the solute transfer between the two phases. Attarakih et al. described the hydrodynamics and mass transfer in counter-current columns in one-dimensional spatial representation by the following equation [2]:

$$\frac{\partial f_{d,c_y}(\psi)}{\partial t} + \frac{\partial [u_y f_{d,c_y}(\psi)]}{\partial z} + \frac{\partial [\dot{c}_y f_{d,c_y}(\psi)]}{\partial c_y} = \frac{\partial}{\partial z} \left[D_y \frac{f_{d,c_y}(\psi)}{\partial z} \right] + u_y^{\text{in}} f_y^{\text{in}}(d, c_y; t) \delta(z - z_y) + S\{\psi\} \quad (1)$$

It is based on the definition of the number distribution function (f), which describes the number distribution of droplet size at a certain section of the extraction column. At the left hand side of the equation are the transient, convection and diffusion terms. The terms on the right hand side of the equation are droplet axial dispersion, droplet-entering rate to extraction column and the source term (S). The source term represents the four rates of droplet birth and death due to breakage and coalescence. This source term is further discussed in details in [2]. The dispersed phase holdup (α_y) is calculated by integrating the number density function over the whole range of drop diameters, where continuous phase holdup (α_x) should satisfy the physical constraint $\alpha_x + \alpha_y = 1$.

Droplet Transport, Interaction and Mass Transfer

Droplet transport and axial dispersion in extraction columns is accounted by droplet velocity that is affected by the compartment internals. Thus, a slowing factor correlation as function of the droplet size and energy input is proposed by Garthe [4]. This correlation contains eight parameters ($s_1 - s_8$):

$$k_v(d) = 1 - \frac{s_1}{N_p^{s_2}} - s_3 \left(\frac{d}{D_c - d_r} \right)^{s_4} - s_5 \left(\frac{h_c}{D_c} \right)^{s_6} + s_7 \varphi_s^{s_8}, \quad N_p = 1.08 + \frac{10.94}{\text{Re}_R^{0.5}} + \frac{257.37}{\text{Re}_R^{1.5}} \quad (2)$$

The correlations for calculating the terminal, relative velocity and droplet velocity in both phases are described in details by Jildeh et al. [5].

Droplet interactions that occur at macro-scale are accounted by droplet breakage and coalescence. These are responsible for the evolution of the droplet size in two-phase flow, which affect the phase fraction and mass transfer rates. In other study for modelling and simulation agitated columns (RDC, Kühni), some well-known models used by different researchers were presented, discussed and compared [5,6]. In this work, Schmidt (2006) breakage probability correlation is used to describe the breakup of droplet with a diameter d and it accounts for the low and high solution

viscosities [7]. The model is based on the modified Weber number and five correlation parameters ($b_1 - b_5$):

$$\frac{p(d)}{1-p(d)} = b_1 \left[\frac{We_{\text{mod}}}{1 + b_3 \cdot Oh \cdot We_{\text{mod}}^{0.5}} \right]^{b_2}, \quad We_{\text{mod}} = \frac{\rho_x^{0.8} \eta_x^{0.2} d D_R^{1.6} (2\pi)^{1.8} (N^{1.8} - N_{\text{crit}}^{1.8})}{\sigma} \quad (3)$$

$$N_{\text{crit}} = b_4 \frac{V_T^{1/3} D_R^{-5/3} \eta_y d^{-4/3}}{2(\rho_x \rho_y)^{1/2}} + \left[\left(b_4 \frac{V_T^{1/3} D_R^{-5/3} \eta_y d^{-4/3}}{2(\rho_x \rho_y)^{1/2}} \right)^2 + b_5 \frac{V_T^{2/3} \sigma}{\rho_x D_R^{10/3} d^{5/3}} \right]^{0.5} \quad (4)$$

Then breakage frequency is given by $\Gamma(d, \phi_y) = p(d)/\tau_m$, where τ_m is droplet residence time. The daughter droplet distribution and mean number of daughter droplets correlations were taken from Jildeh et al. [5].

The model of Coulaloglou and Tavlarides (1977) with two correlation parameters (c_1, c_2) is used for calculating the droplet coalescence frequency [8]:

$$\omega(d, d', \phi_y) = \left[c_1 \frac{\varepsilon^{1/3}}{1 + \phi_y} (d^2 + d'^2) (d^{2/3} + d'^{2/3})^{1/2} \right] \times \left[\exp \left(- \frac{c_2 \eta_x \rho_x \varepsilon}{\sigma^2 (1 + \phi_y)^3} \right) \left(\frac{(dd')}{(d + d')} \right)^4 \right] \quad (5)$$

Another important aspect for predicting droplet interactions is the energy dissipation in extraction compartments. To choose which model to be used in the 1-D simulation, the following approach is used. As it is well known, the 1-D calculations are based on an average compartment value; on the other hand the 3-D simulations require a detailed information for local energy dissipation. Therefore, Wächter et al. [9] and Hlawitschka [10] showed that Kumar and Hartland (1995) model [11] results of 1-D compartment simulation are in good agreement with the predictions of different CFD tools (Fluent, OpenFOAM, FPM).

Finally, to predict the change rate of solute concentration in the droplet, the two-resistance film theory is used, to estimate the overall mass transfer rates between phases [2]:

$$\frac{\partial c_y(z, t)}{\partial t} = \frac{6K_{oy}}{d} (c_y^*(c_x) - c_y(z, t)) \quad (6)$$

The empirical model of Kumar and Hartland (1999) [12] is chosen to calculate the individual mass transfer coefficients because it considers the effect of energy input, phase fraction and droplet diameter and the state of droplet (circulating, oscillating). The overall mass transfer coefficient (K_{oy}) is expressed in terms of the individual mass transfer coefficients for the continuous and the dispersed phases.

Results and Discussion

Parameter Estimation Approach

The previous correlations for slowing factor, breakage and coalescence have many fitting parameters. Traditionally, each researcher presents his own set of fitted parameter to their own experimental data by trial and error method, which cannot be reused later on under other circumstances (geometry, operating conditions). A good example is presented by Maaß and Kraume [3], where a parameter listing of different

literature values for the model of Coulaloglou and Tavlarides (1977) for liquid-liquid extraction is reviewed. In this study, the aim is to obtain an insensitive parameter based on an experimental (single droplet, extraction column) and modelling approach (inverse population balance problem). This is done by using a detailed population balance model [2], which is written in MATLAB and coupled with global optimization toolbox. The approach is presented in Figure 1, which describes the parameter estimation procedure for slowing factor and breakage phenomena using single droplet data. In this step, different literature correlations were collected and then compared to the experimental database (different system, geometry, conditions). In the second step, 3-D CFD model was used to estimate energy dissipation and axial dispersion in single column compartment. Finally, the coalescence parameter estimation can be finally realized under certain constraints [5].



Figure 1. The approach to estimate droplet interaction parameters.

Figure 2 shows the parity plot for simulated slowing factor compared to the experimental data for extraction column diameter DN 32- DN 150, with a maximum deviation of 20% using the following parameters $s_1 - s_8 = [2.28; 3.34; 0.65; 4.00; 1.38; 1.68; 1.55; 0.24]$. On the other hand Figure 3 shows the parity plot for simulated holdup in Kühni extraction column using the estimated interaction parameters $b_1 - b_5 = [0.056; 1.71; 0.68; 0.74; 0.04]$ and $c_1 - c_2 = [0.55; 1.33 \times 10^{11}]$. A maximum deviation of 10% in the experimental data of DN 80 extraction column and 20% deviation of DN 150 extraction column are obtained.

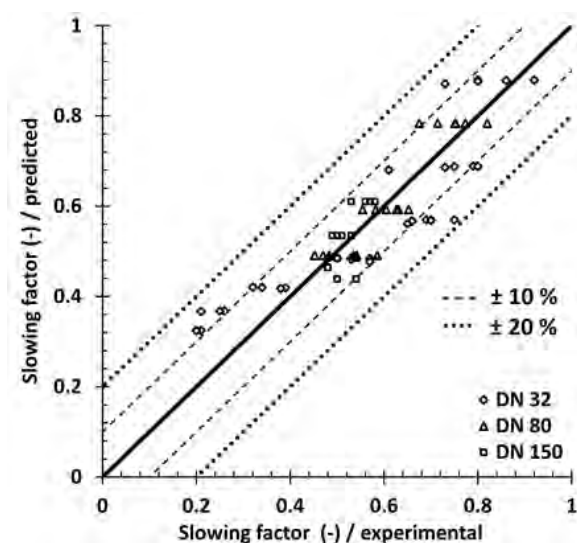


Figure 2. Parity plot for the slowing factor (Exp. DN 32-[13]; DN 80-[4]; DN 150-[7]).

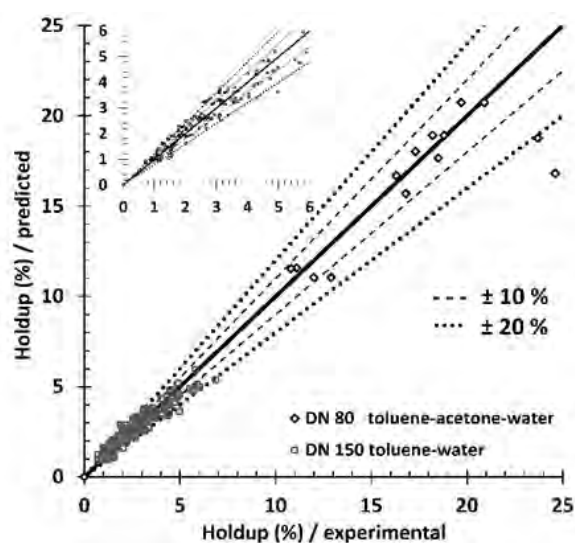


Figure 3. Parity plot for holdup using the set of droplet interaction parameter (Exp. data: DN 80-[4]; DN 150-[5]).

Column Simulation

To evaluate the quality of the droplet interaction parameter, steady and transient predictions are shown in Figure 4 and Figure 5. These are two separate cases under different operating conditions and Kühni extraction column geometry.

In Figure 4 the steady state experimental data are taken from Gomes et al. [14] at 170 rpm, continuous phase flow rate 94 l/h and 120 l/h dispersed phase flow rate. Two cases were investigated: toluene-water (t-w) and the other one using 50 kg/m³ acetone in the continuous phase (t-a-w). The simulated holdup profile along column stages was compared to the measured data without mass transfer (t-w) and with mass transfer (t-a-w). The simulation results compare very well with the experimental data without any further parameter optimization. The effect of the solute on the holdup can be noticed, where it increases the holdup profile due to the reduction in the interfacial tension when compared to toluene-water system. On the other hand, the acetone concentration profile of the aqueous phase is in good agreement with the measured data.

The second case is transient state validation for toluene-water test system in DN 150 Kühni column. Here in this case, the new optimized models and parameters are implemented in an updated version of the in-house tool “Online Monitoring & Simulation Tool” [15]. Figure 5 shows the real-time analysis and prediction response due to a negative step change in the dispersed phase flow rate from 26 l/h to 18 l/h. The results illustrate the agreement between the simulated and measured profiles. As the dispersed flow rate decrease, the holdup tends to decrease while the droplet size remains constant.

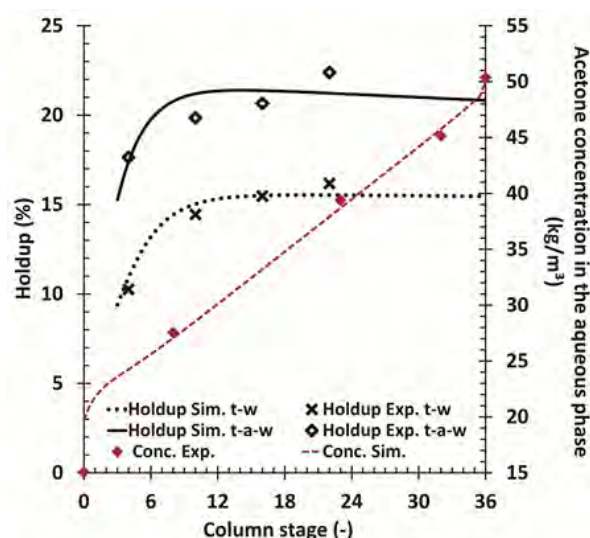


Figure 4. Holdup and concentration profile along column stages (Exp. data: [14]).

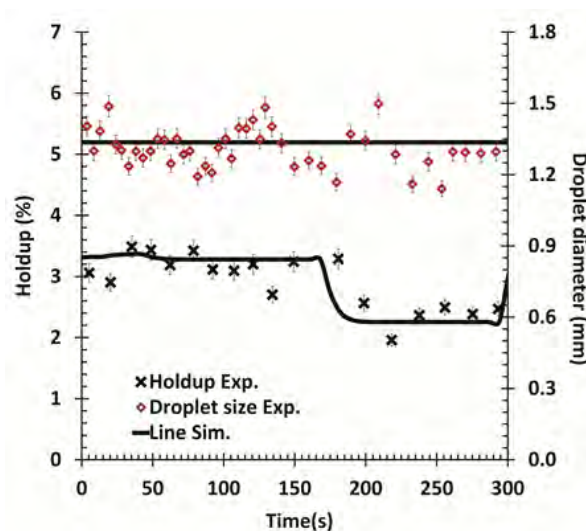


Figure 5. Transient response due to negative step change in dispersed phase flow rate (26l/h-18l/h).

This parameter estimation approach is also applied in CFD simulation: FPM [9] and Fluent [16] were the results show that the methodology to obtain insensitive parameter is accurate enough for column simulations. This presents several advantages especially when designing and simulating extraction columns.

Furthermore, this shows that the accurate prediction of the droplet diameter and holdup is reflected on an accurate prediction of column hydrodynamics and mass transfer profiles. Therefore, this approach is proposed when investigating new test systems such as reactive or in a new industrial project.

Conclusions

In this study, a methodology to obtain insensitive droplet interaction parameters based on coupled experimental and modelling approach under population balance framework is discussed. The estimated parameters for slowing factor, droplet breakage and coalescence, are validated using different test systems in different mini-plant and pilot extraction column geometry. Pure hydrodynamics (droplet diameter, holdup) and concentration profiles prediction, without any further parameter adjustments, show good results when compared to the experimental data. Parity plots show an overall deviation between measured and predicted results is less than 20% using the same parameter set. These results show a high advantage for designing and simulating liquid extraction columns especially during scale-up and scale-down.

Acknowledgement

The authors would like to acknowledge Centre of Mathematical and Computational Modelling (CM)² and TU Kaiserslautern for the financial support.

References

- [1] Bart, H.-J., Stevens, G. (2004), Reactive Solvent Extraction: Ion Exchange and Solvent Extraction, M. Kertes, A.K. Sengupta (Eds.), Vol. 17, 37-82, Marcel Dekker, New York.
- [2] Attarakih, M., Al-Zyod, S., Abu-Khader, M., Bart, H.-J. (2012), *Procedia Engineering* **42**: 1445–1462.
- [3] Maaß, S., Kraume, M. (2012), 14th European Conference on Mixing: 251-256, Warszawa 10-13.09.12.
- [4] Garthe, D. (2006), Fluidynamics and mass transfer of single particles and swarms of particles in extraction columns, Dissertation, Verlag Dr. Hut, München.
- [5] Jildeh, H., Attarakih, M., Mickler, M., Bart, H.-J. (2014), *Can. J. Chem. Eng.* **92** (2): 210–219.
- [6] Jildeh, H., Attarakih, M., Bart, H.-J. (2013), *Chem. Eng. Res. Des.* **91** (7): 1317–1326.
- [7] Schmidt, S. (2006), Populationsdynamische Simulation gerührter Extraktionskolonnen aus Basis von Einzeltropfen- und Tropfenschwarmuntersuchungen, Dissertation, TU Kaiserslautern, Shaker Verlag.
- [8] Coulaloglou, C., Tavlirides, L. L. (1977), *Chem. Eng. Sci.* **32** (11): 1289–1297.
- [9] Wächtler, T., Hlawitschka, M. W., Jildeh, H. (2013), (CM)²-Young Researcher Symposium Proceedings: 84-89, Kaiserslautern, 08.11.13.
- [10] Hlawitschka, M. (2013), Computational Fluid Dynamics Aided Design of Stirred Liquid-Liquid Extraction Columns, Dissertation, TU Kaiserslautern.
- [11] Kumar, A., Hartland, S. (1995), *Ind. Eng. Chem. Res.* **34** (11): 3925–3940.
- [12] Kumar, A., Hartland, S. (1999), *Chem. Eng. Res. Des.* **77** (5): 372–384.
- [13] Steinmetz, T. (2007), Tropfenpopulationsbilanzgestütztes Auslegungsverfahren zur Skalierung einer gerührten Mini-Plant Extraktionskolonne, Dissertation, TU Kaiserslautern, Fortschritts-Bericht VDI Verlag.
- [14] , M., Stichlmair, J., Cruz-Pinto, J. (2009), *Ind. Eng. Chem. Res.* **48** (7): 3580–3588.
- [15] Mickler, M., Jildeh, H., Attarakih, M., Bart, H.-J. (2014), *Can. J. Chem. Eng.* **92** (2): 307–317.
- [16] Jildeh, H., Hlawitschka, M., Attarakih, M., Bart, H.-J. (2012), *Procedia Engineering* **42**: 1692–1710.

Green extraction of aromas from herbs and spices using alternative solvents: Theoretical and experimental solubility study.

**Aurore FILLY^{*1}, Anne Sylvie Fabiano-Tixier¹, Yann Lemasson³, Celine Roy⁴,
Xavier Fernandez², Farid Chemat.¹**

Abstract:

The use of alternative solvents has been possible for the extraction of aromatic components from herbs and spices. This present study was designed to evaluate the performance of nine alternative solvents (α -pinene, MeTHF, Ethyl acetate, Methyl acetate, Ethyl lactate, Butanol, Isopropanol, Ethanol, supercritical fluid CO_2) for extraction of aromas compared to n-hexane. Terpenoids are main constituents of plants. This study of various terpenoids has been performed via simulation using Hansen solubility methodology for comprehension of dissolving mechanism. Experimentally, the extracts of aromatic components in buds Blackcurrant (*Ribes nigrum* L.) were analyzed to compare the solvents' performance in terms of aromas' compositions. The results indicated that MeTHF could be the most promising solvent for n-hexane substitution with good yield and selectivity of aromas.

Keywords: Alternatives solvents, extraction, Aromas, Blackcurrant buds, Hansen solubility parameter.

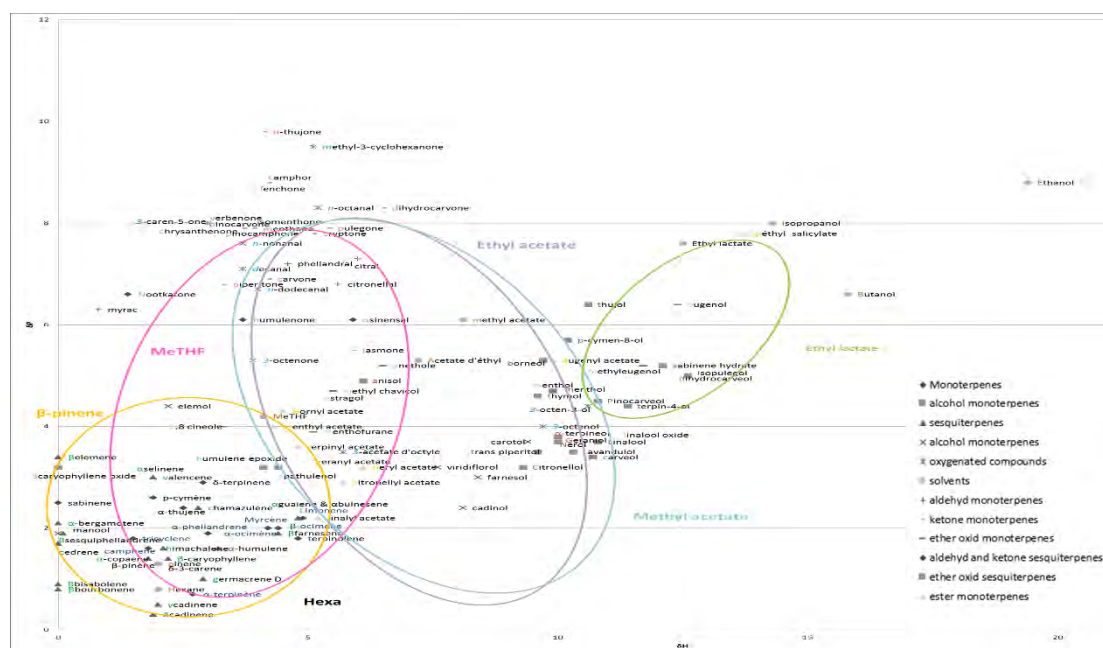


Figure 1: Alternative solvents solubilizing aromas according setting HANSEN

¹Université d'Avignon et des pays du Vaucluse, UMR A 408 INRA-UAPV, Sécurité et Qualité des produits d'Origine Végétale. F-84029 Avignon. France

² Université de Nice Sophia Antipolis, UMR 7272 CNRS, Institut de Chimie de Nice, Parc Valrose, 06108 Nice, France.

³Firmenich-SAS, Parc Industriel Les Bois de Grasse, 06130 Grasse, France.

⁴ERINI, Espace Jacques Louis-Lions, 4 traverses Dupont 06130 Grasse

Thanks Region PACA (Provence Alpes Côte d'Azur) and PASS (Pôle Arômes Senteurs et Saveurs).

**Bioguided Fractionation And Isolation Of Natural Anti-Ulcerogenic Compounds
And Anti- *Helicobacter Pylori* From *Convolvulus austroaegyptiacus***

Asmaa Al-Rifai^{*a}, Amani Awaad^a, Ahmad Aqel^a

^aChemistry Department, College of Science, King Saud University, Riyadh, KSA

ABSTRACT

Bioguided fractionation for the total alcohol extracts of *Convolvulus austroaegyptiacus* were evaluated for its antiulcerogenic activity using an absolute ethanol-induced ulcer model at doses of 500 and 1000 mg/kg. Two main compounds (coumarin and coumarin glycosides) were isolated from the butanol extract of the plant and identified as scopoletin (**A1**) and scopolin (**A2**). Their structures were identified by ¹H and ¹³C NMR. The isolated compounds (50 mg/kg) showed a very promising antiulcerogenic activity with percent protection of control ulcer by; 16.7 and 90.8%, respectively and thought to be responsible for the plant antiulcerogenic activity. The cytoprotective mechanism and the anti-*H. pylori* activity may explain the potent anti-ulcerogenic activity of the total alcohol extract and the isolated coumarins. The acute toxicity study of the extract showed that the extract was highly safe as the LD50 was more than 4000 mg/kg, and these results were well supported by the sub-chronic toxicity, as the extract administrated to rats for 15 consecutive days at dose 1000 mg/kg showed no alteration in the liver and kidney functions.

Salt influence on the partitioning of HMF in aqueous/organic systems

Sultan Mohammad, Christoph Held, Emrah Altuntepe, Gabriele Sadowski

*Technische Universität Dortmund; Laboratory of Thermodynamics, Dortmund,
Germany*

Abstract

Electrolytes influence many biological processes e.g., the production of organic molecules. In biological processes electrolytes might be present as part of a reaction, or electrolytes are added intentionally due to their impact on phase equilibria. Already small amounts of electrolytes can influence the separation performance of a unit operation. An example for a biological process in which electrolytes are used intentionally is the conversion of hexoses to the key chemical component 5-hydroxymethylfurfural (HMF). Extraction is the preferred unit operation for the separation of HMF from the reaction media. The separation strongly depends on the addition of salts, and the determination of the extraction performance requires the knowledge on the liquid-liquid phase equilibrium (LLE). LLEs are accessible via equilibrium measurements and via thermodynamic models.

The LLE of ternary systems containing HMF, water and an organic solvent (e.g. methyl isobutyl ketone (MIBK)) was measured in this work at atmospheric pressure and 298.15 K. The salt influence on the LLE of the system water/HMF/MIBK was measured for salt concentrations up to 3 moles per kg water. The salts under investigation were composed of the anions NO_3^- , PO_4^{3-} , Cl^- and of the alkali cations Li^+ , Na^+ and K^+ . Based on the LLE data, the distribution of HMF between the aqueous and the MIBK phase was calculated and expressed by the distribution coefficient K_{HMF} . It could be shown that K_{HMF} significantly depended on the kind and concentration of the salt. Some of the salts even caused increased K_{HMF} values at low salt concentrations and decreased values at higher salt concentrations.

Based on the experimental data, the electrolyte Perturbed-Chain SAFT (ePC-SAFT) model was applied to describe the salt influence on the LLE of the system HMF/water/organic solvent. Using pure-component parameters for water, organic solvent, HMF and for the ions obtained from independent experimental data, the LLE and the K_{HMF} values could be predicted as function of salt concentrations and HMF concentrations in good agreement with the experiments.

Three-Liquid-Phase Extraction and Gas-Assisted Three-Liquid-Phase Extraction of Anthraquinones from Rhubarb

Xingfu Yang, Xiangfeng Liang, Liangrong Yang, Qingfen Liu, Huizhou Liu**

Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China

Three-Liquid-Phase system (TLPS), which is composed of organic extractant, polymer and brine, is a kind of micro-emulsion extraction system based on the interfacial phenomena. Because the choice of its phase forming components is extensive and physicochemical properties of the system can be easily tuned. Hence TLPS is regarded as a promising technique which could achieve highly-selective separation performance under mild operation condition with simple process.

In this paper, with the model of extraction and separation of anthraquinone compounds from Rhubarb, a kind of traditional Chinese herbal medicine, the partitioning behaviors of emodin and rhein, two typical anthraquinones in Rhubarb, were systematically investigated under various conditions in TLPS, and two structure-similar compounds, 95% emodin and 97% rhein could be simultaneously extracted into the top and middle phase, respectively, and separation factor over 10000 of the two anthraquinones was achieved. Using methyl isobutyl ketone and sodium hydroxide aqueous solution as back extraction medium, both emodin and rhein could be conveniently back extracted by adjusting pH, the one-step back extraction efficiency of both emodin and rhein could be approximately 97%. Furthermore, the novel gas-assisted three-liquid-phase extraction (GATE) composed of butyl acetate-PEG4000-ammonium sulphate aqueous solution was applied to simultaneous separation and concentration of emodin and rhein, and various operation parameters affecting the process were investigated. Within 50 minutes of 30 mL/min nitrogen flow, removal ratio of emodin and rhein from aqueous phase could be over 99% and 97%, respectively. Mass fraction of emodin in the butyl acetate phase and rhein in the PEG phase could reach 97% and 95%, respectively. Experiment results demonstrated that separation ratio and concentration coefficient of GATE are significantly higher than TLPS because of higher phase ratio between aqueous phase and extractant phase.

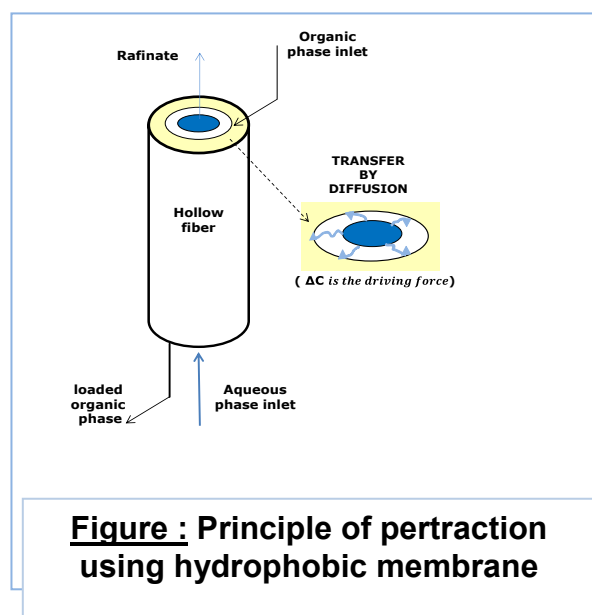
Pertraction of neodymium by a dedicated sovant

Moussa TOURE ^{a, b}, Gilles BORDA ^a, Jean DUHAMET ^a, Stephane PELLET-ROSTAING ^b

^a CEA, DEN, DTEC, SGCS, F-30207 Bagnols-sur-Cèze, France

^b ICSM, UMR5257, LTSM, F-30207 Bagnols-sur-Cèze

The process called pertraction or non-dispersive solvent extraction (NDSX) is a technique which allows the metals recovery from leach solutions. It is a liquid-liquid extractor in which the interfacial area is delimited by a porous membrane separating two immiscible phases, the aqueous phase containing the species to be extracted and the organic phase forming the extractant. In the case of the figure bellow, organic phase passing through the shell side of the module wets the hydrophobic membrane. A non-wetting aqueous phase is passed through the lumen side of the membrane. It is worth noticing that the aqueous-organic (aqueous-membrane) interface is essentially immobilized at the pore mouth of the hydrophobic membrane support through which the solute mass transfer takes place. It has several advantages over conventional solvent extraction method such as dispersion-free operation, very high contact surface area per unit extractor volume (provided by hollow fiber geometry), emulsion formation is avoided and nonrequirement of density difference of the phases.



In the present contribution, the macroporous and the hydrophobic hollow fiber made of polypropylene is used for the extraction of Nd^{3+} in HNO_3 solution in the presence of sodium nitrate NaNO_3 . The studied extractant is used as pure (e.g without diluent) and has been chosen for his relative low solubility in water, his high selectivity for rare earths, and his low viscosity. In view of possible application to actual feeds, Nd^{3+} recovery from varying feed conditions was investigated such as HNO_3 , and Nd^{3+} concentrations. In order to predict scale up of the process, the resistances-in-series model taking account the cylindrical geometry was proposed for the first time to describe the mass transfer trough the membrane. For a model need, Taylor Dispersion Analysis (TDA) coupled to UV-Vis detection is used for determine the diffusion coefficient of Nd^{3+} in aqueous phase and in organic phase.

A new approach to achieve countercurrent multi-stage micro-extraction

Shaowei Li, Institute of Nuclear and New Energy Technology , Tsinghua University , Beijing 100084 , China; Shan Jing, Institute of Nuclear and New Energy Technology , Tsinghua University , Beijing 100084 , China;

Microextraction has been the focus of numerous studies in the past decade. It provides a new solution for the problems of low efficiency, high energy consumption, and large equipment dimensions encountered by the conventional extraction systems. It can reach high extraction performance without any mechanical stirring, mixing, or shaking and can be integrated with other operation units in a small space. However, the existing microextraction systems are mostly cocurrent operated and the recovery efficiency can reach no higher than one theoretical separation stage. Countercurrent microextraction must be used to increase the recovery efficiency. But it is difficult to realize countercurrent flow at the micro-scale because viscosity and surface wetting dominate over gravity and inertial effects. Difficulty in achieving countercurrent operation has been a barrier to the application of micro-extraction.

The human cardiovascular system which transports blood to every part of the body gives us inspiration to solve the problem in the micro-fluidic system. In this work, a bionic system, analogous to the human cardiovascular system, is developed to realize countercurrent, multi-stage micro-extraction. High mass transfer rates and high recovery efficiency were achieved. The system can be applied to any type of micro-extractor and may promote the application of micro-extraction in a wide variety of fields.

Application of Microreactor System in Solvent Extraction Of Metal Ion with Calixarene Derivatives

Masatoshi Maeki^{1,2}, Jee Young Kim³,

*Masaya Miyazaki^{*1,2}, Keisuke Ohto³*

In this study, we investigated the potential of microreactor system with calix[4]arene derivatives for the effective metal ion recovery. Two types of microreactor systems were developed and evaluated the extraction efficiency of silver ion with calix[4]arene derivatives. As a result, the time necessary for silver to reach equilibrium was 15 s in the parallel flow microreactor system. Moreover, the extraction equilibrium in the droplet-based microreactor system reached in only 4 s. In case of batchwise method, the time necessary for silver extraction to reach equilibrium was about 72 hr. These results show that an increasing liquid - liquid interface per unit volume is effective in solvent extraction of metal with calix[4]arene derivatives. We also applied the microreactor system for stripping of silver ion from the silver-loaded ketonic calix[4] arene.

Introduction

Recently, the industrial demand for rare metals have been increasing. However, supply for these metals has been unstable due to instability of international situations and the fact that these metals are eccentrically located. Thus, there is an increasing demand for recycling techniques of these metals [1]. A technique for selective and effective extraction of metal ion is strongly desired, because the variety of metals contained in the source. Many efforts have been made to develop the recycling methods of rare metals. Calixarenes are macrocyclic oligomers which are well known as attractive host compounds. Their ability to recognize and discriminate metal ions is one of their remarkable features. In addition, ring size and functional groups of calixarene derivatives are very important factors for selective and effective extraction [2,3]. These features of calixarenes make specific extraction of rare metal possible. However, slow rate of extraction is an issue to be resolved in using solvent extractant reagent.

Microfluidic reactor has been used as efficient reaction apparatus in chemical engineering field. The microreactor system has several advantages over conventional macroscale reaction processes. For example, microreactor system has larger surface/interface area per unit volume than that of conventional macroscale

*1 Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, mas-maeki@aist.go.jp

*2 National Institute of Advanced Industrial Science and Technology (AIST), m.miyazaki@aist.go.jp

*3 Graduate School of Science and Engineering, Saga University, ohtok@cc.saga-u.ac.jp

apparatuses. Increased interface area yields enhancement of extraction efficiency. Several research groups reported efficient solvent-solvent extraction by using microreactor system[4,5]. In this study, we investigated the potential of microreactor system with calixarene derivatives for the effective metal ion recovery by using the two types of microreactor systems. We also applied the microreactor system for stripping of silver ion from the silver-loaded ketonic calix[4] arene.

Experimental

Materials

Nitric acid, silver nitrate, ammonium thiocyanate, and chloroform were purchased from Wako Pure Chemicals (Osaka, Japan). Ketonic calix[4]arene was used as the extractant. The syntheses of the calix[4]arene derivative have been described in previous papers [6]. The chemical structure of ketonic calix[4]arene was shown in Figure 1. Organic solution was prepared by dissolving the calixarene derivative in chloroform. The concentrations of the ketonic calix[4]arene were 3.3 mM ($M = \text{mol dm}^{-3}$) and 5 mM, for the parallel flow extraction system and droplet-based extraction system, respectively. Aqueous solution was prepared by dissolving the silver nitrate in water. The concentrations of the silver solution were 0.025 mM in 1.77 M HNO_3 and 0.1 mM in 0.1 M HNO_3 , for the parallel flow extraction system and droplet-base system, respectively.

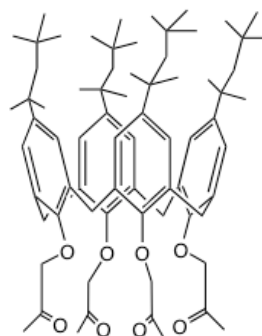


Figure 1. Chemical structure of ketonic calix[4]arene.

Fabrication of Microreactors

The parallel flow microreactor system was fabricated in Pyrex glass and silicon plates using a micromachining process followed by bonding the glass and silicon plates irreversibly [7]. The surface of the silicon-side microchannel was coated with 30 nm-thick titanium using a vapor deposition method, and then coated similarly with 50 nm-thick Au. A microchannel (200 μm width; 200 μm depth) with glass surfaces and Au surfaces was formed on the silicon surface. The Au surface was rendered

hydrophobic by surface treatment with 1 mM 1-octadecanethiol in ethanol solution. The droplet-based microreactor system was also fabricated by using a micromachining process followed by thermal bonding the glass plates irreversibly. Then, the microchannel was treated with 6.0 M KOH solution. Figure 2 shows the microreactor system used in this study. The extraction time was controlled by the flow rate of syringe pumps. The recovered aqueous phase was subjected to ICP analysis (Perkin Elmer Optima 3300 DV) to estimate the amount of extracted rare metal.

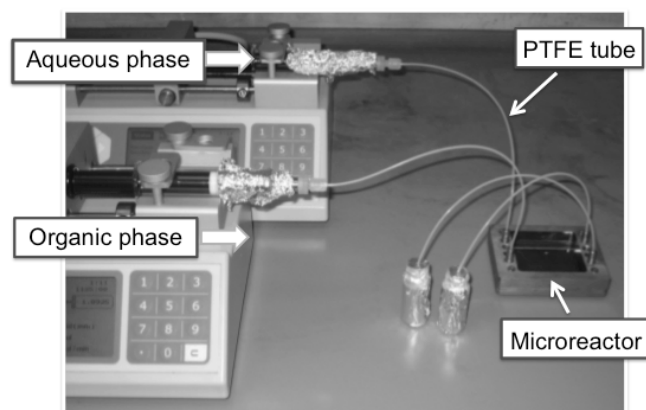


Figure 2. The parallel flow microreactor system.

Results and Discussion

First, the parallel flow microreactor system was employed for extraction of silver ion from aqueous phase. The microchannel surfaces of the glass and silicon sides are hydrophilic and hydrophobic, respectively. Therefore, the aqueous solution flowed through the glass side of the microchannel while the organic solution flowed through the silicon side. The extraction percentage was defined as the following equation;

$$\%E = (1 - C / C_0) \times 100$$

where, C represents the concentration of silver ion in the recovered aqueous phase, and C_0 is the initial concentration of silver ion in the aqueous phase. Figure 3 (a) shows the effect of extraction time on extraction percentage of silver ion with ketonic calix[4]arene in the parallel flow microreactor system. The extraction percentages were gradually increased with increasing the extraction time. The time necessary for silver ion to reach equilibrium was 15 s. According to the literature, ketonic calix[4] required 72 hr to reach equilibrium in the batchwise system[6]. This result suggests that the parallel flow microreactor system dramatically improved the extraction rate in contrast to the batchwise system. Increased liquid-liquid interface per unit volume may have enhanced the extraction efficiency in microreactor systems[8]. Therefore, we demonstrated the extraction of silver ion with ketonic calix[4]arene by using the

droplet-based microreactor system. The extraction condition was slightly modified. The concentration of the ketonic calix[4]arene was 5 mM in chloroform, and the concentration of the silver solution was 0.1 mM in 0.1 M HNO₃. Figure 3 (b) shows the effect of extraction time on extraction percentage of silver ion with ketonic calix[4]arene in the droplet-based microreactor system. The extraction equilibrium in the droplet-based microreactor system reached in only 4 s.

These results suggest that the micro-extraction system dramatically improved the rate of extraction compared with the conventional batchwise method. We consider that the enhanced extraction rate was due to the increased liquid-liquid interfacial area and the smaller diffusion length of the microreactor system. In case of parallel flow system, the inner volume and liquid-liquid interfacial area of the extraction region were 0.8 μL and 0.04 cm^2 , respectively. Therefore, the interface to volume ratio for the micro-extraction system was calculated to be 50 cm^{-1} which value was almost two orders of magnitude more than the value for the batchwise method. In addition, the diffusion length was 200 μm which value was also two orders of magnitude less than the value for the batch method. In addition, the interface to volume ratio of the droplet-based microreactor system was significantly increased compared with other systems. Consequently, the silver extraction efficiency was dramatically improved.

Moreover, the droplet-based microreactor system was applied for the stripping of silver ion from the silver-loaded ketonic derivatives with ammonium thiocyanate. When the extraction time was 100 s, the extraction percentage reached almost 40 %. It was found that the time for stripping required more longer than that for the forward extraction. This result indicates that silver ion was strongly captured by ketonic calix[4]arene. Although the optimized stripping condition is still required for effective silver recovery, the stripping took place within a few minutes.

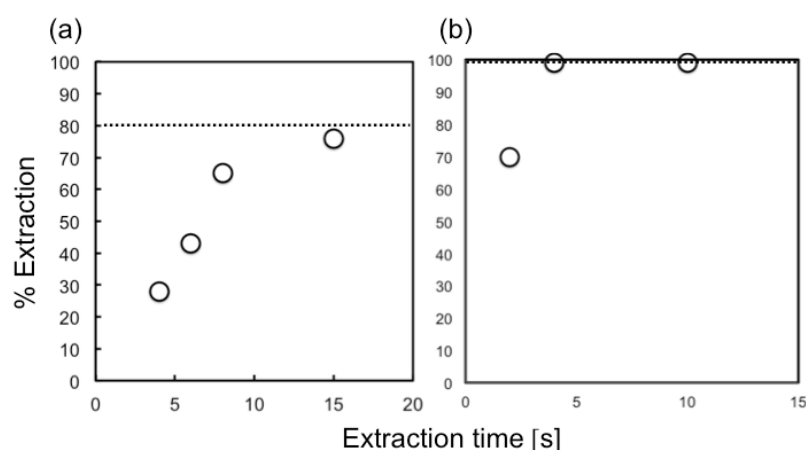


Figure 3. Effect of extraction time on extraction percentage of silver with ketonic calix[4]arene. (a) The parallel flow microreactor system. (b) The droplet-based microreactor system.

Conclusions

In the present study, the micro-extraction system was shown to be an effective tool that enables enhancement of the extraction rate of silver ion using calix[4]arene derivatives, by taking into account the characteristic larger liquid-liquid interface per unit volume. Silver extraction using the ketonic derivatives required 15 s and 4 s, for the parallel flow extraction system and droplet-base system, respectively. Stripping of the loaded silver ion in the droplet-based microreactor system was also achieved. This study shows that the microreactor is a novel efficient apparatus for the extraction of silver ion with calixarene derivatives.

Acknowledgements

Part of this work was supported by The Environment Research and Technology Development Fund (3K-123022) from the Ministry of Environment of Japan, for M. Miyazaki and KO. M. Maeki acknowledges partial support by a Grant-in-Aid for JSPS Fellows.

References

- [1] K. Binnemans, P. T. Jones, B. Blanpain, T. V. Gerven, Y. Yang, A. Walton, M. Buchert, *J. Clean. Prod.*, **51**, 1-22 (2013).
- [2] C. D. Gutsche, "Calixarenes", Royal Society of Chemistry, Cambridge, UK, (1989).
- [3] K. Ohto, *Solvent Extr. Res. Dev., Jpn.*, **17**, 1-18 (2010).
- [4] N. Assmann, A. Ladosz, P. Rudolf von Rohr, *Chem. Eng. Technol.*, **36**, 921-936 (2013).
- [5] M. Tokeshi, T. Minagawa, T. Kitamori, *Anal. Chem.*, **72**, 1711-1714 (2000).
- [6] K. Ohto, E. Murakami, T. Shinohara, K. Shiratsuchi, K. Inoue, M. Iwasaki, *Anal. Chim. Acta.*, **341**, 275-283 (1997).
- [7] T. Honda, M. Miyazaki, Y. Yamaguchi, H. Nakamura, H. Maeda, *Lab Chip*, **7**, 366-372, (2007).
- [8] M. Maeki, Y. Hatanaka, K. Yamashita, M. Miyazaki, K. Ohto, *Solvent Extr. Res. Dev., Jpn.*, **21**, 77-82 (2014).

Concepts for efficient extraction in micro and milli structures

Feasibility of countercurrent extraction with segmented flow

Florian Kaske, Chair of Chemical Reaction Engineering, TU Dortmund, Germany;

David W. Agar, Chair of Chemical Reaction Engineering, TU Dortmund, Germany

Due to raw material shortages, more dynamic markets and a higher number of competitors chemical companies are searching for more flexible plants, less investment costs and shorter to time to market strategies. A concept to overcome these requirements is the miniaturization and modulation of plants. Especially for the case of mass transfer hindered reaction and separation steps the micro reaction technology was introduced as an efficient tool for process intensification [1, 2]. By using a multiphase slug-flow in the microchannels, the mass transfer can be increased even further, because now the mixing is not only driven by diffusion but also by a convective term due to circulations inside the slugs. In addition to this a higher surface to volume ratio is possible in microstructures as in macro structures.

The existing strategies for the multi-phase extraction in microstructures have all advantages and disadvantages. These will be compared to each other to figure out some rules of thumb to make the selection of the best strategy easier. Thereby a focus in the comparison will be laid upon the applicability for high throughput production and how easy it is to achieve a great number of equilibrium stages. A deeper look will then be given into the use of segmented flow for the extraction and how the extraction efficiency is influenced by the operating parameters like slug velocity and slug length.

Strategies for achieving a higher number of equilibrium stages

In most of the microstructures no countercurrent flow is possible due to flooding. To avoid flooding the segmented flow is therefore carried out in concurrent modules which are connected in a specific way so that a countercurrent operation is possible. The total number of pumping devices needed for the operation of n -stages is $n+1$, so great investment costs can arise for the pumps. Alternatives could be the pumping of the fluid through pressurized vessels. For this case an efficient measurement and control concept is necessary, which will be shown. In contrast to this, the use of a couette-contactor could stabilize the interface between the phases and allow a countercurrent operation. The first results for the mass transfer in this contactor will be shown and compared to achievable transfer rates in microstructured apparatus.

Simulation based design of extraction columns for aqueous two-phase systems

Markus Schmidt¹⁾, Matthias Wessling²⁾, Andreas Pfennig³⁾

¹⁾*RWTH Aachen University, AVT – Thermal Process Engineering*

²⁾*RWTH Aachen University, AVT – Chemical Process Engineering*

³⁾*TU Graz, Institute of Chemical Engineering and Environmental Technology*

For the downstream processing of biological products, such as proteins, extraction using aqueous two-phase systems (ATPS) can be used. Due to a high concentration of water in both phases and a very low interfacial tension the gentle conditions for separating fragile components are provided. To establish extraction with ATPS as standard procedure in downstream processing, the continuous operation of extraction columns for ATPS is investigated at AVT-Thermal Process Engineering of the RWTH Aachen University. The aim is the column characterization and design using a combination of lab-scale experiments and simulations based on population-balance models.

This procedure has already been successfully applied for organic-aqueous systems. However, with respect to the physical properties, ATPS strongly differ from organic-aqueous systems for which these methods were developed. For this purpose the simulation tool ReDrop is extended systematically in order to apply this design method for extraction systems with extreme physical properties such as ATPS. At first the fluid dynamics are investigated simultaneously in single-drop and column experiments to adapt the implemented correlations in ReDrop. Therefore, the sedimentation behavior of droplets is characterized experimentally and system-specific model parameters for the description of the sedimentation are determined. In combination with the experimental results of the extraction column on hold-up and flooding the predictions are validated. Afterwards the characterization of mass transfer is performed for a test protein also with single drops. Drop diameter and residence time are varied for these investigations. The predicted separation efficiency with Redrop on the basis of these studies is compared to the results of column experiments on mass transfer. The scale-up capacity of the correlations based on a lab-scale column will further be validated with experimental results of a pilot-plant column.

The results of the single-drop measurements concerning sedimentation and mass transfer will be presented. The simulation results with ReDrop based on these experiments will be shown and be compared with experimental data of a lab-scale extraction column.

Reactive Mass Transfer in a Microstructured Counter-Current Apparatus

*S. Willersinn^{*1}, H.-J. Bart¹*

Abstract

Microstructured devices for solvent extraction (SX) are promising, for process intensification or mechanistic studies of mass transfer. Especially, the advantages of a non-dispersive contacting, with a defined interfacial area, allow a continuous counter-current arrangement. For this, a microstructured apparatus was designed, where both microchannels are physically separated by a porous metal structure and the interface is pinned at the pore mouths. In this study, the reactive mass transfer of Zn(II) from aqueous sulfate solutions by di-(2-ethylhexyl)phosphoric acid (D2EHPA) in isododecane was performed for different metal meshes and at different pH-values to investigate the influence of diffusion and reaction resistances on the overall mass transfer in a mixed regime. The Zn(II) concentration was monitored as a function of residence time and the experimental overall mass transport coefficient was determined within the hydrodynamic limits. The overall mass transport coefficients were compared with models available in literature, predicting only diffusional phenomena.

Introduction

Solvent Extraction (SX) is a well-established separation technique in hydrometallurgical processes and indispensable for the recovery of metals from ores or secondary raw materials ("urban residues"). However, innovative concepts are necessary to address new challenges. In today's massive resource consumption and exploitation, the available primary and secondary raw materials feeds are becoming more complex and low grade, which is also pointed out by the European Union research agenda [1].

One promising approach to intensify existing processes, and hence, increasing the efficiency, is a microstructured apparatus design [2, 3]. In micro process engineering a higher surface-to-volume ratio leads to shorter diffusion and heat transfer paths, and thus, to a lower contact time. Other advantages compared to conventional processes deal with lower equipment investments, smaller space requirements, lower solvent inventories and a safer processing of toxic, explosive or harmful substances. Different techniques for microstructured membrane-stabilized gas-liquid [4, 5, 6] and liquid-liquid interfaces [7, 8] are reported in literature.

This non-dispersive approach has several advantages over traditional dispersion-based extraction equipment (e.g. columns, mixer-settler), as it was discussed earlier for hollow fiber membrane contactors in [9]: independent regulation of the phase ratio over a broad range without flooding at high or unloading at low flow rates; no phase separation/density difference necessary, interfacial area is known and constant, low solvent holdup and no moving parts. However, an additional mass transfer resistance is introduced into the system by the membrane, which has a finite lifetime due to scaling and fouling. Depending on the solvents used for extraction, polymeric hollow fiber contactors may be inappropriate.

¹ Chair of Separation Science and Technology, Technical University of Kaiserslautern, Germany

The prevailing study focuses on the reactive mass transfer of Zn(II) from aqueous sulfate solutions by di-(2-ethylhexyl)phosphoric acid (D2EHPA) in a non-dispersive, membrane-stabilized counter-current apparatus. This entails the stabilization of the interface in the microchannel, which is realized by a solvent-inert porous metal mesh.

Theoretical Considerations

Hydrodynamic Limits

A challenge for operating membrane-based phase contactors is to achieve a stable interface; hence the hydrodynamic conditions and pressure difference across the membrane play an important role for process designing. The interface is immobilized at the pore mouths, as long as the capillary pressure compensates the pressure loss over the pores. A marginal excess pressure (50 – 100 mbar) of the non-wetting phase is sufficient to guarantee stable operating conditions. This breakthrough pressure can be approximated by the Young-Laplace equation for round pores [10]:

$$\Delta p = \frac{2 \cdot \gamma \cdot \cos \theta}{r} \quad (1)$$

Where γ represents the interfacial tension, θ the contact angle and r the pore radius. Consequently, there is a trade-off between the hydrodynamic operating range (break-through) and mass transfer.

Reactive Mass Transfer

Physical mass transfer (without chemical reaction) from an aqueous feed phase through a hydrophobic membrane into an organic extracting phase involves the consecutive diffusion of the solute through the aqueous boundary layer, the porous membrane and the organic boundary layer [11]. Equilibrium is assumed at the liquid-liquid interface, which is characterized by the distribution coefficient. For reactive mass transfer an additional complex formation step of the ion exchanger with the solute at the interface is introduced. The resistance-in-series model accounts for the mass transfer with chemical reaction by integrating single mass transfer resistances due to diffusion and reaction into an overall mass transfer coefficient K_w [12, 13]:

$$\frac{1}{K_w} = \frac{1}{k_a} + \frac{1}{k_r} + \frac{1}{D \cdot k_m} + \frac{1}{D \cdot k_o} \quad (2)$$

k_a , k_m , k_o represent the individual mass transfer coefficients for the aqueous, membrane and organic phase, respectively, k_r is the effective rate of interfacial reaction at the surface (hence $1/k_r$ is the resistance to mass transfer of the interfacial reaction) and D accounts for the distribution coefficient, defined as the ratio of solute concentration in the organic phase and the aqueous phase. The overall Zn(II)-flux across the membrane is accompanied by a counter-flux of H^+ -ions (they encounter the same resistances) according to the following reaction [14], which makes the equilibrium highly pH-dependent:



Materials and Microcontactor

For all experimental investigations di-(2-ethylhexyl)phosphoric acid (Merck-Suchardt, > 98 %), isododecane (Ineos GmbH) and zinc(II) sulfate heptahydrate (Fluka Chemie AG) were used as received. Before preparing the aqueous and organic phases, de-ionized water and isododecane were pre-saturated by contacting for 24 hours. The zinc concentration of the aqueous feed and raffinate phase was analyzed ex situ by atomic absorption spectroscopy (Polarized Zeeman Z-8100). Consequently, the organic phase concentrations were determined by a mass balance. The home-made microcontactor (Fig. 1), which was used for the test system in the prevailing study, consists of an upper and a lower basic plate (polymethylmethacrylate), an upper and a lower channel plate (polytetrafluoroethylene, 3 mm x 452.6 mm x 0.5 mm) and a porous metal structure (GKD Geb. Kufferath AG), which separates both microchannels (Fig. 2). The modular design allows a fast and convenient adaption for a specific separation task. Additionally, the residence time, which is necessary for the chemical reaction, can easily be manipulated by altering the channel geometry and/or flow rates independently.

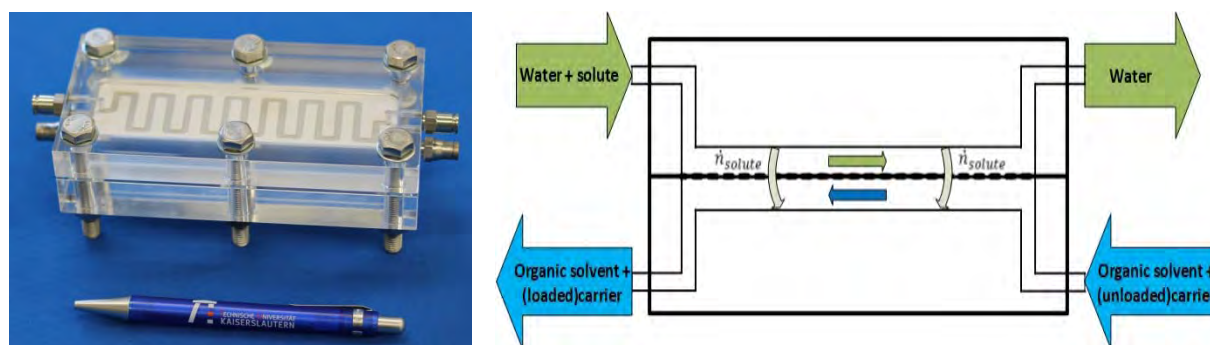


Fig. 1: Microstructured counter-current apparatus.

Table 1: Metal structures.

Mesh type	Material	Geom. Pore diameter	Thickness	Porosity
Optimized Plain Dutch Weave	1.4404	9 μm	89 μm	0.58
Reverse Plain Dutch Weave	1.4404	19 μm	202 μm	0.47

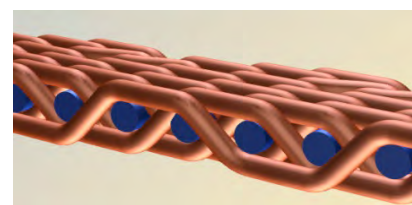


Fig. 2: Optimized Plain Dutch Weave.

Experimental

The aqueous zinc(II) sulfate solution ($1 \text{ g} \cdot \text{l}^{-1}$) and isododecane (with 10 vol.-% D2EHPA) were introduced into the microcontactor with two piston pumps (Merck-Hitachi 655 A-12 and Latek P-700) in counter-current arrangement. First, the apparatus was flooded with the wetting organic phase, filling the pores, and then, the upper channel volume was displaced by the non-wetting aqueous phase. The aqueous phase flow rates were adjusted independently from 0.1 to $0.6 \text{ ml} \cdot \text{min}^{-1}$, the organic phase flow rate was held constantly at $0.5 \text{ ml} \cdot \text{min}^{-1}$ and extraction efficiency was determined by collecting approximately 1 ml sample volume. All experiments were repeated three times. In order to generate a slight pressure difference across the

mesh, the outlet tube of the non-wetting aqueous phase was raised, triggering a hydrostatic pressure. Breakthrough could be observed visually.

Results and Discussion

First, the extraction process of two different mesh types (see Table 1) is investigated under the same experimental conditions. The results for the raffinate concentrations are shown in Fig. 3.

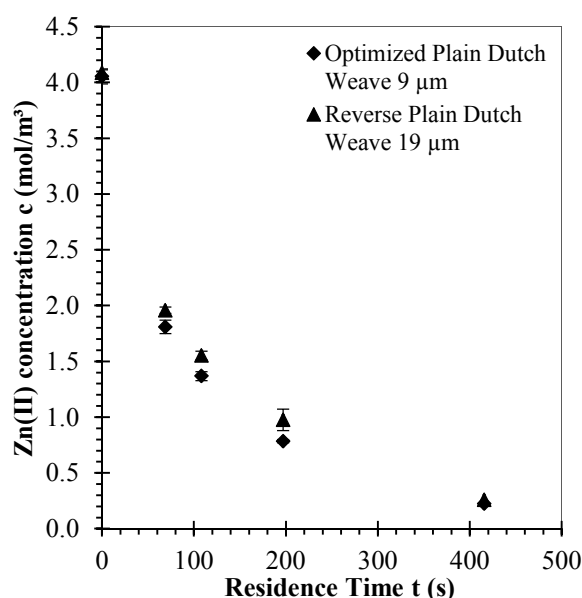


Fig. 3: Aqueous Zn(II) concentration as a function of residence time.

With increasing residence time, the outlet concentration of the aqueous phase decreases. The higher porosity of the Optimized Plain Dutch Weave generates a higher interfacial area, and hence, a favorable extraction performance.

In order to evaluate a comparable extraction efficiency, the experimental overall mass transfer coefficient is determined according to following equation [15, 16]:

$$Q_w \cdot (c_{w,in} - c_{w,out}) = K_w \cdot \Delta c_{w,LM} \cdot A \quad (4)$$

where Q_w is the flow rate of the aqueous phase, $c_{w,in}$ and $c_{w,out}$ the feed and raffinate concentration, respectively, A the contact area (based on mesh porosity) and $\Delta c_{w,LM}$ the mean logarithmic concentration difference. For modeling the overall mass transfer coefficient, each mass transfer resistance is evaluated separately. For physical extraction, the second term on the right-hand side of equation (2) can be neglected. The membrane resistance can be calculated from the Wilson plot method [9, 15, 17] or available correlations from literature [12, 15]. Once the experimental overall mass transfer resistance and membrane resistance is known, the boundary layer resistances can be determined consecutively [15]. On the other hand, the boundary layer resistances can be gained from Sherwood-correlations:

$$Sh \propto Re^\alpha \cdot Sc^\beta \cdot f(geometry) \quad (6)$$

For reactive extraction, the reaction kinetics might have a significant impact on the overall mass transfer resistance (depending on the experimental conditions), and hence, diffusion is coupled with chemical reaction at the interface (mixed regime), where both phenomena can be the rate-determining step. A relatively high pH-value shifts the equilibrium to the right in equation (3) and additionally accelerates the kinetics proposed for this reaction in [14]. Therefore, reaction resistance can be negligible for a fast or instantaneous reaction and the adapted model (6) can account for the mass transfer coefficient. As can be seen from Fig. 4 the overall mass transfer coefficient is higher at a higher pH of 6.5 compared to 4.3. With decreasing residence time, hence, at higher flow rates, K_w increases due to higher Reynolds numbers.

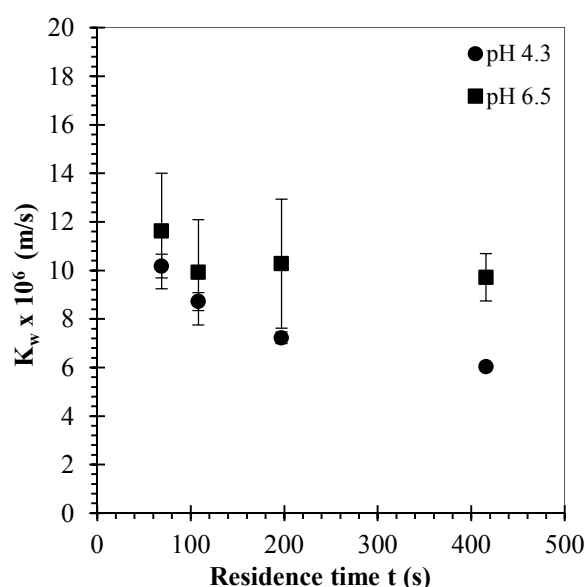


Fig. 4: K_w as a function of residence time and pH for Optimized Plain Dutch Weave.

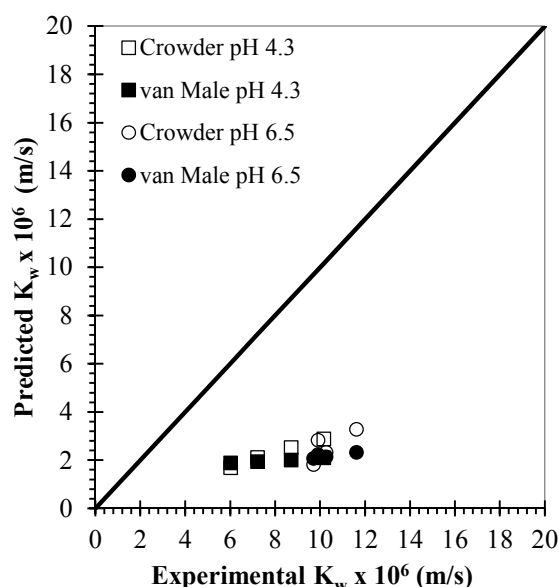


Fig. 5: Predicted K_w vs. experimental K_w for Optimized Plain Dutch Weave.

The available Sherwood-correlations from literature (e.g. Crowder and Cussler [18] in hollow fiber modules and van Male et al. [19] in rectangular microchannels) underestimate the experimental investigated K_w in this study (Fig. 5). Therefore, the models, which only account for the diffusional part of mass transport, need to be optimized, by adapting the geometry-dependent and fluidic parameters in equation (6) to the experimental K_w gained at high pH-values, where the chemical reaction becomes negligible.

Conclusion

The reactive mass transfer of Zn(II) from aqueous sulfate solutions by di-(2-ethylhexyl)phosphoric acid (D2EHPA) in a non-dispersive, membrane-stabilized counter-current apparatus was investigated experimentally. In this study it was shown, that the extraction efficiency is higher for a more porous metal structure within the hydrodynamic limits, which is determined by the pore diameter. By eliminating the chemical reaction resistance (at higher pH) the experimental data was correlated by models found in literature, which only account for diffusional transport phenome-

na. Further research is necessary to adapt existing correlations to the microcontactor-geometry. Therefore, at lower pH-values (mixed regime), the chemical resistance can be approximated by evaluating the difference between the experimentally observed overall mass transport and the predicted diffusional mass transport.

Acknowledgment

This work was financially supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), Bonn.

References

- [1] Horizon 2020 – Work Programme 2014-2015, Retrieved March 2014 from: http://ec.europa.eu/research/participants/data/ref/h2020/wp/2014_2015/main/h2020-wp1415-climate_en.pdf
- [2] Kockmann, N., Kussi, J., Schembecker, G., Hessel, V., Gürsel, I. V., Wang, Q. et al. (2012). Potenzialanalyse von Milli- und Mikroprozesstechniken für die Verkürzung von Prozessentwicklungszeiten - Chemie und Prozessdesign als Intensivierungsfelder. *Chem. Ing. Tech.*, 84 (5), S. 660–684.
- [3] Charpentier, J.-C. (2007). In the frame of globalization and sustainability, process intensification, a path to the future of chemical and process engineering (molecules into money). *Chem. Eng. J.*, 134 (1-3), S. 84–92.
- [4] Sun, X., Constantinou, A., Gavriilidis, A. (2011). Stripping of acetone from isopropanol solution with membrane and mesh gas–liquid contactors. *Chem. Eng. Process.: Process Intensification*, 50 (10), S. 991–997.
- [5] Adiche, C. & Sundmacher, K. (2010). Experimental investigation on a membrane distillation based microseparator. *Chem. Eng. Process.: Process Intensification*, 49 (4), S. 425–434.
- [6] Phattaranawik, J., Leiknes, T., Pronk, W. (2005). Mass transfer studies in flat-sheet membrane contactor with ozonation. *J. Membr. Sci.*, 247 (1-2), S. 153–167.
- [7] TeGrotenhuis, W. E., Cameron, R. J., Butcher, M. G., Martin, P. M., Wegeng, R. S. (1999). Microchannel devices for efficient contacting of liquids in solvent extraction. *Sep. Sci. Technol.*, 34 (6-7), S. 951–974.
- [8] Riedl, W., Mollet, D., Grundler, G. (2011). Using Membrane-Supported Liquid–Liquid Extraction for the Measurement of Extraction Kinetics. *CHIMIA*, 65 (5), S. 370–372.
- [9] Gabelman, A. & Hwang, S. T. (1999). Hollow Fiber membrane contactors. *J. Membr. Sci.*, 159, S. 61–106.
- [10] Reed, B. W., Semmens, M. J., Cussler, E. L. (1995). Membrane contactors, in: Noble, R. D.; Stern, S. A.: *Membr. Sep. Technol.*, Elsevier, Amsterdam.
- [11] Keller, K. H. & Stein, T. R. (1967). A two-dimensional analysis of porous membrane transport. *Meth. Biosci.*, S. 421 – 437.
- [12] Prasad, R. & Sirkar, K. K. (1992). Membrane based solvent extraction, in: *Membrane Handbook*, Van Nostrand Reinhold, New York, pp. 727–763.
- [13] Yang, C. & Cussler, E. L. (2000). Reaction dependent extraction of copper and nickel using hollow fibers. *J. Memb. Sci.*, 166, S. 229–238.
- [14] Rousselle, H.P., Bart, H.-J. (1999). Microkinetics and reaction equilibria in the system ZnSO₄/D2EHPA/isododecane. *Hydrometallurgy*, 51, 285–298.
- [15] Prasad, R. & Sirkar, K. K. (1998). Dispersion-Free Solvent Extraction with Microporous Hollow-Fiber Modules. *AIChE J.*, 34 (2), S. 177–188.
- [16] Darekar, M., Sen, N., Singh, K. K., Mukhopadhyay, S., Shenoy, K. T., Ghosh, S. K. (2014). Liquid–liquid extraction in microchannels with Zinc–D2EHPA system. *Hydrometallurgy*, 144-145, S. 54–62.
- [17] Wilson, E. E. (1915). A basis for rational design of heat transfer apparatus. *Trans. ASME*, 37.
- [18] Crowder, R. O. & Cussler, E. L. (1998). Mass transfer resistances in hollow fiber pervaporation. *J. Membr. Sci.*, 145, 173.

- [19] van Male, P., Croon, M. H. J. M. de, Tiggelaar, R. M., van den Berg, A., Schouten, J. C. (2004). Heat and mass transfer in a square microchannel with asymmetric heating. *Int. J. Heat Mass Transfer*, 47 (1), S. 87–99.

How H-bonding Networks in Reverse Micelles Drive the Extraction of Europium(III) Nitrate

Bao Fu Qiao, Northwestern University, Chicago, USA; Thomas Demars, Argonne National Laboratory, Chicago, USA; Monica Olvera de la Cruz, Northwestern University, Chicago, USA; Ross J. Ellis, Argonne National Laboratory, Chicago, USA

The behavior of solvent extraction systems is complex and often impossible to explain by referring to simple equilibria-based models, particularly when the concentrations of extractant, metal ions, acid, etc resemble those used in real processes. This is because the organic phase does not behave like an 'ideal solution' of metal ions dissolved in hydrocarbon solvent, but is rather more complex. Herein we explore how complex summations of strong and weak interactions manifest in structural hierarchies within the organic phase, connecting the 'hard' metal complex into the 'soft' aggregating solvent structure. Europium(III) nitrate was extracted from acidic and neutral aqueous phases into an oil phase (n-heptane) containing the extractant N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA). Atomistic molecular dynamics (MD) simulations combined with experimental X-ray techniques (SAXS and EXAFS) were used to probe the resulting solution structures on multiple length scales. The presence of water and acid alters the chemical and physical properties of the DMDOHEMA-heptane solvent to give hierarchical structures that hinge on H-bond donors and acceptors. Networks of H-bonding interactions throughout the core of the reverse micelles bridge between the europium nitrate outer-sphere and the aggregating solvent. These interactions appear to stabilize the metal complex in the organic phase and its favor extraction.

Experimental study on extraction of phenol by toluene

Zheng Li, Kathryn A. Mumford, Kathryn H. Smith, Geoff W. Stevens*

Summary

Activity models have previously been used to describe the equilibrium of various metal ions in solvent extraction systems and non-electrolytes in the pharmaceutical industry. However, the use of these kinds of models to describe systems containing weak electrolytes is not common. Due to the need to improve efficiencies and reduce waste, development of improved models that describe these processes is warranted. In this work, the experimental study of the phenol/toluene/water system in the presence of sodium hydroxide is completed as a proxy with the results being readily transferable to similar industrial processes. The data collected includes: distribution of phenol between water and toluene with changing pH and changing concentration of sodium hydroxide and component compositions of the two phases at equilibrium. The data is ready for use in the development of thermodynamic models that enable prediction of separation performance under alternate conditions.

1. Introduction

Extraction of natural products such as alkaloids from plants is a successful application of solvent extraction. In the process of extracting alkaloids, such as morphine, chemical bases are used to increase solubility¹ as well as to enhance selectivity. However, the dissociation/protonation of alkaloids and addition of bases dramatically increases the complexity of the extraction system. To date, mathematical modelling of extraction systems is limited to non-electrolytes and strong electrolytes, while the modelling of systems containing weak electrolytes and bases is very limited. Phenol has a pKa value close to that of many alkaloids and as such is a good model compound to be used to conduct the present study. Phenol is also a water pollutant which has resulted in many studies on the extraction of phenol from aqueous solutions²⁻⁹. However, in these investigations the inclusion of phenol dissociation is limited which makes the use of this data to develop thermodynamic models unsatisfactory.

This study investigates the extraction of phenol using toluene in the presence of sodium hydroxide, including both distribution of neutral phenol and total phenol between the two phases.

2. Experimental

UV-Vis spectrophotometry

A CARY 100 UV-Vis spectrophotometer was used to measure the UV-Vis absorbance spectrum of phenol in water, toluene in water and sodium phenolate. Sodium phenolate was obtained by adding 1.0 M sodium hydroxide into dilute phenol solutions.

Distribution of phenol

Distribution of phenol between water and toluene was measured by completing standard equilibrium shake-up experiments at room temperature. Two sets of experiments were completed: varying pH and varying sodium hydroxide concentration. The aqueous solution was made of phenol (analytical reagent, 99.90%) and miliQ water. Toluene was analytical reagent (99.9%), sodium hydroxide

* Corresponding author. Email address: gstevens@unimelb.edu.au

Author Affiliation: Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, the University of Melbourne, Parkville, Vic, 3010, Australia.

was semiconductor grade (99.99%). Both water and toluene were degassed by vacuum to removed dissolved oxygen which has been shown to oxidize phenol. The room temperature was controlled at 25 ± 0.5 °C.

For the first set of experiments, the initial concentration of phenol in water was 5.0×10^{-4} M and pH was adjusted by sodium hydroxide addition. For each experiment, 25 ml of phenol solution was contacted with 25 ml of toluene in a 100 ml separation funnel, and shaken for three hours to reach equilibrium. After equilibrium, phenol in the aqueous solution was analysed using a UV-Vis spectrophotometer, while phenol in toluene was stripped using 1 M sodium hydroxide (analytical grade, 97%) and then also analysed using a UV-Vis spectrophotometer. Recovery of phenol from toluene using sodium hydroxide was found to be higher than 99.7%.

The second set of experiments was conducted with an initial phenol concentration of 0.78 M in the aqueous phase with varying concentration of sodium hydroxide. The maximum concentration of sodium hydroxide was 0.67 M, thus phenol in aqueous phase was always in excess. At equilibrium, the aqueous solution was neutralized and diluted using 0.01 M hydrochloric acid and the organic phase was diluted using methanol. Phenol concentrations were then measured by Agilent 1200 High Performance Liquid Chromatography (HPLC).

3. Results and discussion

3.1 Dissociation equilibrium of phenol with sodium hydroxide

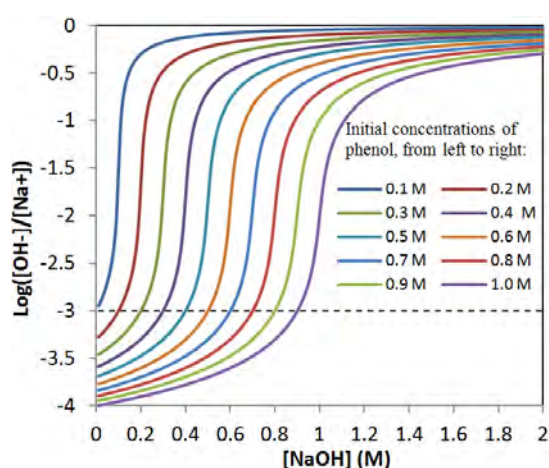


Figure.1 Equilibrium of sodium hydroxide and phenol

As a weak electrolyte, phenol (PhOH) partly reacts with sodium hydroxide, the reaction is given in eq. (1). Determination of species' concentration in the aqueous phase is not possible using UV-Vis spectrophotometer when the solute concentration is high. Mathematical solving of chemical equilibrium for a number of initial phenol concentrations can be performed using eq. (2)-(5), results of which are presented in Figure. 1. The properties of chemicals used in this study are presented in Table 1. When the concentration of phenol is 0.1 M higher than that of sodium hydroxide, the ratio of $[OH^-]/[Na^+]$ is so small that it is assumed sodium hydroxide reacts with phenol completely. Under these conditions, the initial concentration of sodium hydroxide approximately equals that of sodium phenolate.



Dissociation of water

$$[H^+] \times [OH^-] = 10^{-13.995} \quad (2)$$

Dissociation of phenol

$$[PhO^-] \times [H^+] / [PhOH] = 10^{-9.99} \quad (3)$$

Charge balance

$$[Na^+] + [H^+] = [OH^-] + [PhO^-] \quad (4)$$

Mass balance of phenol

$$[PhO^-] + [PhOH] = [PhOH]_{initial} \quad (5)$$

Table 1. Properties of species used in study

Species	Molecular Weight, M_w (g/mol)	Molar Volume ^a , V_i (cm ³ /mol)	Density, ρ (25°C) (g/cm ³)	Dissociation constant (25°C), pK_a	Solubility in water, x_i (25°C) (Mole fraction)
Toluene	92.139	106.85	0.8623		1.04×10^{-4} ¹⁷
Phenol	94.111	87.872	1.071 ^b	9.99	0.0178 ¹⁸
H ₂ O	18.015	18.069	0.9970	15.738 ^c	
NaOH	39.997		2.13		0.3105

Notes: Values come from *CRC Handbook of Chemistry & Physics*¹⁹ except for specified. ^a Calculated from molecular weight and density; ^b Extrapolated from measured value of liquid state at around melting temperature from source²⁰. ^c Calculated from $K_w=13.995$ at 25°C.

3.2 Spectrophotometric properties of phenol

In the aqueous phase, toluene, phenol and phenolate anion absorb ultra violet (UV) light in an overlapped wavelength range, refer to Figure 2. However, at 300 nm only the phenolate anion absorbs UV light. Therefore, absorbance at 300 nm can be used to determine the concentration of phenolate and then the overall phenol concentration (neutral phenol and phenolate) can be measured by converting phenol into phenolate, which was achieved by diluting the aqueous solution with the same volume of 0.2 M sodium hydroxide solution. Extinction coefficients of phenol are presented and compared with literature in Table 2.

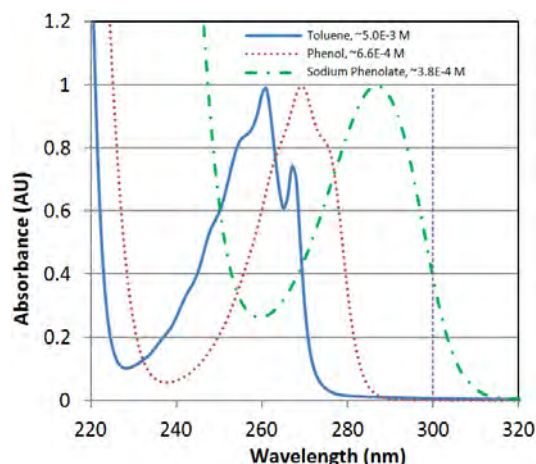


Fig.2 Spectra of toluene, phenol and phenolate anion

Table. 2 Extinction coefficient of phenol

Molar absorptivity (M ⁻¹ cm ⁻¹)			solvent	Reference
270 nm	287 nm	300 nm		
1373			Water	10
1450			Water	11, 12
1430			Water	13
1495			0.01M HCL	14
1660			Water	15
	2560		0.1M NaOH	14
1500.8			Water	This study
	2608.6	1019.4	1M NaOH	This study

3.3 Distribution ratio of phenol with varying pH

Neutral phenol can be extracted into toluene, while dissociated phenol (sodium phenolate) remains in the aqueous phase. The distribution ratio of total phenol (D_{tot}) and neutral phenol (D_{neu}) are defined as follows

$$D_{tot} = \frac{\text{concentration of phenol in organic phase}}{\text{concentration of neutral phenol and phenolate in aqueous phase}} \quad (6)$$

$$D_{neu} = \frac{\text{concentration of phenol in organic phase}}{\text{concentration of neutral phenol in aqueous phase}} \quad (7)$$

The distribution ratio of phenol between water and toluene over a range of pH are presented in Fig.3. With increasing pH, the distribution ratio of total phenol decreases mainly due to the conversion of phenol from neutral molecules to phenolate ions. Distribution of neutral phenol also decreases slightly with increasing pH. The discrepancy from an expected horizontal line is due to the interaction of species in the aqueous phase caused by addition of sodium hydroxide. However, when the distribution ratio of neutral phenol is calculated using a constant pKa, the opposite trend to the experimental result is observed at high pH. This is clearly wrong and is a result of increased interactions of species in solution causing changes in species' activities.

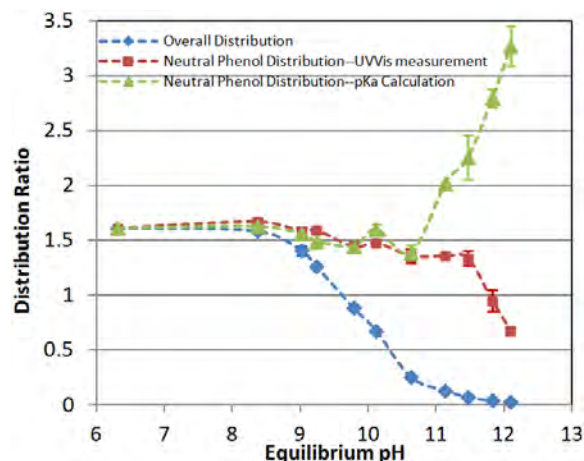


Fig. 3 Distribution of phenol with varying pH

3.4 Distribution ratio of phenol with varying sodium hydroxide concentration

To further investigate the influence of sodium hydroxide concentration on the distribution ratio of phenol, we measured both D_{tot} and D_{neu} with varying concentration of sodium hydroxide. The results are presented in Figure 4. The rapid decrease of D_{tot} is consistent with the results shown in Figure 3 and can again be explained due to the conversion of neutral phenol into sodium phenolate. On the contrary, D_{neu} decreases gradually up to sodium hydroxide concentration of ~0.5 M, and then starts to increase again. This increase is due to the concentration of sodium hydroxide being so high that the excess quantity of phenol is less than 0.1 M, thus sodium hydroxide and phenol coexist. However, the calculation assumes that sodium hydroxide reacts with phenol completely. As a result, data points to the right side of the dotted line in Figure 4 suffer from larger error.

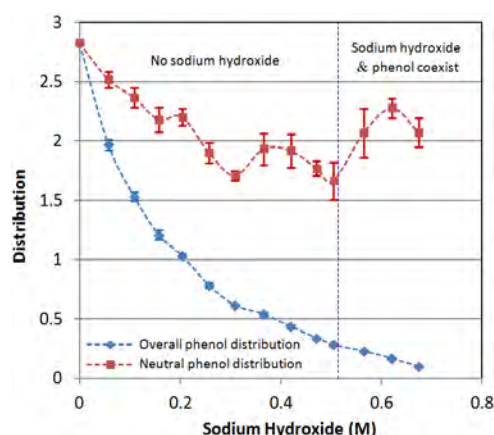


Figure 4 Distribution of phenol with varying sodium hydroxide concentration—initial [PhOH] is 0.78 M

Table 3. Liquid-liquid equilibrium data

Organic phase (I)		Aqueous phase (II)		
Phenol(1)	Toluene(2)	Phenol(1)	Sodium Phenolate(3)	Water(4)
0.05897	0.94103	0.00374	0	0.99626
0.05239	0.94761	0.00397	0.00111	0.99492
0.04799	0.95201	0.00385	0.00209	0.99406
0.0436	0.95641	0.00377	0.00303	0.99319
0.04059	0.95941	0.00346	0.00393	0.99262
0.03529	0.96471	0.00347	0.00495	0.99158
0.03073	0.96927	0.00334	0.00593	0.99073
0.02836	0.97164	0.00272	0.00702	0.99026
0.02468	0.97532	0.00237	0.00805	0.99957
0.02060	0.97940	0.00214	0.00902	0.98884
0.01801	0.98199	0.00198	0.00966	0.98835

In order to quantitatively describe the distribution ratio of phenol in the presence of sodium hydroxide, liquid-liquid equilibrium data of all species in the two phases is required. Considering that the solubility of water in toluene and toluene in water is very small, especially when compared with the concentration of phenol and sodium hydroxide in this study, the water concentration in toluene is neglected along with the toluene concentration in water. Moreover, volume additivity of phenol and toluene is assumed. Addition of phenol into sodium hydroxide solution does not change the ionic strength of the solution, thus volume additivity of phenol and sodium hydroxide solution is also assumed. Based on these assumptions and the correlation of density for sodium hydroxide solution¹⁶ presented by eq (8), the liquid-liquid equilibrium data is calculated for the eleven data points to the left side of the dotted line in Figure 4 (i.e. sodium hydroxide concentrations less than 0.5 M). Results are given in Table 3.

$$\rho(t) = \rho_1(t) + 4.916 \times 10^{-3}c - 9.064 \times 10^{-2}ct + 6.308 \times 10^{-4}ct^2 - 4.907c^3 + 1.633 \times 10^{-2}c^{3/2}t - 1.041 \times 10^{-4}c^{3/2}t^2 \quad (8)$$

where c is concentration (M) of sodium hydroxide, t is temperature ($^{\circ}\text{C}$), $\rho_1(t)$ is density of water (kg/m^3), which is expressed as

$$\rho_1(t) = 999.65 + 2.0438 \times 10^{-1}t - 6.1744 \times 10^{-1}t^{3/2} \quad (9)$$

4. Conclusions

The distribution ratio of total phenol and neutral phenol between water and toluene with varying pH and concentration of sodium hydroxide has been measured. Data

was obtained using UV-Vis spectra properties of phenol. Liquid-liquid equilibrium data of the extraction system was then calculated.

References

- Schiff, P. L., Opium and its alkaloids. *American Journal of Pharmaceutical Education* **2002**, 66, (2), 186-194.
- Won, K. W.; Prausnitz, J. M., Distribution of phenolic solutes between water and polar organic solvents. *The Journal of Chemical Thermodynamics* **1975**, 7, (7), 661-670.
- Alvarez Gonzalez, J. R.; Macedo, E. A.; Soares, M. E.; Medina, A. G., Liquid-liquid equilibria for ternary systems of water-phenol and solvents: data and representation with models. *Fluid Phase Equilibria* **1986**, 26, (3), 289-302.
- Pinto, R. T. P.; Lintomen, L.; Luz Jr, L. F. L.; Wolf-Maciel, M. R., Strategies for recovering phenol from wastewater: thermodynamic evaluation and environmental concerns. *Fluid Phase Equilibria* **2005**, 228–229, (0), 447-457.
- Fan, J.; Fan, Y.; Pei, Y.; Wu, K.; Wang, J.; Fan, M., Solvent extraction of selected endocrine-disrupting phenols using ionic liquids. *Separation and Purification Technology* **2008**, 61, (3), 324-331.
- Brinda Lakshmi, A.; Balasubramanian, A.; Venkatesan, S., Extraction of phenol and chlorophenols using ionic liquid [Bmim]⁺[BF₄]⁻ dissolved in tributyl phosphate. *Clean - Soil, Air, Water* **2013**, 41, (4), 349-355.
- Yang, Q.; Xing, H.; Su, B.; Bao, Z.; Wang, J.; Yang, Y.; Ren, Q., The essential role of hydrogen-bonding interaction in the extractive separation of phenolic compounds by ionic liquid. *AIChE Journal* **2013**, 59, (5), 1657-1667.
- Li, Z.; Wu, M.; Jiao, Z.; Bao, B.; Lu, S., Extraction of phenol from wastewater by N-octanoylpyrrolidine. *Journal of Hazardous Materials* **2004**, 114, (1–3), 111-114.
- Binns, E. H.; Squire, K. H.; Wood, L. J., The distribution of phenol between toluene and water and between toluene and aqueous solutions of sodium phenate. *Transactions of the Faraday Society* **1960**, 56, (0), 1770-1775.
- Chan, C. H.; Escalante-Semerena, J. C., ArsAB, a novel enzyme from *Sporomusa ovata* activates phenolic bases for adenosylcobamide biosynthesis. *Molecular Microbiology* **2011**, 81, (4), 952-967.
- Bhatia, K., Determination of trace phenol in aqueous solution by aqueous liquid chromatography. *Analytical Chemistry* **1973**, 45, (8), 1344-1347.
- Doub, L.; Vandenberg, J. M., The Ultraviolet Absorption Spectra of Simple Unsaturated Compounds. I. Mono- and p-Disubstituted Benzene Derivatives. *Journal of the American Chemical Society* **1947**, 69, (11), 2714-2723.
- Jadhav, S. R.; Verma, N.; Sharma, A.; Bhattacharya, P. K., Flux and retention analysis during micellar enhanced ultrafiltration for the removal of phenol and aniline. *Separation and Purification Technology* **2001**, 24, (3), 541-557.
- Herington, E. F. G.; Kynaston, W., The ultra-violet absorption spectra and dissociation constants of certain phenols in aqueous solution. *Transactions of the Faraday Society* **1957**, 53, (0), 138-142.
- Nakamura, G. R.; Kusafuka, S.; Finne, R. M.; Kearns, J. A., THE USE OF RECORDING SPECTROPHOTOMETER FOR THE DETECTION OF ACID PHOSPHATASES IN SEMINAL STAINS. *Journal of Criminal Law, Criminology & Police Science* **1959**, 49, (6), 608-611.
- Söhnel, O.; Novotny, P., *Densities of aqueous solutions of inorganic substances / Otakar Söhnel, Petr Novotny*. Amsterdam ; New York : Elsevier ; New York : Distribution for the U.S.A. and Canada, Elsevier Science Pub. Co., 1985.: 1985.
- Goral, M.; Wisniewska-Gocłowska, B.; Skrzecz, A.; Owczarek, I.; Blazej, K.; Haulait-Pirson, M. C.; Heffer, G. T.; Kapuku, F.; Maczynska, Z.; Szafranski, A.; Young, C. L., IUPAC-NIST solubility data series. 81. Hydrocarbons with water and seawater-revised and updated. Part 5. C7 hydrocarbons with water and heavy water. *Journal of Physical and Chemical Reference Data* **2005**, 34, (3), 1399-1487.
- Hill, A. E.; Malisoff, W. M., THE MUTUAL SOLUBILITY OF LIQUIDS. III. THE MUTUAL SOLUBILITY OF PHENOL AND WATER. IV. THE MUTUAL SOLUBILITY OF NORMAL BUTYL ALCOHOL AND WATER. *Journal of the American Chemical Society* **1926**, 48, (4), 918-927.
- Haynes, W. M., *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*. 91st. ed.; CRC Press: Boca Raton, London, New York., 2010.
- Badachhape, R. B.; Gharpurey, M. K.; Biswas, A. B., Density and Surface Tension of Phenol, (Mono-, Di-, and Tri-)chlorophenols, Salol, and (o- and m-) Chloronitrobenzenes. *Journal of Chemical & Engineering Data* **1965**, 10, (2), 143-145.

Mass Transfer and Hydrodynamic Investigation of a Hybrid Pulsed Extraction Column

Qinglin Niu; Heng Yi; Yundong Wang¹; Weiyang Fei

Summary

A hybrid pulsed extraction column, which combines a pulsed packed extraction column and a pulsed sieve-plate extraction column has been proposed. Hydrodynamic and mass transfer experiments have been carried out in a 50 mm pulsed extraction column. The system with 30%TBP(kerosene as diluent) / HNO_3 / H_2O was used. The hold-up and drop size of dispersed phase has been measured and investigated. "True" volumetric mass transfer coefficient($K_{oc}a$) based on plug flow model. The hold-up increased with the increase of u_y and Af . d_{32} increased with u_y increasing while decreased with Af increasing. The $K_{oc}a$ increased slowly first and then rapidly with the growth of Af . Besides, higher mass transfer efficiency can be obtained with a hybrid column than a sieve-plate column.

Keywords: liquid-liquid extraction, hybrid pulsed extraction column, pulsed sieve plate extraction column, pulsed packed extraction column, mass transfer

1. Introduction

With the booming of China's industry and economy, plus huge population of China, land resources crisis becomes a critical issue of China which need to be solved. However, in the rare earth industry, the separation and extraction of rare earth elements were mainly carried out in mixer-settlers which occupy large area of land. The usage of land in rare earth industry is of inefficiency. To improve that, it is hoped that liquid-liquid extraction columns, which occupy much smaller area of land, could replace the mixer-settlers in rare earth industry.

Pulsed sieve-plate extraction column is one of the most widely used liquid-liquid extraction columns in chemical industry. And the mass transfer is normally performed in count-current condition. With the pulsation, extra energy input will help to break droplets of dispersed phase that leads to larger interfacial area so as to mass transfer efficiency^[1]. As the pulsator is outside the column and isolated, mechanical parts inside the column can be eliminated and the leakage will therefore be minimized. It is of much more advantage of pulsed extraction columns when processing corrosive or radioactive solutions than other mechanical extraction columns as the pulsation parts can be installed far from the column. As the structure of the internal parts of pulsation columns is simple, the maintenance cost is relatively low. Safari et al^[2] has investigated in mass transfer using plug flow model. Besides, Samani et al^[3] have investigated the drop size distribution affected by the operating conditions in a pulsed packed extraction column. Yu and Fei^[4] has studied the hydrodynamics in a pulsed packed column.

¹ Corresponding Author, The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University Beijing 100084, P. R. China, E-mail: wangyd@tsinghua.edu.cn.

In this work, 30%TBP(kerosene as diluent) / HNO_3 / H_2O has been chosen to study the mass transfer and hydrodynamics in a pulsed sieve-plate column. The hold-up and saute mean diameter of dispersed phase has been investigated. True volumetric mass transfer coefficient has been calculated and investigated using plug flow model. A hybrid pulsed extraction column, which combines a pulsed packed extraction column and a pulsed sieve-plate extraction column has been proposed. A preliminary comparison has been made between the new column and the later two.

2. Experimental

2.1 Equipments

The experiment was carried out in a 50mm inner diameter extraction column which was made of acid-resisting glass with 1.15m active column height. Below and above the active column were two expanded glass settling sections. The four reservoir tanks and pipes were made of stainless-steel. The flow rates of both aqueous and organic phase are controlled and measured by pumps and rotameter. The interface location of the two phases at the top of the column was automatically controlled by an optical sensor. The contents of the column were pulsed at the desired amplitude with a frequency of 1 Hz using compressed air frequently imposed into the air leg jointed to the bottom settling zone of the column. The whole plant is represented in Figure 1.

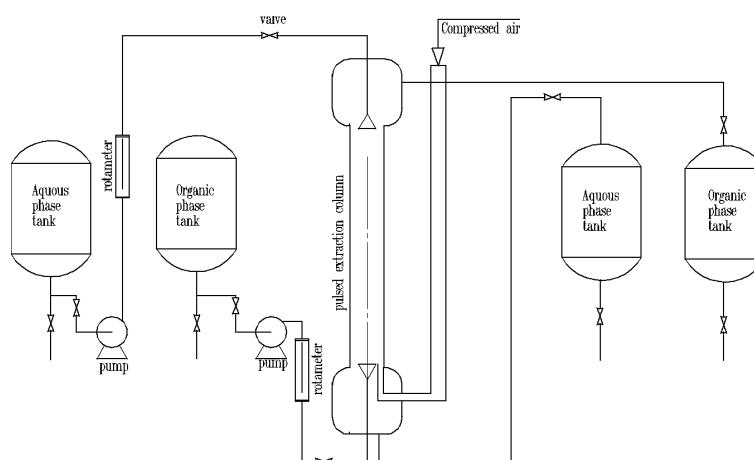


Fig 1 Schematic diagram of pulsed sieve-plate column

The sieve-plates used was made of stainless-steel and its diameter is 0.05m with 23% fractional free area of the perforations. In the experiments, the distance between the two plates is 0.075mm.

2.2 Systems

The system used in this paper was 30%TBP(kerosene as diluent) / HNO_3 / H_2O . Physical properties of the system at room temperature are shown in Table 1. The correlation is as follows:

$$x^* = 4.197y + 0.165 (y > 0.05 \text{ mol/L}) \quad (1)$$

Table 1 Physical properties of the system in temperature of laboratory

	$C_{HNO_3}(\text{mol/L})$	$\rho(\text{kg/m}^3)$	$\mu(\text{Pa}\cdot\text{s})$	$\gamma(\text{N/m})$
Continuous phase	2 ± 0.02	1017.2	0.00106	0.01026
Dispersed phase	0	836.2	0.00211	

2.3 Modeling

In this work, plug flow model(PFM) was adopted. Several assumptions were made for the analysis of the mass transfer using PFM:

- (1) The continuous phase and dispersed phase are effectively immiscible.
- (2) The superficial velocity of both the continuous and dispersed phase keeps constant with the column height changing.
- (3) The mean velocity and concentration of each phase are identical at any given cross-section.
- (4) The distribution coefficient is a constant.
- (5) The volumetric mass transfer coefficient is constant over the column.

The plug flow model assumes that both phases move exactly in plug flow along the column and the flow rate of each phase keeps constant at any given cross-section. Therefore, the PFM is the simplest but the most industrial-scale applicable model.

According to Safari^[2], mass transfer equations in a counter-current extraction column based on PFM can be obtained:

$$\frac{dX}{dZ} - NTU_{oc}(X + Y - 1) = 0 \quad (2)$$

$$\frac{dY}{dZ} - \frac{NTU_{oc}}{\Omega}(X + Y - 1) = 0 \quad (3)$$

The boundary conditions are:

$$\text{At } Z=1: X=0 \text{ and At } Z=1 Y=0$$

The solutions of differential equations (2) and (3) are as follows:

$$X(Z) = \frac{\exp(TZ) - \exp(T)}{1 - \Omega \exp(T)} \quad (4)$$

$$X(Z) = \frac{1 - \exp(TZ)}{1 - \Omega \exp(T)} \quad (5)$$

3. Results and discussion

3.1 Hold-up and sauter mean drop diameter

The hold-up(ϕ) of dispersed phase were mainly affected by pulsation intensity and superficial velocity of dispersed phase (flow rate). The relations of the hold-up and pulsation intensity(Af) and dispersed phase superficial velocity(u_y) are shown in Fig. 2(a).

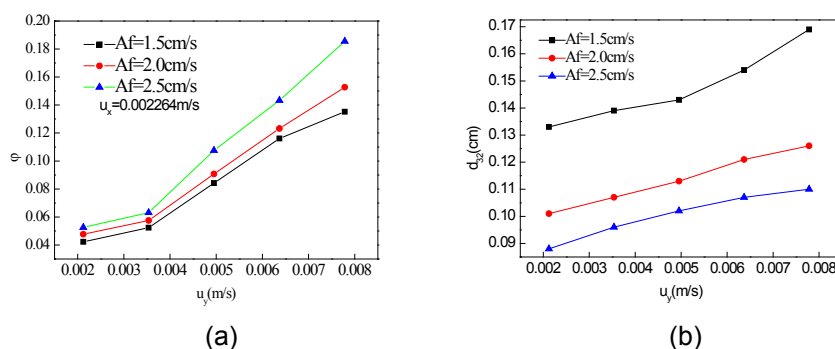


Fig. 2 Effect of u_y and Af on the hold-up and d_{32}

As can be seen in Fig. 2(a), the hold-up increased apparently with the increase of pulsation intensity. Higher energy input could accelerate the drop breakage, which improves the residence time of dispersed phase. This is the reason why increasing pulsation intensity could cause a clear improvement of hold-up of dispersed phase. Besides, the growth of flow rate of dispersed phase also increased dispersed phase hold-up.

The dispersed phase drop size, d_{32} , was also affected by pulsation intensity and superficial velocity of dispersed phase (flow rate). The relations of d_{32} and pulsation intensity(Af) and dispersed phase superficial velocity(u_y) were shown in Fig. 2(b). Dispersed phase drop size decreased with the increase of pulsation intensity with the same reason as the hold-up. In addition, d_{32} increased with the increase of dispersed phase superficial velocity. As the superficial velocity of dispersed phase increased, the volume of dispersed phase in the column increased, which improved the probability of drop coalescence.

3.2 True volumetric transfer coefficient($K_{oc}a$)

$K_{oc}a$ increased as u_y increased when other operating conditions were kept constant, which is shown in Fig. 3(a). As is mentioned above, both the hold-up and d_{32} of dispersed phase increased with the increase of u_y , but the influence of the growth of hold-up on the interfacial area ($a = 6\phi / d_{32}$) is six times more than that of d_{32} . Therefore, the interfacial area increased with the dispersed phase superficial velocity increasing, which led to the increase of $K_{oc}a$. However, too much high dispersed phase superficial velocity which consequently causes high hold-up of dispersed phase might make the system be subject to flooding.

As is shown in Fig. 3(b), $K_{oc}a$ increased as pulsation intensity increased. When the pulsation intensity was relatively low ($Af \leq 2$ cm/s), the flow pattern in the column was close to the mixer-settler area where hold-up and interfacial area did not change too much so that the $K_{oc}a$ increased slowly with pulsation intensity increasing. However,

when pulsation intensity kept growing ($Af > 2.0 \text{ cm/s}$), the hold-up increased remarkably and meantime d_{32} decreased largely. Consequently, the interfacial area increased quickly and so was $K_{oc}a$. But it should be recognized that too much high pulsation intensity will aggravate the axial mixing which contrarily weakens mass transfer efficiency.

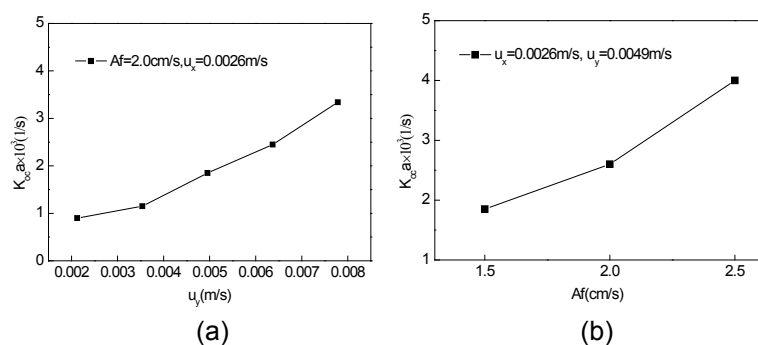


Fig. 3 Effect of u_y and Af on $K_{oc}a$

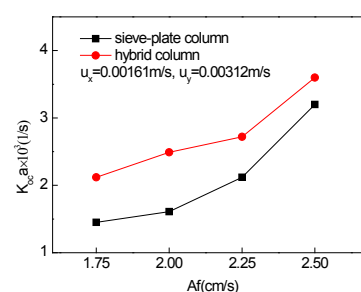


Fig. 4 Comparison of the $K_{oc}a$ of the two columns

3.3 Comparison of $K_{oc}a$ of two different columns

To compare the mass transfer efficiency of two columns, several contrast experiments were performed, the results of which were shown in Fig. 4. As can be seen in Fig. 4, the mass transfer efficiency of hybrid column is higher than that of sieve-plate column under the same operating conditions. The reason may be that the organic phase could be dispersed into more small droplets in hybrid columns which strengthens the mass transfer. However, it should be realized that the margin of the $K_{oc}a$ of the two columns differs from changing Af .

4. Conclusions

An experimental study were carried out on hydrodynamics and mass transfer in a pulsed sieve-plate column. According to the results, the hold up of dispersed phase decreased with the increase of the superficial velocity of dispersed phase and with pulsation intensity increasing. Besides, d_{32} of dispersed phase increased with the growth of the superficial velocity of dispersed phase while decreased with the increase of pulsation intensity. In addition, the true volumetric mass transfer coefficient increased slowly at first with the increase of pulsation intensity. When the pulsation intensity becomes fairly strong, the rise of it becomes tremendous. But too strong pulsation will aggravate the axial mixing which contrarily weakens mass transfer efficiency. Finally, the hybrid column shows much better mass transfer efficiency than the sieve-plate does.

Acknowledgments

This research was carried out under the of National Key Basic Research Program of China (No. 2012CBA01203) and the Specialized Research Fund for Doctoral Program of Higher Education of MOE of China (No. 20130002110018) in the State Key Laboratory of Chemical Engineering of Tsinghua University, Beijing, P. R. China. The authors gratefully acknowledge these grants.

Nomenclature

A	pulse amplitude(cm)	Greek numbers	
a	interfacial area(m ² /m ³)	ρ	density(kg/m ³)
c	concentration of the solute(mol/L)	μ	viscosity(Pa•s)
f	pulse frequency(1/s)	γ	interfacial tension(N/m)
d ₃₂	sauter mean drop diameter(cm)	T	$NTU_{oc}(1-\frac{1}{\Omega})$
K _{oc} a	true volumetric mass transfer coefficient(1/s)	Ω	$\frac{mQ\rho_y}{Q_x\rho_x}$
m	distribution coefficient	Subscripts	
NTU _{oc}	Overall number of transfer unit	x	continuous phase
Q	volumetric flow rate(m ³ /s)	y	dispersed phase
u	superficial velocity(m/s)		
X	dimensionless continuous phase concentration		
Y	dimensionless dispersed phase concentration		
Z	dimensionless height		

References

- [1] Meisam, T-M. and J. Safdari. Mass transfer coefficients in a pulsed packed extraction column. Chem. Eng. Processing: Process Intensification, 2009, 48(2009): 1321-1326.
- [2] Safari, A., H. Abolghasemi, J. Safdari and M. F. Safari. Axial mixing and mass transfer investigation in a pulsed packed liquid-liquid extraction column using plug flow and axial dispersion models. Chem. Eng. Res. Des., 2012, 90(2012):193-200.
- [3] Samani, G., H. Asl, J. Safdari and T-M. Meisam. Drop size distribution and mean drop size in a pulsed packed extraction column. Chem. Eng. Res. Des., 2012, 90(2012):2148-2154.
- [4] Yu, J. and W. Y. Fei. Hydrodynamics and mass transfer in a pulsed paced column. The Canadian J. Chem. Eng., 2000, 78(2000):1040-1045.

A new electrochemical approach for solvent extraction processes

Nima Sadeghi¹, Eskandar Keshavarz Alamdari^{1},*

Summary

Presence or absence of ion species at solutions can be predicted with a thermodynamic point of view so that use extensively for mineral's leaching processes. Nernst equation is efficient tools for electrochemical equilibrium in aqueous system that there are pourbaix diagram as outcomes of that. Different parameters can change structure of diagram such a temperature, vapor pressure of components and Concentration in solution. This research, extraction of Au(III) and Fe(III) from chloride media by tri n-butyl phosphate (TBP), ionic species concentration on Electrochemical potential was evaluated. Sensitized aqueous solution was prepare by AuCl_4H , FeCl_3 and HCl that Gold, Iron and acid concentration is 500, 1000mg/l and 0.1-7 mol/l, respectively. Considering to the dynamic change of chemical concentration in the solvent extraction process, it can be concluded electrochemical potential changes of aqueous systems. Electrochemical potential was measured by ORP meter and then data was comprised with pourbaix diagram that depicted by Fact-Sage software. The results almost confirm together, increasing acid concentration (HCl) or Reducing the concentration of metal ions in aqueous phase drops oxidation-reduction potential(ORP). According to Au(III) and Fe(III) ions extraction by TBP at specified condition, ORP variation was interpreted. Consider to metallic ions oxidation strength, significant differences in electrochemical potential can be attributed to metallic ions extraction by TBP from chloride solution.

Key words: oxidation-reduction potential (ORP), chloride solution, Gold, Iron

1. Introduction:

In solvent extraction processes dissolved species concentration in aqueous - or organic- solution are changed. The ions concentration changes will affect other properties of solution, such as pH, conductivity, density and Etc.

pH is main parameter that studies on solvent extraction research (Rydberg, 2004) H^+ exchange in ion exchange extractant and acid extraction are the main agent for pH variation. The ion exchange solvents extract metallic ions with hydrogen (H^+) or hydroxide (OH^-) ions release that alters pH dramatically. With monitoring pH content process progress is estimated.

conductivity is other parameter that be changed of ionic speasies. Percences different ionic species changes conductivity of solution. Mironov (Mironov, 2013) measured the electro-conductivity of extracts and solutions of $\text{HAuCl}_4 \cdot 3.3\text{H}_2\text{O}$ in dry DBC. Due to electrochemical nature of different Au chloride complexes (H^+ , AuCl_4^- , HAuCl_4 , $(\text{HAuCl}_4)_2$, $\text{H}(\text{AuCl}_4)_2^-$, and $\text{H}_2(\text{AuCl}_4)^+$) in solvent extraction process, the variation of solution conductivity was notable. By measuring aqueous solution

¹ Department of mining and metallurgical Eng., Amirkabir University of Technology, Tehran, IRAN

* Corresponding Author, Email: alamdari@aut.ac.ir, Telephone: +98 21 6454 2971

conductivity, Au chloride complexes and concentration was determined.

In addition to the above parameters, other variables can also be used to investigate the solvent extraction process. Electrochemical variables are the most important ones. Electrochemical relations in the equilibrium system are defined based on the Nernst equation which is shown for component A in eq.1.

$$E_A = E_0 + \frac{RT}{nf} \ln a_A \quad (1)$$

In leaching process oxidation Potential is used to study the dissolution of mineral specimen, extensively. Electrochemical potential of solution (Oxidation-reduction potential) is a thermodynamic parameter that changes by Temperature, pressure and activity of component. High oxidation-reduction potential (ORP) indicate strong oxidative media and vice versa. Hence, ORP of solution depend on activity of components at ambient temperature. Thus, it seems that extraction process change potential. Based on equilibrium qualification, variation of potential is sensible when extracted species is strong oxidative or reductive. Oxidizing species selection appears to be more useful for the study of the solvent extraction method. Due to electrochemical nature of different chloride complexes and High oxidation potential Au and Fe was selected for electrochemical survey in chloride media.

Oxidation-reduction potential (ORP) can be considered as the tendency of the system for accepting or donating electrons when a change occurs in the ionic species of the system. The aim of the present work was to identify and analyze the effect of pertinent parameters – i.e. temperature, HCl, Au, Fe and TBP concentrations – in Au and Fe solvent extraction process from chloride media.

2. material and method

The stock gold chloride solution was prepared by dissolution of analytical grade of Hydrogen gold tetrachloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, FeCl_3 , MERK, chemical company, Germany) in double distilled water. Analytical grade of Tri-n-Butyl Phosphate (FLUKA, Switzerland) as the extractant and commercial grade kerosene(Isfahan Refinery Co) as the diluents were used for preparing of stock organic solutions.

The Oxidation-Reduction potential (ORP) based on SHE (Hach Company, 2012) and pH of extracted and equilibrated aqueous solutions were measured by ORP meter (Eutech instrument, pH300) and pH meter (Mettler Toledo, FE30), respectively.

Initial Metal concentration in aqueous phase for Au and Fe was 500 and 1000 mg/l respectively. Batch experimental was done in flask containing equal volume of aqueous and organic phase. The mixture was mechanically agitated (400 rpm) at ambient temperature (20 °C). The time required to reach equilibrium, based on our previous studies (sadeghi et al., 2013), was set to 30 minutes. The mixtures were then separated by a decanting funnel for 15 min to allow complete separation. The metal content of the aqueous phase was determined by atomic absorption

spectroscopy (Varian, A240) and that of for the organic phase was estimated by mass balance calculations. The Oxidation-Reduction potential (ORP) based on SHE (Hach Company, 2012) and pH of extracted and equilibrated aqueous solutions were measured by ORP meter (Eutech instrument, pH300) and pH meter (Mettler Toledo, FE30), respectively.

3. Results and discussion

3.1 E-pH diagram for Au

Equilibrium E-pH diagram for Au-Cl-H₂O was depicted in fig1 for 500 mg/l, 3 mol/l HCl and ambient temperature. As shown Au can be formed AuCl₄⁻, Au(OH)₃ and Au. Practical parameters, such as ion concentration, pH and temperature, can change pourbaix diagram structure. solvent extraction process changes ions composition of aqueous solution. So composition parameters changing on pourbaix diagram was investigated. Fig 2.a and Fig 2.b shows effect of AuCl₄⁻ and Cl⁻ concentration on E-pH diagram, respectively. In fig2 Cl⁻ increases drops electrochemical potential. When chloric acid concentration is 0.5-10 M, potential is changing 975 to 870. Hence it seems that chlorine ions are reductive agent in chloride media. In Fig. 2.b, decreasing au concentration drops potential 937-907 mv.

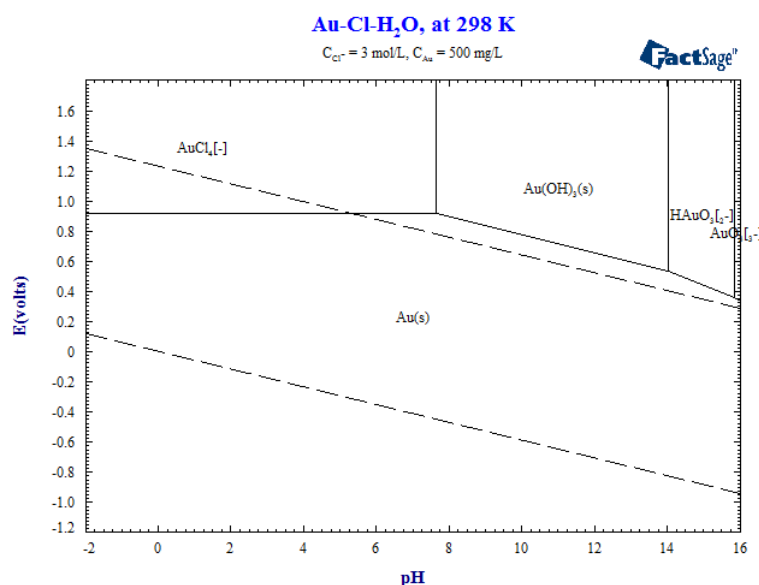


Fig. 1. purbax diagram of Au-Cl-H₂O system in [Cl⁻]= 3 mol/l and [Au]= 500 mg/l

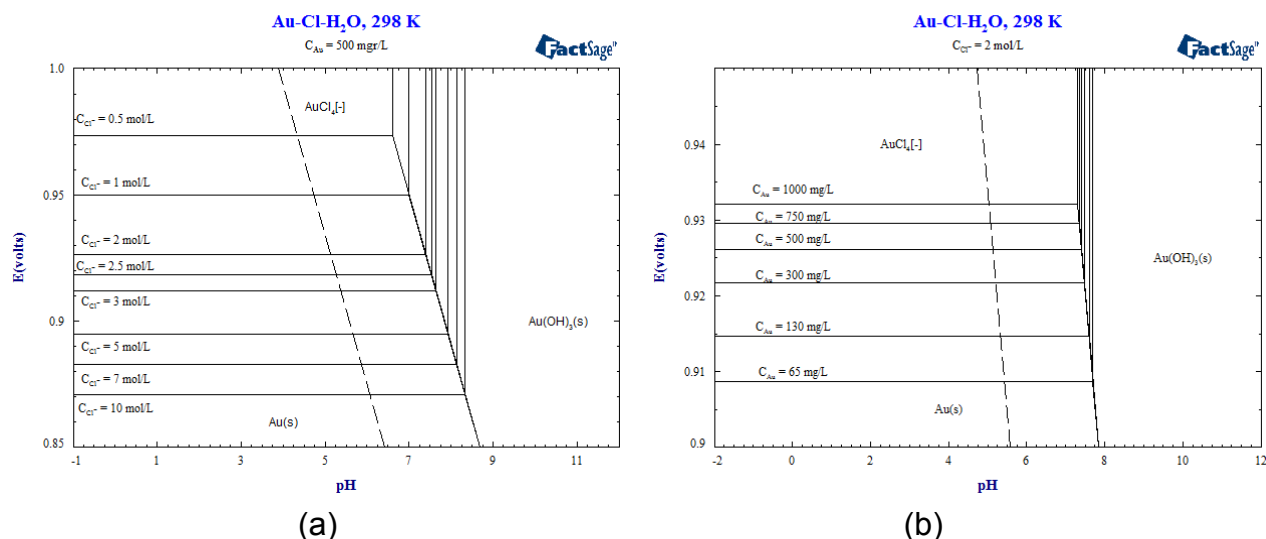


Fig.2.purbaix diagram for Au-Cl-H₂O at a) [Au] = 500 mg/l and different Cl⁻ Concentration, b) [Cl⁻] = 2 Mol/l and different [Au] Concentration.

3.2 E-pH diagram for Fe

Iron pourbaix diagram for 1 g/l Fe, 3 M HCl and 25 C was shown in Fig 3. Iron in reductive position (<-420mv) and acidic pH is stable. When electro chemical potential is up to -0.420 , Fe²⁺ cations is formed in the system but in high potential value (>0.610 mv), iron was dissolved in the form FeCl₃.

Chlorine and iron changes in the system have a similar effect as gold. Chloric ions increases and Fe decrease drops potential of aquaous system. Hence Fe extraction process can be monitored by ORP.

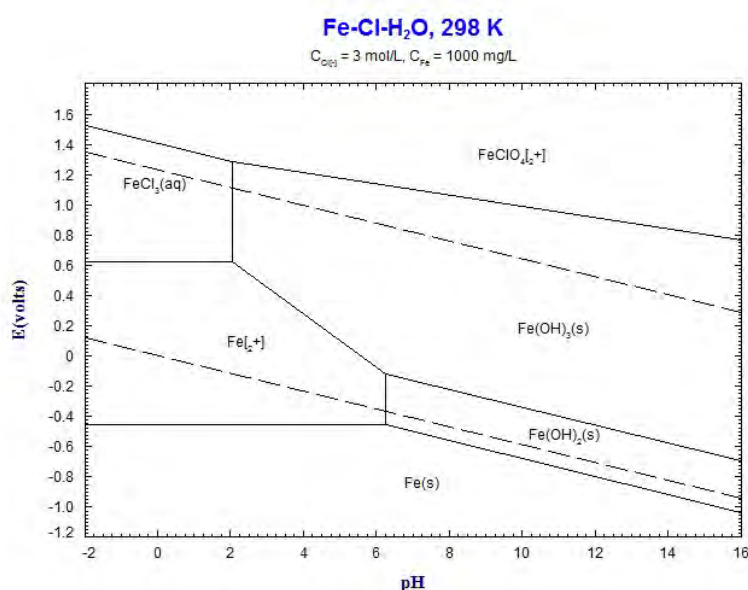


Fig. 3. purbax diagram of Au-Cl-H₂O system in [Cl⁻] = 3 mol/l and [Au] = 500 mg/l

3.2 chlorine ions effect on ORP

As seen in section 3.1, chlorine concentration changes ionic species region in pourbaix diagram. So, potential changes should be measured in various chlorine concentrations. In Fig 4, influence of Cl^- ions on electrochemical potential was shown in different Au concentrations. High concentration of Au increase ORP value but Cl^- ions drop ORP and increase reducing power of aqueous solution by Cl^- . In Fig 5, effect of chlorine ions on ORP of Fe aqueous solution was shown. Cl^- have similar effect of fig. 5 on ORP and Cl^- appears in the role of a reducing agent.

3.3 effect of solvent extraction process on electrochemical potential

TBP is one of the most popular extractant that can extract gold and iron from chloride media (Sadeghi et al., 2013, Mishra et al, 2011) hence, SX practice did by this extractant. Initial gold concentration was 500 mg/l and TBP concentration changes 0.005-0.25 M. Two phases (aqueous and organic) was agitated and after that ORP of aqueous solution was measured. ORP monitoring for gold extraction was reported in

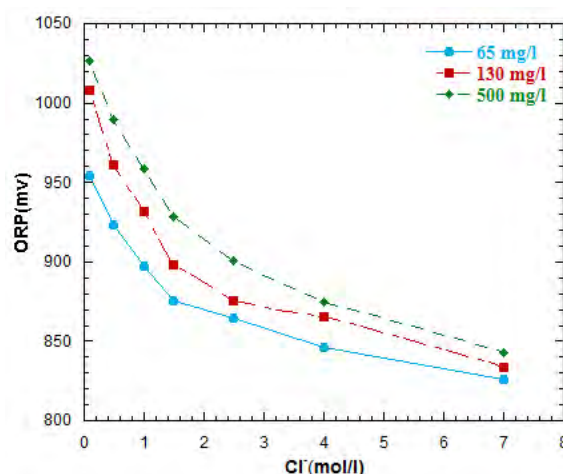


Fig 4. influence of Cl^- concentration on oxidation-reduction potential (ORP) in various Au concentration

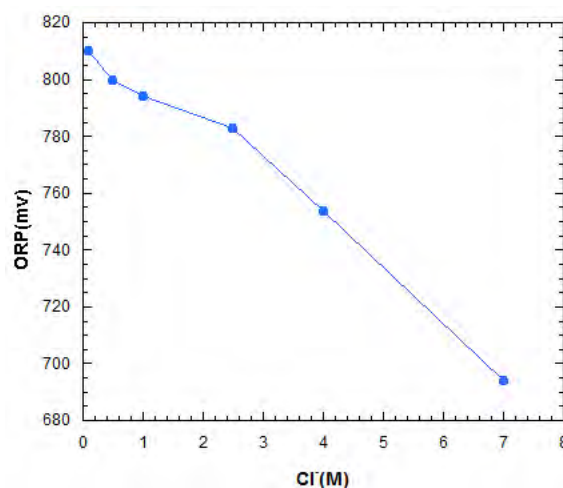


Fig 5 influence of Cl^- concentration on oxidation-reduction potential (ORP) IN 1000 mg/l Fe

Fig. 6. Potential variation in low Cl^- is negligible but high concentration (2.5, 4, 7M) of Cl^- is salient. Extraction percent and Cl^- increases are main reason for this difference.

For studying potential changes in Fe extraction, 0.05-0.25 M TBP was agitated 1000 mg/l Fe in different Cl^- concentration. ORP variation by Fe extraction by TBP was reported in Fig. 7. In low Cl^- concentration, ORP isn't changes tangibly but in high concentration of Cl^- is.

Studies show that chloride plays an important role in the extraction of iron from aqueous solution. In high concentration of Cl^- (0.05-1.5M), extraction percent is considerable. So, ORP drops can show Fe Extraction from aqueous solution.

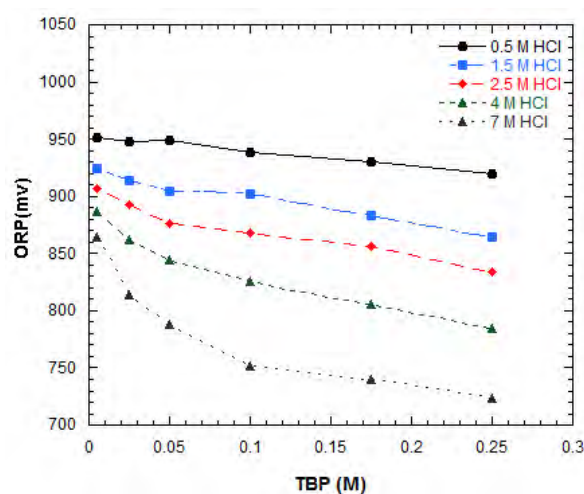


Fig. 3 Effect of Au Extraction on ORP by TBP in difference acid concentration and 500 mg/l Au

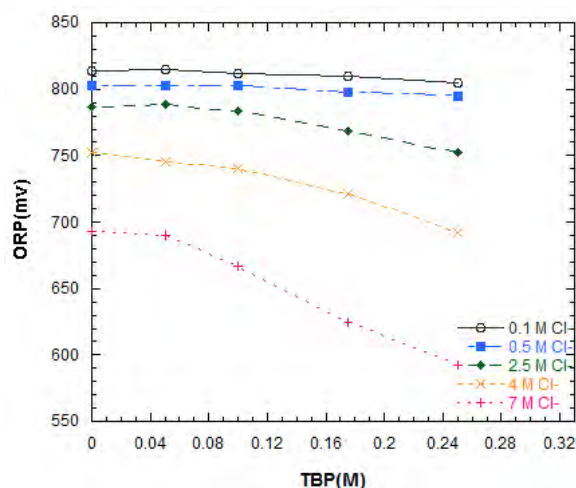


Fig. 4 influence of Fe extraction by TBP in different Cl^- concentration and 1000 mg/l Fe

4. Conclusion

- Studying on ionic species stability in different condition by pourbaix diagram is helpful for determine extracted ions

- ORP changes can be used for monitoring of reductive or oxidant species extraction
- ORP changes dynamically during solvent extraction operations
- Initial concentration of target metals, such as Au and Fe, changes ORP value
- Presence and concentration of other ionic species, such as Cl^- , effect on ORP changes

References:

Mironov, I. V., Some additional aspects of gold(III) extraction by dibutyl carbitol, Hydrometallurgy 133, 2013, 15–22

Mishra. R.K., Rout P.C., Sarangi. P.C., Nathsarma. K.C. A comparative study on extraction of Fe(III) from chloride leach liquor using TBP, Cyanex 921 and Cyanex 923, Hydrometallurgy 104, 2010, 298–303

Rydberg, J., Cox, M., Musikas, C., Chappin, G., Solvent Extraction Principles and Practice, Revised and Expanded, 2nd edition, CRC press, 2004

Sadeghi N., Alamdari E.K., Fatmehsari D. H., Darvishi D., Alamdari A. K., kafash Rafsanjani A. B., Solvent Extraction of Gold from Chloride Solution by Tri-Butyl Phosphate (TBP), 23rd International Mining Congress & Exhibition of Turkey, 16-19 April 2013

Numerical Modelling of Centrifugal Settlers

Based on Experimental Data

*Robert Macher¹, Andreas Pfennig^{*1}*

Summary

The separation of a liquid-liquid dispersion is a regular task in today's industry. However the separation of mixtures containing electrolytes or surfactants, high viscosity systems or liquid mixtures with small density differences may still pose a problem. It is possible to separate these systems using centrifugal settlers, but the scale up is still based mostly on experience.

A powerful model to determine the size of gravity settlers using experimental results has been developed by Henschke et al. [1] This method is modified to estimate the size of centrifugal settlers utilizing standardized lab-scale settling experiments. This allows the exact adjustment of length and diameter of the centrifugal settler to the specifications of the separation system. The model uses the results from experiments as well as input specified by the user to calculate the dimensions of the centrifugal settler.

Experimental results using different systems with varied concentration and type of surfactants are used to validate the numerical model to describe centrifugal settlers. In addition these experimental results are compared with the settling behaviour in conventional gravity settlers. One objective of these investigations is the comparison of these two types of settlers to see the advantages of centrifugal settlers directly and to validate the design model.

Introduction

There are many processes in chemical engineering, e.g. liquid-liquid extraction, liquid-membrane permeation or azeotropic distillation, where dispersions of immiscible liquids have to be separated. This often leads to small drops and therefore to problems concerning the separation process [1]. To perform this separation for industrial purposes, it is common to use continuous settlers. However, using conventional gravity settlers, it is often not possible to reach sufficient separation between light and heavy phase. As a consequence, alternative separation processes like centrifugal separation are necessary. Especially the centrifugal acceleration is greater than the gravitational acceleration by orders of magnitude, which leads to larger buoyancy and, therefore, to faster settling. Nevertheless the scale up of centrifugal settlers is still a big challenge and needs to be improved.

* Corresponding Author

E-mail address: andreas.pfennig@tugraz.at

¹ Graz University of Technology, Inffeldgasse 25/C/II, 8010 Graz, Austria

Background

Unlike the distillation process, where it is common to determine the size of the apparatus based on data of the vapour-liquid equilibrium, the determination of the dimensions of extraction equipment is much more demanding. The reason for this is that different effects like sedimentation, mass transfer, coalescence or separation take place simultaneously. Additionally they are strongly interrelated. Another issue is that coalescence is strongly affected by smallest amounts of impurities of the system. Therefore, prediction of the size of extraction equipment is difficult [2].

To perform extraction in mixer-settler batteries a method has been developed to design a gravity settler solely based on simple lab-scale experiments, shown in Fig. 1. In this example, the light phase is dispersed in the heavy phase. After stirring for a distinct time, the sedimentation of drops towards the interface can be observed. There they coalesce with the corresponding phase, in this case the light phase, or accumulate in a dense-packed zone. This depends on both the sedimentation velocity and the frequency of coalescence. If sedimentation is faster than coalescence this layer occurs otherwise the drops coalesce directly with their corresponding phase. When all drops have vanished at t_E the sedimentation curve meets the coalescence curve and a distinct interface is visible and the experiment is finished [1].

The data from this experiment, shown in Fig. 1 on the right hand side, is used in the model developed by Henschke et al. [1] to determine the Sauter mean diameter as well as the coalescence parameter. The Sauter mean diameter can be calculated from the sedimentation curve with the knowledge of hold-up and the properties of the liquids, like density and viscosity. The coalescence parameter is derived from the coalescence curve. These parameters are used for further characterization of the system. Using the Sauter mean diameter it is possible to determine the velocity of sedimentation whereas the coalescence parameter is used to describe the coalescence of drops in more detail. Based on these two values the drop-based model is able to describe drop sedimentation, effects concerning coalescence also in other geometries and drop deformation in the dense-packed zone. This method has been extended to determine the size of horizontal settlers with internals [3, 4].

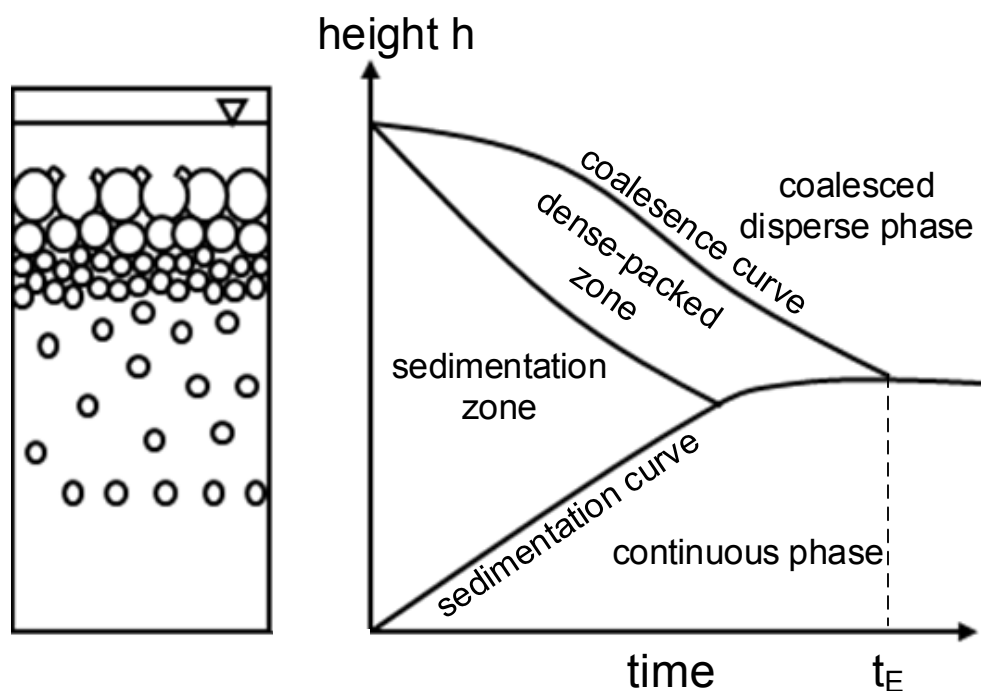


Fig. 1: Batch-settling experiment and settling curve [1]

Targets

The main goal of this work is to develop a mathematical model, which is able to describe phase separation in centrifugal settlers as accurate as it is already possible for horizontal and vertical settlers only using standardized lab-scale settling experiments. For this reason feasible models for sedimentation, coalescence and drop deformation in the dense-packed zone for horizontal and vertical settler are adopted to describe the behavior of dispersions in the centrifugal field. The model originally has been developed by Henschke et al. [1]. It is adopted and expanded step by step in a way that it accounts for the centrifugal field. For calculating the size of a centrifugal settler only the results of the batch-settling experiment, e.g. settling and coalescence time, and some user inputs like flow rate or required height of the dispersion at the end of the settler are necessary. The idea is to transfer the sedimentation and the coalescence models, which are based on equilibrium of forces. These forces, which have an effect on the droplets, are evaluated corresponding to the distance of the axis of the rotor's shaft. This leads to different sedimentation and coalescence behavior depending on where the drop is located inside the centrifuge.

Due to the need of validating the mathematical model, experiments using different standard test systems are evaluated. This is done in a centrifuge the flowrate of which is comparable with that of a DN 100 horizontal gravity settler. To get an impression of the power of centrifugal settlers in general systems, which hardly separate in horizontal gravity settlers, such as systems containing salts or surfactants, are analyzed as well. All experimental results are compared with the corresponding ones derived from experiments using a horizontal gravity settler.

References

- [1] Henschke M, Schlieper L, Pfennig A. Determination of a coalescence parameter from batch-settling experiments. Chem Eng J 2002 1/28;85(2–3):369-378.
- [2] Kopriwa N. Quantitative Beschreibung von Koaleszenzvorgängen in Extraktionskolonnen. Dissertation, Aachen; 2013.
- [3] Chatterjee M. Dimensionierung liegender Flüssig-Flüssig-Abscheider mit Platten-einbauten. Dissertation, Aachen; 1998.
- [4] Schlieper L, Chatterjee M, Henschke M, Pfennig A. Liquid-liquid phase separation in gravity settler with inclined plates. AIChE J 2004;50(4):802-811.

Influence of the Nature of an Extragent on the Rate of Extraction a REE at Vibration on a dynamical interfacial Layer

Kizim N.F., Novomoskovsk Institute of Mendeleev University of Chemical Technology, Novomoskovsk, Russia; Golubina E.N., Novomoskovsk Institute of Mendeleev University of Chemical Technology, Novomoskovsk, Russia

At the extraction and separation of rare-earth elements (REE) wide utilization was received by two reagent these are tributylphosphate (TBP) and di-(2-ethylhexyl)phosphoric acid (D2EHPA). TBP belong to neutral extragents and possess higher solubility in water, than D2EHPA which shows lower propensity to formation of cruds. D2EHPA belong to acid extragent for which formation of the cruds takes place and the influenced on the rate of extraction. Therefore the studying of kinetics of extraction a REE by solutions D2EHPA or TBP at vibration in a dynamical interfacial layer was of interest.

To estimation influence of various factors at the rate of extraction with vibrations imposed we used the enhancement factor (E) at the time set, which is defined by the relation of concentration REE in an organic phase with vibration in dynamic interfacial layer and at their absence. At the extraction of REE by the use of solutions D2EHPA, the dependence of E on time can be divided into three areas. The first area corresponds to occurrence and development in system spontaneous superficial convection (SSC), the enhancement factor and accepting values of an order 5. The second area corresponds to formation of temporal structure in a dynamical interfacial layer and the enhancement factor decreases to 1. The third area corresponds to destruction of structure of a dynamical interfacial layer and the enhancement factor accepts close to 4. The value of E and length of areas is defined by entry conditions of carrying out the process. In particular, if initial concentration D2EHPA increases from 0,01 to 0,05 M the enhancement factor decreases 2 times than that is caused by approach of front reaction to interface and higher rate of formation of a dynamical interfacial layer. At extraction of REE by solutions TBP at the time the value of E decreases, however in all cases its value exceeds 1. It is caused by reduction of the intensity SSC in interfacial layer and in near-boundary layers. At the value of the enhancement factor influences to render initial concentration of an extraction element, extragent and the nature of solvent.

The received experimental data are of interest for engineering microfluid extraction.

**Thermodynamics of the solvation
of Lead nitrate in mixed DMF-H₂O
solvents at 301.15 K.**

By

Esam A. Gomaa

**Chemistry Department, Faculty of Science,
Mansoura University, 35516-Mansoura, Egypt.**

Abstract:

The Gibbs free energies as very important thermodynamic property were evaluated for $\text{Pb}(\text{NO}_3)_2$ in mixed dimethylformamide (DMF)- H_2O solvents at 301.15 K from the experimental solubility measurements. The ratio of the ionic between lead and nitrate ions was used to divide the total Gibbs free energy of the salt into its individual contribution in the mixtures used. Libration Gibbs free energy associated with moving $\text{Pb}(\text{NO}_3)_2$ in standard gas state to standard state in solution was calculated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid $\text{Pb}(\text{NO}_3)_2$ (Cr) was also calculated and used for further evaluation.

The conventional Gibbs free energies for the cation (Pb^{2+}) and anion (NO_3^-) were estimated theoretically and also the Gibbs free energy of NO_3^- gas was evaluated and all values were discussed.

**Thermodynamics of the solvation
of Lead nitrate in mixed DMF-H₂O
solvents at 301.15 K.**

By

Esam A. Gomaa

**Chemistry Department, Faculty of Science,
Mansoura University, 35516-Mansoura, Egypt.**

Abstract:

The Gibbs free energies as very important thermodynamic property were evaluated for $\text{Pb}(\text{NO}_3)_2$ in mixed dimethylformamide (DMF)- H_2O solvents at 301.15 K from the experimental solubility measurements. The ratio of the ionic between lead and nitrate ions was used to divide the total Gibbs free energy of the salt into its individual contribution in the mixtures used. Libration Gibbs free energy assoicated with moving $\text{Pb}(\text{NO}_3)_2$ in standard gas state to standard state in solution was calculated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid $\text{Pb}(\text{NO}_3)_2$ (Cr) was also calculated and used fro further evaluation.

The conventional Gibbs free energies for the cation (Pb^{2+}) and anion (NO_3^-) were estimated theoretically and also the Gibbs free energy of NO_3^- gas was evaluated and all values were discussed.

Heteropolynuclear 3d/4f Metal Complexes in Solvent Extraction

*Norman Kelly¹, Kathleen Schnaars¹, Thomas Doert¹, Felix Hennersdorf¹, Axel Heine¹, Franziska Taube¹, Margret Acker¹, Kerstin Gloe¹, Karsten Gloe¹, Jan J. Weigand^{*1}*

Heteropolynuclear 3d/4f metal complexes with multidentate imine ligands have attracted much attention due to their interesting physicochemical properties. The studies reported here focus on the extraction behaviour of hexadentate diimine (H_2L^1 - H_2L^7) and related diamine ligands (H_2L^8 , H_2L^9) towards Zn(II), Eu(III) and Yb(III) using the extraction system $Ln(NO_3)_3$ -Zn(NO_3)₂-NaNO₃-buffer- H_2O /ligand-*n*-caprylic acid- $CHCl_3$. Significant synergistic enhancement has been observed for the Ln(III) extraction in presence of Zn(II) and *n*-caprylic acid. These effects can be interpreted by formation of heterodinuclear Zn(II)/Ln(III) complexes in the organic phase taking into account solution and solid state structural data of relevant complexes isolated by separate crystallization experiments.

Introduction

Synergistic solvent extraction of metal cations represents a successful way to control efficacy and selectivity of the phase transfer for selected species. Typical synergistic systems are characterized by combination of two extractants, mostly of neutral and acid type, leading to an enhancement of extraction in comparison with the related single systems. The effects are mainly based both on the formation of an optimum coordination sphere for the metal ion and the improvement of lipophilicity of the extracted complex [1, 2]. Supramolecular chemistry offers novel approaches [3] to the design of synergistic systems using self-assembly processes of two extractants [4] or two chelate complexes of 3d- and 4f-block metals [5, 6]. The latter suggests a further possibility for synergistic extractions namely the formation of one combined heterodinuclear metal complex binding two different metal ions by one ligand molecule in the organic phase. Chelating 2-hydroxy-3-alkoxy substituted diarylimines or diarylamines (Figure 1) are promising ligand candidates forming such heterodinuclear complexes [7]. Overall, the presented study aims towards the role of defined mixed metal complexes in selected solvent extraction systems.

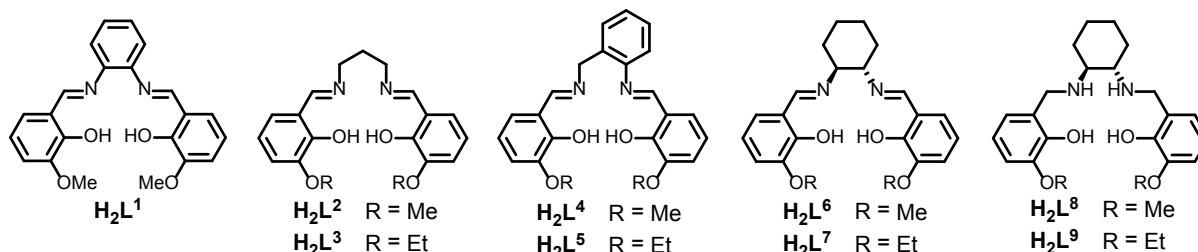


Figure 1. Structural formulas of multidentate diimine and diamine ligands studied.

¹ Technical University Dresden, Department of Chemistry and Food Chemistry, 01062 Dresden, Germany.

Methodology

All extraction experiments were performed at room temperature in microcentrifuge tubes (2 mL) by mechanical shaking. The phase ratio $V_{(org)}:V_{(w)}$ was 1:1 (0,5 mL each); the shaking time was 60 min. The organic phase consists of CHCl_3 as diluent, the ligand ($1 \cdot 10^{-2}$ M) and in some cases *n*-caprylic acid ($2 \cdot 10^{-4}$ M). The aqueous phase contained the buffer HEPES/NaOH or MES/NaOH, furthermore NaNO_3 ($5 \cdot 10^{-3}$ M) and $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{Eu}, \text{Yb}; 1 \cdot 10^{-4}$ M). In some cases $\text{Zn}(\text{NO}_3)_2$ ($1 \cdot 10^{-4}$ M) was added. All samples were centrifuged after extraction. The metal concentration in both phases (100 μL samples each) was determined radiometrically using γ -radiation ($^{152/154}\text{Eu}$, ^{169}Yb , ^{65}Zn ; NaI(Tl) scintillation counter Cobra II/Canberra-Packard).

The diimine ligands were synthesized using *Schiff*-base condensation reaction between related diamines and aldehydes in dry alcohol in a molar ratio of 1:2. The corresponding diamines are formed by the reduction of the diimines with sodium borohydride. Crystalline heterodinuclear complexes are obtained from the microwave assisted reaction (100 °C) of equimolar amounts of ligand, $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Ln}(\text{NO}_3)_3$ in alcohol or THF. Single crystals suitable for X-ray diffraction studies were formed after slow diffusion of diethylether/hexane ($v/v = 1:1$) into that solution. All structural data were collected on a Bruker AXS Kappa APEX II CCD diffractometer equipped with a graphite monochromator and Mo-K α radiation at RT.

Extraction studies

Figure 2 depicts an overview of the results of the Eu(III) and Yb(III) extraction with all imine (H_2L^1 - H_2L^7) and amine ligands (H_2L^8 , H_2L^9) at pH 6.8 with and without the addition of *n*-caprylic acid. Only the 3-methoxy substituted salophen ligand H_2L^1 extracts both metal ions quantitatively, which is in good agreement with the well-known strong complexation ability of salophen type ligands [8].

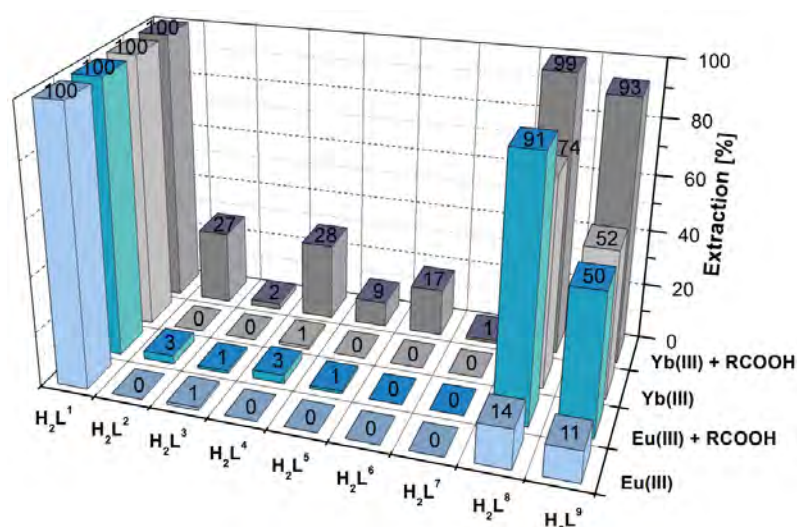


Figure 2. Eu(III) and Yb(III) extraction by H_2L^1 - H_2L^9 at pH = 6.8 with or without addition of *n*-caprylic acid (RCOOH).

Interestingly, diimines with different linkers such as ligands H_2L^2 - H_2L^7 show no extraction capability for Eu(III). In case of Yb(III) the results are quite different. There is no extraction of Yb(III) with these ligands in absence of *n*-caprylic acid. However, distinct synergistic effects are observed after addition of the acid to the organic phase containing the 2-methoxy substituted ligands H_2L^2 , H_2L^4 and H_2L^6 . The corresponding 2-ethoxy derivatives show only minor effects. In contrast to the diimines a graded extraction behavior is characteristic for the structurally related diamine derivatives H_2L^8 and H_2L^9 . Generally, these ligands show significantly higher extractabilities for both cations. The extraction of Yb(III) is also favoured over Eu(III) with strong synergistic effects in the presence of *n*-caprylic acid.

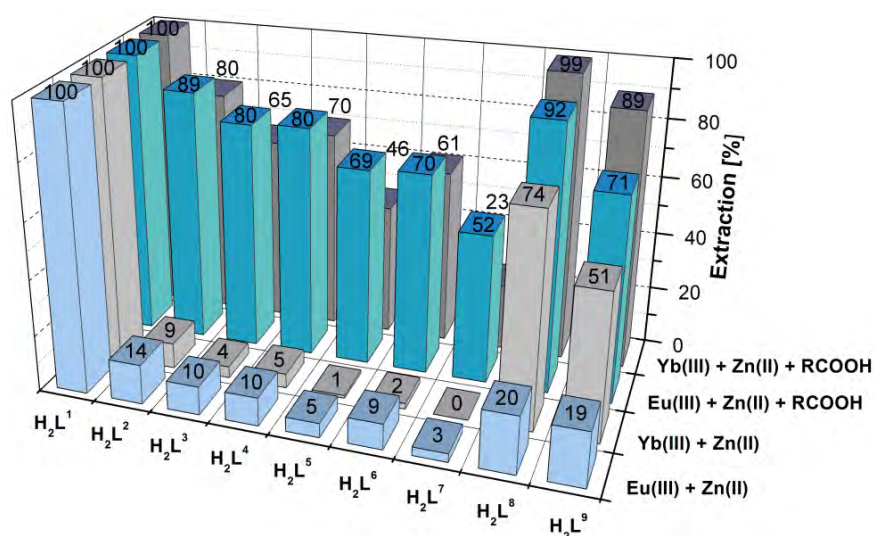


Figure 3. Eu(III) and Yb(III) extraction by H_2L^1 - H_2L^9 at pH = 6.8 in the presence of Zn(II) or Zn(II)/*n*-caprylic acid (RCOOH).

Figure 3 depicts the influence of the presence of Zn(II) with and without the addition of *n*-caprylic acid with respect to the extraction of Eu(III) and Yb(III). Except for H_2L^1 , the extractabilities are slightly higher in presence of Zn(II) in all other cases. The highest extraction is observed when the extraction system contains both Zn(II) and *n*-caprylic acid. Thus, clear evidence for the existence of a strong combined synergistic effect for the diimine ligands H_2L^2 - H_2L^7 can be derived and, to the best of our knowledge, has not been discussed in the literature so far. Under comparable conditions, the addition of Cu(II) did not or only slightly improve the extraction of Eu(III) and Yb(III). In the case of diamine ligands H_2L^8 and H_2L^9 the Eu(III) and Yb(III) extraction are only weakly influenced by the addition of Zn(II).

Interestingly, we could observe that under the chosen experimental conditions and the presence of Zn(II) and *n*-caprylic acid, the diimines H_2L^2 - H_2L^7 extract Eu(III) much better than Yb(III). This contrasts the typically observed order for the extraction of Eu(III) and Yb(III) by different extractants [6, 9]. The extraction efficiency for ligands with 2-methoxy groups (H_2L^2 , H_2L^4 and H_2L^6) is higher compared to the structure-analogous 2-ethoxy substituted ligands (H_2L^3 , H_2L^5 and H_2L^7). This

difference might be a result of slightly different steric requirements of the bulkier ethoxy groups.

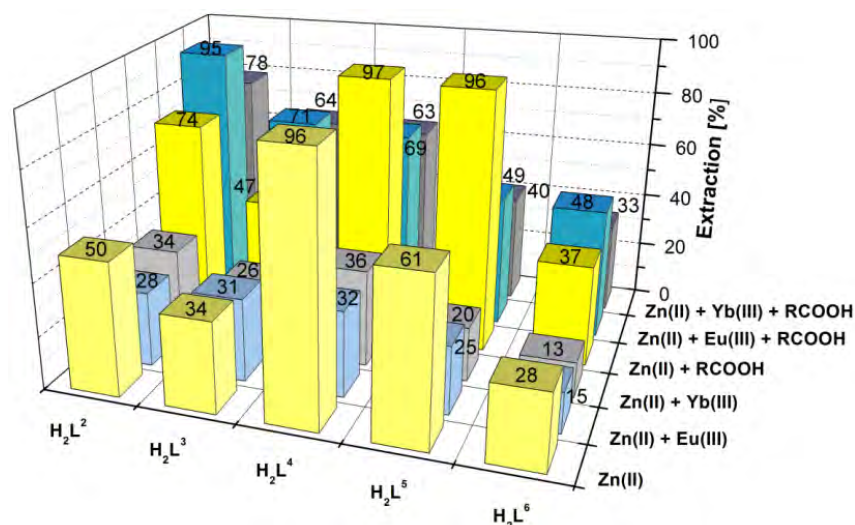


Figure 4. Zn(II) extraction by H_2L^2 - H_2L^6 at pH = 6.8 in absence and presence of Eu(III), Yb(III) or *n*-caprylic acid (RCOOH).

Figure 4 shows the results for the Zn(II) extraction by the diimine ligands H_2L^2 - H_2L^6 with and without the presence of Eu(III), Yb(III) and *n*-caprylic acid. It can be clearly demonstrated (row 1) that in the presence of Zn(II) the extractabilities rise in the order $H_2L^4 > H_2L^5 > H_2L^2 > H_2L^3 \approx H_2L^6$. The addition of Eu(III) (row 2) and Yb(III) (row 3) to the mixtures leads to a decrease of extraction capability, and a leveling of the distribution ratios is observed. In contrast the highest Zn(II) extraction has been achieved for ligands H_2L^4 and H_2L^5 in presence of *n*-caprylic acid (row 4). It was observed, that the addition of the lanthanide ions Eu(III) and Yb(III) lowers the Zn(II) extraction (row 5, 6) as in absence of *n*-caprylic acid (row 2, 3). H_2L^2 and H_2L^3 show the highest extraction capability in the presence of both ions Eu(III) or Yb(III) and *n*-caprylic acid.

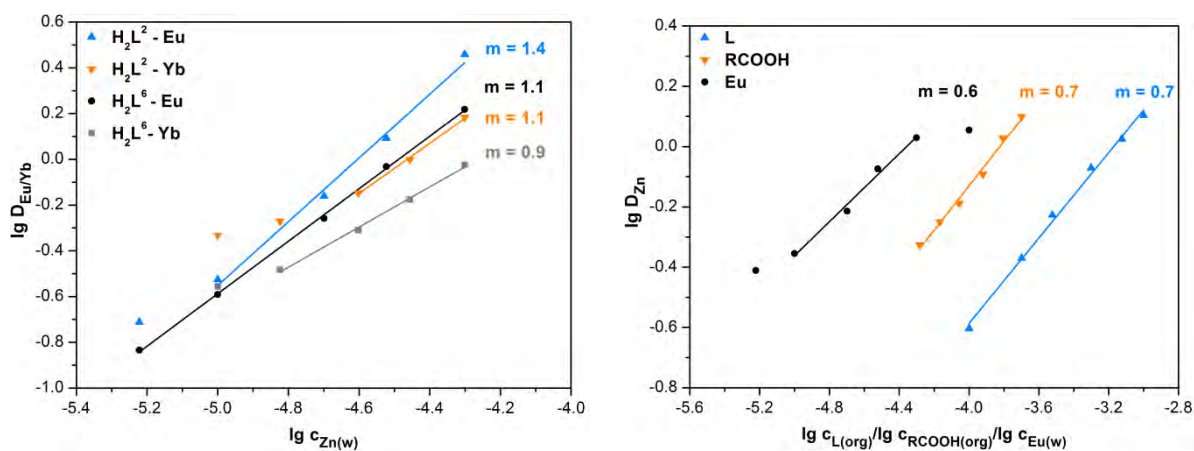


Figure 5. Eu(III) and Yb(III) extraction by H_2L^2 and H_2L^6 at pH = 6.8 in dependence on concentration of Zn(II) (left); Zn(II) extraction by H_2L^2 at pH = 6.8 in dependence on concentration of ligand, *n*-caprylic acid (RCOOH) and Eu(III) (right).

In order to gain information about the composition of the extracted complexes with diimine ligands, a series of experiments was performed involving extraction of the three metal ions in dependence on the concentration of metals, ligand and *n*-caprylic acid. Figure 5 shows selected diagrams. These results indicate apparent stoichiometries of 1:1:1:1 (Zn(II):Ln(III):H₂L:RCOOH) for the extracted complexes.

Structural studies

Significant information can be derived from solid state structures since they show possible binding patterns within complexes that play an important role in the extraction. Thus, crystal structure studies are key-important and where successful in the case of the heterodinuclear Zn(II)/Yb(III) complexes with the diimine **H₂L⁶** and the diamine **H₂L⁸** ligands (Figure 6). Both structures show a similar arrangement of the deprotonated ligands around the two metal centers with a N₂O₂ donor set for Zn(II) and O₄ donor set for Yb(III). In both complexes, one acetate anion acts as bridging ligand between the two metals. Two additional bidentate nitrate anions complete the coordination sphere of Yb(III) and compensate the positive charge of the heterodinuclear complex species. This binding motif allows optimum coordination numbers of five for zinc and nine for ytterbium.

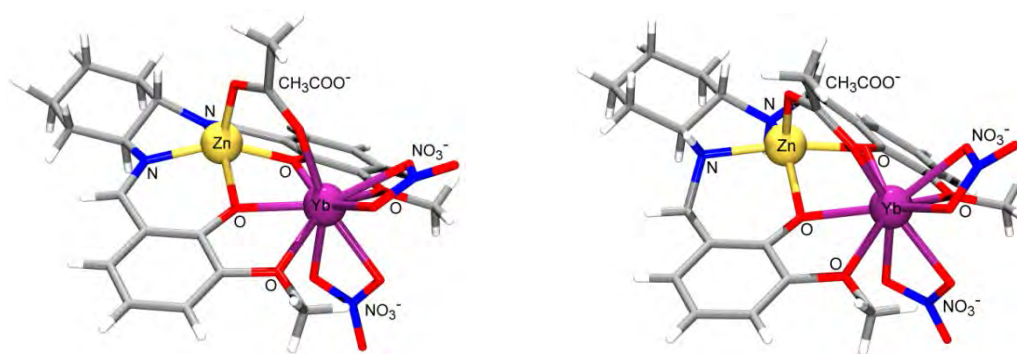
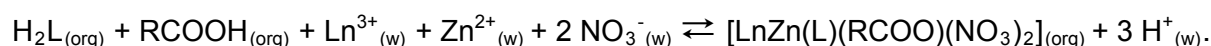


Figure 6. Molecular structures of dinuclear complexes $[Zn(L^6)(\mu\text{-CH}_3\text{COO})Yb(NO_3)_2]\cdot\text{MeOH}$ (left) and $[Zn(L^8)(\mu\text{-CH}_3\text{COO})Yb(NO_3)_2]$ (right).

It is well likely that the composition of both solid-state structures correlates well with the proposed composition of the extracted complex in the organic phase derived from extraction experiments, thus, helps to understand the observed synergistic effect.

Conclusions

Studies on the Eu(III) and Yb(III) extraction with a series of 3-alkoxy-2-hydroxyphenyl substituted diimine and diamine ligands show a graded synergistic enhancement for both cations in presence of Zn(II) and *n*-caprylic acid. This interesting behaviour is obviously based on the formation of heterodinuclear Zn(II)/Ln(III) complexes with the ligand and *n*-caprylic acid in the organic phase which can be expressed with the following equation:



According to the results of the extraction experiments together with X-ray crystal structure determination of related complexes, a three step mechanism is proposed for the synergistic extraction (Figure 7).

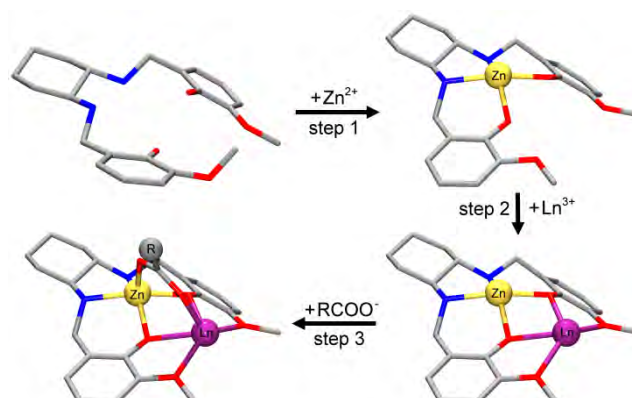


Figure 7. Proposed mechanism of synergistic extraction of Ln(III) with hexadentate diimines and diamines in presence of Zn(II) and a lipophilic carboxylic acid.

We assume that in the first step the Zn(II) forms a neutral 1:1 complex with the ligand. This preorganization is key-important to bind the lanthanide ion to form the heterodinuclear Zn(II)/Ln(III) complex in the second step. These complexes typically would coordinate up to three nitrate anions in order to compensate the positive charge. However, according to X-ray crystal structure analysis, substitution of at least one nitrate anion by at least one lipophilic carboxylate anion leads to an increased hydrophobic environment of the complex, thus, allows a better extraction capability of the complex from the aqueous solution into the organic phase in the third step 3.

Further detailed studies of such extraction systems will provide a better understanding of the proposed mechanism and the manifold influencing factors. Additionally, experiments are also planned for the entire lanthanide series and selected actinides.

Acknowledgements

The authors thank the Federal Ministry of Education and Research in Germany (BMBF-project 02NUK014A) for financial support.

References

- [1] J. Rydberg, M. Cox, C. Musikas, G. R. Choppin, Eds., *Solvent Extraction Principles and Practice*, M. Dekker, New York, **2004**.
- [2] A. H. Bond, M. L. Dietz, R. Chiarizia, *Ind. Eng. Chem. Res.* **2000**, 39, 3442-3464.
- [3] K. Gloe, K. Gloe, M. Wenzel, L. F. Lindoy, F. Li, in *Solvent Extraction and Ion Exchange: A Series of Advances*, Vol. 21, B. A. Moyer, Ed., CRC Press, Boca Raton, **2013**, pp. 1-48.
- [4] V. Gasperov, K. Gloe, A. J. Leong, L. F. Lindoy, M. S. Mahinay, H. Stephan, P. A. Tasker, K. Wichmann, in *Proc. Int. Solvent Extraction Conference, ISEC 2002*, Cape Town, K. C. Sole, P. M. Cole, J. S. Preston, D. J. Robinson, Eds., South African Institute of Mining and Metallurgy, Johannesburg, **2002**, Vol. 1, pp. 353-359.
- [5] H. Imura, M. Ebisawa, M. Kato, K. Ohashi, *J. Alloys Compd.* **2006**, 408-412, 952-957.
- [6] H. Imura, Y. Hasegawa, *Solv. Extr. Ion Exch.* **2013**, 31, 345-357.
- [7] M. Sakamoto, K. Manseki, H. Okawa, *Coord. Chem. Rev.* **2001**, 219-221, 379-414.
- [8] P. A. Vigato, S. Tamburini, *Coord. Chem. Rev.* **2004**, 248, 1717-2128.
- [9] I. Matsubayashi, E. Ishiwata, T. Shionoya, Y. Hasegawa, *Talanta* **2004**, 63, 625-633.

Solvent Extraction and Separation of Samarium(III) using Hexaacetato Calix(6)arene

D. D. Malkhede^{*1}, Y. S. Thakare², S.T. Gawhale³

Summary: Solvent extraction of samarium(III) was carried out at pH 9.0 by equilibrating five min with 10 mL of 0.0001 M of acetyl derivative of calix(6)arene in xylene. Samarium(III) was stripped quantitatively with 0.25 N HCl and determined photometrically by complexation with xylenol orange at 580 nm. The method affords the binary separation of samarium(III) from associate elements and was further extended to analysis of synthetic mixtures. The nature of the extracted species was determined from the log-log plot and has been found to be an ion-pair complex $[\text{Sm}(\text{HR})_3]_{\text{org}}$ in the organic phase. The temperature dependence of the extraction equilibrium was examined by the temperature variation method. The value of $\Delta H^\circ = -171.019 \text{ kJ mol}^{-1}$ indicates that the extraction reaction was exothermic. The metal loading capacity was also evaluated. This method was successfully used for the extraction and separation of multicomponent mixtures.

Keywords acetyl derivative, calix(6)arene, samarium(III), solvent extraction.

Introduction

The element, samarium is one of the materials used in making optical glass, carbon-arc lamps and it helps in absorbing infrared light^[1]. Today, samarium is primarily obtained through solvent extraction process of light and heavy rare earth minerals. Other techniques for the extraction and separation of samarium(III) like solid phase extraction^[2], electrochemical extraction^[3], chromatography^[4]. But there are some limitations like high reagent concentration, high equilibration period, tedious and incomplete extraction^[5-7].

Liquid-liquid extraction was widely used for the separation of rare earths. Many researchers were studied the synergetic solvent extraction and separation of Sm(III) with oxygen and phosphorous containing group and the nature of the extracted species were reported^[8-12]. It was found that the stripping with several mineral acids was only 78%. The solvent extraction of lanthanum(III) and samarium(III) from nitrate solutions by cyanex 921, cyanex 923 and cyanex 925 phosphine oxide compounds in kerosene was investigated. But stripping of samarium(III) was about 5.2% in two stages^[13].

The supramolecular compounds crown ethers, cryptands and calixarenes were found to be the best extractant for the separation of samarium(III)^[14-15]. Extraction of trivalent rare earth metal ions was carried out using different derivatives of calix(4)arene having cone-conformation^[16-17]. However, there is no systematic study carried out with calix(6)arene and its derivative for the extraction and separation of samarium(III). Therefore, an endeavor is made to explore the possibility of utilizing acetyl derivative of calix(6)arene for solvent extraction and separation of samarium(III) under microgram concentration.

Experimental

Instrumentation and Reagents

A systronics UV-Visible spectrophotometer (Model No-108) with matched 10 mm quartz cuvettes and a digital pH meter. Samarium(III) was prepared from samarium trioxide in D/W containing 1 mL concentrated HCl. Acetate buffer of pH 5.0, 0.05% xylenol orange.

Corresponding author :^{*1}Department of Chemistry, University of Pune, Pune-411 007, India, Tel.: 020-25696061; E-mail address: ddm@chem.unipune.ac.in; ²Department of Chemistry Shri Shivaji Science College, Amravati- 444 603 India; ³Department of Chemistry, AISSMS-COE, Pune-411001, India.

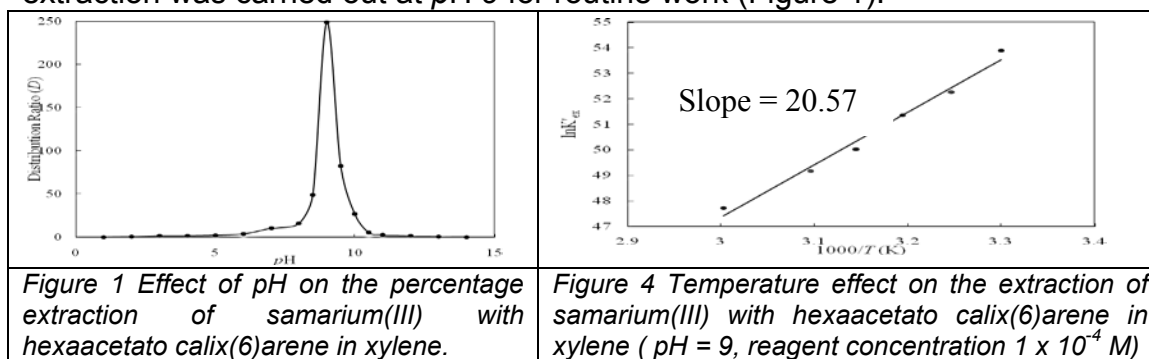
Solvent extraction procedure for determination of samarium(III)

Solvent extraction studies were carried out by mixing 10 mL of an aqueous solution containing 20 ppm of metal ion, at pH 9.0 and 10 mL, 0.0001 M hexaacetato calix(6)arene in xylene. The mixture was shaken vigorously for five min to achieve the equilibrium. The two phases were allowed to settle and separate. The organic phase was shaken with 10 mL of 0.25 N hydrochloric acid solution to back extract samarium(III). The aqueous phase was evaporated to dryness and concentration of samarium(III) present in the aqueous phase was determined spectrophotometrically with xylenol orange at 580 nm [18]. The distribution ratio and percentage extraction values for extraction of samarium(III) were calculated from concentration of samarium in each phase.

Results and Discussion

Extraction of samarium as a function of pH

Samarium(III) was extracted at different pH with 0.0001 M hexaacetato calix(6)arene in xylene. Above and below pH 9 the extraction was incomplete. Since poor complexation takes place under these conditions Therefore extraction was carried out at pH 9 for routine work (Figure 1).



Effect of period of equilibration

The kinetics of samarium extraction was studied by variation of shaking time from 30 sec to 25 min by equilibrating aqueous solution containing 20 ppm of samarium with 0.0001 M hexaacetato calix(6)arene in xylene at aqueous pH 9. The extraction of samarium was quite rapid and obtained the equilibrium within a four min.

Effect of extracting solvents

Diluents play an important role in the solvent extraction of metals. The diluent has to be cheap, non-toxic, give practically negligible losses and give good stability to the extractant. The extraction becomes quantitative in toluene and xylene because the ion-pair complex has high value of distribution ratio (249) in them. The distribution ratio for cyclohexene (4.0), chloroform (0.32), dichloromethane (0.47), 1,2 dichloroethane (0.14), benzene (0.52) were found to be less and hence were poor solvents for the solvent extraction of samarium(III). However xylene alone was preferred as it was relatively less toxic in nature, did not exhibit phenomenon of emulsification, offered a clear phase separation and easily available at low cost.

Effect of reagent concentration

Samarium(III) was extracted at pH 9 in xylene with different concentrations of acetyl derivative of calix(6)arene. The concentration was varied from 1×10^{-6} M to 2×10^{-4} M. The percentage extraction for 0.8×10^{-4} and 0.9×10^{-4} M was found to be 97.2% and 98.8% respectively. It was found

that from 1×10^{-4} and above, the extraction was quantitative. Hence 1×10^{-4} M of extractant was used for the routine work.

Nature of extracted species

The composition of extracted species was ascertained by plotting $\log D$ against $\log$ of the reagent [hexaacetato calix(6)arene] concentration at a fixed pH 9 (Figure 2) shows a slope 2.96. Therefore, the probable composition of extracted species is 1:3 i.e. $[\text{Sm}(\text{Reagent})_3]$.

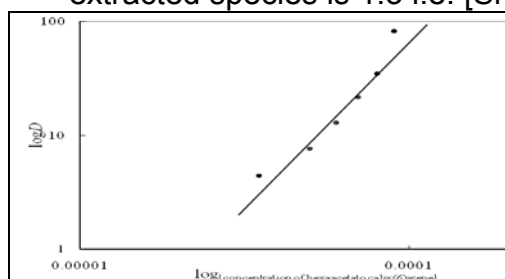


Figure 2 Effect of reagent concentration on the extraction of samarium(III)

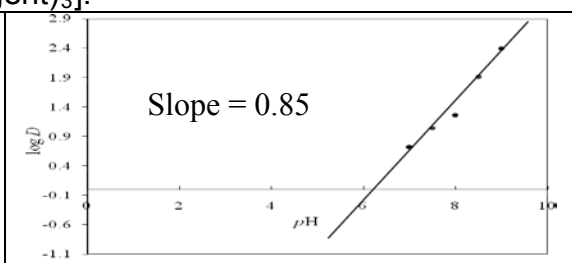


Figure 3 Plot of $\log D$ against pH for the extraction of samarium(III)

Stoichiometry of the extracted species

The possible mechanism of formation of the extracted species appeared by plotting a graph of $\log D$ versus $\log$ [Hexaacetato calix(6)arene] in xylene (Figure 2). It gives a linear graph with slope 2.96 i.e. 3.0 indicating that three ligands react with one mole of samarium(III) ion while the graph between $\log D$ and pH (Figure 3) shows a linear plot with slope 0.85, which is nearly equal to integer one, clearly shows that one ligand is being associated with one mole of metal ion in the extracted species to form an ion-pair complex $[\text{Sm}(\text{HR})_3]_{\text{org}}$ in the organic phase.

Mechanism of extraction

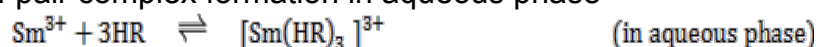
Hexaacetato calix(6)arene is a neutral ligand having six donor acetyl groups. It extracts uncharged metal complexes and undergoes the ion-pair formation. The formation of $[\text{Sm}(\text{HR})_3]_{\text{org}}$ involved cationic ion pair complex formation mechanism. It can be summarized as

1. Distribution of acetyl derivative of calix(6)arene (HR)



2. Formation of uncharged complex

Cationic ion-pair complex formation in aqueous phase



3. Transformation of ion-pair complex to organic phase



The equilibrium constant K_{ex} is defined as

$$K_{\text{ex}} = \frac{\{[\text{Sm}(\text{HR})_3]^{3+}, 3\text{OH}^{-}\}_{\text{org}}}{[\text{Sm}^{3+}]_{\text{aq}} [\text{HR}]_{\text{org}}^3 [\text{OH}^{-}]_{\text{aq}}^3} \quad (1)$$

Effect of temperature on the extraction of samarium(III)

The extraction of samarium(III) with hexaacetato calix(6)arene was carried out in the range of 298 to 353 K, following equations were used,

$\frac{d(\ln K'_{ex})}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^o}{R}$	$\Delta G^o = -2.303 RT \log K'_{ex}$	$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$
--	---------------------------------------	--

The change in enthalpy (ΔH^o), standard free energy (ΔG^o) and standard entropy change (ΔS^o) at room temperature (T) 298 K were calculated using above equations (Figure 4), (Table 1). The high negative value of standard Gibb's free energy indicates the transport of cation from the aqueous to organic phase. It favors the formation of ion-pair complex. The negative value of enthalpy indicates the reaction is exothermic and percentage extraction decreases with increase in temperature.

Table 1 Thermodynamic parameters for solvent extraction of samarium(III) with hexaacetato calix(6)arene

Temp/(K)	log D	dlog K'_{ex}	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J K ⁻¹ mol ⁻¹
298	2.396	23.396		-133.492	-125.931
303	2.396	23.396		-135.731	-116.461
308	1.69	22.69		-133.797	-120.849
313	1.297	22.298	-171.019	-133.627	-119.463
318	0.72	21.72		-132.245	-121.929
323	0.351	21.351		-132.042	-120.671
333	-0.28	20.719		-132.116	-116.826
343	-0.491	20.508		-134.686	-105.927
353	-0.624	20.576		-137.732	-94.297

Effect of stripping agents for samarium(III)

After extraction of samarium(III) using 0.0001M hexaacetato calix(6)arene at pH 9, it was stripped using various stripping agents, Table 2. For routine work, 0.25 N of hydrochloric acid was used as a stripping agent.

Table 2 Effect of stripping agents on percentage extraction of samarium(III)

Stripping agents	% Extraction					
	0.01 N	0.1 N	0.25 N	0.5 N	1 N	2 N
HNO ₃	82.4	99.6	72.8	56.0	21.6	12.0
HCl	77.2	83.6	99.6	99.0	69.6	61.2
CH ₃ COOH	99.6	99.6	99.6	92.0	76.0	65.2
HClO ₄	99.6	99.6	99.00	86.8	84.0	70.0
H ₂ SO ₄	79.2	83.6	99.6	92.0	61.2	45.6

Applications:

Foreign ions effect:

The suitability of the above developed method was examined by applying it to the separation and determination of samarium(III) in different binary mixtures which are commonly associated with it. (Table 3).

Table 3 Effect of foreign ions on the extraction and determination of samarium(III): Sm(III) = 20 ppm, equilibration period = 5 min, extractant = 10 mL of 0.0001 M of acetyl derivative of calix(6)arene in xylene, strippent = 0.25 N hydrochloric acid, A:O = 1:1

Foreign ion	Added as	Tolerance limit
Cl ⁻ , Br ⁻ , I ⁻ , Thiocynate, Thiourea, Thiosulphate, Nitrite, Carbonate	Potassium chloride, Potassium bromide, Potassium iodide, Ammonium thiocynate, Thiourea Sodium thiosulphate, Sodium acetate trihydrate, Sodium nitrite, Sodium	1000

Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Ni ²⁺ , Mo ⁶⁺ , Hf ⁴⁺ , Hg ²⁺ , Th ⁴⁺ , Pb ²⁺ , As ³⁺ , Oxalate, Tartaret Sulphate, Fluoride Bisulphite	nitrate, Sodium hydrogen carbonate LiCl, NaCl, KNO ₃ , BeCl ₂ .2H ₂ O MgCl ₂ .6H ₂ O, CaCl ₂ .2H ₂ O Ni(NO ₃) ₂ .6H ₂ O, (NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O, HfCl ₄ , HgCl ₂ , Th(NO ₃) ₄ .5H ₂ O, Pb(NO ₃) ₂ , As ₂ O ₃ , Potassium oxalate, Sodium potassium tartaret, Potassium sulphate, Sodium fluoride, Sodium bisulphite	800
Ba ²⁺ , V ⁵⁺ , Cr ³⁺ , Mn ²⁺ Fe ³⁺ , Fe ²⁺ , Co ²⁺ , Cu ²⁺ Zr ⁴⁺ , La ³⁺ , Ce ⁴⁺ , Au ³⁺ Sn ²⁺ , Sb ³⁺ , Bi ³⁺ , Citrate	BaCl ₂ .2H ₂ O, V ₂ O ₅ , Cr(NO ₃) ₃ .9H ₂ O MnCl ₂ .4H ₂ O, Fe(NO ₃) ₃ .9H ₂ O FeSO ₄ .7H ₂ O, Co(NO ₃) ₂ .6H ₂ O CuSO ₄ .5H ₂ O, ZrOCl ₂ .8H ₂ O LaO ₃ (NH ₄) ₄ , Ce(SO ₄) ₄ .2H ₂ O, HAuCl ₄ .xH ₂ O, SnCl ₂ .2H ₂ O, SbCl ₃ Bi(NO ₃) ₃ .5H ₂ O, Trisodium citrate	400
Ti ⁴⁺ , Zn ²⁺ , Y ³⁺ , Rh ³⁺ Ag ⁺ , Cd ²⁺ , Ga ³⁺	TiO ₂ , Zn(NO ₃) ₂ .6H ₂ O, Y ₂ O ₃ , RhCl ₃ .H ₂ O AgNO ₃ , CdCl ₂ .2H ₂ O, GaCl ₃	100
Orthophosphate EDTA	Sodium dihydrogen orthophosphate Disodium salt of EDTA	20
Sc ³⁺ , Al ³⁺ , In ³⁺	Sc ₂ O ₃ , AlK(SO ₄) ₂ .12H ₂ O, InCl ₃	10

Separation and determination of samarium(III) from binary mixtures:

This method permits the extraction and separation of Sm(III) from commonly associated metal ions Th(IV), Zr(IV), La(III), Y(III), Cr(III) and Fe(III) by taking advantage of difference in the extraction conditions like pH, equilibration time and stripping agents of the other metal ions (Table 4).

Table 4 Binary separation of samarium(III)

Metal ion	Amount taken(μg)	pH	Stripping agent	% Recovery	Determination method
Sm(III)	20	8.5	0.005 N HClO ₄	99.0	Xylenol orange, 580 nm
Th(IV)	25	8.5	0.05 N HNO ₃	99.2	Thoron, 545 nm
Sm(III)	20	2.0	Unextracted	99.6	Xylenol orange, 580 nm
Zr(IV)	25	2.0	2 M H ₂ SO ₄	99.5	Xylenol orange, 560 nm
Sm(III)	20	8.5	0.25 N HCl	99.5	Xylenol orange, 580 nm
La(III)	30	8.5	4 N HNO ₃	99.3	Arsenazo(III), 655 nm
Sm(III)	20	9.0	0.25 N HCl	99.5	Xylenol orange, 580 nm
Y(III)	20	6.0	4 N HNO ₃	99.35	Arsenazo(III), 660 nm
Sm(III)	20	9.0	0.25 N HCl	99.5	Xylenol orange, 580 nm
Cr(III)	30	6.5	4 N HNO ₃	99.5	Xylenol orange, 520 nm
Sm(III)	20	9.0	0.25 N HCl	99.5	Xylenol orange, 580 nm
Fe(III)	25	7.0	3 N HNO ₃	99.6	Thiocynate, 500 nm

Determination of samarium(III) in a synthetic mixtures

As it is very difficult to study the real samples for samarium(III). Its synthetic mixtures were prepared as its composition in the ores like andradite

(SmCaFe), uravorite (SmCaCr), biotite (SmMgFe), aeschynite (SmThFe), manacite (SmThLa), columbite (SmFeMn), samarskite (SmYFe) etc. (Table5).

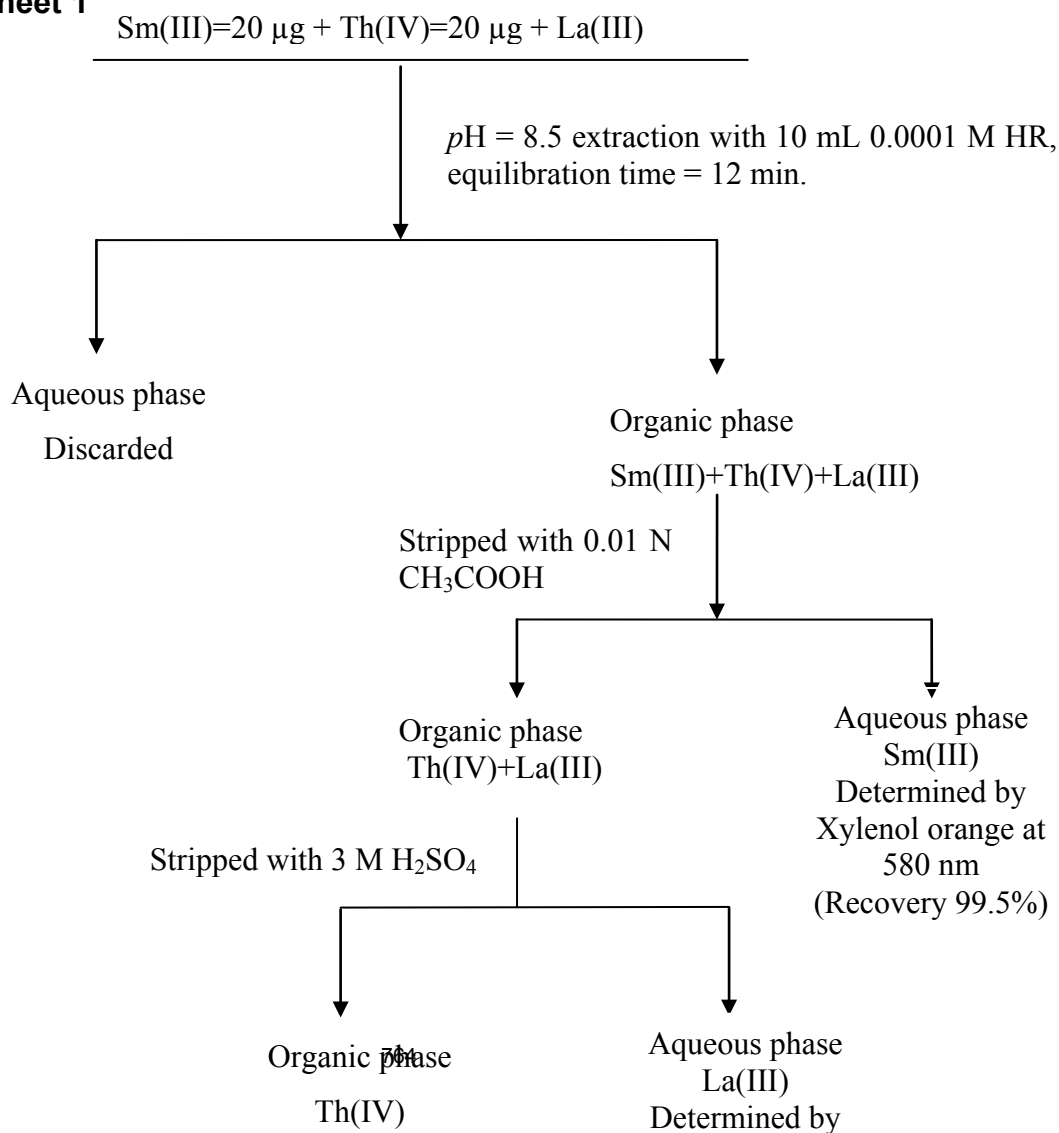
Table 5 Extraction separation and determination of samarium(III) from synthetic mixtures

Composition (ppm)	Samarium(III) found (ppm)	Mean (ppm)	% Recovery	% RSD
Sm(20)+Ca(20)+Fe(20)	19.92,19.69,19.77,19.85,19.77	19.80	99.0	0.44
Sm(20)+Ca(20)+Cr(20)	19.75,19.75,19.85,19.85,19.78	19.81	99.02	0.21
Sm(20)+Cr(20)+Fe(20)	19.84,19.77,19.84,19.92,19.69	19.81	99.06	0.45
Sm(20)+Mg(20)+Fe(20)	19.86,19.79,19.72,19.79,19.86	19.80	99.0	0.30
Sm(20)+Th(20)+Fe(20)	19.84,19.92,19.69,19.84,19.92	19.84	99.22	0.49
Sm(20)+Th(20)+La(20)	19.92,19.84,19.92,19.76,19.68	19.83	99.12	0.53
Sm(20)+Th(20)+Ce(20)	19.69,19.85,19.85,19.92,19.77	19.81	99.05	0.45
Sm(20)+Th(20)+Y(20)	19.76,19.76,19.84,19.92,19.76	19.81	99.04	0.36
Sm(20)+Mn(20)+Fe(20)	19.85,19.85,19.92,19.77,19.77	19.83	99.15	0.33
Sm(20)+Y(20)+Ce(20)	19.85,19.93,19.85,19.78, 19.78	19.84	99.18	0.32
Sm(20)+Y(20)+La(20)	19.92,19.84,19.84,19.68,19.76	19.81	99.04	0.46
Sm(20)+Ce(20)+La(20)	19.84,19.92,19.76,19.92,19.68	19.83	99.12	0.52
Sm(20)+Y(20)+Fe(20)	19.70,19.70,19.93,19.93	19.81	99.03	0.57

Extraction and separation of multicomponent mixtures

The monacite is one of the ore of samarium having composition of (SmThLa). For separation of Sm(III), Th(IV) and La(III) the pH of the mixture was maintained to 8.5 and extracted with 10 mL of 0.0001 M of hexaacetato calix(6)arene by equilibrating 12 min. Details are given in Flow Sheet 1.

Flow Sheet 1



Conclusions:

The important features of the method described herein are:

The proposed method is simple, rapid, selective and reliable. The use of relatively less toxic solvent like xylene is favorable. A very low reagent concentration 0.0001 M is required for the quantitative recovery of samarium(III). Samarium(III) can be easily stripped by low concentration of mineral acid. The equilibrium constant and thermodynamic parameters ΔH , ΔS and ΔG in the extraction of samarium(III) with acetyl derivative of calix(6)arene are evaluated. The extraction is an exothermic process and the extraction of samarium(III) decreases with increasing temperature. The extraction mechanism corresponds to an ion-pair formation in which a complex stoichiometric formula $[\text{Sm}(\text{HR})_3]_{(\text{org})}$ is formed in the organic phase. The large number of diverse ions are tolerated in high ratio. The method is free from interference from a large number of foreign ions which are often associated with naturally occurring samarium(III). Also the method is applicable to separate and determine very low concentration of samarium(III) in synthetic mixtures. The proposed method permits the selective separation of multicomponent mixtures of rare earth elements.

References:

1. John, E., *Samarium Nature's Building Blocks: An A-Z Guide to the Elements*. England, UK: Oxford University Press, 371-374 (2001).
2. Shirvani-Arani, S., Ahmadi, S.J., Bahrami-Samani, A., Ghannadi-Maragheh, M., *Anal. Chim. Acta*, **623** (1), 82-88 (2008).
3. Castrillejo, Y., Fernandez, P., Medina, J., Hernandez, P., Barrado, E., *Electrochim. Acta*, **56** (24), 8638-8644 (2011).
4. Pin, C., Briot, D., Bassin, C., Poitrasson, F., *Anal. Chim. Acta*, **298** (2), 209-217 (1994).
5. Sun, G-X., Cui, Y., Zhang, Z-W., Xu, R-Q., Jiang, R-T., Sun, S-X., *J. Serb. Chem. Soc.*, **69** (8-9), 675-681 (2004).
6. Lee, M-S., Lee, G-S., Lee, J-Y., Kim, S-D., Kim, J-S., *Taehan Kumsok, Chaeryo Hakhoechi*, **42** (10), 829-834 (2004).
7. Fujino, O., Kometani, Y., Sugiyama, M., Matsui, M., *Bunseki Kagaku*, **33** (9), 465-471 (1984).
8. Hasegawa, Y., Tamaki, S., Yajima, H., Hashimoto, B., Yaita, T., *Talanta*, **85** (3), 1543-1548 (2011).
9. Wang, X., Du, M., Liu, H., *Sep. Purif. Technol.*, **93** (1), 48-51 (2012).
10. Jia, Q., Tong, S., Li, Z., Zhou, W., Li, H., Meng, S., *Sep. Purif. Technol.*, **64** (3) 345-350 (2009).
11. Maharana, L.N., Nair, V.R., *Light Metals*, 1163-1166 (2005).
12. Rabie, K.A., *Hydrometallurgy*, **85** (2-4), 81-86 (2007).
13. El-Nadi, Y.A., El-Hefny, N.E., Daoud, J.A., *Solvent Extr. Ion Exch.*, **25** (2), 225-240 (2007).
14. Kim, J.S., Lee, C.H., Han, S.H., Suh, M.Y., *Talanta*, **45** (2), 437, (1997).
15. Ohto, K., Yano, M., Inoue, K., Yamamoto, T., Goto, M., Nakashio, F., Shinkaj, S., Nagasaki, T., *Anal. Sci.*, **11** (6), 893-902 (1995).
16. Ohto, K., Ota, H., Inoue, K., *Solvent Extr. Res. Dev. Jpn.*, **4**, p-167 (1997).
17. Yafian, M.R., Burgard, M., Matt, D., Dieleman, C.B., Rastegar, F., *Solvent Extr. Ion Exch.*, **15** (6), 975-989 (1997).
18. Snell, F.D., *Photometric and Fluorometric Methods of Analysis Metals*, Part II, Wiley Interscience Publication, New York, 1908 (1978).

Numerical analysis and experimental validation of droplet collision

*Felix Gebauer^{*1,2}, Mark W. Hlawitschka^{1,2} and Hans-Jörg Bart^{1,2}*

Computational fluid dynamics (CFD) studies were performed to describe the collision of two differently sized single droplets. The focus of attention here is on the numerical analysis of the droplet behavior during the collision and the experimental verification and validation of the numerical results, which was done with standardized high-speed imaging studies. The simulations are based on the open source code "OpenFOAM" extended by an experimental based algorithm to account for the droplet contact time. A test cell was designed to achieve a reproducible investigation of single drop coalescence. The EFCE test system toluene/water with a high interfacial tension was used for the experimental investigation and for the numerical calculation as well. The obtained numerical results could reproduce the experimental observed coalescence behavior. In addition, a deeper insight in local phenomena otherwise difficult to notice, like film rupture, the occurring velocities, pressures and micro-droplet entrainment could be obtained.

INTRODUCTION

The droplet coalescence is one of the most important and complex processes in liquid-liquid extraction, which is applied in many chemical, petrochemical and biochemical processes. The complex relationships between the various factors are not well represented by published models, although it is part of scientific research in many research groups since many years [1, 2, 3, 4]. These models need to be adjusted in the simulation by using fitting parameters for each test system and apparatus geometry. Many influence factors as ions and their concentrations (pH value, salts) and collision parameters are not correctly considered. For this reason, it is necessary to further improve the available correlations to account for e.g. surface-acting forces (van der Waals force, static electricity). For model improvement the basic understanding requires a high spatial and temporal resolution of the local phenomena. However, there is a limitation for the experimental approach to investigate the fluid hydrodynamics close to the film rupture, and an alternative is to use CFD to get locally resolved information (e.g. velocity and pressure profile between the droplets).

EXPERIMENTAL SETUP

The test cell is designed to accommodate a variety of requirements to guarantee reproducible droplet collisions (s. Fig. 1). The basic principle is an adaption to the setup described by Kamp and Kraume [5], with simple modifications, as additional side windows, to achieve a better optical accessibility. Due to the intention of well re-

¹ Chair of Separation Science and Technology, TU Kaiserslautern, Kaiserslautern, 67663, Germany

² Center for Mathematical and Computational Modelling, Kaiserslautern, 67663, Germany

producible droplet collisions a semi-dynamic approach is applied. The usage of a pendant droplet at the top and a second free rising droplet combines the advantages of a dynamic and static experimental setup. Especially an optical analysis with a high spatial and temporal resolution requires a defined and reproducible collision area due to a small image section and a short depth of field. The sufficient resolution to investigate the film drainage and the film rupture at the droplet-droplet-interface requires a macro-lens for high a magnification and a powerful backlight because of the short exposure time.

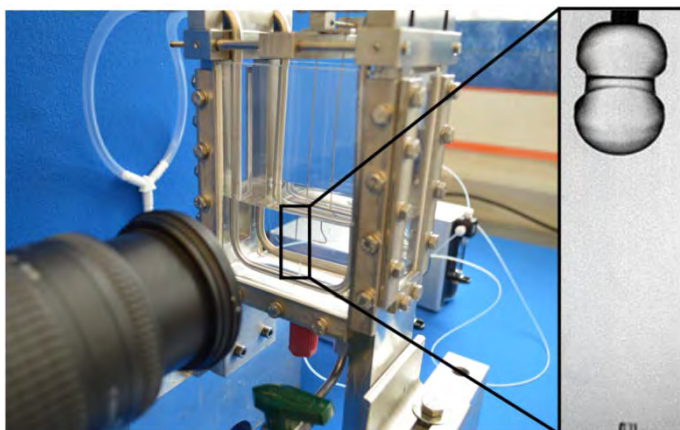


Fig. 1: Single drop test cell with high speed camera (left) and a coalescence snapshot (right).

The setup allows a high repetition rate up of to two collisions per minute and a temporal resolution up to 30000 frames per second. A careful selection of construction materials was made (PTFE, glass and stainless steel), which come into contact with a wide range test systems and is easy to clean in order to avoid impurities. The control routine for a process automatization to realize serial experiments with LabVIEW is given in Kamp and Kraume [5]

NUMERICS

The simulations are based on the OpenSource Toolbox OpenFOAM® version 2.3.0 using the multiphase Volume of Fluid (VoF) approach called *multiphaseInterFoam* with the extension of adaptive mesh refinement. Direct numerical coalescence is inhibited by the use of three phases, two for the toluene droplets and a surrounding water phase. After initial contact, artificially defined by a phase fraction of 0.999 of both dispersed phases in a single computational cell and a phase fraction of more than 0.2 for each phase, the coalescence of the droplets is initiated after the experimentally derived contact time by switching the second dispersed phase to the first dispersed phase.

For the numerical framework, a purely structured hexahedral mesh representing the experimental single droplet cell was created using the pre-processing utility blockMesh. The used boundary conditions are given in Tab. 1. The water and droplet

regions were initialized using the setFields OpenFOAM® utility. It is then on the solver to adapt the time step to keep the Courant number below 0.5. The used refinement conditions and initial solve options are given in Tab. 2. In final simulations a mesh refinement at each time step was used. The simulations were done on a single core (Xeon E5345, 2.33 GHz, with a maximum requested 8GB RAM) using the ELWE-Cluster from the University of Kaiserslautern.

Tab. 1: Boundary conditions

	Velocity	Phase fraction
Needle	zeroGradient	
Outer box	zeroGradient	zeroGradient
Inlet	fixedValue (0 0 0)	zeroGradient

Tab. 2: Refinement conditions and solve options

Boundary	Value
Refinement	Every step
Maximum cell number	2 000 000
Maximum refinement	3
Initial time step	0.00001 s
Max Courant number	0.5
Write interval	0.00005 s

EXPERIMENTAL AND NUMERICAL RESULTS

In a first step, a new CFD model with the geometrical specifications of the experimental test cell was implemented (s. Fig. 2). A result for the adaptive mesh refinement is shown in Fig. 3 prior the collision of the pendant and the rising droplet. Due to the dynamic refinement of the transient simulation the maximum number of grid cells reaches nearly 1.6 million. The relevant area around the droplet interface is covered with a very fine mesh, where the continuous phase is surrounding the droplets, and the inside of the droplets is described with a coarser mesh.

In Fig. 4, the simulated droplet coalescence is compared to the experimental coalescence investigations. The example shows a droplet coalescence of two unequal sized droplets (2.2 mm and 3 mm), where the upper one is fixed at the cannula. The simulated data is shown as a cut through the center of the domain (2D plot). The lower droplet rises and it comes to elliptical deformations of both droplets

before the actual contact. The coalescence occurs after a time of 19.1 ms, leading to an entrainment of water in the simulation, which could also be observed experimental studies.

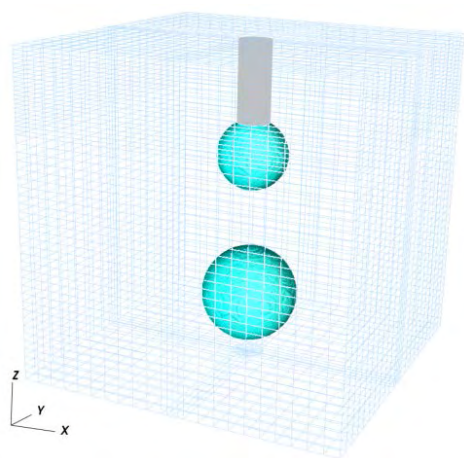


Fig. 2: CFD Model of the experimental setup.

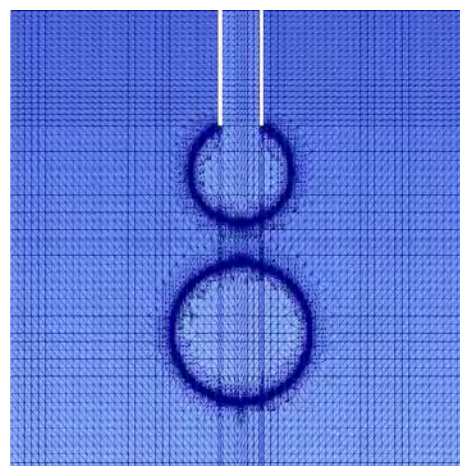


Fig. 3: Refined mesh at the droplets interfaces.

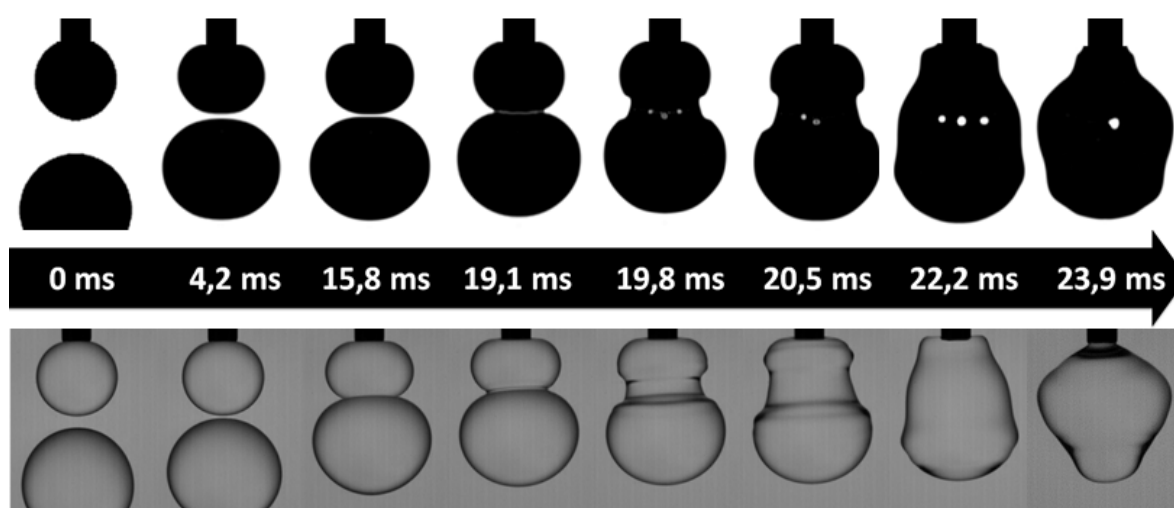


Fig. 4: Image sequence of coalescence; CFD (top); experimental (bottom).

The simulated droplet coalescence with our implemented contact time fits very well to the experimental observed coalescence behavior. Fig. 5 (left, phase fraction) shows the formation of the entrainment during coalescence, which can be attributed to the fact that the critical film thickness or the film confluence is achieved in the edge region of the contact area before the continuous phase can completely flow out of the contact area. Fig. 5 (right) shows an increase in pressure in the contact area by forming micro water droplets inside the toluene droplets.

During the collision of both droplets, a parabolic profile of the liquid film thickness is observed and given by the phase fraction plot in Fig. 5. In the circular edge region, the smallest film thickness can be observed, which finally leads to the entrainment of the continuous phase after the film rupture in the edge region (Fig. 6).

Experimental investigations to describe the processes around the droplet-droplet-interface showed the limits of the optical accessibility. With the help of the CFD, the local velocity and pressure profile could be visualized during the coalescence process (s. Fig. 7). The local velocity maximum during the formation of a coalescence bridge directly after the film rupture becomes particularly visible. Furthermore, a significant local increase of pressure is noticed with the entrainment of continuous phase after the coalescence.

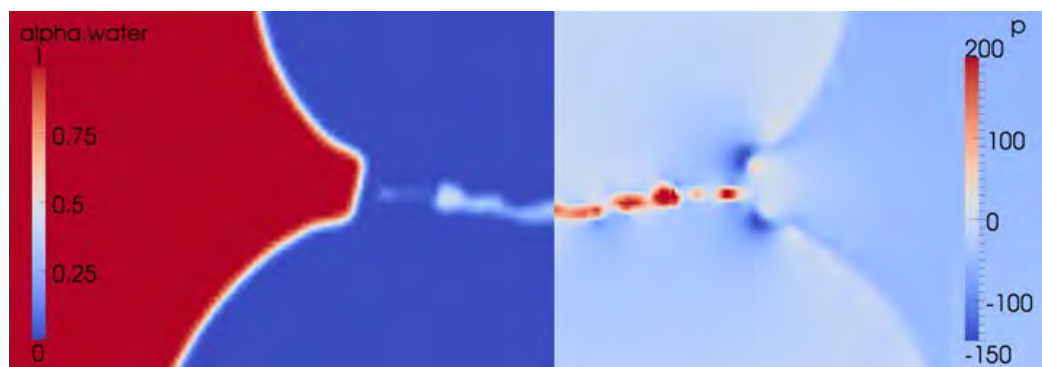


Fig. 5: Entrainment of continuous phase after coalescence; phase fraction (left); pressure (right).



Fig. 6: Sequence of film rupture and coalescence bridge building, water phase fraction is monitored.

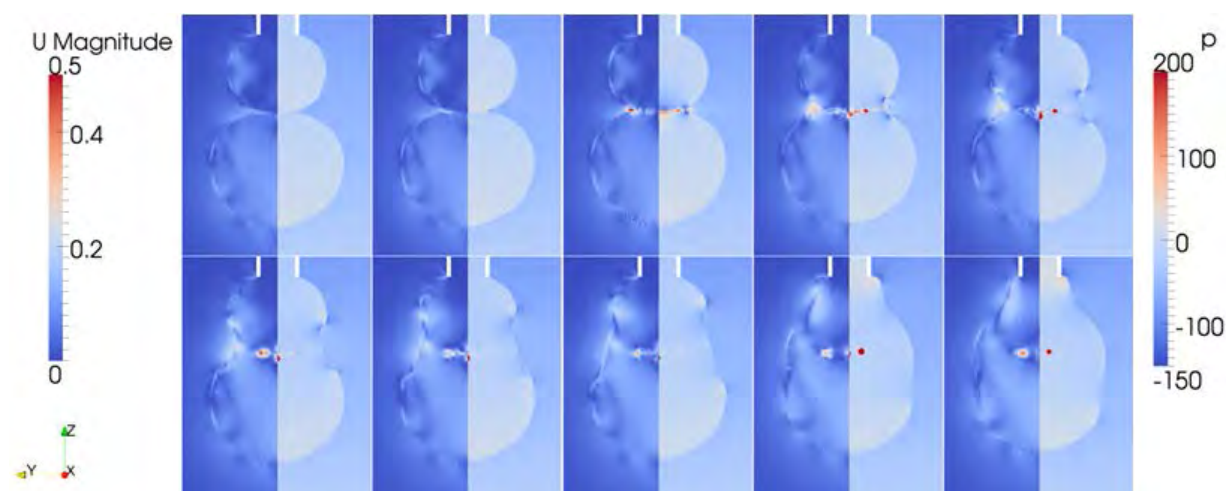


Fig. 7: Velocity (left) and pressure (right) gradient between the droplets.

CONCLUSIONS AND OUTLOOK

The experimental investigations of droplet coalescence are limited by the spatial accessibility of the experimental setup and the measurement techniques, which can be overcome by CFD simulations. Therefore, an OpenSource CFD code was extended to account for the droplet contact time before a coalescence event. The simulation of a single droplet coalescence is in good agreement with experimental data, where the temporal development of the droplet deformation could be described. Local spatial and time resolved information is given by the CFD simulation regarding the increase of pressure during droplet approach and the parabolic film thickness. The entrainment of continuous phase after coalescence can be described by the CFD simulations, where further studies regarding the mesh influence and contact time are required. The final aim will be the implementation of surface acting forces (e.g. van-der-Waals, static electricity) to describe the influence of ionic ingredients on the coalescence.

REFERENCES

- [1] T. Tobin, D. Ramkrishna, *AIChE J.* 1992 38 (8), 1199-1205. DOI: 10.1002/aic.690380807.
- [2] C. Coulaloglou, L. Tavlarides, *Chem. Eng. Sci.* 1977 32 (11), 1289-1297. DOI: 10.1016/0009-2509(77)85023-9.
- [3] G. Scheele, D. Leng, *Chem. Eng. Sci.* 1971 26 (11), 1867-1879. DOI: 10.1016/0009-2509(71)86030-X.
- [4] R. T. Eiswirth, H.-J. Bart, *Experimental Investigation of Droplet-Droplet-Coalescence in Liquid-Liquid-Systems, Solvent Extraction: Fundamentals to Industrial Applications*, ed. C.A. Moyer, Vol. II, Can. Inst. Min. Met. & Petroleum, Montréal 2008.
- [5] J. Kamp, M. Kraume, *Chem. Eng. Res. Des.* 2014. DOI: 10.1016/j.cherd.2013.12.023.

ACKNOWLEDGEMENT

The authors want to thank the DFG for their financial support (BA 1569/55-1) and the RHRK for the computational resources (ELWE-Cluster).

Activity coefficients of di-(2-ethyl hexyl) phosphoric acid by vapor pressure osmometry and slope analysis

Michael Gray^{*1} *Dr. Peter Zalupski*², *Dr. Giuseppe Modolo*³ and *Dr. Mikael Nilsson*¹

Activity coefficients have been calculated for the extractant di(2-ethyl hexyl) phosphoric acid (HDEHP) in the diluent *n*-dodecane using both vapor pressure osmometry and slope analysis techniques. Thermodynamic equilibrium models to determine metal distribution ratios in a liquid-liquid extraction process should be formulated in terms of chemical activity and not chemical concentration for accurate results over a wide range of conditions. Concentration data on HDEHP can be converted to chemical activity using the activity coefficient results presented here, aiding in the fundamental thermodynamic treatment of processes involving this extractant. As HDEHP is used both industrially and features in many advanced separations processes for components in spent nuclear fuel, this data is of immediate value. In addition to the VPO and slope analysis results for HDEHP in *n*-dodecane, VPO results are presented for HDEHP in several additional low polarity diluents at different temperatures, including toluene and *n*-octane. The analysis of the osmometry data is based on the theory of Scatchard and Hildebrand to obtain the solubility parameter for HDEHP dimer at multiple temperatures. This parameter provides a versatile tool to determine activity coefficients for components in the organic phase. However, the analysis results also demonstrate certain limitations to this one parameter model as will be discussed. A diluent dependence of the calculated solubility parameter for HDEHP dimer is contrary to the theory of Scatchard and Hildebrand which suggests that making use of this one parameter model to calculate activity coefficients requires caution when applied to different classes of diluents. Similarly, the advantages and limitations to the activity coefficient for HDEHP calculated using slope analysis are presented.

Introduction

Di-2-(ethylhexyl) phosphoric acid, known as HDEHP and DEHPA, is present in industrial solvent extraction processes and features in many advanced spent nuclear material separations, and has been the subject of an extensive number of studies. Yet there are aspects of the behavior of HDEHP relevant to these solvent extraction systems that are unclear on a fundamental thermodynamic level and would benefit from further study and characterization.

Baes investigated the solution behavior of HDEHP using both isopiestic techniques and slope analysis techniques to determine the activity coefficient of HDEHP dimer and explain the deviation from the ideal hypothesized extraction mechanism.¹ However, the two techniques showed unresolved discrepancy. Later Danesi et al. published additional slope analysis studies on the activity coefficient of HDEHP

1 University of California Irvine, Dept. of Chemical Engineering, nilssonm@uci.edu

2 Idaho National Laboratory, Aqueous Separations Division

3 Forschungszentrum Jülich, IEK-6

dimer.² Despite obtaining results with some overlapping values for the activity coefficients, the trends did not match between these newer extraction studies and the isopiestic study done by Baes.

In an effort to improve the characterization of HDEHP and determine activity coefficients, investigations were carried out using vapor pressure osmometry (VPO), and those initial results have been recently published.³ The data was modeled using the theory of Scatchard and Hildebrand, as summarized in the earlier article, for HDEHP in toluene, *n*-dodecane, and cyclooctane at different temperatures due to differences in vapor pressure. The solubility parameter obtained for HDEHP allows calculation of the activity coefficient. This current study reports the results for additional diluents and temperatures, and provides comparison with both the slope analysis results of Danesi et al, and also activity coefficients calculated from slope analysis performed on new data.

Methods

Binary solutions of HDEHP or *n*-tetracosane (as the VPO standard) in *n*-dodecane, toluene, and *n*-octane were prepared gravimetrically with concentrations ranging from approximately 0.005 to 0.05 mole fraction. Solutions of HDEHP and *n*-tetracosane in toluene in these concentration ranges were contacted with 0.95 M nitric acid to determine the effect of aqueous saturated phases on the solution behavior of HDEHP and the performance of the osmometer.

HDEHP with 95% purity from Acros Organics was further purified using the copper precipitation method.⁴ After purification the result was checked by titration, and was above 99.5% for all batches. All other chemical were used as received at greater than 99% purity.

These solutions were injected as samples in the UIC 833 Vapor pressure osmometer to obtain data on the diluent activity. The new osmometry data sets were collected in the same manner as the data presented in an earlier paper.³ Triplicate measurements were taken for each solution concentration, and the average value was used. When a solution is injected onto a temperature sensitive thermistor in the thermostatted osmometer chamber, diluent vapor condenses on the solution droplet leading to a temperature increase. The temperature increase of the thermistor leads to a voltage imbalance created in the circuit, which is the instrument output. This voltage readout is related to the diluent activity via Eq. 1. A more extensive treatment of the theory is available in literature.⁵

$$\Delta V = K(1 - \gamma_1 x_1) \quad \text{Eq. 1}$$

Where ΔV is the voltage readout of the osmometer; γ_1 and x_1 are the activity coefficient and mole fraction of the solvent, respectively; and K is the machine constant, which must be determined by calibration using standards of known solution behavior for each diluent and temperature. For these experiments the standard was *n*-tetracosane.

Europium distribution data was collected to characterize HDEHP using slope analysis. Batch extractions were carried out using europium-152 tracer. Fourteen concentrations of HDEHP were prepared from $5.5 \cdot 10^{-4}$ M to 0.103 M in dodecane. The aqueous phase was $3.9 \cdot 10^{-3}$ M nitric acid in 1.0 M ammonium nitrate. Equal phase volumes were used for each extraction of 500 μ l or 700 μ l. Each sample was contacted at 25°C using a vortex mixer for 15 minutes followed by 15 minutes in a centrifuge for phase disengagement. Then 200 μ l samples were then taken for spectroscopy using an HPGE detector.

Results

Figure 1 presents an example of the raw data from the osmometer. This data is for HDEHP-toluene and *n*-tetracosane-toluene binary solutions at a temperature of 45°C. The data set also shows the VPO data for solutions contacted with the 0.95M nitric acid, given by the gray points. These aqueous contacted solutions give results exactly following the trend of the non-contacted “dry” solutions, within experimental uncertainties. A total of eight data sets have been collected similar to the set shown here except for the water contact. The other sets did not include data on water contacted phases. Some of these have been presented and discussed previously.³

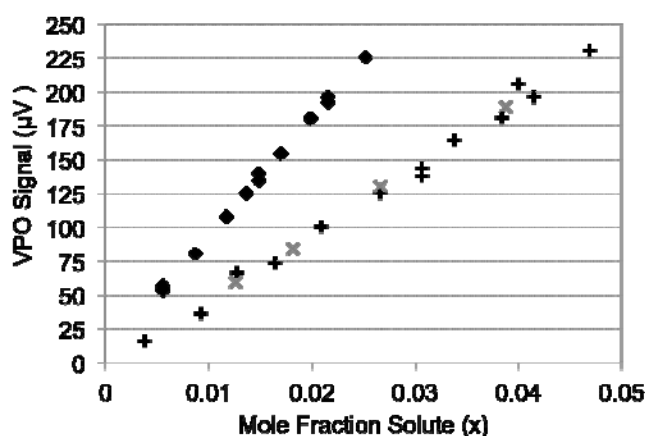


Fig. 1. VPO data for HDEHP and tetracosane in toluene at 45°C. ◆ Tetracosane, + HDEHP, x HDEHP contacted with 0.95M nitric acid.

The results for europium extraction by HDEHP as a function of concentration are presented in Fig. 2. The line indicates a slope of 3, which corresponds to the idealized extraction mechanism under low metal loading conditions where three dimers bind to one trivalent metal ion to bring it into the organic phase. The dashed line shows the empirical fit that was integrated to obtain the activity coefficients of HDEHP dimer.

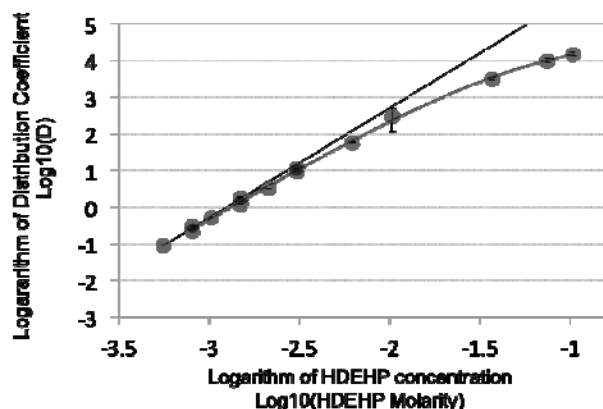


Fig. 2. Extraction results for europium distribution between 0.0039M nitric acid at 1.0M ionic strength and varying concentration of HDEHP in Dodecane. The high distribution values show deviation from the line showing a slope of 3. Error bars show the uncertainty in the distribution coefficients due to peak fitting and the inherent randomness in radioactive decay. Phase contamination might cause more scatter in the deviation.

Analysis

The VPO data yields the diluent activity after the machine constant for each VPO data set, K , in Eq. 1 is determined by fitting to the data for the standard, *n*-tetracosane. With K determined, Eq. 1 yields the diluent activity for the solutions of HDEHP. This data can then be used to fit for the Hildebrand solubility parameter, $\bar{\delta}$, shown in Eq. 2 for the activity coefficient.⁶

$$\ln(\gamma_i) = \frac{V_i}{RT} (\delta_i - \bar{\delta})^2 + \ln\left(\frac{V_i}{V_m}\right) + 1 - \frac{V_i}{V_m} \quad \text{Eq. 2}$$

Where V_i (cm³/mol) is the molar volume of component i ; δ_i (MPa^{1/2}) is the solubility parameter of component i ; V_m is the number average molar volume; and $\bar{\delta}$ is the volume average solubility parameter. Physical properties were obtained from the DIPPR database,⁷ except for the molar volume of HDEHP, which was extrapolated from published data.⁸

After the solubility parameter for HDEHP dimer was obtained by fitting Eq 2. to the VPO data for each diluent and temperature, the activity coefficient of HDEHP dimer may be calculated at each of these temperatures. In theory, the activity coefficient of HDEHP can be calculated in diluents other than the one used to determine the solubility parameter. However, some caution must be used as a difference was found for the solubility parameter of HDEHP dimer when calculated using data for toluene at 45°C versus the data for HDEHP in *n*-octane at 45°C. This data is illustrated in Fig. 4 showing the temperature trend of the solubility parameter as calculated for each diluent. The different temperatures are required due to the differing vapor pressures, as the VPO requires a sufficient vapor pressure to operate effectively.

At this point, it is undetermined whether the discrepancy between the results from the toluene data and *n*-octane data is due to a shortcoming of the theory, or quality of the *n*-octane data. Two sets of data were collected for toluene at 45°C, and both yielded the same value for the solubility parameter, within error. A second run for HDEHP in *n*-octane is planned as the current result does not match the temperature trend of the solubility parameter that is apparent from the graph. However, the theory underlying the solubility parameters when applied to HDEHP in these diluents may lead to this

inaccuracy. The Scatchard-Hildebrand equation is best suited for mixtures where dispersion forces dominated the interaction, such as alkanes, rather than systems where polar or hydrogen bonding forces become significant, as is the case for HDEHP or toluene.

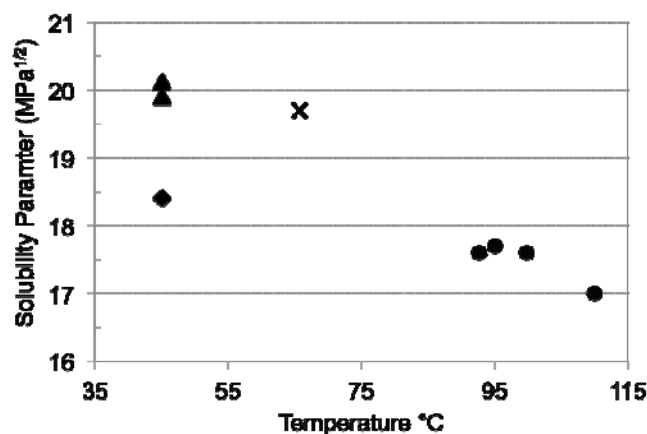


Fig. 3. The temperature trend for HDEHP dimer solubility parameter.
 • Data from *n*-dodecane X Data from Cyclooctane ▲ Data from Toluene
 ◆ *n*-octane

To analyze the data on the extraction of Eu-152 tracer by HDEHP, the parameters in the empirical function given in Eq. 3 were fit to the data

$$\log_{10} D = 3 \log_{10}[HA] + A[HA]^B + C \quad \text{Eq. 3}$$

where D is the distribution ratio of europium; $[HA]$ is the molar concentration of HDEHP; and A , B , and C are fitting parameters. These were determined to be -6.01, 0.564, and 8.77, respectively.

This empirical equation allows easy integration of the model for determining the dimer activity from slope analysis using Eq. 4²

$$\frac{\partial \log_{10} D}{\partial \log_{10}[HA]} = 3 + \frac{\partial \log_{10} \gamma_{[HDEHP]_2}}{\partial \log_{10}[HA]} \quad \text{Eq. 4}$$

Based on the fitted parameters, and referencing the activity coefficient to be 1 for dilute systems of HDEHP, the activity coefficient of HDEHP dimer is given by the empirical equation

$$\log_{10} \gamma = -2.00[HA]^{0.5644} \quad \text{Eq. 5}$$

The activity coefficient for HDEHP dimer calculated from both the VPO data and the extraction data is presented in Fig. 4 along with the activity coefficient results presented by Danesi et al. As is evident, the VPO results and the results of Danesi are the same at some values, but show slightly disagreeing trends. However, the slope analysis results for HDEHP from the 0.0039M nitric acid/1.0M ammonium nitrate solutions show significant deviations from the results based on the europium extraction from the 0.0524M hydrochloric acid/ 0.95M sodium chloride solution results by Danesi et al.

At the high distribution ratios in the extraction study, phase contamination or a secondary interaction involving the ammonium nitrate may be leading to the lower

distribution ratios rather than pure activity effects of HDEHP, and further experiments are being conducted.

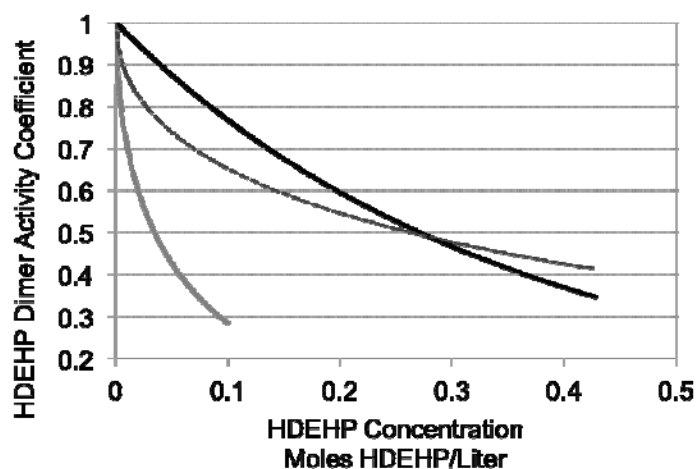


Fig. 4 Comparison of calculated activity coefficients for HDEHP dimer in dodecane. — Solubility parameter results from toluene data at 45°C, - - - Slope analysis by Danesi² Dodecane/HCL at 25°C, - Slope analysis in Dodecane/HNO₃ at 25°C

Conclusions

Continued VPO experiments are needed to resolve the difference with the value of the activity coefficient of HDEHP found from *n*-octane, and additional europium extractions are being carried out.

Acknowledgements

Work was supported under subcontract number 107827 with the Idaho National Laboratory, Fuel Cycle Research and Development program (FCR&D), U.S. DOE, Office of Nuclear Energy.

References

1. C. F. BAES, J. Phys. Chem. 66, 1629-1634 (1962)
2. P. R. DANESI; G. F. VANDEGRIFT, Inorg. Nucl. Chem. Lett. 17, 3-4, 109-115 (1981)
3. M. F. GRAY; P. ZALUPSKI; M. NILSSON, Solvent Extr. Ion Exch. 31, 5, 550-563 (2013)
4. J. A. PARTRIDGE; R.C. JENSEN, J. Inorg. Nucl. Chem. 31, 8, 2587-2589 (1969)
5. K. KAMIDE, 高分子化学 (Kobunshi Kagaku), 25, 282, 648-656 (1968)
6. A.F.M BARTON, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, Ch. 4, CRC Press: Boca Raton, FL; 1991.
7. Design Institute for Physical Properties, DIPPR Project 801 Design Institute for Physical Property Research/AIChE. Online at: <http://www.knovel.com>
8. L. D. KOEKEMOER; M.J.G. BADENHORST; R. C. EVERSON, J. Chem. Eng. Data 50, 587-590 (2005)

Study of the aggregation of Cyanex 272 and Ionquest 290 by Vapor Pressure Osmometry

Marie Dehestru ^{*1,2}, Moncef Stambouli ¹, Morgan Gohin ², Dominique Pareau ¹,
Yves Le Quesne ²

Summary

The extractant molecule bis-2,4,4-trimethylpentyl phosphoric acid (BTMPP), is the active component of Cyanex 272 and Ionquest 290. BTMPP is known to form aggregates, especially dimers, in nonpolar organic diluents. The aggregation results from strong intermolecular hydrogen bonding between the P=O and P-OH groups. The knowledge of this aggregation is important, as it influences solvent extraction equilibria by reducing the amount of extractant molecules available for the extraction.

In the present work, aggregation of BTMPP was studied by Vapor Pressure Osmometry (VPO). The average numbers of aggregation were calculated for several solutions containing various concentrations of extractant for both Cyanex 272 and Ionquest 290. The average numbers of aggregation are around 2 – 2.2 at 50°C, depending on the concentration of BTMPP. It was concluded that BTMPP forms monomers, dimers and trimers. Then the equilibrium constants of dimerization and trimerization were estimated by a numerical optimization procedure developed on Matlab. The logarithms of the constants of dimerization and trimerization are respectively estimated at 3.0 ± 0.2 and 4.8 ± 0.2 at 50°C (constants in L/mol and L²/mol² resp.). VPO measurements were also conducted at 43°C and 60°C. Only small differences were observed for the average numbers of aggregation and the equilibrium constants calculated at 43°C, 50°C and 60°C. It was concluded that the temperature dependence of the aggregation of BTMPP is low from 43°C to 60°C.

Introduction

The extractant molecule bis-2,4,4-trimethylpentyl phosphoric acid (BTMPP), is the active component of Cyanex 272 and Ionquest 290 (CX272 and IQ290 resp.). BTMPP is widely studied for its hydrometallurgical applications of metals separation, especially cobalt and nickel. It is generally accepted that monobasic organophosphorus acid extractants like BTMPP form dimers in diluents of low polarity. The dimer arises from strong intermolecular hydrogen bonding between the P=O and P-OH groups as shown Figure 1. [1], [2].

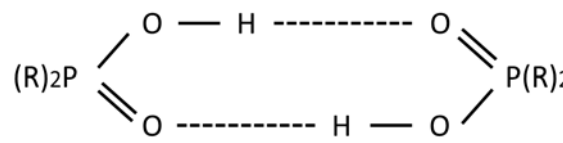


Figure 1: Schema of dimer BTMPP

The knowledge of the aggregation of an extractant is important, as it influences the extraction equilibria by reducing the amount of extractant molecules available for the extraction. Most of the studies on solvent extraction by BTMPP consider that BTMPP exists only as dimer in the organic phase. The predominance of the dimer form was demonstrated in toluene by Vapor Pressure Osmometry (VPO) [2], [3]. The existence of monomers and of other more aggregated forms such as

* marie.dehestru@erametgroup.com

+33 1 30 66 55 79, 1 av. Albert Einstein – BP120 – F – 78193 TRAPPES CEDEX – FRANCE

¹ Process Engineering and Material Lab, Ecole Centrale Paris, France

² Eramet Research, France

trimer is also suggested [4]. Indirect methods involving biphasic equilibriums were used to estimate the value of the equilibrium constant of dimerization (Table 1). The dimerization constant is optimized together with the constants of the other equilibriums involved (distribution, dissociation...), in order to fit measured data such as pH, distribution of BTMPP or conductivity [5]–[9].

Authors/ ref	Experimental conditions	Log(K_{dim})	Method of determination
Biswas et al. [5]	Pure BTMPP in kerosene, 30°C	2.28	Biphasic distribution
Ke-An et al. [6]	CHCl ₃ , 25°C	2.26	Biphasic distribution
	CDCl ₃ , 25°C	2.31	
Fu et al. [7]	Pure BTMPP in Kerosene, 25°C	4.2	Conductivity measurement
Nagaosa et al. [8]	CX272 in kerosene, 25°C	4.56	Biphasic potentiometric titration
Sella et al. [9]	CX272 in Kerosene, 25°C	3	Biphasic potentiometric titration
Sastre et al. [10]	Pure BTMPP in toluene, 30°C	3.07	VPO
	37°C	2.92	
	50°C	2.57	

Table 1: review of the dimerization constants of CX272 or pure BTMPP available in the literature, with the conditions and the methods used for their estimation.

It was pointed out that dimerization constant cannot be determined precisely from these biphasic methods, because of the too low impact of the variation of the constant on the measured data [7], [9]. This could explain the dispersion observed between the constants reported in Table 2. Furthermore, some studies are conducted with BTMPP purified from CX272 whereas others use non-purified CX272. Sastre et al. estimated the dimerization constant of BTMPP by VPO [10].

In the present work, the aggregation of BTMPP is studied by VPO at 50°C, temperature commonly chosen for industrial applications. The aggregation constants are calculated by least square optimization method. In order to know the impact of temperature, tests were also conducted at 43°C and 60°C.

Material and methods

Reagents

The extractants Cyanex 272 (Cytec) and Ionquest 290 (Rhodia) are used without further purification. The diluents chosen for the VPO tests are n-hexane (Sigma-Aldrich) for the measurements at 43°C and 50°C, and n-heptane (Panreac) at 60°C, because their boiling points (69°C and 98°C resp.) are adapted to VPO at such temperatures and they have dielectric properties similar to kerosene. We assumed that the length of chain of the alkane diluent does not modify the aggregation of BTMPP. Tri-octylamine (TOA) (Sigma-Aldrich) is used as standard because it is known to be monomeric and to dissolve well in alkane diluents [11]. All the solutions are prepared by weighting.

VPO technique

VPO consists in measuring the difference of resistance ΔR between two thermistors: one containing a drop of pure diluent suspended, and the other a drop of solution (diluent + solute). The two thermistors are located in an atmosphere saturated with

diluent vapor. ΔR is directly proportional to the difference of temperature between the thermistors. It is also a function of the difference in vapor pressure of the two drops, and so directly related to the activity of the diluent, or to the apparent molar fraction of solutes in the solution (X_{app}). X_{app} is the molar fraction of all the solute species present in the solution:

$$X_{app} = \frac{n_{monomer} + n_{dimer} + \dots}{n_{diluent} + n_{monomer} + n_{dimer} + \dots}$$

The simplification of the equation of Clausius Clapeyron leads to a proportional relation between ΔR and X_{app} [12].

$$\Delta R = K \cdot X_{app} \quad (\text{constant } K \text{ determined by calibration})$$

This proportional relation, valid for low X_{app} , can also be used with molalities instead of molar fractions for solutions of low molalities. Although most of the VPO studies work with molalities for convenience, we chose to work with molar fractions that led to better calibrations than molalities because of the high concentrations of our solutions.

VPO experiments are carried out at 43°C, 50°C and 60°C using a Knauer K-7000 Vapor pressure osmometer. The drop size is kept as constant as possible. Due to the time dependence of the signal, the measurements are taken when the maximum of ΔR is attained and stabilized for a short period of time. Three measurements are done for each sample showing a good repeatability. The average of the three measurements is calculated.

Calculation method

ΔR are measured by VPO for several solutions containing extractant at various analytical molar fractions, called X_{tot} . $X_{tot} = \frac{n_{BTMPP} + n_{impurities}}{n_{diluent} + n_{BTMPP} + n_{impurities}}$

X_{app} are calculated from the ΔR and K . The average numbers of aggregation (N_{agg}) are obtained from the couples X_{tot} and X_{app} : $N_{agg} = X_{tot} / X_{app}$

Then an optimization procedure developed on Matlab based on the least square method is used to estimate the equilibrium constants of aggregation from the experimental average number of aggregation. For convenient use of the constants, the molar fractions are converted into molar concentrations.

Results and discussion

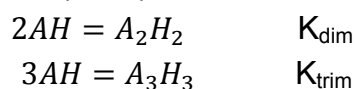
Presence of impurities

CX272 and IQ290 are respectively 88% and 95% pure. The presence of impurities influences the estimation of N_{agg} obtained by VPO because they are included in X_{app} and X_{tot} . The main impurity is tri(2,4,4-trimethylpentyl) phosphine oxide. For simplification, we assumed that the phosphine oxide impurities are monomeric, although mixed aggregates phosphine-oxide / BTMPP could be formed, as it was suggested for TOPO and D2EHPA [13]. Other assumptions were tried: similar

aggregation behavior of the impurities and BTMPP, formation of mixed aggregates... However these assumptions (results not presented here) led to different values of aggregation constants between CX272 and IQ290.

Comparison of Cyanex 272 and Ionquest 290 at 50°C

Depending on the concentration of BTMPP, its average number of aggregation varies from 1.8 to 2.2 (Figure 2), so it was concluded that BTMPP forms monomers (AH), dimers (A_2H_2) and trimmers (A_3H_3):



The procedure of optimization developed on Matlab is used to estimate the aggregation constants (for calculations in concentrations):

CX272: $\text{Log}(K_{\text{dim}}) = 3.1 \pm 0.2$ $\text{Log}(K_{\text{trim}}) = 4.9 \pm 0.2$ (at 50°C)
 IQ290: $\text{Log}(K_{\text{dim}}) = 3.3 \pm 0.2$ $\text{Log}(K_{\text{trim}}) = 4.9 \pm 0.2$ (at 50°C)

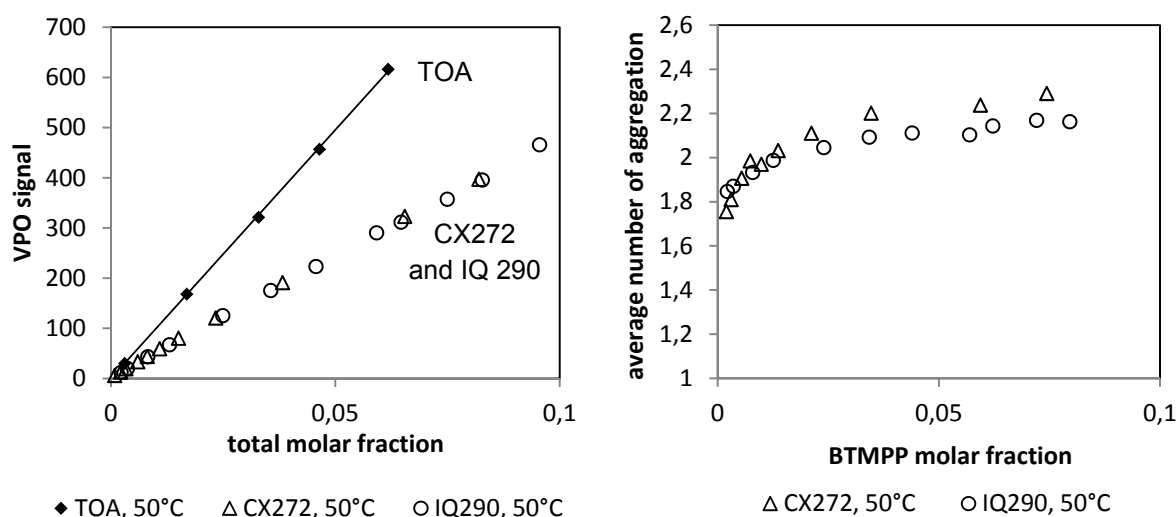


Figure 2: Calibration curve with TOA, VPO signals and average numbers of aggregation obtained at 50°C with CX272 and IQ290 at various concentration of extractant

The optimized aggregation constants allow calculating the experimental average numbers of aggregation with good agreement. However, we observe that the method is very sensitive to small variations of the experimental average numbers of aggregation. Moreover, the aggregation constants are only approximations due to the presence of impurities and the assumption on their aggregation. Therefore the incertitude on the logarithm of the optimized aggregation constant is around 0.2.

Influence of temperature

Experimental tests were also conducted at 43°C (in n-hexane) and 60°C (in n-heptane) with CX272, in order to see the influence of such temperature variations (Figure 3). The differences obtained between the three couples of constants are low, comparable to the incertitude

CX272	$\text{Log}(K_{\text{dim}})$	$\text{Log}(K_{\text{trim}})$
43°C	2.8	4.8
50°C	3.1	4.9
60°C	3.0	4.8

Table 2: Logarithm of BTMPP equilibrium constants of aggregation estimated with CX272 at 43°C, 50°C and 60°C.

of the method (Table 2). So it is concluded that temperature variations from 43 to 60°C have small influence on the aggregation. At first approximation, it can be considered that aggregation is independent on temperature from 43°C to 60°C, taking the average of the constants calculated at each temperature:

$$\text{Log}(K_{\text{dim}}) = 3.0 \pm 0.2$$

$$\text{Log}(K_{\text{trim}}) = 4.8 \pm 0.2$$

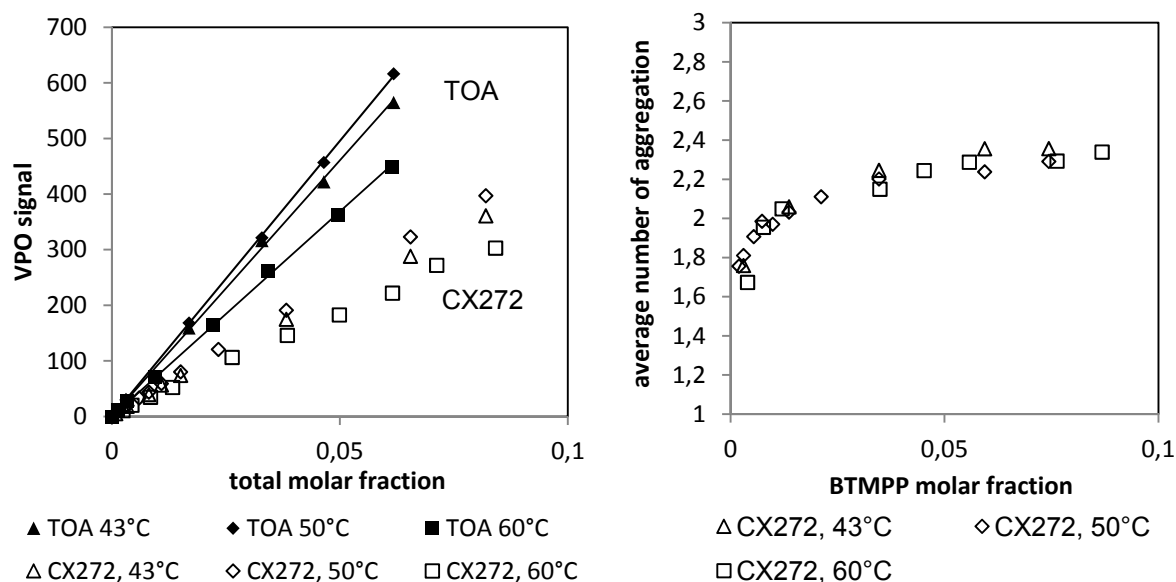


Figure 3: Calibration curves with TOA, VPO signals and average numbers of aggregation obtained at 43°C, 50°C and 60°C with CX272 at various concentration of extractant

Knowing the equilibrium constants of dimerization and trimerization, the distribution of BTMPP between monomers, dimers and trimers can be calculated at various analytical concentrations of BTMPP (Figure 4).

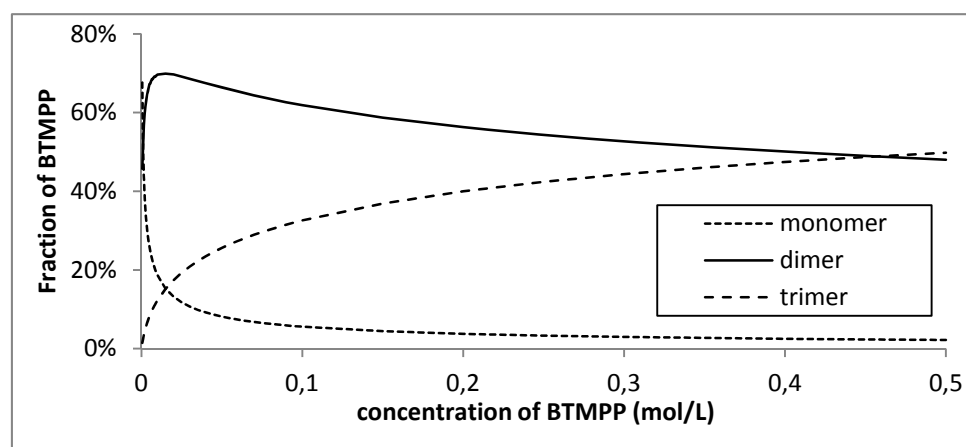


Figure 4: fraction of BTMPP that is present in the form of monomer, dimer or trimer, as a function of the analytical concentration of BTMPP.

Contrarily to the common assumption that BTMPP is only dimeric, the proportion of BTMPP present in the form of monomer or trimer can be elevated. For concentrations higher than 0.15 mol/L, the proportion of BTMPP present in the dimers is lower than 60%, and higher than 35% in the trimers.

Conclusion

The aggregation of BTMPP has been studied by VPO. The average numbers of aggregation of CX272 and IQ290 are measured for various concentrations of extractant at 43°C, 50°C, 60°C. As the average number of aggregation reaches 2-2.2, it was concluded that BTMPP exists as monomer, dimers and trimers. The equilibrium constants of dimerization and trimerization are estimated by least square optimization method. Nearly similar values of equilibrium constants were obtained for both CX272 and IQ290 when assuming impurities of the commercial extractants are monomeric. No significant influence of temperature has been detected on the average aggregation number in the range 43 - 60°C. $\text{Log}(K_{\text{dim}})$ and $\text{Log}(K_{\text{trim}})$ are respectively estimated at 3.0 ± 0.2 and 4.8 ± 0.2 . At low concentrations of BTMPP (0.005-0.1 mol/L), the extractant is mainly present as dimer. However at higher concentrations the fraction of BTMPP that is present as trimer becomes elevated.

References

1. G. M. Ritcey, *Solvent extraction, principles and applications to process metallurgy*, vol. 1, 2006
2. B. K. Tait, *Hydrometallurgy*, vol. 32, 365–372, 1993.
3. P. R. Danesi, L. Reichley-Yinger, G. Mason, L. Kaplan, E. P. Horwitz, and H. Diamond, *Solvent Extr. Ion Exch.*, vol. 3, 435–452, 1985.
4. K. Sole and B. Hiskey, *Hydrometallurgy*, vol. 37, 129–147, 1995.
5. R. K. Biswas, M. A. Habib, and H. P. Singha, *Hydrometallurgy*, vol. 76, 97–104, 2005.
6. L. K. Ke-An, S. Muralidharan, and H. Freiser, *Solvent Extr. Ion Exch.*, vol. 3, 895–908, 1985.
7. X. Fu, Z. Hu, and Y. Liu, *Solvent Extr. Ion Exch.*, vol. 8, 573–595, 1990.
8. Y. Nagaosa and Y. Binghua, *Talanta*, vol. 44, 327–337, 1997.
9. C. Sella and D. Bauer, "Diphasic acido-basic properties of organophosphorus acids.," *Solvent Extr. Ion Exch.*, vol. 6, no. 5, pp. 819–833, 1988.
10. A. M. Sastre, N. Miralles, and M. Martinez, *Monatshefte Für Chem. Chem. Mon.*, vol. 126, 401–409, 1995.
11. A. Buch, D. Pareau, M. Stambouli, and G. Durand, *Solvent Extr. Ion Exch.*, vol. 19, 277–299, 2001.
12. I. J. Goldfarb and A. C. Meeks, Air Force Materials Laboratory, USA, *Technical report AFML-TR-66-80*, 1966.
13. D. Beltrami, G. Cote, H. Mokhtari, B. Courtaud, and A. Chagnes, *Hydrometallurgy*, vol. 129–130, 118–125, 2012.

Multi-scale modelling of droplet interactions in liquid–liquid systems

Lachlan R. Mason; Geoffrey W. Stevens; Dalton J. E. Harvie, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Melbourne, Australia

Understanding droplet–surface and droplet–droplet interactions is important in the design and optimisation of multi-phase industrial processing equipment. Simultaneous modelling of droplet and thin-film dynamics is challenging due to the large differences in characteristic length scales present. This study outlines an efficient subgrid-scale modelling approach for droplet–surface interactions, suitable for inclusion in standard interface-capturing techniques.

The model couples a level-set method to a concurrent numerical solution of the Reynolds lubrication equation using the finite-volume solver *arb*^[3]; the coupling is achieved via incorporating the lubrication film pressure into the continuum-surface-force (CSF) framework of Brackbill et al.^[1].

Two collision-energy scenarios are investigated: (i) low-energy collisions between a droplet and porous membrane and (ii) moderate-energy collisions between a droplet and wall. Low-energy results are in good agreement with the semi-analytical Stokes–Reynolds–Young–Laplace framework, and the determined film-thicknesses at moderate energy compare favourably with the experimental collision sequences of Hartland^[2].

Results presented will aid in the future improvement of simulation techniques for droplet interactions in liquid–liquid systems: the simulation technique can be readily extended to model droplet–droplet interactions, aiding in the assessment of coalescence kernels for large-scale stochastic models.

Brackbill, J. U., Kothe, D. B., and Zemach, C. A continuum method for modeling surface tension. *J. Comput. Phys.* 100, 2 (1992), 335–354.

Hartland, S. The profile of the draining film beneath a liquid drop approaching a plane interface. *Chem. Eng. Prog. Symp. Ser.* 91, 65 (1969), 82–89.

Harvie, D. J. E. An implicit finite volume method for arbitrary transport equations. *ANZIAM J.* 52 (2012), C1126–C1145.

Mary R. Healy¹, Euan D. Doidge¹, Adam J. Fischmann², Jason B. Love¹,
Carole A. Morrison¹, James W. Roebuck¹, Thomas Sassi², Peter A.
Tasker^{*1}

Introducing hydrogen-bond acceptor groups adjacent to the OH group in phenolic pyrazoles greatly enhances their strength as copper extractants. Density functional theory calculations suggest that H-bond buttressing, which favours inter-ligand interactions, makes an important contribution to the extractant strengths; these strengths are also influenced by the resonance and inductive effects that the substituents have on the acidity of reagents and their binding strengths to Cu(II). A very good correlation has been observed between the predicted energies of formation of the copper complexes and the observed strength as solvent extractants.

Substituents in phenolic oxime extractants (Figure 1) have been shown to influence their strength greatly, with hydrogen-bond acceptor groups in the *ortho* position appearing to “buttress” inter-ligand H-bonding, favouring the formation of copper complexes.¹ In this paper, we consider whether similar buttressing effects can be used to tune strength and selectivity of phenolic pyrazole extractants that have similar H-bonding motifs which could favour the formation of metal-free dimers (HL)₂ and 2:1 complexes [M(L)₂] with metal dications (Figure 1).

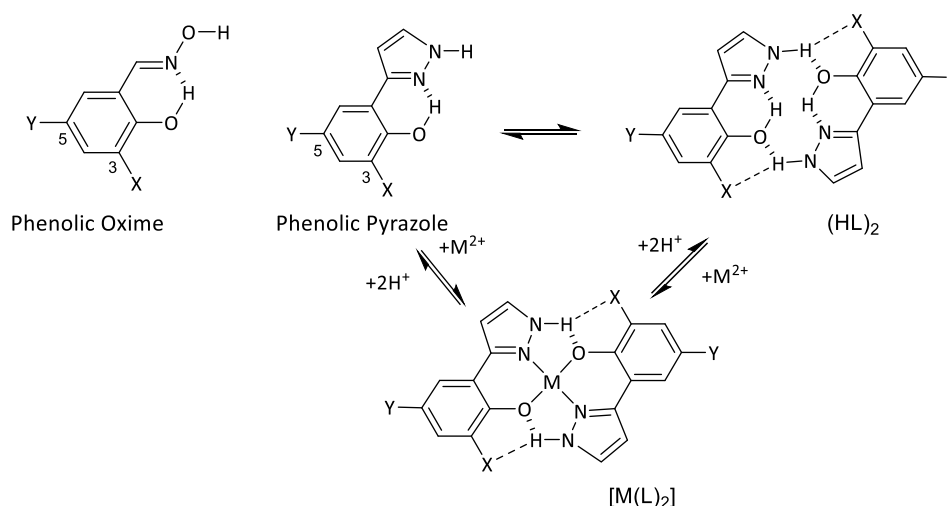


Figure 1: Phenolic-oxime and -pyrazole extractants, indicating how 3-X substitution could influence inter-ligand H-bonding in preorganised ligand dimers and pseudomacrocyclic metal complexes.

¹ EaStCHEM School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

² Cytec Industries Inc., 1937 W. Main Street, Stamford, Connecticut 06902, USA

The phenolic pyrazole pro-ligands (HL1-HL8, Figure 2) were used in this study, five (HL1-HL5) for computational work, and three octyl derivatives (HL6-HL8) that exhibit high solubilities in chloroform, in solvent extraction experiments.

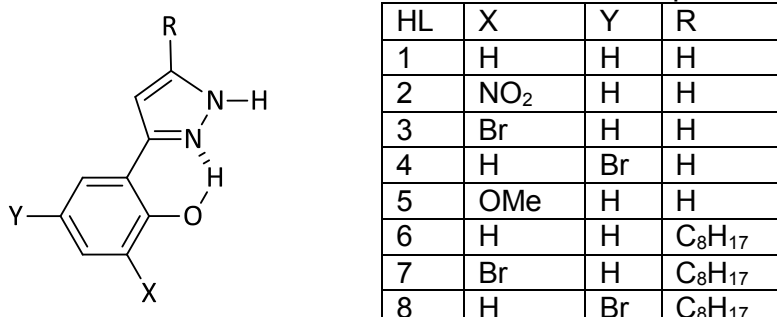
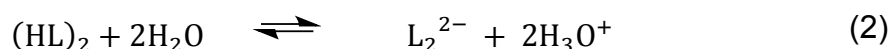


Figure 2: Reagents used in this study

Results and Discussion

Density functional theory calculations were used to predict how substituents influence the overall energy of formation of copper complexes in the gas phase (Equation 1), a reaction analogous to that in a solvent extraction process. This is influenced by the effects of substituents on the deprotonation of the extractant (Equation 2) and on the binding of the resulting anionic ligand to the copper dication (Equation 3).



In order to make valid comparisons of the energies of these reactions it is essential that the lowest energy conformations of all products and reactants are used. An important issue in this context is the dimerization of the pro-ligands (Equation 4) to form pre-organised sites for Cu binding (Figure 1, top right).



Energy of Dimerization, (ΔU_{dim})

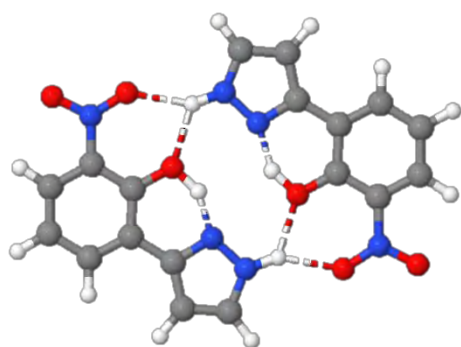


Figure 3: Inter and intra-ligand H-bonding in NO₂-substituted proligand dimer (HL2)₂

It was found that the formation of dimers (HL)₂ is favourable in all cases (Table 1) and consequently these were used as precursors in the energy calculations for the reactions in equations 1-3. Dimer formation is most favoured for the NO₂-substituted reagent, HL2, because the nitro group allows the formation of very symmetrical, bifurcated H-bonds from the pyrazolic NH group to oxygen atoms of the phenol and nitro groups (Figure 3). The least stable dimer is formed by the

para-Br-substituted reagent HL4. This substituent reduces the basicity of the H-bond-accepting phenolic oxygen and its location does not allow buttressing of the H-bonds. Dimerization is more favourable for all reagents with H-bond acceptors in the *ortho* position.

HL			ΔU Dimerization (ΔU_{dim})	ΔU Deprotonation (ΔU_{dp})	ΔU Binding (ΔU_{b})	Relative ΔU_{b}	ΔU Formation (ΔU_{f})	Relative ΔU_{f}
	X	Y	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol ⁻¹)	(kJ/mol)
1	H	H	-66.225	1707.20	-1183.35	0	523.850	0
2	NO ₂	H	-116.235	1549.63	-1067.06	116.29	482.574	-41.277
3	Br	H	-78.683	1634.48	-1132.26	51.089	502.220	-21.628
4	H	Br	-64.037	1621.00	-1113.89	69.454	507.106	-16.743
5	OMe	H	-84.639	1734.26	-1221.95	-38.604	512.311	-11.539

Table 1: Calculated dimerization energies of HL1-HL5 (Equation 4) and deprotonation, binding and complex formation energies of their dimers (Equations 2, 3 and 1 respectively).

Energy of Deprotonation, (ΔU_{dp})

As might be expected, the lowest energy of deprotonation of a pro-ligand dimer to give the 'active' form of the extractant (calculated for the reaction in Equation 3) is found for (HL2)₂ which has the strongly electron withdrawing (EWG) NO₂ group (see Table 1). EWGs also stabilize the deprotonated forms of the Br-substituted extractants HL3 and HL4. Greater stabilization is seen for the deprotonated *para*-substituted dimer (Y = Br) than for the *ortho*-isomer (X = Br) because the latter experiences repulsion between the electronegative Br atom and the negative charge on the phenolate O-atom. As expected, the electron-donating properties of the OMe group cause the (HL5)₂ dimer to have a higher deprotonation energy than the parent compound, (HL1)₂, (X=Y=H).

Binding Energy, (ΔU_{b})

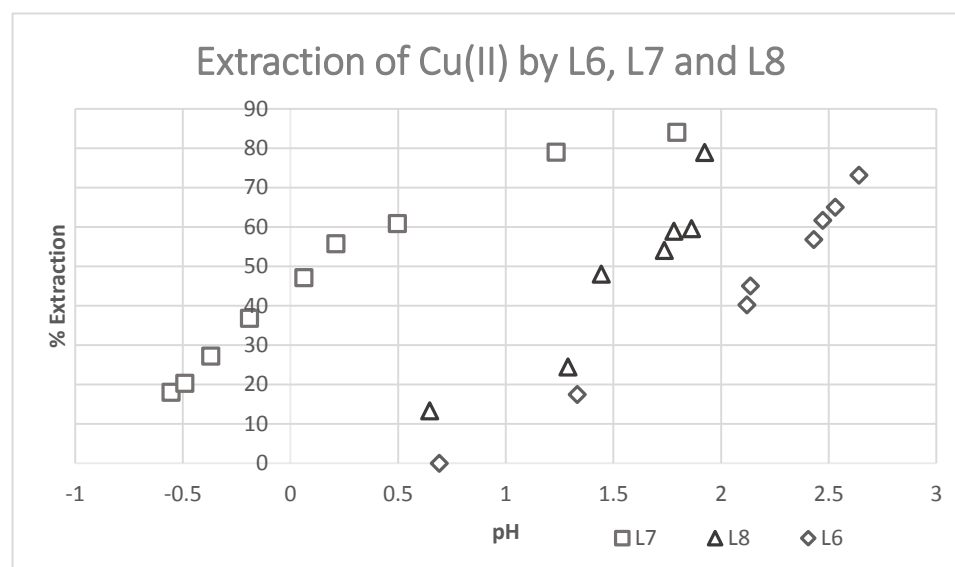
The calculated binding energies (Equation 3) reflect differences in the Cu-O and Cu-N bond strengths resulting from variations in the basicity of the phenolate oxygen and pyrazole N atoms. As expected, the most favourable binding energy is seen for the OMe-substituted reagent and the least favourable for the NO₂-substituted reagent as their substituents are the most electron-donating and electron-withdrawing, respectively.

Energy of Complex Formation (ΔU_{f}) and solvent extraction results

The calculated energies of formation of the copper complexes, ΔU_{f} (Table 1), predict that all of the substituted reagents are stronger extractants than HL1 and that strengths of HL1-HL5 vary in the order NO₂(*ortho*) > Br(*ortho*) > Br(*para*) > OMe(*ortho*) > H.

Significantly, the experimentally determined extractant strengths of HL6-HL8[#] in experiments undertaken with chloroform as the organic phase are in the same order (Figure 5). The extraction equilibrium constant for the *ortho*-bromo-substituted reagent (HL7) is almost 2.5 orders of magnitude greater than that for the unsubstituted reagent (HL6). This remarkable increase in strength arises in part from the increased acidity accompanying bromo-substitution. The deprotonation energies (ΔU_{dp} in Table 1) become more favourable in the order $H < Br(ortho) < Br(para)$, but in terms of copper complex formation, this is offset by the decreasing basicity of the resulting $N_2O_2^{2-}$ donor set which leads to variation in the binding energies (ΔU_b in Table 1) of $H > Br(ortho) > Br(para)$. Substitution has a striking influence on the dimerization energies of the reagents (ΔU_{dim} in Table 1) which relates to the H-bonding buttressing.

Figure 5: Cu extraction by L6 (unsubstituted), L7 (*ortho*-Br) and L8 (*para*-Br) phenolic pyrazoles as a function of pH.



It can be argued that the buttressing is the dominant effect in determining strength. If changing the acidity of the extractant was the most important factor then the *para*-bromo-substituted reagent should be stronger than its *ortho*-isomer, but the reverse is the case with both the calculated ΔU_f values for LH3 and LH4 in Table 1 and the experimentally observed $pH_{1/2}$ values for LH7 and LH8 in Figure 4 indicate that the *ortho*-isomers are stronger reagents. Despite *decreasing* the acidity of the reagent, methoxy substitution leads to a stronger extractant HL5 as a consequence of its more favourable dimerization and binding energies.

Work is in progress to define the nature and strength of the secondary bonding in the pre-organised dimers and the copper complexes. Whilst there is good agreement between gas-phase structures and those determined by X-ray crystallography in the solid state (Figure 5), the difficulty in accurately defining the positions of H-atoms in the latter is probably responsible for the disparity between the calculated and

[#] Preliminary results (J Roebuck, PhD thesis 2014) on extraction by related NO_2 - and MeO -substituted compounds also fall in line with the strengths predicted by the calculations

determined lengths of pyrazole N-H to phenol O hydrogen bonds. Structures of the free pro-ligand dimers show that the cavity in the free ligand dimer is significantly larger than that in the complex. A significant rearrangement is seen in complex formation. The bite distance in the complex increases in length by more than 0.2 Å as does the length of the inter-ligand hydrogen bond.

Structure	a	b	c	d
(HL1) ₂ - gas phase	1.851	2.511	3.112	1.584
(HL1) ₂ - crystal structure ²	2.22	2.594	3.316	1.78
[Cu(L1) ₂] - gas phase	2.017	2.754	2.729	-
[Cu(L1) ₂] - crystal structure ³	2.23	2.732	2.689	-

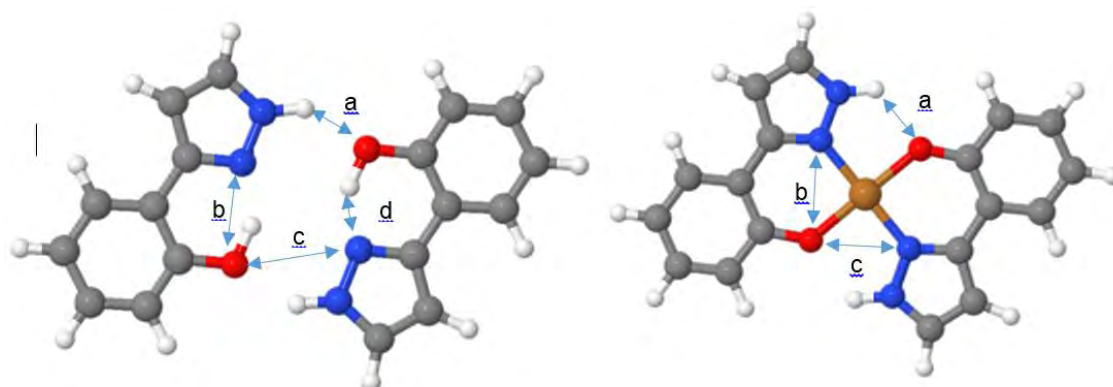


Figure 5: Calculated and experimentally determined interatomic contacts (Å) in the phenolic pyrazole pro-ligand, HL1, and its copper complex [Cu(L1)₂].

Conclusions

Gas-phase calculations of energies of formation of metal complexes can be used to predict the relative extraction strength for substituted phenolic pyrazoles. Electron withdrawing groups in the *ortho* or *para* positions of the phenolate increase the stability of the deprotonated structure but decrease its binding energy in the metal complex; the opposite is apparent for an electron donating group such as a methoxy unit. Groups in the *ortho* position with the potential for outer-sphere buttressing interactions provide additional stability to dimers of the ligand and their complexes. Significantly, this additional interaction results in a large decrease in the pH_{1/2} in copper(II) extraction by phenolic pyrazole reagents, and therefore should facilitate the tailoring of these reagents to a variety of different processes and feed streams.

Computation Details

All calculations were executed using the Gaussian '09 program⁴. Full structural optimizations were carried out using the H-DFT method B3LYP/LANL2DZ for each of the pro-ligands, pro-ligand dimers, ligand dimers and copper complexes. Frequency calculations were carried out on all optimized structures to ensure energy minima had been reached. Assembly formation energies, dimerization and deprotonation energies are calculated using the difference internal energy values of the sum of the products and the sum of individual reactants.

Experimental Procedure

Extractions were carried out by contacting chloroform solutions (2.5 mL) of the ligands at concentrations of 0.005 mol L^{-1} with aqueous solutions (2.5 mL) of copper(II) sulphate at concentrations of 0.005 mol L^{-1} . The pH of the aqueous copper sulphate solution was varied by adding 0.5 mL of sodium hydroxide/water or sulphuric acid/water solutions of varying concentrations to 2.0 mL of $0.00625 \text{ mol L}^{-1}$ copper(II) sulphate solution.

After vigorous stirring for 22 h at 40°C , the phases were separated and 0.2 mL of each evaporated and diluted into 10.00 mL 1-methoxy-2-propanol for copper analysis by ICP-OES. The equilibrium pH of the aqueous phase was measured by titration of 0.5 mL of the aqueous phase against varying concentrations of sodium hydroxide. The calculated percentage copper(II) uptake into the organic phase was plotted against the measured equilibrium pH of the aqueous phase to give S-curves.

1. R. S. Forgan, B. D. Roach, P. A. Wood, F. J. White, J. Campbell, D. K. Henderson, E. Kamenetzky, F. E. McAllister, S. Parsons, E. Pidcock, P. Richardson, R. M. Swart, and P. A. Tasker, *Inorg. Chem.*, 2011, **50**, 4515–22.
2. J. Catalan, F. Fabero, R. M. Claramunt, M. D. Santa Maria, M. de la C. Foces-Foces, F. Hernandez Cano, M. Martinez-Ripoll, J. Elguero, and R. Sastre, *J. Am. Chem. Soc.*, 1992, **114**, 5039–5048.
3. L. Emeleus, *PhD Thesis, Univ. Edinburgh, UK*, 1999.
4. D. J. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenb, *Gaussian, Inc., Wallingford CT*, 2009.

Influence of the Nature of an Extragent on the Rate of Extraction a REE at Vibration on a dynamical interfacial Layer

*N.F. Kizim^{*1}, E.N. Golubina²*

In this work presented, the influence of mechanical vibrations in the frequency range 3–12 kHz on extraction of Ln(III) with solutions of D2EHPA or TBF in various solvents. We detected for the first time that vibrations in the medium-frequency sound range affect the extraction of rare-earth elements with solutions of D2EHPA in organic diluents. These results allow one in a fundamentally different way to solve the problem of enhancement of the interfacial mass transfer in heterogeneous liquid systems in which there is dynamical interfacial layer formation. The role of forced surface vibrations in the formation of the interfacial layer increases, since the interface near the vibrator remains uncoated with the film and the extraction mainly occurs through this portion of the surface. Further dissolution of the interfacial film because of the solvation of lanthanide di-(2-ethylhexyl)phosphate with free D2EHPA contained in the organic phase leads to the fact that, at low metal concentrations, the film is sometimes ruptured, extraction through the free surface begins, and a new interfacial layer forms.

Introduction

Typically, solvent extraction is performed in the emulsion regimes using stirrers or pulsates. The disadvantage of these methods is a complicated apparatus, elevated energy expenditure, as when using stirrer agitators, energy being expended in dispersing one liquid in another, the need to break the emulsion.

Therefore it is necessary to search for new methods to reduce the resistance of the transfer through the interfacial layer in the emulsion regime. A literary analysis of the data showed that the use of force fields: electrical, ultrasonic, electromagnetic means leads to faster extraction [1-5].

In the extraction of rare earth element (REE) with solutions of di (2 - ethylhexyl)phosphoric acid (D2EHPA) in the presence of the vibrational effects in the interfacial region for two reasons are considered to accelerate the extraction process: the removal and change of the interfacial film transport mechanism of the system through the transition region.

This report presents the results of a study of the kinetics of the extraction of rare earth elements solution of D2EHPA or tributylphosphate (TBF) when applied to a system of mechanical oscillations of the resonance frequency.

Experimental

Our experiments used the following Lantanoid salts: PrCl_3 , $\text{Nd}(\text{NO}_3)_3$, ErCl_3 , $\text{Ho}(\text{NO}_3)_3$ of chemical pure (c.p.) qualification, D2EHPA or TBF, Heptane, Toluene and Carbon Tetrachloride (c.p.) as (dis)solvents. D2EHPA was purified according to a well-known method [6].

^{*1} Kizim Nicolay F., nphk@mail.ru, Novomoskovsk Institute of Mendeleyev University of Chemical Technology, Russia

² Golubina Elena N. Novomoskovsk Institute of Mendeleyev University of Chemical Technology, Russia

Experiments were conducted on a setup comprised of a glass cell, vibrator and generator of low-frequency signals. 8 ml of Ln(III) salt in aqueous solution was placed into a conical cell and 2 ml of D2EHPA (TBF) in Heptane or Toluene solution were carefully added along the cell wall. The cell's geometric area of interface for the two-layer system was 6.07 cm². By the specified time period our experiments stopped, the phases were divided and Ln(III) concentrations in both organic and aqueous phases were measured.

The concentration of Ln(III) in aqueous phase was measured according to the known technique [7]. One aliquot of aqueous solution was placed into 25 ml - volumetric flask, ammonium hydrate was added up to pH = 6, 2 ml of Arsenazo I (indicator) solution was introduced as well as 5 ml of borate buffer, then the solution volume was filled with water up to the scale label. The solution's optical density was measured by means of photoelectric colorimeter using a 590 nm light filter. The concentration of Ln(III) was estimated with calibration dependency that had been preliminary drawn using solutions with known Ln(III) concentration. The measurements were performed in linear calibration line that was achieved by changing of absorption medium thickness and selecting the cavity appropriate size.

The concentration of Ln(III) in organic phase was measured via stripping using 0.5 M aqueous solution of nitric acid (preliminary experiments showed that Ln(III) re-extraction was quantitative). For that purpose, the extract was placed into the separating funnel, 8 ml of 0.5 M nitric acid solution was added, then shook for 5 min. The system was sustained until the emulsion was entirely divided. The aqueous phase was separated and Ln(III) concentration in aqueous phase was measured as previously described.

Vibration on the process rate were examined by means of the same glass cell and vibrator comprising a high-frequency electro-dynamic head with a stainless steel bar (0.05 cm - diameter, 4.3 cm – length) tightly fastened to a diffuser center, a vibrating element was attached to its end. The element was a Teflon triangular prism, its length - 1.1 cm, its rib facing the interface. The prism cross-section was isosceles triangle (0.5 cm – height, 0.3 cm – base) [8,9].

Prior to the experiment, the rib of prismatic vibration element was installed onto the surface between Ln(III) salt aqueous solution and air so that the rib touched the solution and the electro-dynamic head's clamps transmitted sinusoidal voltage of appropriate frequency. Then 2 ml of extraction reagent in organic solvent were carefully placed along the cell wall onto aqueous solution. All the experiments performed at 20 ± 1°C.

In order to assess effects of various factors on extraction with mechanical vibrations imposed, we used enhancement factor (E). It was calculated according to the following:

$$E = C_f / C,$$

where C_f is Ln(III) concentration in organic phase for certain period of time with vibration effect on dynamic interfacial layer, C - is Ln(III) concentration in organic phase for the same time period but free of vibration.

Statistical handling of experimental data revealed its repeatability and ratio error was within 7 %.

Results and discussion

REE extraction solutions D2EHPA is accompanied by several interfacial phenomena, the main ones are the chemical reaction between the cation and extractable REE extraction reagent, spontaneous surface convection, adsorption, the formation of interfacial suspensions (cruds). These phenomena, their existence in a natural way affects the rate of extraction of REE.

In the regime of spontaneous surface convection (SSC), the interface performs a complicated movement with the tangential and normal components. Such motion can be represented as a superposition of oscillations at specific frequencies. The study of the spectral composition of the interface forms by the method of [10], shows that there is frequency, intensity fluctuations, interfacial surface on which the maximum.

Picking up the vibration frequency vibroelement can ensure that it aligns with any vibrational mode of the interface element and the oscillation amplitude increases due to the phenomenon of resonance (Figure 1).

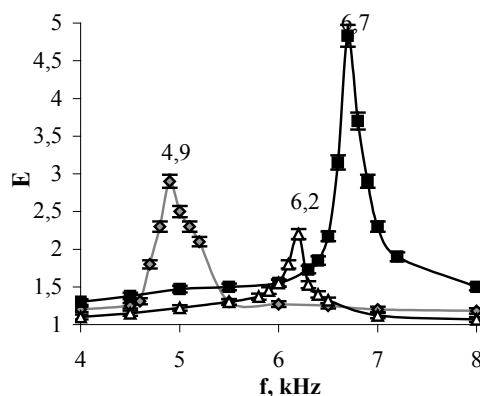


Figure 1 Correlation between enhancement factor and vibration frequencies applied. Aqueous phase: 0.01 M Pr (III) salt solution; pH 5.3. Organic phase: 0.05 M D2EHPA solution in Heptane (1), Toluene (2) and Carbon Tetrachloride (3). The data was registered 50 min. after the beginning of experiment

The enhancement factor at the time can be divided into three regions (Figure 2): the first region corresponds to the emergence and development of the system of spontaneous surface convection and the enhancement factor extraction of the value of the order takes 5, the second region corresponds to the formation of a temporary structure in the interface and the enhancement factor is close to 1, and the third region corresponds to the destruction of structures in the interfacial layer and the enhancement factor has a value close to 4. The value of enhancement factor extraction and extension areas also depend on the initial composition of the system.

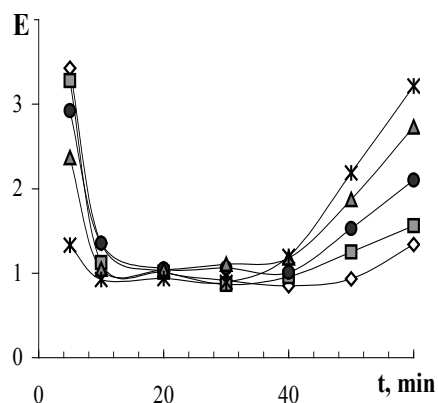


Figure 2 Effect of initial concentration of D2EHPA on the enhancement factor at the extraction $Er(III)$. System: 0.05 M solution $Er(III)$; pH 5.3 / D2EHPA solution in heptane with a concentration of 0.01 M (1), 0.02 M (2), 0.03 M (3), 0.04 M (4), 0.05 M (5). The frequency is resonance

For example, an increase in the initial concentration of D2EHPA from 0.01 to 0.05 M leads to a decrease in the acceleration factor extraction two times, due to displacement of the formation time of interfacial layer to lower values of time.

In the extraction of REE by the solutions TBP the enhancement factor extraction decreases over time (Figure 3). Increasing the initial concentration of TBP in heptane with 0.1 to 0.5 M in the case of REE extraction reduces the enhancement factor extraction, *ceteris paribus*; approximately 4-fold at a time process of 0-60 min (Figure 3) and more important is the system with TBP concentration of 0.1 M. The intensity of the SEC decreases with time (due to the formation of interfacial layer) and the enhancement factor extraction, trying in most cases 1.

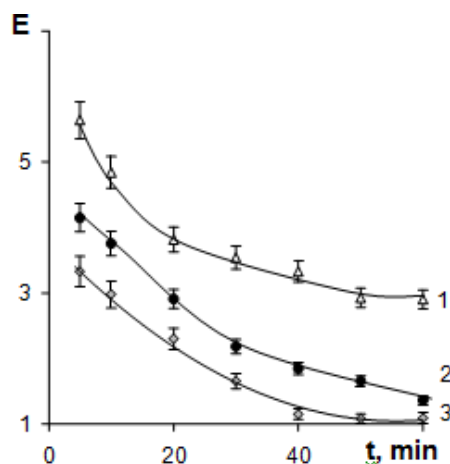


Figure3 Effect of initial concentration of TBP on the enhancement factor. Aqueous phase: 0.05 M solution of $ErCl_3$; pH 2.4. The organic phase: 0.1 M (1), 0.2 M (2) and 0.5 M (3) was dissolved in heptane TBP

Thus, the role of vibrational effects is local additional energy in the dynamic interfacial layer increases the amplitude of oscillation at the resonant frequency change of hydrodynamic conditions in the transition region of the system and as a consequence, a change in the permeability of the interfacial layer.

References

1. Dib Y. J. *Colloid and Interface Sci.*, 1997. V. 186. № 1, p. 29
2. Bart H-J. *Int. Solv. Extr. Conf. (ISEC'02)*. Cape Town. South Africa, 2002, p. 45
3. Riera E., Golás Y., Blanco A., Gallego J.A., et al. *Ultrasonics & Sonochemistry*, 2004. V. 11. N 3-4, p. 241
4. Brodard P.; Vauthey E. *Rev. Sci. Instrum.*, 2003. V. 74. p. 725
5. Kizim N.F., Golubina E.N. Solvent extraction: fundamentals to industrial application (*ISEC'2008*). Tucson, Arizona, USA, 15-19 September, 2008, p. 1255
6. McDowell, W.J., Perdue, P.T., Case, G.N. *J Inorganic and Nuclear Chemistry*. 1976. 11, p. 2127
7. Busev A.I., Tiptsova V.G, Ivanov V.M. *Rukovodstvo po analiticheskoy khimii redcikh elementov*. Moscow. Chemistry. 1978. 432 p.
8. Kizim N.F., Golubina E.N., Chekmarev A.M. *Doklady Physical Chemistry*, 2006. V. 411. P.2, p. 331
9. Golubina E.N., Kizim N.F., Chekmarev A.M. *Doklady Physical Chemistry*, 2012. V. 447. P.2, p. 220
10. Kizim N.F., Golubina E.N. *Russian J Physical Chemistry*, 2003. V.77. № 12, p. 2064

Nitrate based ionic liquid as a new solvent for extraction of aromatic from alkane

Babak Mokhtarani¹, Javad Musavi², Ali Sharifi¹, Mehdi Parvini²

1- Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran.

2- Department of Chemical Engineering, 35196-45399 Semnan University, Semnan, Iran

Summary

In this research, liquid – liquid equilibria (LLE) data for the ternary systems {hexane + ethyl benzene+ 1-butyl 3-methylimidazolium nitrate [Bmim][NO₃] or 1-methyl 3-octylimidazolium nitrate [Omim][NO₃] }, {hexane + toluene + [Bmim][NO₃] or [Omim][NO₃] } and {hexane+ ethyl benzene + [Bmim][NO₃] or [Omim][NO₃] } was determined at 298.15 K and atmospheric pressure. The reliability of the LLE data was tested by the Othmer-Tobias and Hand equations. In order to evaluate the ILs capacities as a solvent for extraction of aromatic from hexane, the selectivity (*S*) and distribution ratio factor (β) were calculated. The selectivities for [Bmim][NO₃] are higher than [Omim][NO₃] systems. The comparison of selectivity values of both types of studied ILs indicate that an increase of the alkyl chain length of the IL cation leads to a decrease of the values of selectivity. The distribution coefficient values of [Omim][NO₃] are more than the [Bmim][NO₃] that indicate, in equal conditions less amount of [Omim][NO₃] will be used as a solvent. The NRTL thermodynamic model was used for correlating the LLE data and the binary interaction parameter were estimated. The LLE data were successfully correlated by the NRTL model.

1. Introduction

Extraction of aromatic from alkane is a major process in the oil refineries. the mixtures of these components have a close boiling point and several azeotropes are formed [1]. Liquid extraction is the common process for separation of these compounds and the typical solvent are polar component such as sulfolane, N-methylpyrrolidone (NMP), N- formylmorpholine (NFM) and ethylene glycol [1]. These solvents are toxic, flammable and volatile those generate different problems in process. Ionic liquids (ILs) are a good alternative for these solvents. These non-flammable solvents have negligible vapor pressure, low melting point, and high solubility for polar and nonpolar substances [2].

extractions of aromatic from alkane using ILs were studied by many researchers in last decades [3-9]. Pereiro et al. reviewed the application of ILs in separation of azeotropic mixtures [10]. This research is the continuation of our previous work on the extraction of aromatic from their mixtures with alkane and ILs [11-12].

* Corresponding author *E-mail:* mokhtaranib@ccerci.ac.ir Tel.: +98 21 44580751; fax: +98 21 44580781.

In this research, liquid – liquid equilibria (LLE) data for the ternary systems {hexane + ethyl benzene + 1-butyl 3- methylimidazolium nitrate [Bmim][NO₃] or 1-methyl 3-octylimidazolium nitrate [Omim][NO₃] } were measured at 298.15 K and atmospheric pressure. The experimental data was compared with our previous data for aromatic systmes {hexane + toluene + [Bmim][NO₃] or [Omim][NO₃] } [3] and {hexane+ benzene + [Bmim][NO₃] or [Omim][NO₃] } [4] inorder to investigate the behavior of IL for extraction of different aromatic compound.

2. Materials and methods

Hexane and ethyl benzene with purity more than 99% were supplied from Merck vompany. [Bmim][NO₃] and [Omim][NO₃] were synthesized in our laboratory from [Bmim][Cl] or [Omim][Cl] according to the procedure in literature [19]. The purified ILs was dried and degassed for 24 h at 343.15 K under vacuum, and was kept in bottle under argon gas.

The ternary mixtures of aromatic + hexane + IL ([Bmim][NO₃] or [Omim][NO₃]) were prepared in glass vials. The total mass of each mixture was 20 g using a laboratory balance with the precision of $\pm 10^{-4}g$. The mixtures were shaken (IKA HS-260) for 180 min at 300 rpm and inserted into a water bath (Julabo, FP50) at 298.15 K for 12 h. After equilibrium, the two phase are formed and the samples of the top and bottom phases were taken for composition analysis. The compositions were analyzed by a gas chromatography (Varian, cp 3800) with a FID detector and capillary column (Chrompack, 30 m× 0.25 mm× 1.2 μ m).

3. Results

Experimental data for ternary systems of IL (1) + hexane (2) + ethyl benzene (3), IL (1) + hexane (2) + benzene (3) and IL (1) + hexane (2) + toluene (3) are reported in Tables 1-3. The selectivity (S) and distribution ratio (β) were calculated as:

$$\beta = \frac{x_3^{II}}{x_3^I} \quad (1)$$

$$S = \frac{x_3^{II} x_2^I}{x_3^I x_2^{II}} \quad (2)$$

where x is the mole fraction, the superscripts II and I refer to the hexane- and IL-rich phase, and the subscripts 2 and 3 refer to hexane and aromatic, respectively.

Table 1. Experimental LLE data in mole fraction for ternary systems IL (1) + hexane(2) + ethyl benzene (3) at 298.15 K and calculated aromatic distribution coefficient (β) and selectivity (S) values.

Feed			Hexane rich phase ¹		IL rich phase ²		β	S
x_1	x_2	x_3	x_2^I	x_3^I	x_2^{II}	x_3^{II}		
[Bmim][NO3] (1) + hexane (2) + ethyl benzene (3)								
0.306	0.577	0.117	0.841	0.159	0.006	0.027	0.17	22.64
0.316	0.444	0.240	0.664	0.336	0.008	0.051	0.15	12.89
0.322	0.309	0.368	0.473	0.527	0.010	0.079	0.15	7.52
[Omim][NO3] (1) + hexane (2) + ethyl benzene (3)								
0.257	0.611	0.132	0.849	0.151	0.105	0.092	0.61	4.90
0.255	0.453	0.292	0.667	0.333	0.122	0.227	0.68	3.72
0.274	0.400	0.326	0.622	0.378	0.117	0.259	0.68	3.63

Table 2. Experimental LLE data in mole fraction for ternary systems of IL (1) + hexane (2) + toluene (3) at 298.15 K and calculated aromatic distribution coefficient (β) and selectivity (S) values [3].

Feed			Hexane rich phase ¹		IL rich phase ²		β	S
x_1	x_2	x_3	x_2^I	x_3^I	x_2^{II}	x_3^{II}		
[Bmim][NO ₃] (1) + hexane (2) + toluene (3)								
0.303	0.564	0.133	0.832	0.168	0.008	0.060	0.36	38.88
0.305	0.428	0.267	0.644	0.356	0.009	0.0961	0.27	19.94
0.306	0.359	0.335	0.548	0.452	0.010	0.115	0.26	14.12
[Omim][NO ₃] (1) + hexane (2) + toluene (3)								
0.254	0.605	0.141	0.846	0.154	0.093	0.115	0.75	6.84
0.256	0.458	0.286	0.677	0.323	0.100	0.224	0.69	4.71
0.257	0.384	0.359	0.583	0.417	0.101	0.278	0.67	3.68

Table 3. Experimental LLE data in mole fraction for ternary systems IL (1) + hexane(2) + benzene (3) at 298.15 K and calculated aromatic distribution coefficient (β) and selectivity (S) values [4].

Feed			Hexane rich phase ¹		IL rich phase ²		β	S
x_1	x_2	x_3	x_2^I	x_3^I	x_2^{II}	x_3^{II}		
[Bmim][NO3] (1) + hexane (2) + benzene (3)								
0.295	0.552	0.153	0.834	0.166	0.011	0.127	0.76	55.65
0.291	0.409	0.300	0.635	0.365	0.013	0.185	0.51	25.51
0.286	0.344	0.370	0.536	0.464	0.010	0.208	0.45	23.48
[Omim][NO3] (1) + hexane (2) + benzene (3)								
0.244	0.600	0.159	0.849	0.151	0.109	0.175	1.16	8.98
0.240	0.443	0.317	0.675	0.325	0.092	0.306	0.94	6.89
0.241	0.360	0.399	0.571	0.429	0.090	0.361	0.84	5.37

The experimental results show that the S value for [Bmim][NO₃] are greater than [Omim][NO₃] for ethyl benzene, toluene and benzene. The higher selectivity means the lower stages required for extraction process and the higher distribution coefficient means lower solvent need for extraction. The comparison of the selectivity values in Tables 1-3 indicate that the selectivity values are decreasing with increasing the aromatic molecule. It means that the selectivity values for ethyl benzene is lower than toluene and benzene.

The NRTL model [13] was used for correlating of the experimental data. The binary energy parameters were determined by minimizing the differences between the experimental and calculated mole fractions for each component as an objective function.

$$F = \sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{exp} - x_{ijk}^{cal}}{x_{ijk}^{exp}} \right)^2 \quad (1)$$

where m is the number of tie lines, n is the number of component, k is the number of phases, and superscripts of *exp* and *cal* referred to experimental and calculated mole

fraction values, respectively. The optimum binary energy parameters was calculated and the root mean square deviation is defined according to this equation:

$$rmsd = \left[\frac{\sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{exp} - x_{ijk}^{cal}}{x_{ijk}^{exp}} \right)^2}{2mn} \right]^{1/2} \times 100 \quad (2)$$

Where m is the number of the tie lines and n is the number of the components in the mixtures. The results of NRTL correlation indicated the rmsd value for [Bmim][NO₃] (1) + hexane (2) + ethyl benzene (3) and [Omim][NO₃] (1) + hexane (2) + ethyl benzene (3) are 0.20 and 0.42 respectively. This imply, NRTL model can correlated the LLE data with a good accuracy.

4. Conclusion

The potential of nitrate based IL([Bmim][NO₃] and [Omim][NO₃]) for extraction of aromatic from hexane was tested and compared to the previous data. LLE data for the ternary systems {hexane + ethyl benzene or toluene or benzene + [Bmim][NO₃] or [Omim][NO₃] } were measured at 298.15 K and atmospheric pressure. The selectivity and distribution coefficient values were calculated. The selectivity values are decreasing with enlargement the alkyl chain length of IIs. This means [Bmim][NO₃] is superior than [Omim][NO₃] for extraction of aromatic from hexane. The NRTL model was used for correlating of the experimental data. The result of thermodynamic modeling shows, the NRTL model can correlate the experimental data with a good accuracy.

References

- [1] G.W. Meindersma, A. R. Hansmeier, A.B. de Haan, Ind. Eng. Chem. Res. 49 (2010) 7530- 7540.
- [2] B. Mokhtarani, A. Sharifi, H. R. Mortaheb, M. Mirzaei, M. Mafi, F. Sadeghian, J. Chem. Thermodyn. 41 (2009) 1432-1438.
- [3] B. Mokhtarani, J. Musavi, M. Parvini, Fluid Phase Equil. 363 (2014) 41-47.
- [4] B. Mokhtarani, J. Musavi, M. Parvini, M. Mafi, A. Sharifi, M. Mirzaei, Fluid Phase Equil. 341 (2013) 35-41.

- [5] T.M. Letcher, N. Deenadayalu, J. Chem. Thermodyn. 35 (2003) 67–76.
- [6] T.M. Letcher, P. Reddy, J. Chem. Thermodyn. 37 (2005) 415–421.
- [7] N. Deenadayalu, K.C. Ngcongco, T.M. Letcher, D. Ramjugernath, J. Chem. Eng. Data 51 (2006) 988–991.
- [8] G. W. Meindersma, A.J.G. Podt, A.B. Haan, Fluid Phase Equil. 247 (2006) 158–168.
- [9] G. W. Meindersma, A.J.G. Podt, A.B. Haan, J. Chem. Eng. Data 51 (2006) 1814–1819.
- [10] A. B. Pereiro, J. M. M. Araujo, J. M. S. S. Esperanca, I. M. Marrucho, L. P. N. Rebelo, J. Chem. Thermodyn. 46 (2012) 2-28.
- [11] B. Mokhtarani, A. Sharifi, H. R. Mortaheb, M. Mirzaei, M. Mafi, F. Sadeghian, J. Chem. Eng. Data 55 (2010) 3901-3908.
- [12] M.R. Heidari, B. Mokhtarani, N. Seghatoleslami, A. Sharifi, M. Mirzaei, J. Chem. Thermodyn. 54 (2012) 310-315.
- [13] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.

Solvent extraction of precious metal ions with phenylurea type of trident molecule

*Y. Ueda, S. Morisada, H. Kawakita, K. Ohto**¹

A phenylurea derivative of trident molecule and the corresponding monopodal analogue have been prepared as a novel solvent extraction reagent for precious metal ions in nitrate media. The phenylurea type of extraction reagents exhibited extractive selectivity for Pd(II) over Ag(I), Pt(IV), Ru(III), Fe(), Co(II), Ni(II), Cu(II), and Zn(II) in nitrate media. The extractability of the trident extraction reagent for Pd(II) was higher than that of the monopodal analogue. The extraction mechanism of palladium with the phenylurea type of extraction reagents were determined by slope analysis and from the peak shift for the FT-IR and ¹H-NMR spectra of the extraction reagents before and after palladium loading.

Introduction

Precious metals are indispensable metal elements in modern industries, particularly in the automotive industry, petrochemical and bio fuel processes [1-2]. However, the natural abundance of precious metals is extremely small and they exist in limited locations [3]. Therefore, it is necessary to establish an efficient recovery process for precious metals. Solvent extraction is one of the most important metal separation methods in hydrometallurgical process. For example it has been used in the Vale-INCO process and the Matthey Rustenberg Refiners process [4-5]. However, the conventional solvent extraction reagents for precious metals are not fully effective and mutual separations are not complete. Separation of precious metals is still quite difficult since precious metal ions in acidic media form different types of anion complexes with chloride and nitrate ions [6-7], have different charges, and the size of precious metal anion complexes is extremely large [8]. Consequently, it is necessary to prepare more effective and selective solvent extraction reagents for precious metals.

Various types of extraction reagents based on macrocycles and pseudomacrocycles, such as calixarene [9-10] and tripodal alkyltrimethylol compounds as “trident” molecules [11-12] have been prepared for metal separation in our group. The derived primary amino type of trident molecule employed as a precursor in the present work also provides the following characteristics:

1. three primary amino groups for chemical modification at the metal coordinating groups,
2. relatively narrow coordination site for size recognition,

*Department of Chemistry and Applied Chemistry, Saga University, 1-Honjo, Saga 840-8502, Japan

ohtok@cc.saga-u.ac.jp

3. high coordination ability due to the chelating and preorganized effects.

The urea compounds have four advantages in that they are completely incinerable at the end of the process as they only contain hydrogen, carbon, nitrogen, and oxygen atoms [13], they are hardly eluted into the aqueous phase because of the neutral ligand, and they have strong coordination ability by the carbonyl oxygen atoms with high charge density [14], and they have an anion recognition site consisting of urea hydrogen atoms [15].

In the present work, a phenyl urea type derivative of a trident molecule together with the corresponding monopodal analogue have been synthesized to investigate the solvent extraction of some precious and base metal ions from nitrate media.

Experimental

Reagents

The phenylurea type of trident molecule and the corresponding monopodal analogue were prepared in a similar manner to that described in a previous paper [16]. Chemical structures and abbreviations of the phenylurea type of extraction reagents in the present study are shown in Figure 1.

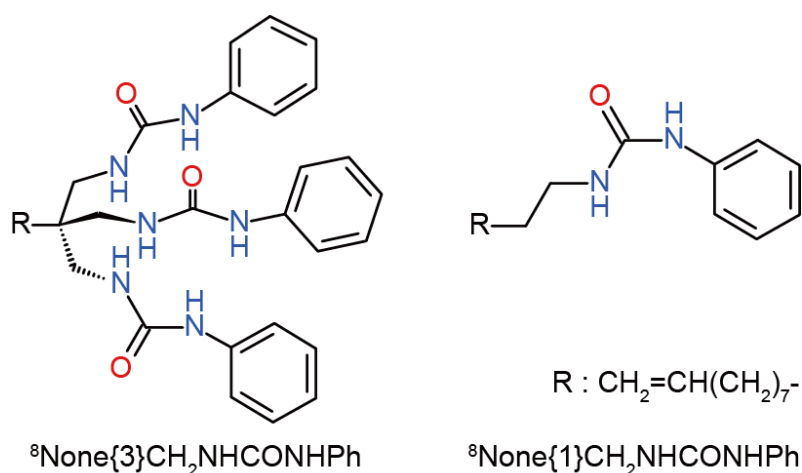


Figure 1 Chemical structures of phenylureatype of extraction reagents.

Extraction of metal ions

Organic solutions were prepared by dissolving the trident extraction reagent in analytical grade chloroform to a concentration of 5 mM. The concentration of the monopodal analogue was adjusted to be 15 mM so that the concentration of the phenylurea groups for the monopodal extraction reagent is equal to that for the trident reagent. Aqueous solutions were prepared by dissolving each metal salt in nitric acid solution to the desired acid and metal concentrations. Equal volumes of both phases were mixed and vigorously shaken at 303 K for 15 h. After phase separation, the

metal concentrations in the aqueous phase were measured by ICP-AES (Shimadzu ICPS-8100).

Proton NMR spectrum

Organic solutions were prepared by dissolving the extraction reagent in analytical grade deuterated chloroform to the desired concentrations. Aqueous solutions were prepared by dissolving the metal salt in analytical grade nitric acid solution to the desired acid and metal concentrations. Both phases were mixed and vigorously shaken at 303 K for 15 h. After phase separation, the spectra of the extraction reagent in the organic phase were measured by a ^1H -NMR spectrophotometer (Jeol JNM-GX300). The metal concentration in the aqueous phase was measured by ICP-AES.

Results and Discussions

Extraction of metal ions

The effect of nitric acid concentration on the extraction percentage of precious and base metals with the trident extraction reagent and the corresponding monopodal analogue is shown in Figure 2. From the results, the extraction percentage of Pd^{2+} with the trident extraction reagent is more than 80% over the whole nitric acid concentration range. In the case of the corresponding monopodal analogue, the extraction percentage of Pd^{2+} increased with increasing nitric acid concentration from 0.01 to 1.0 M. There after the extraction percentage decreased with increasing nitric acid concentration from 1.0 to 8.0 M. The trident extraction reagent exhibited a higher extraction ability for Pd^{2+} than the corresponding monopodal one due to the preorganized effects of the tripodal coordination site. The detailed extraction behavior will be described below.

The extraction percentage of Ag^+ was approximately 70% over the whole nitric acid concentration range. The extraction percentage of Pt^{4+} was 40% at lower nitric acid concentrations, and the extraction percentage significantly decreased with increasing nitric acid concentration. The extraction percentage of Ru^{3+} was 30% over most of the nitric acid concentration range although the extraction percentage decreased at high nitric acid concentration.

Base metals, such as Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} were poorly extracted at any concentration of nitric acid, because such base metals exist as cationic species in nitrate media. In the case of the extraction of cationic species with the neutral ligand, counter anions are necessary for neutralization, consequently it is difficult to extract multivalent cationic species. From these results, the group separation of precious from base metals was achieved.

To confirm the stoichiometries between both phenylurea extraction reagents and Pd^{2+} , the effects of the extraction reagent concentration on the distribution ratio of

Pd^{2+} with both extraction reagents were investigated. The results are shown in Figure 3. For trident molecule extraction reagents, the experimental data lie on the straight lines with a slope of 1 from 1.0 to 3.0 mM and of 2 from 3.0 to 6.0 mM, respectively. On the other hand, for monopodal analogue extraction reagents, the experimental data lie on the straight lines with a slope of 1 from 3.0 to 6.0 mM and of 2 from 9.0 to 18 mM, respectively. Consequently, the stoichiometry was determined to be 1 : 1 (Pd^{2+} : extraction reagent) at relatively low extraction reagent concentration, while a 1 : 2 complex was formed at relatively high extraction reagent concentrations.

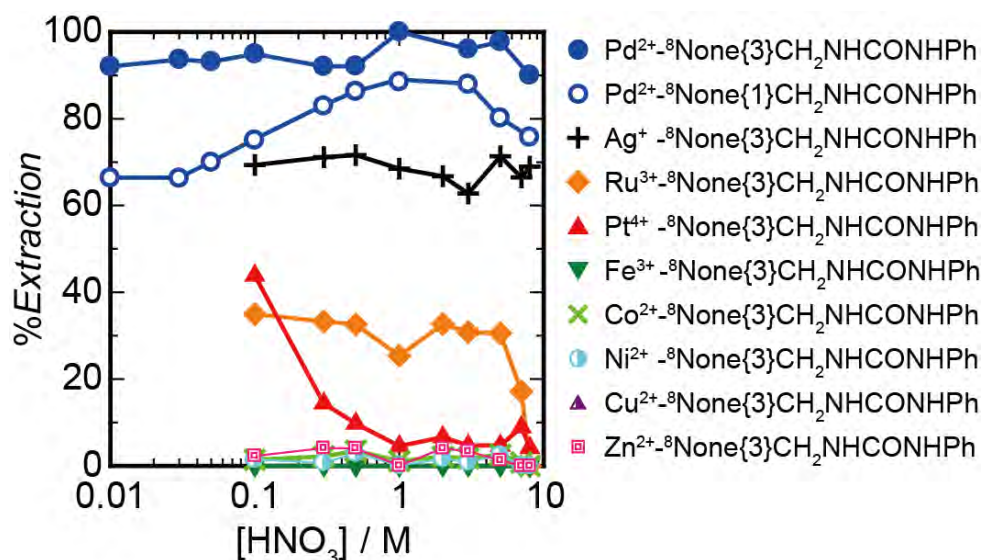


Figure 2 Effect of nitric acid concentration on the extraction percentage of precious and base metals with the trident extraction reagent and the corresponding monopodal analogue.

$[\text{Metal}] = 0.1 \text{ mM}$ each, $[\text{trident}] = 5.0 \text{ mM}$,

$[\text{monopodal}] = 15 \text{ mM}$.

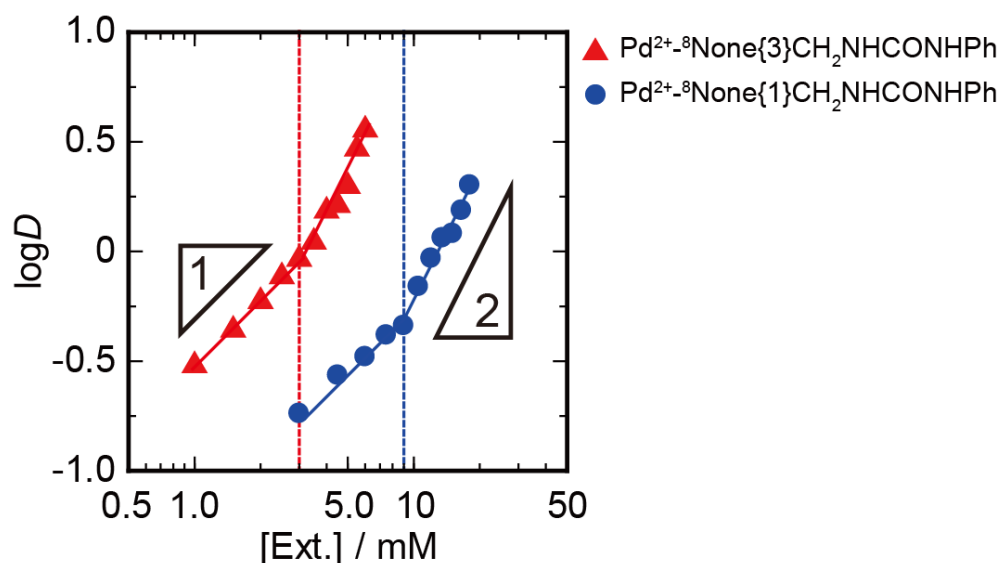


Figure 3 Effect of extraction reagent concentration on the distribution ratio of Pd^{2+} with the both Phenylurea type of extraction reagents. $[\text{Pd}^{2+}] = 0.1 \text{ mM}$, $[\text{HNO}_3] = 1.0 \text{ M}$.

Proton NMR spectrum

To elucidate the extraction mechanism of Pd^{2+} with the trident reagent, a ^1H -NMR spectrophotometric study was carried out. The ^1H -NMR spectra of the phenylurea trident extraction reagent before and after Pd^{2+} loading in nitrate media are shown in Figure 4. The methylene protons next to the branched carbon ($\text{C}-\text{CH}_2-\text{NH}$) and phenyl groups ($\text{NH}-\text{C}_6\text{H}_5$) shift to a lower magnetic field after Pd^{2+} loading. The peaks of the free methylene protons next to the branched carbon and phenyl groups were not observed after Pd^{2+} loading. The peak shifts took place *via* a change in the electron density of the coordinating atoms. From these results, three carbonyl oxygen atoms coordinate in a complementary manner with the palladium and the structure of the tripodal site changed after palladium loading. This result is supported by FT-IR, together with the slope analysis [16].

Consequently, palladium recognition took place at the inner tripodal site. It was suggested that the preorganized effects of the trident extraction reagent contributed to palladium extraction.

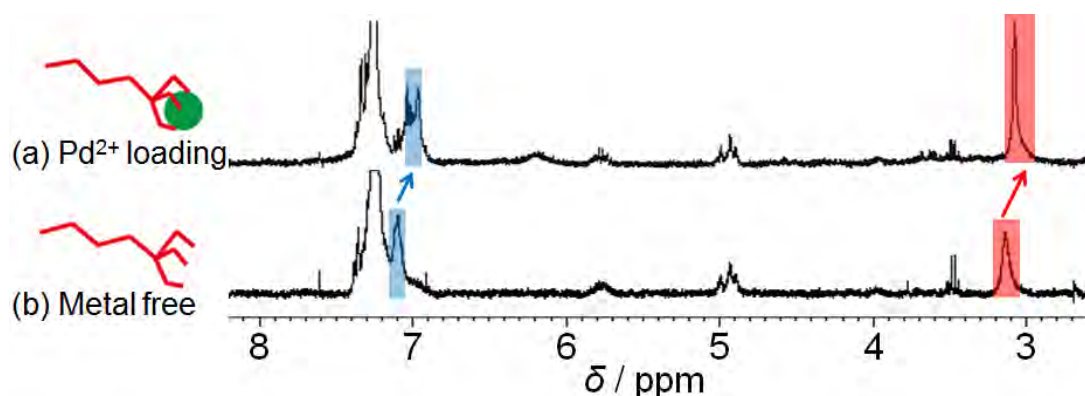


Figure 4 ^1H -NMR spectra of the phenylurea type of trident molecule extraction reagent (a) before and (b) after Pd^{2+} loading in nitrate media. $[\text{Pd}^{2+}]_i = 5.0 \text{ mM}$, $[\text{HNO}_3] = 1.0 \text{ M}$, $[\text{None}\{3\}\text{CH}_2\text{NHCONHPh}] = 5.0 \text{ mM}$, Aq. phase = 17 cm^3 , Org. phase = 3 cm^3 .

Conclusions

The phenylurea type of the trident extraction reagent exhibited selectivity for palladium and silver over other precious and base metals. The extractability of the trident extraction reagent for $\text{Pd}(\text{II})$ was higher than that of the monopodal analogue due to the complementary effects of metal recognition groups as indicated by the FT-IR spectra and ^1H -NMR spectra. From slope analysis, the stoichiometry for the trident extraction reagent and palladium was 1 : 2 (metal : extraction reagent) at high concentration of the extraction reagent.

References

1. J. T. Kummer, *Prog. Energy Combust. Sci.*, **6**, 177-199 (1980)
2. J. Wei, E. Iglesia, *J. Catal.*, **225**, 116-127 (2004)
3. B. J. Glaister, G. M. Mudd, *Miner. Eng.*, **23**, 438-450 (2010)
4. E. Benguerel, G. P. Demopoulos, G. B. Harris, *Hydrometallurgy*, **40**, 135-152 (1996)
5. J. Rydberg, M. Cox, C. Musikas, G. R. Choppin, *Solvent Extraction Principles and Practices* Second Edition, Marcel Dekker, Inc., New York, (2004) 455-505
6. G. Levitin, G. Schmuckler, *React. Funct. Polym.*, **54**, 149-154 (2003)
7. T. Fujii, H. Yamana, M. Watanabe, H. Moriyama, *J. Radioanal. Nucl. Chem.*, **247(2)**, 435-437 (2001)
8. K. J. Naidoo, G. Klatt, K. R. Koch, D. J. Robinson, *Inorg. Chem.*, **41**, 1845-1849 (2002)
9. M. Kawashima, H. Kawakita, K. Ohto, Y. Shiwa, *Solvent Extr. Res. Dev., Jpn.*, **19**, 41-50 (2012)
10. B. B. Adhikari, M. Gurung, H. Kawakita, K. Ohto, *Chem. Eng. Sci.*, **78**, 144-154 (2012)
11. Y. Ueda, S. Morisada, H. Kawakita, K. Ohto, *Solvent Extr. Res. Dev., Jpn.*, **20**, 53-63 (2013)
12. R. Yamaguma, A. Yamashita, H. Kawakita, T. Miyajima, C. Takemura, K. Ohto, N. Iwachido, *Sep. Sci. Technol.*, **47(9)**, 1303-1309 (2012)
13. H. Narita, M. Tanaka, K. Morisaku, T. Abe, *Hydrometallurgy*, **81**, 153-158 (2006)
14. T. Fujii, H. Yamana, M. Watanabe, H. Moriyama, *J. Radioanal. Nucl. Chem.*, **247(2)**, 435-437 (2001)
15. N. Busschaert, P. A. Gale, *Angew. Chem. Int. Ed.*, **52**, 1374-1382 (2013)
16. Y. Ueda, S. Morisada, H. Kawakita, K. Ohto, *Solvent Extr. Res. Dev. Jpn.*, **21**, 9-19 (2014)

Non-steroidal analgesics and β -lactam antibiotics extraction with binary extracting agents

Alexandr L. Gulevich, Prof., Dr. rer. nat. habil., Belarusian State University, Minsk, Belarus

a.l.gulevich@mail.ru

Volga I. Kuksa, Belarusian State University, Minsk, Belarus

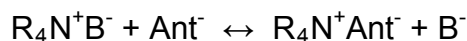
Summary

Constants of anion-exchange extraction of non-steroidal analgesics (ibuprofen, ortofen, naproxen, ketoprofen) and some β -lactam antibiotics (ampicillin, amoxicillin, oxacillin, ceftazidime, ceftriaxone, cefaclor etc.) with higher quaternary ammonium salts solutions were determined to increase by up to 5 orders of magnitude in the presence of nitro- and chlorine-substituted 2,2,2-trifluoro-1-phenyl-ethanone. Effect value varies in direct proportion to concentration of solvating agent and correlates well with sum of Hammett σ -constants of substituents. With the use of analysis of log-log dependences $\lg K_{\text{ex}} - \lg[S]$ formation constants of solvates ($K_S \approx 10^3 \div 10^5$) and stoichiometry of forming solvate complexes ($p \approx 1$) were calculated. Linear correlation between formation constants of solvates and exchange constants was found.

The most promising way for intensification of extraction of hydrophilic anions, including non-steroidal analgesics (ibuprofen, ortofen, naproxen, ketoprofen) and some β -lactam antibiotics (benzylpenicillin, ampicillin, amoxicillin, oxacillin, ceftazidime, ceftriaxone, cefaclor, cefuroxime), is the use of binary extracting agents, i.e. mixtures of liquid anion exchanger (higher quaternary ammonium salt) and solvating agent in organic solvent. In the presence of solvating agent tight solvates in organic phase occur:

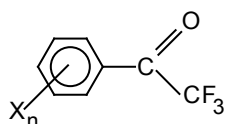


and the equilibrium of the main anion-exchange reaction



shift to the right (where $R_4N^+B^-$ - higher quaternary ammonium salt in B-form, $R_4N^+Ant^-$ - analgesic or β -lactam antibiotic anion).

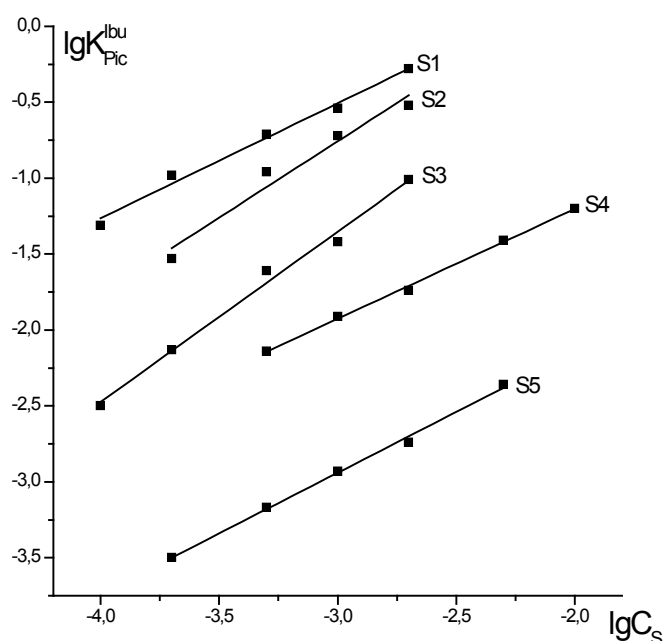
Substituted derivatives of 2,2,2-trifluoro-1-phenyl-ethanone are used as solvating agent.



Carbon atom of carbonyl group of fluoroketones is a hard electrophilic center, for which it is typical to attach hard nucleophilic reagents. Since electrophilicity of carbonyl group changes proportionally to polar effect of substituents X_n , characterized by Hammet constants, purposeful synthesis of highly efficient solvating agents is possible.

Several derivatives of 2,2,2-trifluoro-1-phenyl-ethanone with different substituents were synthesized and their efficiency in extraction system with non-steroidal analgesics and β -lactam antibiotics anions was investigated.

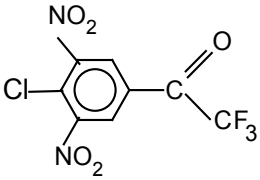
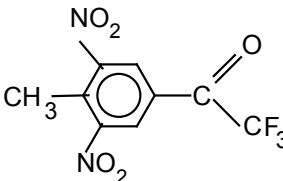
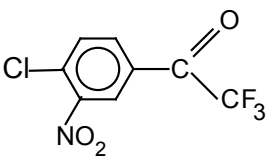
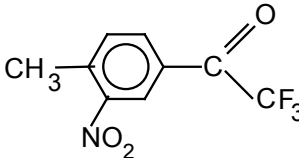
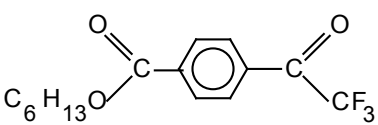
All of the synthesized solvating agents were determined to be highly efficient at extraction of non-steroidal analgesics and β -lactam antibiotics anions. In pic.1 log-log dependence between conditional exchange constants of ibuprofen and concentrations of the solvating agents is shown. As seen in pic.1, efficiencies of the solvating agents differ greatly, but all the dependences are linear.



Picture 1. Comparative plot of log-log dependence $\lg \tilde{K}_{Pic}^{Ibu} - \lg C_s$ for different solvating agents

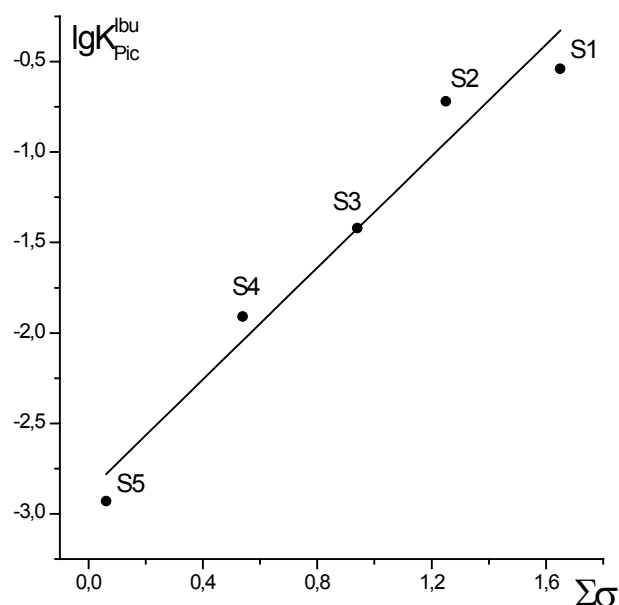
Efficiency of synthesized solvating agents is shown in table 1. As seen in table 1, exchange constants naturally increase according to the rise of electron-accepting affinity of substituents and correlate well with the sums of Hammet constants (pic.2).

Table 1. Comparative rating of solvating agents' efficiency at extraction of ibuprofen anions

Designation	Solvating agent	$\lg \tilde{K}_{\text{Pic}^-}^{\text{ibu}^-}$	$\Delta \lg \tilde{K}_{\text{Pic}^-}^{\text{ibu}^-}$
	without solvating agent	-3,48	0
S1		-0,54	2,94
S2		-0,72	2,76
S3		-1,42	-2,06
S4		-1,91	1,57
S5		-2,93	0,55

* Concentration of solvating agent in organic phase was $1,0 \cdot 10^{-3}$ M

As expected, the greatest effect was gained for structure S1, which had three substituents – chlorine in para position and two nitro-groups in meta positions. At equal concentrations of solvating agents (10^{-3} M) the greatest effect value comparatively to hexyl 4-(2,2,2-trifluoroacetyl)benzoate was 2,39 orders of magnitude, in comparison to extracting agent solution without solvating agent – 2,94 orders of magnitude.



Picture 2. Hammett correlative dependence at ibuprofen-anions extraction with toluene solution of trionyloctadecylammonium picrate in the presence of substituted 2,2,2-trifluoro-1-phenyl-ethanone. Straight-line equation: $\lg \tilde{K}_{\text{Pic}}^{\text{Ibu}} = -2,87 + 1,54 \cdot \Sigma\sigma, R = 0,98$

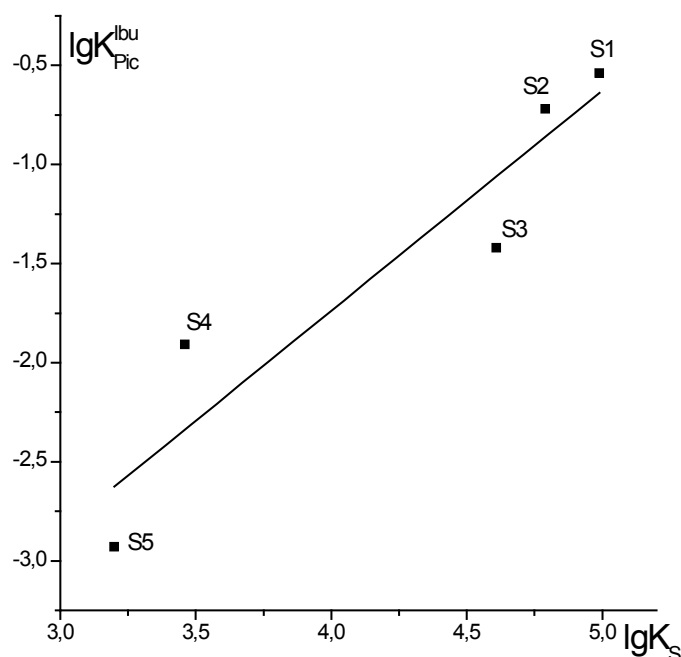
Hammett equation $\lg K = \lg K_0 + \rho \Sigma\sigma$ also contains coefficient ρ , which reflects sensitivity of anion-exchange reaction to variation of electrophilicity of 2,2,2-trifluoro-1-phenyl-ethanone. Obtained high value of $\rho = 1,54 \pm 0,17$ can be explained by low polarity of toluene and correlates with values of ρ obtained by other authors from study of anion-exchange in chlorobenzene ($\rho = 1,89 \pm 0,04$) and methyl n-butylketone ($\rho = 1,71 \pm 0,06$).

Analysis of log-log dependence in pic.1 allowed calculating formation constants of solvates and stehiometry of the forming solvate complexes (table 1). As seen from calculated data, average solvation numbers for all the solvating agents are close to 1 and formation constants of solvates correlate with exchange constants.

Table 3. Logarithms of solvation constants and average solvation numbers in extraction system Ibu/(R₄N⁺Pic + S) in toluene

Designation	$\lg K_s \pm \delta$	$\bar{p} \pm \delta$
S1	4,99±0,47	0,93±0,12
S2	4,79±0,38	0,93±0,10
S3	4,61±0,38	1,07±0,12
S4	3,46±0,28	0,92±0,10
S5	3,20±0,37	1,05±0,14

For the studied solvating agents good correlation with their influence on exchange constants was observed (pic. 3).



Picture 3. Log-log dependence $\lg \tilde{K}_{Pic}^{Ibu} - \lg K_s$ for different solvating agents. Straight-line equation: $\lg \tilde{K}_{Pic}^{Ibu} = -6,18 + 1,11 \cdot \lg K_s$, $R = 0,94$.

Thereby substituted 2,2,2-trifluoro-1-phenyl-ethanone has high solvation properties and can increase exchange constants by 3 orders of magnitude when used at concentration as low as $10^{-3}M$.

Taking into consideration that rise in concentration of solvating agent causes proportional rise in exchange constant, it's possible to gain more efficiency (up to 5 orders of magnitude) using higher concentrations of solvating agents.

Analogous results were achieved in studies of anion-exchange extraction of β -lactam antibiotics.

Sorption behaviour of Cd(II) sorption from aqueous solutions using polymeric microcapsules containing an acidic organophosphonic extractant

*Viviana Ide O.^{*1}, Carlos Basualto², Jaime Sapag², Claudio Araneda², Fernando Valenzuela L.²*

The equilibrium, kinetics, and thermodynamics of Cd(II) sorption from aqueous solutions onto polymeric microcapsules has been studied. Microcapsules were prepared by immobilizing an acidic organophosphonic extractant in a polymeric matrix prepared from styrene and ethylene glycol dimethacrylate following in situ free-radical suspension polymerization. Scanning electronic microscopy showed that the microcapsules were spherical and exhibited a rough surface with an average BET surface area of $12\text{--}20\text{ m}^2\text{ g}^{-1}$ and an approximate pore size of 7.0 nm. The microcapsules were contacted with aqueous solutions containing Cd(II) approximately 100 mg L^{-1} at an initial pH = 4.0 to study their sorptive behaviour over a temperature range of 293–323 K. The results of equilibrium experiments showed that the results fitted the Langmuir isotherm model. The experimental kinetics followed a pseudo-second order model with an activation energy of $47.1 \pm 2.2\text{ kJ mol}^{-1}$. Thermodynamics measurements showed that sorption is spontaneous and exothermic and that entropy had a negative value.

Introduction

Ion-exchange provides valuable options for the treatment of solutions contaminated with low concentrations of metallic ions that may exceed the concentration limits set by various environmental regulations. Ion-exchange systems are normally easy to employ in simple processing systems because most function by using solid ion-exchange resins in continuous columns or by using liquid extractants in mixer–settler reactors. In previous articles, we have reported the sorption of several metallic ions from aqueous solutions using different microcapsules containing diverse extractants in various polymers matrices.^[1–3] In this work, we report the synthesis and characterization of polymeric microcapsules containing an acidic organophosphonic extractant for the sorption of Cd(II) from aqueous solutions. Cadmium was chosen because it is present in many industrial aqueous waste solutions arising from its industrial applications and its high level of toxicity.

Experimental

Reagents and Solutions: the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (Daihachi Chemical Industry Co. Japan), was used without further purification. Styrene (St) and ethylene glycol dimethacrylate (EGDMA) were supplied by Sigma-Aldrich in purities >98% and were used as received to synthesize the polymeric matrix with benzoyl peroxide USP-grade (Sigma-Aldrich) as a polymerization initiator. Toluene and gum arabic, both reagent grade, were used as a

^{*1}Universidad de Chile, mail: vivideopa@hotmail.com

²Universidad de Chile.

solvent and a dispersant, respectively, during the microcapsule synthesis. Sorption tests were conducted using aqueous cadmium solutions prepared by dissolving CdCl_2 (Merck r.g.) in distilled water with the initial pH adjusted to approximately 4.0.

Synthesis and Characterization of Microcapsules

The polymeric matrix of P(St-co-EGDMA) was synthesised by in situ radical suspension polymerization in a three-necked round-bottom flask equipped with mechanical stirring and immersed in a water bath at 343 K.^[3] First, a solution of gum arabic in water was heated and after reaching the desired temperature, a toluene solution of the phosphonic extractant, the monomers (St and EGDMA), and benzoyl peroxide initiator were added and dispersed in the continuous aqueous phase with stirring. After reacting for 3 h, the resulting microcapsules were filtered, washed with distilled water, and dried overnight at room temperature. The alkylphosphonic extractant content immobilized within the microcapsules was measured potentiometrically as previously reported.^[1] The microcapsules were also examined by scanning electron microscopy (SEM) using a JEOL JSM-25SII. Porosimetry analyses were conducted using a Micromeritics ASAP 2010 porosimeter, and the mean particle size determined using a Malvern Mastersizer Hydro 2000 MU apparatus.

Equilibrium, Kinetics, and Thermodynamics Experiments

To obtain information about the equilibrium and kinetics governing the metal adsorption and to obtain data on the thermodynamic aspects of the process, several experiments were conducted by contacting microcapsules (0.2 g) and aqueous solutions containing Cd(II) (25 mL, 100 mg L⁻¹) at pH 4.0 in a Polyscience orbital-shaker apparatus with the temperature varied between 293–323 K. After the experiments were completed, the metal-loaded microcapsules were separated by conventional filtration and the concentrations of metallic ions in the raffinate solutions were measured by atomic absorption spectrophotometry (Perkin Elmer 3110).

Results and discussion

Microcapsule synthesis, and characterization

Immobilization of the extractant in the porous structure of the microcapsules was almost quantitative, and the resulting microcapsules were easily separated from the reaction medium by settling and filtration. The results of hydrophobicity tests indicate high stability of the organic liquid extractant in the polymeric matrix, even after a prolonged time period. SEM micrographs of the microcapsules confirmed the results of previous studies that these microcapsules are spherical and exhibit quite rough surfaces. The porosimetry analyses indicate that the microspheres present reproducible characteristics from one production batch to another with respect to their size and porosity with average pore diameters = 7.0 nm, pore volumes = 0.0320 cm³ g⁻¹, average mean particle sizes = 15 – 22 µm, and BET surface areas = 12–20 m² g⁻¹.

Adsorption Equilibrium

The relationship between the quantity of metal adsorbed by the microcapsules and the experimental conditions were determined in batch operations. The amounts of metal adsorbed were plotted against the equilibrium metal concentration and the resulting data modelled using the Langmuir isotherm. The parameters of this equation express the surface properties and the affinity of the sorbent by the adsorbate under certain temperature and pH conditions. The model can be expressed (Eq 1).

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad [Eq\ 1]$$

where q_e = amount adsorbed at equilibrium (mmol g^{-1}), q_m = maximum charge capacity (mmol g^{-1}), K_L = Langmuir's constant (L mmol^{-1}) and C_e = equilibrium metal concentration (mmol L^{-1}). The parameters were evaluated by non-linear regression using the Lavenberg–Marquardt iteration routine. Linear models can cause errors in the determination of sorption constants; therefore, it is more appropriate to minimize the error by determining χ^2 , which represents the error between experimental data and the values obtained from the model.^[4]

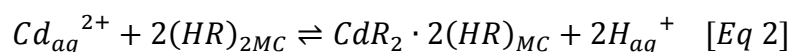
Table 1 presents values of the parameters of the equilibrium sorption model. Analysis of χ^2 and R^2 values reveals that the Langmuir isotherm model fits the experimental results well. This goodness of fit likely results from the active adsorption sites being constantly renewed, which causes a nearly ideal representation of the processes represented by this model. The results in Table 1 indicate a slight increase of adsorbed metal at equilibrium, q_e , with increasing temperature.

This is consistent with the expected increase of the diffusion of the metallic ion active species in the aqueous phase towards the interfacial site of the chemical reaction with the extractant. The Langmuir constant values decrease with temperature indicating an exothermic chemical reaction between the metallic ions and the extractant in the microcapsule surface.

Temperature [°C]	q_e [mmol g ⁻¹]	K_L [L mmol ⁻¹]	R^2	χ [mmol g ⁻¹]
20	0.1074	2.7251	0.9901	0.00001
30	0.1116	1.9200	0.9889	0.00001
35	0.1108	1.8370	0.9826	0.00002
40	0.1221	1.5336	0.9829	0.00002
50	0.1351	1.1814	0.9869	0.00002

Table 1 Parameters of Langmuir equilibrium model for the sorption of Cd(II) onto microcapsules with PC-88A.

This favorable adsorption necessitates the use of a large amount of stripping agent for metal desorption to shift the equilibrium towards the reagents and regenerate the microcapsules for a new extractive cycle. If it is assumed that the extraction chemical reaction between the metal and the extractant (HR) occurs at the surface of the microcapsules, sorption and desorption reactions would proceed according to the following ion-exchange equation:



where $(HR)_2$ and $CdR_2 \cdot 2(HR)$ denote the dimerised alkylphosphonic extractant and the metal–extractant complex. Additionally, the subscripts *aq* and *MC* denote aqueous solution and microcapsule surface, respectively. This extractant dimerizes in many organic diluents, and from other studies^[5,6] $CdR_2 \cdot 2(HR)$ is the most probable complex formed and immobilized inside the microspheres. Equation (2) shows that a high concentration of acid (approximately 200 g L⁻¹) is required to shift the sorption equilibrium towards metal desorption from the microcapsules, as represented by the reverse equation.

Adsorption Kinetics

Experiments were conducted over 2 h time spans, which provided ample time to attain equilibrium, using a Cd(II) feed solution (100 mg L⁻¹) at an initial pH = 4.0. Results of this work were analyzed by applying a pseudo-second order kinetics model based on the sorption capacity of the solid phase—the microcapsule with the extractant—and could be applied to higher concentrations of the adsorbate on the surface of the microcapsules as follows:^[7]

$$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \quad [Eq\ 3] \qquad \ln k = \ln A - \frac{E_a}{RT} \quad [Eq\ 4]$$

(Eq 3) where q_t = molarity of the metal adsorbed onto the MC at any time *t* (mmol g_{MC}⁻¹), k_2 = pseudo-second order reaction rate constant (g_{MC}/mmol·sec) and q_e is as previously defined.

(Eq 4) where k = the rate constant of the pseudo-second order kinetic model; E_a = activation energy of the process (kJ mol⁻¹), R = gas constant (8.314 J mol⁻¹K⁻¹); T = temperature (K), and A = temperature independent frequency factor (g mg⁻¹min⁻¹).

Equation (3) was applied as a non-linear model and the rate-constant values were obtained through iteration as described above. Table 2 shows the results of applying this model to the observed experimental values from 293–323 K. The values for R^2 and χ^2 show that the pseudo-second order kinetic model fits well with the experimental results, confirm those of our previous report that microcapsules behave as granular sorbents in which the extractant is retained almost in a pure state.

Results in Table 2 indicate that the rate constants of the model increase with increasing temperature, consistent with the values in Table 2 for the parameter $k_2 q_e^2$ (mg·g⁻¹·min⁻¹), which reflects the initial adsorption rate when approaches 0 in the pseudo-second order kinetic model. The initial adsorption rate clearly increases with increasing temperature of the process.

Temperature [°C]	q_e [mg g ⁻¹]	k_2 [g/mg·min]	$k_2 q_e^2$	R^2	χ [mg g ⁻¹]
20	5.584	0.072	2.235	0.9962	0.01260
30	5.363	0.143	4.119	0.9899	0.02598
35	5.387	0.180	5.223	0.9937	0.01604

40	5.442	0.217	6.435	0.9902	0.02509
50	5.937	0.460	16.222	0.9958	0.01805

Table 2 Parameters of the pseudo-second order kinetic model applied to Cd(II) adsorption with PC-88A immobilized in P(S-coEGDMA) microcapsules.

The activation energy is determined by the Arrhenius equation (Eq 4) and is equally valid for chemical reaction as for the diffusion steps because both depend on the Arrhenius temperature. The experimental results were plotted according to Eq. (4) over the temperature range from 293–323 K, giving a linear Arrhenius plot with fairly good correlation of the plotted data ($R^2 = 0.9872$). An activation energy of $47.1 \pm 2.2 \text{ kJ mol}^{-1}$ was obtained from the slope and the intercept, representing a characteristic activation energy of a rate-determining step shared between diffusion steps ($E_a < 30 \text{ kJ mol}^{-1}$) and chemical reaction ($E_a > 60 \text{ kJ mol}^{-1}$).^[8] An activation energy of 47.1 kJ mol^{-1} indicates that although chemical reaction plays a significant role in the adsorption process of the metal onto the microcapsule, diffusion of the metal ions towards the surface of the microcapsule and the intraparticle diffusion of the metal–extractant complex inside the pores of microspheres must be taken into account to develop an overall kinetic model for the system.

Thermodynamic Aspects

Based on the results reached in the equilibrium study, the Langmuir model was considered appropriate for interpretation of the thermodynamics. Thus the Langmuir constant, K_L , can be considered as the equilibrium constant for the overall extraction process based on chemisorption. The Van't Hoff equation can now be applied to determine the thermodynamics parameters as follows:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T} \quad [\text{Eq 5}] \quad \Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad [\text{Eq 6}]$$

where K_L = Langmuir constant (L mol^{-1}); ΔH^0 = standard enthalpy (kJ mol^{-1}); ΔS^0 = standard entropy change ($\text{J mol}^{-1}\text{K}^{-1}$); and T and R are the equation defined above (Eq 4). Measured values of K_L vs T were plotted according to Eq. (5) giving a linear plot with a good correlation ($R^2 = 0.9879$). The standard enthalpy and standard entropy were obtained respectively from the slope and intercept and from these values the Gibbs free energy (ΔG^0 ; J mol^{-1}) can be calculated, the value of which indicates the spontaneity of the process (Eq 6).

Temperature [K]	$\Delta S^0 [\text{J mol}^{-1}\text{K}^{-1}]$	$\Delta H^0 [\text{kJ mol}^{-1}]$	$\Delta G^0 [\text{kJ mol}^{-1}]$	R^2
293	-8.8 ± 0.3	-21.8 ± 0.8	19.26 ± 0.72	0.9879
303			-19.17 ± 0.96	
308			-19.13 ± 0.87	
313			-19.09 ± 0.72	
323			19.00 ± 0.76	

Table 3 Thermodynamics parameters according to the Van't Hoff equation for Cd(II) adsorption onto microcapsules.

Table 3 shows the values for ΔG^0 , ΔH^0 , and ΔS^0 over the temperature range studies which indicate a spontaneous sorption process for the metal with the microspheres loaded with extractant, consistent with the fast adsorption of the metal from aqueous solution. The sorption process is exothermic given the decrease, although slight, of the Gibbs free energy with temperature. The exothermicity of the process is also consistent with a Langmuir constant that decreases with decreasing temperature (Table 1). Furthermore, the negative entropy change introduces the possibility of reusing the same microcapsules in different cycles of adsorption with fresh feed aqueous solutions because the microcapsules would not suffer physical modifications, especially with regard to their form, size, and pore structure during the process.

Conclusions

The synthesis provides an immobilized extractant in the porous structure of the solid matrix of the spherical and roughly surfaced microcapsules.

The equilibrium determinations fitted well to the experimental results suggesting that the active adsorption sites are permanently renewed.

Kinetic determinations provided a good fit, confirming that the microcapsules act as granular sorbents. The activation energy of $47.1 \pm 2.2 \text{ kJ mol}^{-1}$ indicates that the rate-determining step is shared between diffusion and chemical reaction.

Thermodynamic determinations indicate a spontaneous sorption process and the process is exothermic. Finally, we conclude from this study that the extractant inside the microcapsules retains its effectiveness as an ion exchanger as observed in conventional liquid-liquid solvent extraction.

Acknowledgments

The authors gratefully acknowledge the support of The National Fund of Science and Technology of Chile (CONICYT) through project FONDECYT No 1100151. V. Ide acknowledges a Doctoral Fellowship from CONICYT.

References

1. Araneda, C.; Fonseca, C.; Sapag, J.; Basualto, C.; Yazdani-Pedram, M.; Kondo, K.; Kamio, E.; Valenzuela, F. *Sep. Purif. Technol.* 172, 262–268.
2. Fonseca, C.; Araneda, C.; Yazdani-Pedram, M.; Borrmann, T.; Basualto, C.; Sapag, J.; Valenzuela, F. *J. Chil. Chem. Soc.* 55(3), 408–414.
3. Barassi, G.; Valdés, A.; Araneda, C.; Basualto, C.; Sapag, J.; Tapia, C.; Valenzuela, F. *J. Hazard. Mater.* 172, 262–268.
4. Ho, Y.S. *Carbon*. 42, 2115–2116.
5. Nakashio, F.; Kondo, K.; Murakami, A.; Akiyoshi, Y. *J. Chem. Eng. Jpn.* 15, 274–279.
6. Sato, Y.; Valenzuela, F.; Tsuneyuki, T.; Kondo, K.; Nakashio, F. *J. Chem. Eng. Jpn.* 20, 317–321.
7. Ho, Y.S. *J. Hazard. Mater.* 136, 681–689.
8. Kamio, E.; Matsumoto, M.; Valenzuela, F.; Kondo, K. *Ind. Eng. Chem.* 44, 2266–2272.

Formation and extraction ability of reverse micelle by intermolecular interaction between di (2-ethylhexyl) phosphoric acid and ethanolamines

K. Shiomori, K. Ejima, Dept. Applied Chem., Univ. Miyazaki, Miyazaki 889-2192, Japan,; S. Kiyoyama, Dept. Chem. Sci. Eng., Miyakonojyo Natnl. Collage Tech., Miyakonojyo 885-8567, Japan; T. Sana, Sansei Giken Co. Ltd., Yoshikawa 342-0008, Japan

The molecular interaction of ionic surfactants with counterionic molecules affects their interfacial properties and formation of molecular assemblies. In order to control these interactions, it is expected to develop new functional molecular assemblies to show stimuli-responsive properties and molecular recognition. In this study, formation of reverse micelle by intermolecular interaction between di (2-ethylhexyl) phosphoric acid and ethanolamines and extraction ability of proteins by the reversed micellar system developed have been investigated.

Di (2-ethylhexyl) phosphoric acid (DEHPA) dissolved in isooctane has low ability to form reverse micelles in the two-phase partitioning method. By the addition of ethanolamines, such as diethanolamine, triethanolamine and tris(hydroxymethyl) amino methane, in the aqueous phase, reverse micelles of DEHPA were formed with high extraction of water. Furthermore the addition of octanol in the organic phase was drastically stabilized the reverse micelles. Extraction of water into the mixed micellar systems was controlled by pH in the aqueous phase. When triethanolamine was added in the aqueous phase, the extraction of water was enhanced at pH between 5.5 and 8.5. The ethanolamines added to the aqueous phase would be extracted into the water pool of the reverse micelles by the electrostatic interaction with the head group of DEHPA and enhance the ability to form the reverse micelles. The reverse micellar system consisted of DEHPA and the ethanolamines shows a high ability to extract cytochrome-c which was back-extracted at pH higher than its pI value. The effects of the extraction condition on the extraction properties of water and proteins by the reverse micellar system of DEHPA were investigated under various conditions.

The new and effective reverse micellar system has been developed using molecular interaction between DEHPA and ethanolamines.

Solvent Extraction of Palladium from Hydrochloric Acid Media by *N,N*-disubstituted Thioamides

A.P. Paiva^{*1}, *O. Ortet*²

Summary

Two new *N,N*-disubstituted thioamides are proposed as efficient and selective extractants for palladium(II) recovery from hydrochloric acid solutions. It was found that Pd(II) is effectively extracted from 0.5 to 8.0 M HCl aqueous phases by both extractants in toluene, with a favourable kinetics, and easily stripped by thiourea in HCl. The different alkyl groups of both thioamides do not remarkably affect the overall solvent extraction performance towards Pd(II). Sequential extraction-stripping tests for Pd(II) have been carried out for the two extractants, and the results obtained denote good stability profiles. Data collected from extraction isotherms, supported by UV-visible and ¹H NMR spectra, allow suggestions for the composition of the involved Pd(II) extracted species. Selectivity tests based on the extraction of binary and ternary metal solutions involving Pd(II), Pt(IV) and Rh(III), in 4 M and 6 M HCl, evidence the promising behavior these solvents may have to achieve the successful separation of Pd(II), from Pt(IV) and Rh(III), through a one-stage solvent extraction process.

Introduction

Platinum, palladium and related rare metals are nowadays considered critical raw materials. Platinum-group metals (PGMs) are scarce in the Earth's crust, therefore the maintenance of their supply is a necessity. In addition to the large PGMs utilization in areas such as jewelry and health, their hardly replaceable technological applications in last years – for example, in electronics, fuel cells, and in automobile and industrial catalysts [1] – motivates a wide research aiming to their efficient and selective recycling from secondary sources. Hence, the development of new and modified hydrometallurgical processes to achieve the separation and concentration of PGMs from specific industrial leaches or effluents becomes an important task [2], and solvent extraction may play an important role to accomplish those objectives.

The hydrometallurgical industry applies solvent extraction to recover Pd(II) from chloride leaching solutions of minerals and concentrates through the main utilization of alkyl sulfides, hydroxyoximes and 8-hydroxyquinolines [3]. These extractants are generally not so appropriate to process leaches resulting from the recycling of secondary sources, with more complex and specific compositions. Accordingly, research focusing on the development of new types of extractant compounds, which may show a more versatile behavior regarding kinetics and selectivity, for example, is currently quite active.

Some alternative extractant molecules have recently been proposed for Pd(II) recovery from complex chloride aqueous phases, namely those coming from the leaching of spent automobile catalysts. Sulfide-containing monoamides [4] have been

^{*1} CQB, DQB-FCUL, Universidade de Lisboa, 1749-016 Lisbon, Portugal. E-mail: appaiva@fc.ul.pt

² CQB, DQB-FCUL, Universidade de Lisboa, 1749-016 Lisbon, Portugal, and DCT, Universidade de Cabo Verde, Praia, Santiago Island, Cape Verde.

specifically reported as fast and efficient extractants for Pd(II) from such matrices, being selective over other metals, and easily stripped by a 28% ammonia solution. A similar application has been found for a dithioether derivative [5], but the use of 1,2-dichlorobenzene as diluent and extraction rates ranging from 50 to 500 minutes, depending on the aqueous HCl concentrations, can be pointed out as major drawbacks. Thiodiglycolamides have also shown potentialities to efficiently recover Pd(II) from complex chloride media [6,7]. In sequence of all these works, *N,N'*-disubstituted thioamide derivatives came to mind to be tested as PGMs extractants, as the corresponding “non-thio” monoamides have already been produced in the laboratory [8], and their conversion to the respective thio derivatives could be easily achieved [9]. The general solvent extraction characteristics shown by two new thioamide compounds towards Pd(II) - *N*-methyl-*N*-phenyl-octanthioamide (MPHTA) and *N*-methyl-*N*-cyclohexyl-octanthioamide (MCHTA) - are described herein.

Experimental

Syntheses of MPHTA and MCHTA were carried out from the corresponding amides [8] using the Lawesson reagent [9]. Both compounds were conveniently characterized by chromatographic and spectroscopic techniques, revealing purities above 88% and 98%, respectively. 0.03 M MPHTA and MCHTA solutions in toluene were generally used as organic phases.

For the preparation of the feed aqueous solutions, atomic absorption spectroscopy standards of Pt(IV), Pd(II) or Rh(III) were arranged. Metal ion concentrations were typically of about 100 mg/L, prepared for several HCl aqueous media. Distilled water, 0.5 M aqueous ammonia, 0.5 M NaCl, 1 M HCl, 0.1 M thiourea in 1 M HCl, were used as stripping agents.

General extraction and stripping experiments were performed at room temperature through contact of equal volumes of the organic and aqueous phases ($A/O = 1$) by mechanical shaking, adopting a rotation speed between 900 and 1000 rpm. The contact times were generally of 30 minutes, both for extraction and stripping. After phase separations, both solutions were always filtrated, to minimize mutual entrainments. In reutilization, the same volume of organic phase suffered sequential extraction and stripping contacts, with $A/O = 1$. Fresh portions of aqueous solutions containing 100 mg/L and 200 mg/L Pd(II), in 4.54 M HCl, were successively contacted with the same fraction of 0.03 M MPHTA or 0.033 M MCHTA in toluene, using A/O ratios of 2 and 3, to achieve their maximum Pd(II) loading saturation paths.

Pd(II) concentrations in the aqueous solutions, before and after extraction, were determined by flame atomic absorption spectrophotometry (AAS, novAA 350, Analytik Jena). Inductively coupled plasma–atomic emission spectrometry (ICP-AES, Horiba Jobin-Yvon, Ultima) was used to analyze the multi-metallic solutions. Metal concentrations in organic phases were found by mass balance. The coefficient of variance calculated for the extraction and stripping results presented in this article is about $\pm 5\%$.

UV-visible spectra of Pd(II) loaded MPHTA and MCHTA organic solutions were recorded in an UV Shimadzu 1800 CE 230V apparatus, connected to a TCC controller fixed at 25°C. Quartz cells were used. ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance 400 (400 MHz for ^1H and 100 MHz for ^{13}C nuclei) using deuterated chloroform as solvent.

Results and Discussion

Dependence of Pd(II) extraction on HCl concentration and extraction kinetics

Extraction experiments were carried out with 100 mg/L Pd(II) in 0.50 M to 8.00 M HCl solutions, and 0.03 M MPHTA or MCHTA in toluene as organic phases. The results obtained for both compounds are displayed in Figure 1.

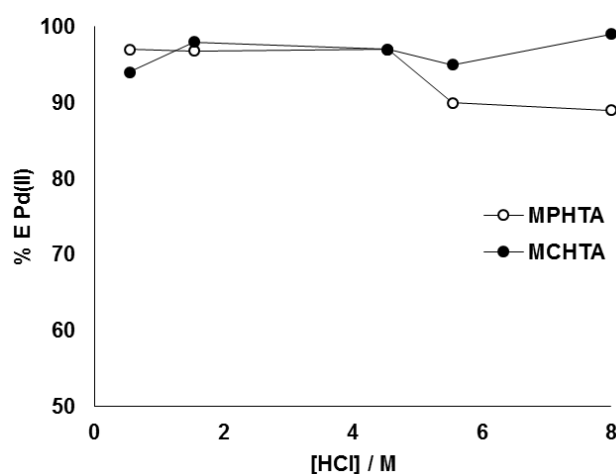


Figure 1 – Effect of HCl concentration on Pd(II) extraction by 0.03 M MPHTA or MCHTA solutions in toluene. [Pd(II)] = 100 mg/L, A/O=1, room temp., 30 min. contact. Standard deviations: $\pm 5\%$.

It can be observed that Pd(II) is effectively extracted by both compounds in a large range of HCl concentrations, with %E typically above 90%. Kinetic experiments were subsequently carried out, for feed solutions bearing 1.54 M and 4.54 M HCl, in order to evaluate if the systems had reached equilibrium or not. The data collected is presented in Figure 2.

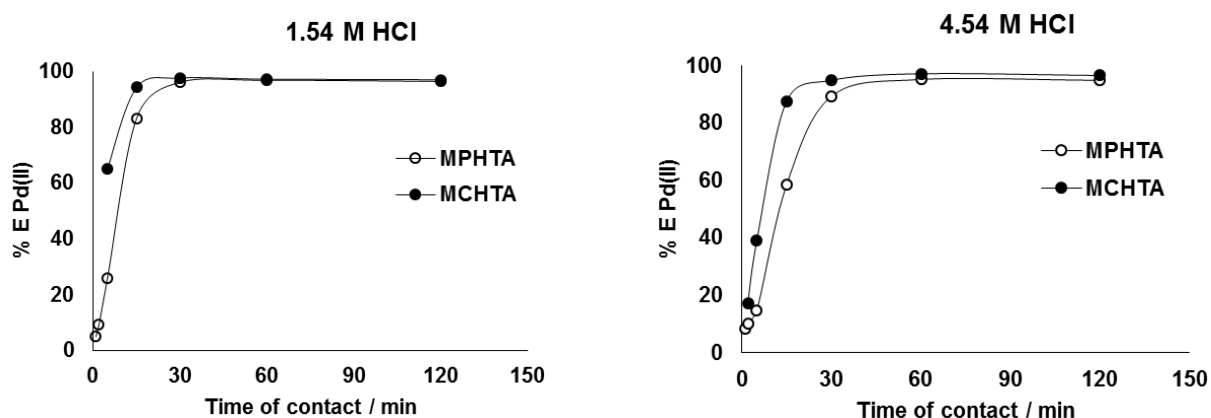


Figure 2 - Effect of contact time on Pd(II) extraction from 1.54 M and 4.54 M HCl solutions by 0.03 M MPHTA or MCHTA in toluene. [Pd] = 100 mg/L, A/O=1, room temp. Standard deviations: $\pm 5\%$.

Figure 2 shows that equilibrium is reached by both MPHTA and MCHTA in 30 minutes for 1.54 M HCl. When a 4.54 M HCl is involved, particularly for MPHTA, it seems 60 minutes are advisable. However, contacts of 30 minutes were generally adopted throughout the whole work.

Composition of the Pd(II) extracted species

The time necessary to reach equilibrium conditions, varying between 30 to 60 minutes, suggests that Pd(II) extraction should not occur through the formation of ion-pairs between protonated MPHTA or MCHTA and $[\text{PdCl}_4]^{2-}$ [7]. Additionally, UV-visible spectra of both Pd(II) loaded solvents do not evidence the presence of a band at 476 nm, typical of this Pd(II) chlorocomplex [10], and the ^1H and ^{13}C NMR spectra of MPHTA, after equilibration with a 4.54 M HCl solution, did not suffer any change. Extraction isotherms were obtained both for MPHTA and MCHTA from 4.54 M HCl solutions, which are depicted in Figure 3.

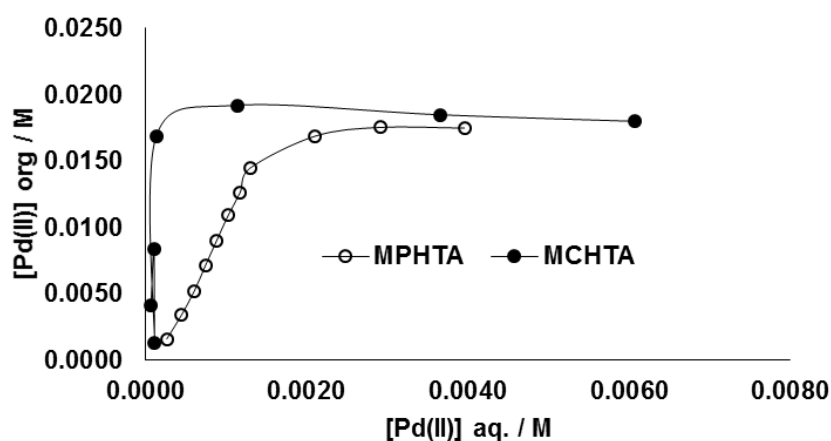


Figure 3 – Extraction isotherms obtained by successive contacts of 0.03 M MPHTA, and 0.033 M MCHTA, in toluene. $[\text{Pd}] = 100$ and 200 mg/L in 4.54 M HCl, A/O = 2 or 3, 30 minutes contact, room temp. Standard deviations: $\pm 5\%$.

MPHTA and MCHTA reveal a quite good capacity to load Pd(II), and both saturate at a mole ratio extractant: Pd(II) of 1.7. Therefore, at these conditions, a mixing of 2:1 and 1:1 species should exist. Proposals for those Pd(II) extracted species by MPHTA and MCHTA are $[\text{PdCl}_2\text{L}_2]$ and $[\text{Pd}_2\text{Cl}_4\text{L}_2]$, respectively (L being MPHTA or MCHTA), and assuming that the two organic compounds exist under a monomeric form in toluene. These compositions are in accordance with those of the Pd(II) species formed upon extraction by pyridine carboxamides, reported in [11].

Stripping and reutilization

Several stripping agents were tested to release Pd(II) from the loaded organic phases of both MPHTA and MCHTA. Pd(II) recovery by water, 1 M HCl and 0.5 M NaCl did not exceed 10%, whereas 0.5 M ammonia permitted a stripping of 25% Pd(II). More concentrated ammonia solutions caused the formation of stable emulsions. The use of 0.1 M thiourea in 1 M HCl allowed almost quantitative Pd(II) recoveries. In order to evaluate the stability of both extractants when successively

reused, four sequential cycles of extraction / stripping were carried out for the same portion of organic solvent. The results obtained are presented in Figure 4.

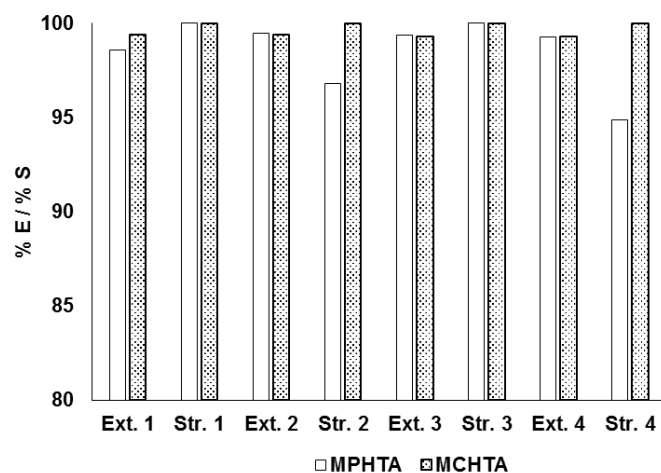


Figure 4 – Sequential extraction and stripping experiments for Pd(II) recovery by 0.03 M MPHTA or MCHTA in toluene. [Pd] = 100 mg/L in 4.54 M HCl, 0.1 M thiourea in 1 M HCl for stripping. A/O=1, room temp., 30 minutes contact. Standard deviations: $\pm 5\%$.

It can be observed that both extraction (%E) and stripping (%S) values shown by MPHTA and MCHTA towards Pd(II) do not appreciably change after reutilization.

Selectivity

Binary mixtures of Pd(II) and Pt(IV), and ternary metallic solutions containing Pd(II), Pt(IV) and Rh(III), in 4 M and 6 M HCl, were contacted with both extractants in toluene, under the usual set of experimental conditions. The results obtained are displayed in Figure 5.

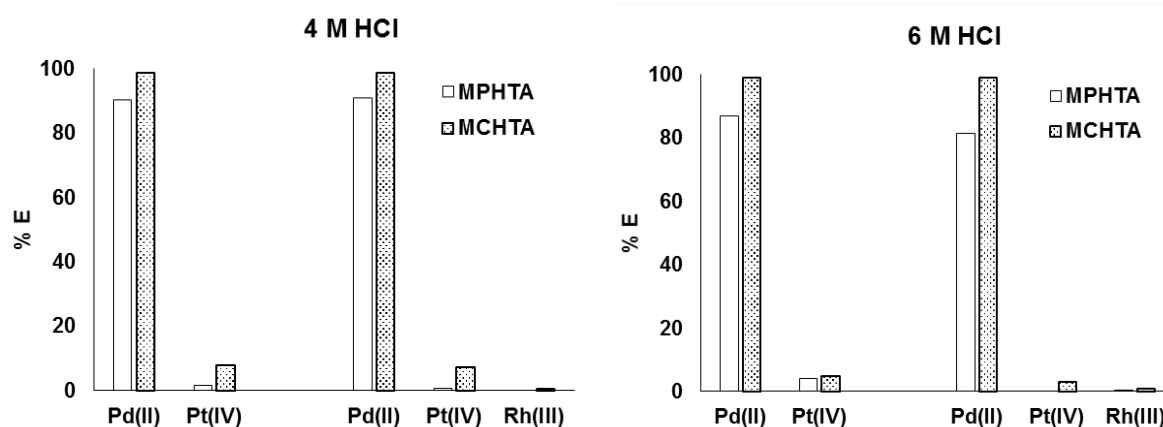


Figure 5 – Extraction and stripping experiments for Pd(II) recovery by 0.03 M MPHTA or MCHTA in toluene. [Pd] = 100 mg/L in 4 or 6 M HCl, 0.1 M thiourea in 1 M HCl for stripping. A/O=1, room temp., 30 minutes contact. Standard deviations: $\pm 5\%$.

The data presented in Figure 5 reveal that MPHTA and MCHTA slightly co-extract Pt(IV), and do not extract Rh(III). These overall results point out to a better selectivity of MPHTA for Pd(II) recovery than MCHTA.

Conclusions

N-methyl-*N*-phenyl-octanthioamide (MPHTA) and *N*-methyl-*N*-cyclohexyl-octanthioamide (MCHTA), dissolved in toluene, are suitable solvents to recover Pd(II) from a wide range of HCl concentrations, with typical efficiencies of 90% or higher. Extraction equilibria are reached in 30 to 60 minutes. Equilibrium and spectroscopic data point out to the formation of Pd(II) inner-sphere complexes involving either MPHTA or MCHTA. The information collected from reutilization tests, using thiourea in 1 M HCl as stripping solution, indicate an adequate robustness of both extractants. Selectivity results obtained from the extraction of complex solutions containing Pd(II), Pt(IV) and Rh(III) support the potential interest this solvent extraction scheme may have to attain the separation of Pd(II), from Pt(IV) and Rh(III), when these metals are included in leaching solutions coming from the hydrometallurgical treatment of spent automobile catalytic converters, for example.

Acknowledgements

The financial support for this work has been kindly provided by FCT, “Fundação para a Ciência e a Tecnologia” (Lisbon, Portugal) under the projects PTDC/QUI-QUI/109970/2009 and PEst-OE/QUI/UI0612/2013, and through the PhD grant SFRH/BD/78289/2011, offered to O. Ortet.

References

1. Saurat, M., Bringezu, S. *J. Ind. Ecol.* **2008**, 12, 754–767.
2. Hagelüken, C. *Chim. Oggi* **2006**, 24(2) suppl., 14–17.
3. Cox, M., in *Principles and Applications of Solvent Extraction*, 2nd Ed.; Rydberg, J., Musikas, C., Choppin, G.R., Eds.; Marcel Dekker Inc.: New York, 2004.
4. Narita, H., Tamura, K., Tanaka, M. *US Patent 2009178513-A1*, July 2009.
5. Traeger, J., König, J., Städtke, A., Holdt, H.-J. *Hydrometallurgy* **2012**, 127-128, 30–38.
6. Narita, H., Tanaka, M., Morisaku, K. *Proc. ISEC 2005*, Beijing, China, Conf. Proc. Ed. Dep., Ed.; 2005, pp. 227–232.
7. Paiva A.P., Carvalho, G.I., Costa, M.C., Costa, A.M.R., Nogueira C. *Solv. Extr. Ion Exch.* **2014**, 32, 78-94.
8. Figueira J.L., Paiva, A.P. *Sep. Sci. Technol.* **2009**, 44, 2928–2941.
9. Ortet, O., Paiva, A.P. *Sep. Sci. Technol.* **2010**, 45, 1130–1138.
10. Zhidkova T.I., Belova V.V., Brenno Yu.Yu., Zhidkov L.L., Khol'kin A.I. *Theoret. Found. Chem. Eng.* **2009**, 43, 826–830.
11. Szczepanska, I., Borowiak-Resterna, A, Wisniewski, M. *Hydrometallurgy* **2003**, 68, 159-170.

Synthesis of alkylpiperazine and its application to a polymer inclusion membrane for selective separation of Cd(II) over Zn(II) and Ni(II)

Yoshinari Baba^{*1}, Chisato Aso¹, Shintaro Kanemaru¹, Tatsuya Oshima¹

Summary

1,4-Di[[di(2-ethylhexyl)carbanoyl]methyl]piperazine (DDCMP) has been newly synthesized to develop extractants with high selectivity and extraction abilities for Cd(II) over Zn(II) and Ni(II) from the viewpoints of environmental protection and metal recycle from such wastes as Ni/Cd batteries and home electronics. The extraction selectivity for metals from hydrochloric acid was investigated using DDCMP in toluene at 303 K. DDCMP exhibited a high selectivity for Cd(II) over Zn(II). In order to determine the reason for the high selectivity for Cd(II), the extraction equilibria of Cd(II) and Zn(II) were quantitatively studied by examining the concentration dependence of chloride and hydrogen ions on the extraction equilibria. Cd(II) was extracted as a 1:2 complex through ion pair formation and coordination bonding with the two nitrogen atoms of the piperazine moiety, respectively, while Zn(II) was extracted as a 1:1 complex through coordination bonding with the two nitrogen atoms. We found that the selective extraction of Cd(II) over Zn(II) is due to the difference in the extracted species with DDCMP. Stripping of Cd(II) and Zn(II) was quantitatively performed by a single contact batch method using distilled water and dilute acids such as nitric acid, hydrochloric acid, sulfuric acid. DDCMP-embedded membrane was prepared using cellulose triacetate, and its membrane exhibited selective and uphill transport of Cd(II) over Zn(II).

Introduction

Cd(II) is harmful to health. WHO warns that Cd(II) causes cancer in humans. However, Cd(II) is utilized in various functional materials and also in various fields. Cd(II) is contained in the zinc ore sphalerite (ZnS), and Cd(II) is produced as a by-product of Zn(II) ore refining. The selective separation of Cd(II) from Zn(II) is difficult because the chemical properties of Cd(II) are similar to those of Zn(II). Soft metals are selectively extracted with extractants containing soft-donors (nitrogen and sulfur donor atoms), for example calixarenes with pyridine and thioamide, 2,4,6-(2-pyridyl)triazine (TPTZ), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), Bis(2,4,4-trimethylpentyl)monothiophosphonic acid (Cyanex 302) [1-4]. Precious metals, Pd, Au, and Ag, and highly toxic metals, Cd and Hg, are classified as soft metals. The recovery and removal of these metals are important and valuable from the viewpoints of environmental protection and metal recycle. If an environmentally-friendly soft-donor extractant could be developed, the extraction process would be applicable to the recovery of these highly toxic metals from wastewater or polluted soil as an environmentally recommended technology. The development of an extractant to recover soft metals selectively would be of great value industrially as well as of interest scientifically. Thus much work on the selective extraction of Cd(II)

*Corresponding Author: Yoshinari. Baba, Tel.: +81-985-58-7307, E-mail address: t0g202u@cc.miyazaki-u.ac.jp

¹ Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, Miyazaki, JAPAN

from Zn(II) with extractants containing thiol groups has been carried out[5,6]. However, these extractants are easily oxidized during the process. In addition, the selective separation of Cd(II) from Ni/Cd battery wastes is of particular interest.

In this study, 1,4-di[[di(2-ethylhexyl)carbanoyl]methyl]piperazine (DDCMP) as shown in Fig.1 was newly synthesized as an extractant with high selectivity and extraction abilities for target metals such as precious metals and toxic metals. Especially, since DDCMP exhibited a high selectivity for Cd(II) over Zn(II), the extraction equilibria of Cd(II) and Zn(II) with DDCMP were quantitatively measured at 303 K to elucidate the selective extraction mechanism of cadmium(II) over Zn(II) from hydrochloric acid.

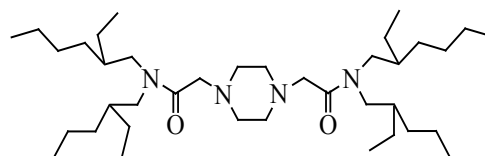


Fig. 1 Chemical structure of DDCMP

Experimental

Materials and reagents

Metal chlorides of analytical-grade (Wako Pure Chemical Ind. Ltd.) were used to prepare the test solutions containing the metals. Piperazine (Tokyo Kasei Kogyo Co. Ltd.) was used as the raw material for synthesis of the new extractant. Other chemicals were of analytical reagent grade and used as received. 1,4-Di[[di(2-ethylhexyl)carbanoyl]methyl]piperazine (DDCMP) was synthesized by alkylation of piperazine with 2-chloro-*N,N*-di-(2-ethylhexyl)acetamide(CDEHAA)[7]. Nuclear magnetic resonance spectra were recorded on a Bruker AV400M for ^1H NMR (400 MHz) in CDCl_3 with TMS as the internal standard for the identification of products.

Extraction procedures

The aqueous phase was prepared by dissolving the metal chlorides in hydrochloric acid. The initial concentration of metal was about 1.0×10^{-4} M. The organic phase was prepared by diluting with toluene gravimetrically. The initial concentration of DDCMP was 1.0×10^{-2} M for measurement of the extraction selectivity of the metals. The extraction equilibrium for metal ions was performed by a batchwise method at 303 K for 24 h. Equal volumes (10 cm^3) of both phases were mixed in an Erlenmeyer flask and vigorously shaken mechanically. After phase separation, the concentrations of hydrochloric acid and metal ions in the aqueous phase were determined by acid-base titration, AAS or ICPS, respectively. The metal ion concentration in the organic phase was calculated from the mass balance between the aqueous and organic phases. Extraction percentage ($E\%$) and metal distribution ratio (D) were calculated according to Eqs. (1) and (2), respectively.

$$E\% = \frac{[\text{M}]_{\text{org,eq}}}{[\text{M}]_{\text{aq,init}}} \times 100 = \frac{[\text{M}]_{\text{aq,init}} - [\text{M}]_{\text{aq,eq}}}{[\text{M}]_{\text{aq,init}}} \times 100 \quad (1) \quad D = \frac{[\text{M}]_{\text{org,eq}}}{[\text{M}]_{\text{aq,eq}}} = \frac{[\text{M}]_{\text{aq,init}} - [\text{M}]_{\text{aq,eq}}}{[\text{M}]_{\text{aq,eq}}} \quad (2)$$

where $[\text{M}]_{\text{aq,init}}$ represents the initial concentration of metal ion in the aqueous phase. $[\text{M}]_{\text{aq,eq}}$ and $[\text{M}]_{\text{org,eq}}$ are the total concentrations of metal ion in the aqueous and organic phases at equilibrium, respectively.

Results and discussion

Extraction selectivity for metal ions with DDCMP

The extraction selectivity for metal ions in hydrochloric acid with DDCMP in toluene was examined. Figure 2 shows the effect of the hydrochloric acid concentration on the extraction percentage of metal ions with DDCMP. DDCMP exhibited high selectivity for Au(III), Pd(II) and Pt(IV) over Cu(II), Ni(II), Co(II) and Fe(III) over the whole hydrochloric acid concentration region.

On the other hand, Cd(II) was selectively extracted from Zn(II) at hydrochloric acid concentrations of more than 0.2 M. In addition, Cd(II) was selectively extracted from Ni(II) which is not extracted at all from high concentrations of hydrochloric acid from the practical point of view of removal and recovery of toxic and industrially useful Cd(II) from electronic wastes such as Ni-Cd batteries.

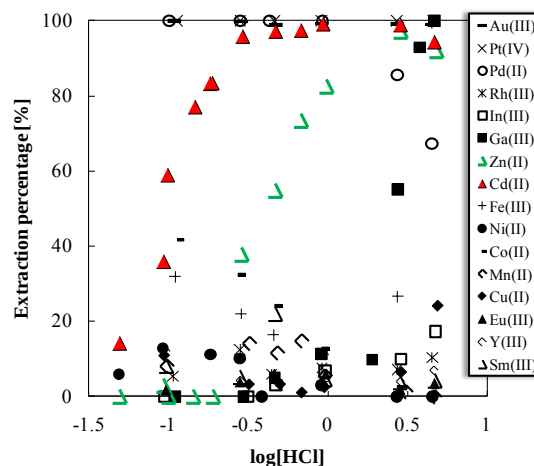


Fig. 2 Effect of the hydrochloric acid concentration on the extraction percentage of metal ions with 0.01 M DDCMP.

Extraction equilibrium of Cd(II)

Effect of the hydrogen ion and chloride ion concentrations on the distribution of Cd(II)

In order to evaluate separately the effects of hydrogen ion and chloride ion concentrations on the distribution ratio of Cd(II), the effect of hydrogen ion concentration was examined at a constant chloride ion concentration ($[Cl^-] = 0.3$ M) while the effect of chloride ion concentration was examined at a constant hydrogen ion concentration ($[H^+] = 0.1$ M). Figure 3 shows the effect of hydrogen ion and chloride ion concentration on the Cd(II) distribution ratio.

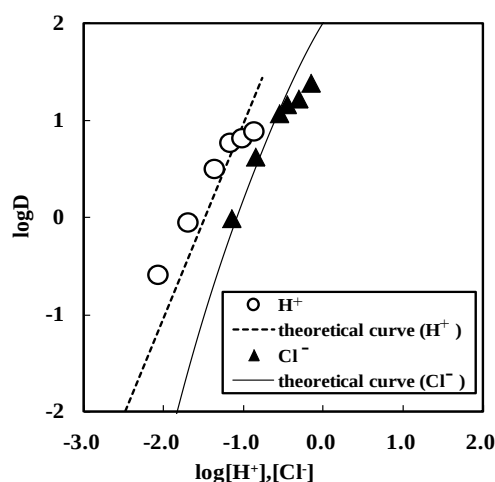


Fig. 3 Effect of the chloride ion and hydrogen ion concentrations on the distribution ratio of Cd(II).

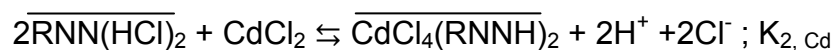
The distribution ratio increased with increasing hydrogen ion concentration. The distribution ratio lies on a straight line with a slope of 2. While, in the effect of the chloride ion concentration, the distribution ratio increased with increasing chloride ion concentration. The plotted points lie on a straight line with a slope of 2.

Effect of DDCMP concentration on the distribution ratio of Cd(II)

Figure 4 shows the effect of DDCMP concentration on the Cd(II) distribution ratio. As seen from this figure, the distribution ratio increased

with increasing extractant concentration. The plotted points lie on a straight line with a slope of 2, indicating that two molecules of DDCMP participate in the extraction reaction of Cd(II) from hydrochloric acid

From these experimental results, it may be concluded that Cd(II) is extracted according to the following equations. The extractant reacts with hydrochloric acid and this hydrochloride salt of the extractant reacts with CdCl₂, respectively, as follows:



The over-all stability constants of the chloro complexes of cadmium(II) are known to be $\beta_1 = 59 [\text{mol dm}^{-3}]^{-1}$, $\beta_2 = 1.7 \times 10^3 [\text{mol dm}^{-3}]^{-2}$, $\beta_3 = 9.3 \times 10^2 [\text{mol dm}^{-3}]^{-3}$ and $\beta_4 = 8.3 \times 10^2 [\text{mol dm}^{-3}]^{-4}$ [8]. The values of the equilibrium constants were $K_{1, \text{Cd}} = 3.24 \times 10 [\text{mol dm}^{-3}]^{-4}$ and $K_{2, \text{Cd}} = 1.09 \times 10^5 [\text{mol dm}^{-3}]^{-2}$.

Extraction equilibrium of Zn(II)

Effect of hydrogen ion and chloride ion concentrations on the distribution of Zn(II)

In order to evaluate separately the effects of hydrogen ion and chloride ion concentrations on the distribution ratio of Zn(II), the effect of the hydrogen ion concentration was examined at a constant chloride ion concentration ($[\text{Cl}^-] = 1 \text{ M}$) while the effect of chloride ion concentration was examined at a constant hydrogen ion concentration ($[\text{H}^+] = 0.1 \text{ M}$).

Figure 5 shows the effects of hydrogen ion and chloride ion concentrations on the Zn(II) distribution ratio. The distribution ratio lies on a straight line with a slope of 0. While, in the effect of the chloride ion concentration, the distribution ratio increased with increasing chloride ion concentration. The plotted points lie on a straight line with a slope of 2.

Effect of DDCMP concentration on the distribution ratio of Zn(II)

Figure 6 shows the effect of DDCMP and hydrochloric acid concentration on the Zn(II) distribution ratio. As is seen from this figure, the distribution ratio of Zn(II)

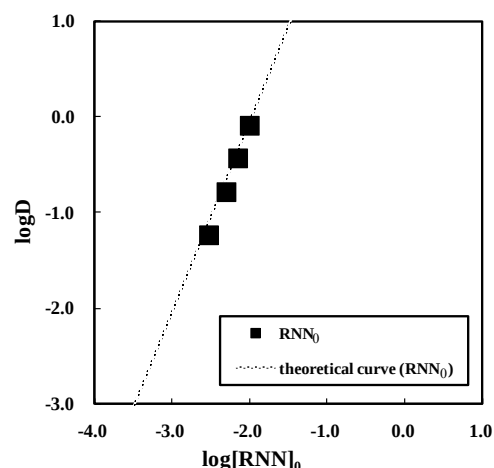


Fig. 4 Effect of the DDCMP concentration on the distribution ratio of Cd(II).

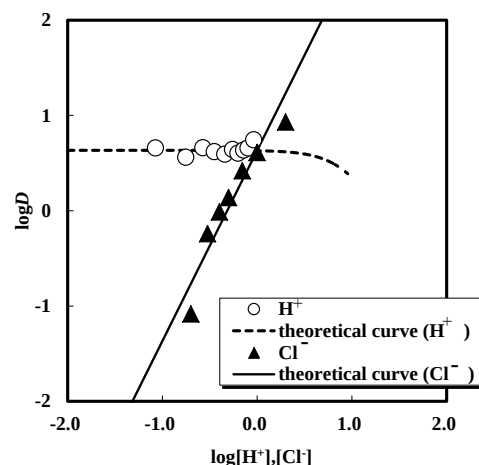
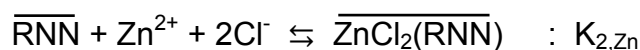
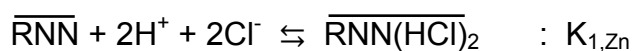


Fig. 5 Effect of chloride ion and hydrogen ion concentrations on the distribution ratio of Zn(II).

increased with increasing the extractant concentration. The plotted points lie on a straight line with a slope of 1, indicating that one molecule of DDCMP participates in the extraction reaction of Zn(II) from hydrochloric acid.

From these experimental results, it may be concluded that Zn(II) is extracted according to the following equations.



The over-all stability constants of the chloro complexes of Zn(II) are known to be $\beta_1 = 0.65 \text{ [mol dm}^{-3}\text{]}^{-1}$, $\beta_2 = 1.5 \text{ [mol dm}^{-3}\text{]}^{-2}$, $\beta_3 = 0.04 \text{ [mol dm}^{-3}\text{]}^{-3}$ and $\beta_4 = 0.03 \text{ [mol dm}^{-3}\text{]}^{-4}$ [8]. The values of the equilibrium constants were $K_{1,\text{Zn}} = 9.34 \times 10^{-3} \text{ [mol dm}^{-3}\text{]}^{-4}$ and $K_{2,\text{Zn}} = 4.31 \times 10^2 \text{ [mol dm}^{-3}\text{]}^{-3}$.

Back extraction of Cd(II) and Zn(II)

Cadmium(II) and zinc(II) extracted with DDCMP were effectively stripped into the aqueous phase using aqueous HCl and HNO₃ solutions. In particular, it should be noted that cadmium(II) and zinc(II) was quantitatively stripped with distilled water owing to the decrease in the hydrochloric acid concentration.

Application of DDCMP to the inclusion membrane

Cellulose triacetate(CTA) was used as the membrane. CTA and DDCMP was dissolved in THF and then was dried over a night to prepare the DDCMP-embedded CTA membrane by the casting method. The DDCMP inclusion membrane exhibited the selective uphill-transport of cadmium(II) over zinc(II) by use of water as a stripping solution in the received side.

Conclusions

A new extractant, 1,4-di[[di(2-ethylhexyl)carbanoyl]methyl]piperazine (DDCMP), was synthesized to develop a selective extractant for cadmium(II). DDCMP is designed so as to exhibit a high selectivity for anion chemical species through the electrostatic force of the protonated tertiary amine and the coordination ability of the oxygen atom of the amido groups. DDCMP in toluene exhibited high selectivity for precious metals over base metals, while cadmium(II) was selectively extracted from zinc(II) in hydrochloric acid solution. In this study, the extraction equilibria of cadmium(II) and zinc(II) were quantitatively determined by examining the effect of the chemical species

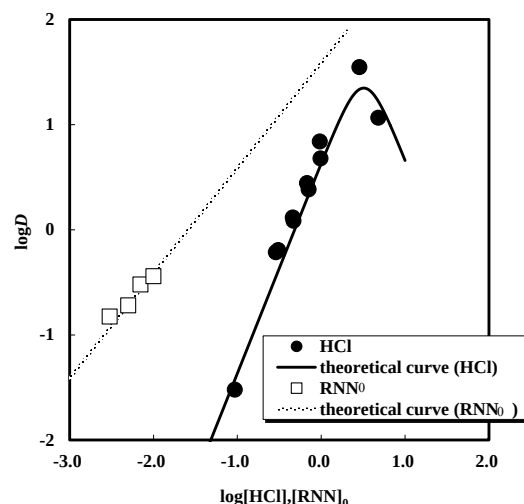


Fig. 6 Effect of DDCMP and hydrochloric acid concentrations on the distribution ratio of Zn(II).

such as hydrogen ion and chloride ion in order to elucidate the reason for the high selectivity for cadmium(II) over zinc(II). Cadmium(II) was extracted as a 1:2 complex through ion pair formation and coordination bonding with the two nitrogen atoms of the piperazine group, respectively, while zinc(II) was extracted as a 1:1 complex through coordination bonding with the two nitrogen atoms. It is probable that the selective extraction of cadmium(II) over zinc(II) is due to the difference in the extracted species with DDCMP. CTA membrane embedding DDCMP prepared by the casting method was efficient for selective and active transport of Cd(II) over Zn(II).

Acknowledgement

We thank The Environment Research and Technology Development Fund (ERTDF) from the Ministry of the Environment in Japan for financial support of this research.

References

1. Belhamel, K., Dzung, N. T.K., Benamor, M. and Ludwig, R., *Proc. ISEC 2002*, South Africa.
2. Abdel-Rahman, L. H., *Trans. Metal Chem.*, 26, 412-416 (2001).
3. Singh, R., Khwaja, A. R., Gupta, B. and Tandon, S. N., *Solv. Extr. Ion Exch.*, 17, 367-390 (1999).
4. Mimura, H., Akiba, K. and Onodera, Y., *J. Nucl. Sci. Technol.*, 38(5), 342-348 (2001).
5. K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, *Solv. Extr. Ion Exch.*, 22(2), 203-218 (2004)
6. K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, *Hydrometall.*, 70, 63-71 (2003).
7. Shintaro KANEMARU, Tatsuya OSHIMA, Yoshinari BABA, *Solv. Extr. Res. Dev. Jpn.*, 16, 57-67 (2009).
8. Lars Gunnar Sillen, Erik Hogfeldt, Arthur E. Martell, Robert M Smith, *STABILITY CONSTANTS SUPPLEMENT*. The Chemical Society London, 1971.

Synergistic effect of 8-quinolinol derivatives on the supercritical carbon dioxide extraction of gallium(III) with D2EHPA

Akira Ohashi, Natsumi Kawashima, Haeng-Boo Kim*

Ibaraki University, Mito, Japan

The synergistic effect of five 8-quinolinol derivatives (HQs) on the extraction of gallium(III) with di(2-ethylhexyl)phosphoric acid (D2EHPA) from weak nitric acid into supercritical carbon dioxide (SC-CO₂) was investigated. 8-Quinolinol (Hq), 5-ethoxymethyl-8-quinolinol (HO₂q), 5-hexyloxymethyl-8-quinolinol (HO₆q), 5-(2,2,2-trifluoroethoxymethyl)-8-quinolinol (HFO₂q), and 5-chloro-8-quinolinol (5-Cl-Hq) were used as synergists. Synergism was observed for all of the HQs. This result indicates that the synergism using D2EHPA and HQ in the extraction of gallium(III) is able to apply to the SC-CO₂ extraction. The synergistic effect increased in the following order: Hq < HO₂q < HFO₂q < HO₆q ≈ 5-Cl-Hq. The extent of synergism can be related to both the distribution constant and the acid dissociation constant of the HQ. The effect of pressure on the synergistic extraction was also investigated.

Introduction

Gallium is one of the most important elements in industry, because it is used in many industrial products such as semiconductors, optical devices and so on. Therefore, development of an effective method to recover gallium(III) is important. Solvent extraction is widely used to separate and concentrate gallium(III) from aqueous solutions. Recently, reduction of usage of organic solvents, however, is demanded due to rising of environmental awareness.

The supercritical carbon dioxide (SC-CO₂) extraction of metal ions from aqueous media has become a viable separation method, and an alternative to solvent extraction.¹⁻⁴ SC-CO₂ is an environmentally-acceptable media, because it is non-toxic and has a relatively mild critical point. The use of SC-CO₂ as the solvent in the extraction of metal ions gives several advantages: i) The use of organic solvents is dramatically decreased. ii) The pollution of the aqueous phase by the organic solvent is greatly reduced. iii) The extraction rate may become fast because the diffusion coefficient of the solute in SC-CO₂ is generally higher than that in an organic solvent. iv) The solubility of a solute in SC-CO₂ can be controlled with relatively small changes in the pressure and temperature. v) The extracted substances can be rapidly and completely separated from CO₂ by the gasification of CO₂. However, SC-CO₂ has some disadvantages: i) The solubility of metal complexes in SC-CO₂ is generally much lower than that in conventional organic solvents, such as chloroform, dodecane, and toluene. ii) The pH of a non-buffered aqueous solution in contact with CO₂ shifts downward, and becomes approximately 2.8 because of the carbonic acid/carbonate equilibrium of dissolved CO₂.⁵ These disadvantages prevent the application of SC-CO₂ as a medium for extracting metal ions with organic acid chelators from aqueous solution. The use of synergism is one method for resolving these problems with SC-CO₂ extraction. Several workers reported on synergistic extraction of metal chelates in the SC-CO₂ extraction.⁶⁻⁹ However, there are far

fewer reports on synergism in SC-CO₂ extraction than those on synergism in solvent extraction. A detailed investigation of synergism in SC-CO₂ extraction is important for extending its applicable range. Synergisms of an acidic organophosphorus compound and 8-quinolinol derivative (HQ) in solvent extraction of gallium(III) were reported.^{10,11} This synergism may be applied to SC-CO₂ extraction.

In this study, the synergistic effect of HQs on the extraction of gallium(III) with di(2-ethylhexyl)phosphoric acid (D2EHPA or HA) from a weak nitric acid solution into SC-CO₂ was investigated.

Experimental

Reagents

D2EHPA (EP, Nacalai Tesque) was purified by a precipitation method of copper(II) according to the literature.¹² 8-Quinolinol (Hq, GR) and 5-chloro-8-quinolinol (5-Cl-Hq, GR) were purchased from Wako and Tokyo Kasei, respectively, and purified by vacuum sublimation. The other HQs (5-Ethoxymethyl-8-quinolinol (HO₂q), 5-hexyloxymethyl-8-quinolinol (HO₆q) and 5-(2,2,2-trifluoroethoxymethyl)-8-quinolinol (HFO₂q)) were prepared in a manner similar to that reported previously.¹³⁻¹⁵ A gallium(III) stock solution was prepared by the dilution of an AAS gallium(III) standard solution (Kanto Chemical) with a dilute nitric acid solution. Each stock HQ solution was also prepared by dissolution with a dilute nitric acid solution. Liquid CO₂ (99.99 %) was purchased from Taiyo Nissan Co. Ltd. Water was doubly distilled and further purified with a Milli-Q (Millipore) device. All other chemicals were of reagent grade, and were used without further purification.

SC-CO₂ extraction procedure

An acidic aqueous solution (25 ml) containing gallium(III) and an HQ and a known amount of D2EHPA were added to the 50-ml stainless-steel extraction vessel. This vessel was placed in a thermostat-controlled oven with a magnetic stirrer. CO₂ gas was compressed by a syringe pump (Isco, Model 500D) and introduced into the extraction vessel. The solutions were stirred with the magnetic stirrer for 30 min and left standing for 10 min. Then, the outlet valve was opened to take the aqueous phase (approximately 5 ml) through the back-pressure regulator (Jasco, 880-80) into the sampling vessel. After the pH was measured, the concentration of gallium(III) in the sampled aqueous phase was determined by ICP-AES (Shimadzu, ICPS-7510). The extraction percentage (%E) was calculated from the concentrations of gallium(III) in the aqueous phase before and after SC-CO₂ extraction. As mentioned above, the pH value of the non-pH-buffered solution shifts downward in an SC-CO₂ extraction system because of the dissolution of CO₂. All of the experiments in the SC-CO₂ extraction system were conducted at below pH 2.8, because the pH change caused by contact with SC-CO₂ was reported to be negligibly small below pH 2.8.¹⁶ The pH

value of the aqueous phase was measured by a pH meter (HORIBA, F-51) both before and after the SC-CO₂ extraction. The gallium concentration was constant at $5.0 \times 10^{-5} \text{ mol dm}^{-3}$. The ionic strength was maintained at 0.1 mol dm^{-3} with (H, Na)NO₃. The CO₂ pressure was varied from 10 to 20 MPa.

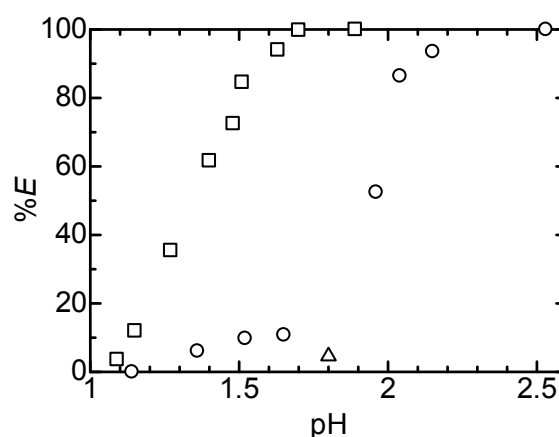


Figure 1. Extraction behavior of gallium(III) with D2EHPA and 5-Cl-Hq into SC-CO₂ at 13 MPa and 318K. Ga(III), $5.0 \times 10^{-5} \text{ mol dm}^{-3}$; D2EHPA, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; 5-Cl-Hq, $5.0 \times 10^{-4} \text{ mol dm}^{-3}$. □, D2EHPA + 5-Cl-Hq; ○, D2EHPA alone; △, 5-Cl-Hq alone

Results and Discussion

Synergism of 8-quinolinol derivatives

Figure 1 shows the extraction behavior of gallium(III) with D2EHPA and 5-Cl-Hq into SC-CO₂. Little gallium(III) was extracted with $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ 5-Cl-Hq. On the other hand, The extraction percentage, %E, value was enhanced in the presence of both D2EHPA and 5-Cl-Hq. This result implies that the synergism of D2EHPA and HQ in the extraction of gallium(III) is able to apply to the SC-CO₂ extraction. To reveal the influence of the physical properties of HQ on the synergism, The %E of gallium(III) with D2EHPA into SC-CO₂ at 13 MPa was investigated in both the absence and presence of an HQ. The concentrations of D2EHPA and HQ were $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. The pH of the aqueous solution was maintained at 1.7. The obtained %E values are summarized in Table 1, which also lists the acid dissociation constant of H₂Q⁺, K_{a1} ,¹⁷ and the distribution constant of HQ, K_{D,CO_2} , between SC-CO₂ at 13 MPa and water. The K_{D,CO_2} values at 13 MPa were estimated from the dependency of K_{D,CO_2} on the CO₂ density, given in a previous report.¹⁷ Synergism was observed among all the HQs. The synergistic effect increased in the following order: Hq < HO₂q < HFO₂q < HO₆q ≈ 5-Cl-Hq. The extent of the synergism can be related to both the K_{D,CO_2} and K_{a1} values of the HQ. The greater are these values,

Table 1. Physical properties of HQ, the concentration of HQ in SC-CO₂, and extraction percentage of gallium(III) with D2EHPA in the presence of HQ as a synergist into SC-CO₂

HQ	pK _{a1} ^a	log K _{D,CO2} ^b	[HQ] _{CO2} / mM	%E
none	-	-		36.0
Hq	4.80 ^c	0.65 ^d	1.5	39.5
HO ₂ q	4.54	1.02 ^e	5.9	53.2
HFO ₂ q	3.59 ^c	0.07 ^d	7.4	79.5
HO ₆ Q	4.45 ^c	1.88 ^d	55.8	97.9
5-Cl-Hq	3.66 ^c	1.16 ^d	66.4	99.8

the larger does its synergistic effect tend to be. That is, the concentration of an HQ as a synergist in SC-CO₂ influences mainly the magnitude of the synergism.

Effect of pressure on the SC-CO₂ extraction

One of the characteristics of SC-CO₂ extraction is that the analyte extractability can be changed with a relatively small change in pressure. The effect of the CO₂ density (ρ) on the SC-CO₂ extraction of gallium(III) with $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ D2EHPA was investigated in both the absence and presence of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ HQ (Hq, 5-Cl-Hq, and HFO₂Q). Figure 2 shows the dependencies of half-extraction pH

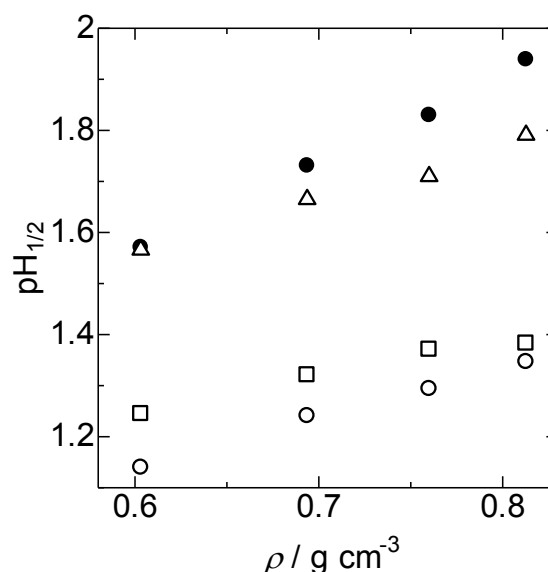


Figure 2. Dependencies of Half-extraction pH on the CO₂ density in the SC-CO₂ extraction with D2EHPA in the absence and presence of HQ. Ga(III), $5.0 \times 10^{-5} \text{ mol dm}^{-3}$; D2EHPA, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; HQ, $5.0 \times 10^{-4} \text{ mol dm}^{-3}$; pressure. ●, D2EHPA alone; □, D2EHPA + HFO₂Q; ○, D2EHPA + 5-Cl-Hq; Δ, D2EHPA + Hq

(pH_{1/2}) on the CO₂ density. The pH_{1/2} value increased with increasing the CO₂ density in the system with D2EHPA alone. This indicates that the extractability of gallium(III) with D2EHPA into SC-CO₂ is reduced by an increase in the CO₂ pressure. This is explained on the basis of the solvation number of D2EHPA and its gallium(III) complex in SC-CO₂.¹⁸ The pH_{1/2} values also increased with increasing pressure in the system with a mixture of D2EHPA and HQ. However, the increasing trends of pH_{1/2} against ρ in the system with a mixture of D2EHPA and HQ are smaller than that in the system with D2EHPA alone. This may be caused by the increasing the HQ concentration in SC-CO₂ with an increase in the pressure. However, further investigation is needed to clarify this pressure effect.

Conclusion

The synergistic effects of five HQs on the extraction of gallium(III) with D2EHPA from a weak nitric acid into SC-CO₂ was investigated. The effect increased in the following order: Hq < HO₂q < HFO₂q < HO₆q ≈ 5-Cl-Hq. The extent of synergism can be related to both the K_D and K_{a1} values of the HQ. Synergistic extraction is useful for enhancing the extractability of metal ions in SC-CO₂ extraction as well as solvent extraction. The result obtained in this study may provide a useful guide for selecting the optimal experimental conditions and synergist in SC-CO₂ extraction, and forms the basis for further development of SC-CO₂ extraction.

References

1. F. V. Bright, M. E. P. McNally, “*Supercritical Fluid Technology*”, **1992**, ACS, Washington DC.
2. L. T. Taylor, “*Supercritical Fluid Extraction*”, **1996**, Wiley & Sons, New York.
3. C. Erkey, *J. Supercrit. Fluids*, **2000**, *17*, 259.
4. A. Ohashi, K. Ohashi, *Solvent Extr. Res. Dev.*, **2008**, *15*, 11.
5. K. L. Toews, R. M. Shroll, C. M. Wai, N. G. Smart, *Anal. Chem.*, **1995**, *67*, 4040.
6. Y. Lin, C. M. Wai, *Anal. Chem.*, **1994**, *66*, 1971.
7. Y. Meguro, S. Iso, J. Ougiyani, Z. Yoshida, *Anal. Sci.*, **2001**, *17*, i72, Supplement.
8. S.-Y. Choi, Z. Yoshida, K. Ohashi, *Talanta*, **2002**, *56*, 689.
9. M. Koh, K. Park, D. Yang, H. Kim, H. Kim, *Bull. Korean Chem. Soc.*, **2005**, *26*, 423.
10. K. Kondo, K. Yano, M. Matsumoto, *J. Chem. Eng. Jpn.*, **1996**, *29*, 836.
11. K. Kondo, M. Matsumoto, T. Okubo, *Kagaku Kogaku Ronbun.*, **2000**, *26*, 535.
12. J. A. Partridge, R. C. Jensen, *J. Inorg. Nucl. Chem.*, **1969**, *31*, 2587.
13. K. Ohashi, H. Imura, S. Mochizuki, K. Hiratani, *Min. Pro. Ext. Met. Rev.*, **1997**, *17*, 169.
14. K. Ohashi, R. Iwata, S. Mochizuki, H. Imura, K. Hiratani, H. Sugihara, *Talanta*, **1996**, *43*, 1481.
15. H. Hoshino, A. Ohashi, K. Ohashi, *Bunseki Kagaku*, **2003**, *52*, 775.
16. J. Ougiyani, Y. Meguro, Z. Yoshida, K. Ohashi, *Talanta*, **2002**, *57*, 213.
17. A. Ohashi, K. Yamato, H. Imura, K. Ohashi, *J. Supercrit. Fluids*, **2009**, *49*, 315.
18. Y. Meguro, S. Iso, Z. Yoshida, *Anal. Chem.*, **1998**, *70*, 1262.
19. I. Komazawa, T. Otake, Y. Higaki, *J. Inorg. Nucl. Chem.*, **1981**, *43*, 3351.
20. R. K. Biswas, M. A. Habib, M. N. Islam, *Ind. Eng. Chem. Res.*, **2000**, *39*, 155.
21. K. Ohashi, K. Tatenuma, *Chem. Lett.*, **1997**, 1135.
22. J. Ougiyani, Y. Meguro, Z. Yoshida, H. Imura, K. Ohashi, *Talanta*, **2003**, *59*, 1189.
23. F. Dehghani, T. Wells, N. J. Cotton, N. R. Foster, *J. Supercrit. Fluids*, **1996**, *9*, 263.
24. Y. Meguro, S. Iso, Z. Yoshida, *Anal. Chem.*, **1998**, *70*, 1262.
25. S. N. Joung, S. J. Yoon, S. Y. Kim, K.-P. Yoo, *J. Supercrit. Fluids*, **2000**, *18*, 157.

Effect of aggregation on synergistic mechanism for liquid/liquid extraction

S. Dourdain, J. Rey, S. Pellet-Rostaing, T. Zemb, ICSM/LTSM, CEA/CNRS/UM2/ENSCM
UMR5257, Site de Marcoule, Bat 426, 30207, France;

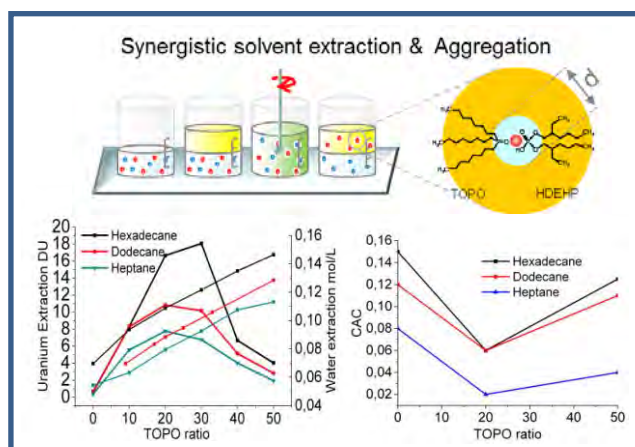


Fig. 1 Extraction and aggregation in 3 aliphatic solvents.

distribution coefficients for some salts from a mixture. The origin of synergism is a mystery in chemical engineering because modelling implies complexation and not micellisation. A better understanding of synergistic mechanism in liquid/liquid extraction renders possible thermodynamic simulation.

¹HDEHP/TOPO was chosen to be our model system. Synergistic system was studied in different diluents to observe their **influence on extraction and aggregation**. Experiments have shown that, for TOPO from 0-30%, uranium extraction reaches a maximum which is the synergistic ratio and then decrease to 50% TOPO. When increasing the carbon chain length of diluent, uranium extraction increases. This may be due to an increase of hydrophobic interaction, before the synergistic ratio, while adding TOPO. Aggregates are destabilized (leading to a decrease of uranium extraction) since water and acid extraction increase with TOPO ratio. Systems with long chain diluent contain less water, thus extraction is improved. **To highlight diluent effect on aggregation**, critical aggregation concentrations (CAC) was determined by drop surface tensiométrie. Two important phenomena were notice. First, for one diluent used, CAC is minimized when extraction is maximized whatever the diluent. This means extraction may be related to a minimization of aggregation energy. Secondly, CAC decrease when the chain length of the diluent increase. This phenomenon may be explained by the theory of penetration of short chain diluent in the apolar crown of aggregate. This may stabilize aggregates and decrease aggregation energy. SANS experiment allowed us to confirm this hypothesis.

1 Dourdain S, Hofmeister I, Pecqueur O, et al., Synergism by Coassembly at the Origin of Ion Selectivity in Liquid-Liquid Extraction, Langmuir 2012, 28, 11319–11328

Separation of nickel from calcium and magnesium by using mixtures of Cyanex 272 and D2EHPA

Alexandre Silva Guimarães¹, Priscila Siqueira da Silva¹, Marcelo Borges Mansur ^{*1}

The separation of nickel sulfate from laboratory aqueous solutions containing calcium and magnesium, at similar concentration levels of industrial liquors obtained from the HPAL process, has been investigated using mixtures of extractants Cyanex 272 (20%v/v) and D2EHPA (0 to 20%v/v). Simultaneous extraction of nickel ($\approx 25\%$) and magnesium ($\approx 75\%$) with low calcium extraction ($<10\%$) was achieved using only Cyanex 272. The addition of 5-10%v/v of D2EHPA mixed with Cyanex 272 improved the purification of nickel from calcium and magnesium. In fact, the system containing 5%v/v of D2EHPA and 20%v/v of Cyanex 272 extracted about 60% of calcium, 72% of magnesium and less than 2% of nickel at pH 4.8, while the system containing 10%v/v of D2EHPA and 20%v/v of Cyanex 272 extracted about 45% of calcium, 51% of magnesium and approximately 2% of nickel at pH 4.8. Both systems could be used to purify nickel in continuous multiple stages operation. The mixture containing 20%v/v of D2EHPA was not selective.

Introduction

Nickel is widely used in the production of stainless steel, ferrous and nonferrous alloys, rechargeable batteries, electroplating processes, and many other applications. It can be obtained industrially from lateritic ores using the HPAL (High Pressure Acid Leaching) process (Ndlovu and Mahlangu, 2008). The obtained sulfuric leach liquor is highly concentrated in nickel (up to 100 g/L) and contain other metals such as iron, copper, magnesium, manganese, zinc, calcium and cobalt. After iron removal by precipitation as hematite (Rydberg *et al.*, 2004), the liquor is purified by solvent extraction. Acid extractants such as D2EHPA (di(2-ethylhexyl)phosphoric acid) and Cyanex 272 (di(2,4,4-trimethylpentyl)phosphine acid) are normally used, the latter being more efficient to promote the cobalt/nickel separation (Flett, 2005). The liquor is subjected to a purification step using 20%v/v Cyanex 272 in pH ≈ 4 and 50°C in order to remove cobalt, copper, manganese and zinc. The purification of nickel related to calcium and magnesium, however, is not effective with Cyanex 272 (Flett, 2005; Guimaraes, 2013).

Synergistic extractive systems to separate nickel from sulfuric liquors containing calcium and magnesium has been investigated elsewhere (Cheng and Urbani, 2003; Cheng, 2006; Cheng *et al.*, 2010). In this context, the aim of the present study is investigate the use of mixtures of Cyanex 272 and D2EHPA in order to obtain a purified stream containing nickel to be sent to electrowinning.

Experimental

Reagents and solutions

Synthetic sulfuric liquor containing 1.5 mol/L of nickel, 0.125 mol/L of manganese and 0.013 mol/L of calcium was prepared. Such concentration levels are similar to industrial process liquors obtained by the HPAL after removal of cobalt, copper, manganese and zinc with Cyanex 272. The reagents used are all analytical grade (Synth, purity $> 98\%$) and their salts were dissolved in distilled water. The initial pH of the aqueous solution is approximately 3.9 and it was filtered before contacting with

^{1*} Corresponding author, Dept. de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG, Brazil, Tel: +55 (31) 3409-1811, Fax: +55 (31) 3409-1715, Email: marcelo.mansur@demet.ufmg.br

the organic solution to remove any suspended solids because such condition is near the saturation of calcium (Guimaraes, 2014).

The organic phase was prepared by dissolving D2EHPA (Aliaba, purity 95%) and/or Cyanex 272 (Cytec Canada, purity 85%) in n-heptane (Synth, purity 98%). Both extractants were used as received. No modifier was added and no third phase observed.

Solvent extraction tests

Tests were carried out by contacting 200 mL of each phase in a glass reactor of 1 L, which was placed in a water bath (Kacil brand, model BM-02). The experimental setting-up used in the experiments is similar to employed in previous studies (Mansur and Morais, 2004; Mantuano *et al.*, 2005). Once solutions reached the specified temperature (50°C), stirring was initiated (400 rpm) using a mechanical stirrer (IKA, model RW 20N) for 5 minutes. After that, stirring was turned out and disengagement of phases lasted for 3 minutes. The pH of the aqueous phase was measured using a pH meter (Quimis, model 0400AS). Samples (10 mL) were withdrawn and aqueous phase was submitted to chemical analysis. Stirring was turned on again and the pH of the aqueous phase was changed by adding some drops of NaOH solution (5 and 10 mol/L), thus repeating the same procedure in a higher pH value. The following operating values were investigated: (i) pH of the aqueous phase (from approximately 2.0 to 7.5, with increments of nearly 0.5), and (ii) D2EHPA concentration (0, 5, 10, and 20% v/v). The concentration of Cyanex 272 was fixed (20%v/v) in all trials based on the concentration level used in previous investigation (Guimaraes, 2014).

Chemical analysis

The samples of the aqueous phase were analyzed by atomic absorption spectrophotometry (GBC, model Avanta) for nickel, calcium and magnesium. The metal concentration in the organic phase was calculated by mass balance.

Results and discussion

The effect of D2EHPA concentration (0 to 20% v/v) at fixed concentration of Cyanex 272 (20% v/v) with pH on the extraction of metals Ca, Mg and Ni is shown in Figure 1. The calculated separation factors $\beta_{Ca/Ni}$ and $\beta_{Mg/Ni}$ are shown in Table 1. It has to be said that tests at pH > 6.5 resulted in quite difficult phase disengagement, so such operating conditions require strict pH control and should be avoided for practical applications; in some tests, the viscosity of the organic phase increased to prohibitive values.

In the absence of D2EHPA (Figure 1-a), the extraction of magnesium increases monotonically with pH, reaching approximately 75% at pH = 6.35. A significant increase on the extraction of nickel is verified solely at pH > 6, reaching 28% at pH = 6.35. Low extraction of calcium (below 10%) is verified along the whole range of pH investigated. Such result reveals low selectivity of Cyanex 272 to separate nickel from alkaline earths calcium and magnesium (see Table 1), thus corroborating Flett (2005).

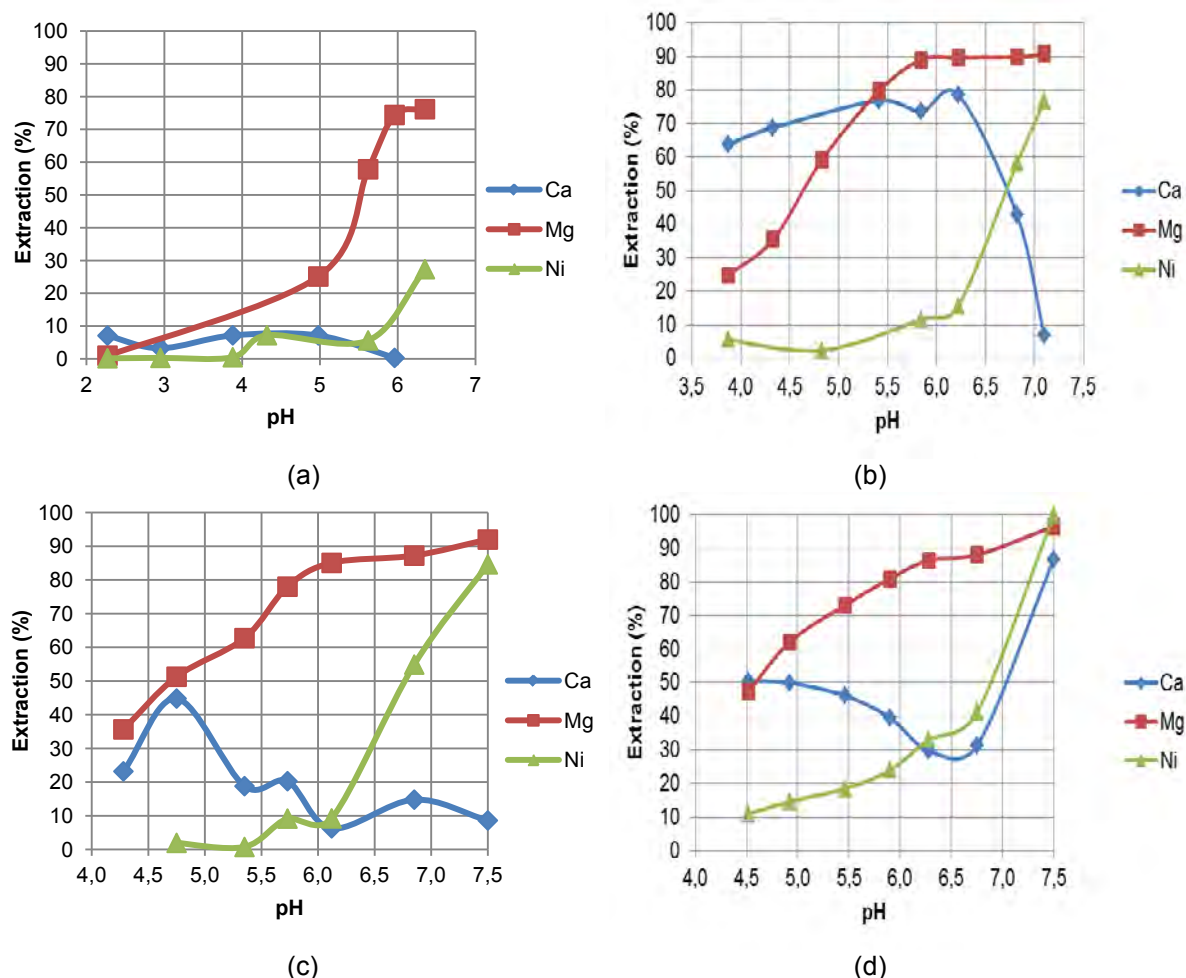


Figure 1: Extraction of calcium, magnesium, and nickel as a function of pH in different concentrations of D2EHPA maintaining the concentration of Cyanex 272 in 20% v/v ($T = 50^{\circ}\text{C}$; ratio A/O = 1): (a) [D2EHPA] = 0% v/v, (b) [D2EHPA] = 5% v/v, (c) [D2EHPA] = 10% v/v, and (d) [D2EHPA] = 20% v/v.

Table 1: Separation factor ($\beta_{\text{Ca/Ni}}$ and $\beta_{\text{Mg/Ni}}$) for the separation of nickel from calcium and manganese with Cyanex 272 (20% v/v) and D2EHPA (0 to 20% v/v) at changing pH values.

[D2EHPA] (% v/v)	equilibrium pH	$\beta_{\text{Ca/Ni}}$	$\beta_{\text{Mg/Ni}}$
0	4.3	0.05	0.02
	5.6	0.04	1
	6.4	0.06	3
5	4.8	36	61
	5.8	22	62
	6.8	0.5	6.4
10	4.8	40	52
	5.7	2.5	35
	6.9	0.1	5.6
20	4.9	5.9	9.6
	5.9	2.1	14
	6.8	0.7	11

The mixing of Cyanex 272 (20% v/v) with D2EHPA resulted in a quite different extraction system regarding its higher affinity to extract alkaline earths calcium and manganese over nickel from sulfate medium. In general terms, the addition of 5 to 10% v/v of D2EHPA mixed with 20% v/v of Cyanex 272 resulted in significant increase on the extraction of calcium and manganese, as well as their selectivity over

nickel. Best results were obtained in the pH range between 4.0 and 5.5 probably due to more acidic character of D2EHPA, thus allowing the purification of nickel by using multiple contacting stages. The best result was obtained using an organic phase containing 5% v/v of D2EHPA and 20% v/v of Cyanex 272, at pH 4.8, thus corresponding to $\beta_{\text{Mg/Ni}} = 61$ and $\beta_{\text{Ca/Ni}} = 36$ (Table 1), and extractions of about 60% of calcium, 72% of magnesium and approximately 2% of nickel (see Figure 1-b). In this condition, a purified nickel solution could be obtained using at least 2-3 contacting stages. At higher pH values, however, the selectivity Ca/Ni is significantly affected probably due to a metal competition by the extractant and/or to a metal exchange between nickel and calcium (similar to a scrubbing operation).

An even interesting operating condition was obtained using 10% v/v of D2EHPA with 20% v/v of Cyanex 272. The contact of this organic phase at pH 4.8 resulted in quite high selectivity ($\beta_{\text{Mg/Ni}} = 52$ and $\beta_{\text{Ca/Ni}} = 40$, see Table 1), associated to satisfactory extraction levels of approximately 45% of calcium, 51% of magnesium and around 2% of nickel (see Figure 1-c).

Increasing the concentration of D2EHPA to 20% v/v in the organic phase containing 20% v/v of Cyanex 272 resulted in lower selectivity (see Table 1) due to the relative increase on the extraction of nickel (> 10% as shown in Figure 1-d) for the whole pH range studied.

Conclusions

The results obtained revealed that small quantities of D2EHPA mixed with Cyanex 272 (20% v/v) associated to lower pH values of the aqueous phase favor the selectivity of alkaline earth metals calcium and magnesium over nickel. The higher acidity of D2EHPA in comparison to that of Cyanex 272, its higher affinity to calcium and magnesium, as well as the lower concentrations of alkaline earths relative to nickel may explain such results. For the conditions investigated, the best results in terms of selectivity Ca/Ni and Mg/Ni, as well as metal extractions, were obtained using an organic phase containing 5% v/v of D2EHPA mixed with 20% v/v of Cyanex.

Acknowledgements

The authors acknowledge the financial support from CNPq (CT-Mineral, Project n° 550243/2011-9), FAPEMIG, CAPES and INCT-Acqua (National Institute of Science and Technology in Minerals, Water Resources and Biodiversity, www.acqua-inct.org), as well as to Cytec for supplying the Cyanex 272 samples.

References

- Cheng, C.Y., Urbani, M.D. Purification of laterite leach solutions by direct solvent extraction. In: Kongoli, F., Itagaki, K., Yamauchi, C., Sohn, H.Y. (Eds), Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies. *Aqueous and Electrochemical Processing*, 3, 251-265, 2003.
- Cheng, C.Y., Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime. *Hydrometallurgy*, 84, 109-117, 2006.
- Cheng, C.Y., Boddy, G., Zhang, W., Godfrey, M., Robinson, D.J., Pranolo, Y., Zhu, Z., Wang, W. Recovery of nickel and cobalt from laterite leach solutions using

- direct solvent extraction: Part 1 - selection of a synergistic SX system. *Hydrometallurgy*, 104, 45-52, 2010.
- Flett, D.S. Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. *Journal of Organometallic Chemistry*, 609, 2426-2438, 2005.
- Guimaraes, A.S. Purificação de níquel a partir de soluções sulfúricas por extração por solventes utilizando-se Cyanex 272 e misturas de extratantes. Dissertação, Mestrado em Engenharia Metalúrgica, Materiais e de Minas. Belo Horizonte, Minas Gerais, Universidade Federal de Minas Gerais; 145p., 2014.
- Mansur, M.B., Morais, B.S. Characterization of the reactive test system $\text{ZnSO}_4/\text{D2EHPA}$ in n-heptane. *Hydrometallurgy*, 74, 11-18, 2004.
- Mantuano, D.P., Dorella, G., Elias, R.C.A., Mansur, M.B. Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. *Journal of Power Sources*, 159, 1510-1518, 2008.
- Ndlovu, B., Mahlangu, T. Calcium and magnesium rejection from sulphate solutions in lateritic nickel solvent extraction using Versatic 10 acid-LIX[®] 84 IC system. *Template Journal*, 108, 223-227, 2008.
- Rydberg, J., Cox, M., Musikas, C., Choppin, G.R. Principles and practices of solvent extraction. 2ed. Marcel Dekker, New York, 723p., 2004.

Solvent extraction reaction of uranium (VI) sulfate with Alamine 336

Érica Cristina Avelar¹, Georgio Patrício de Souza Resende¹, Marcelo Borges Mansur^{*1}

The solvent extraction equilibrium reaction of uranium (VI) sulfate with Alamine 336 as an extractant dissolved in Exxsol D-100 and 5% v/v of tridecanol as a modifying agent at room temperature (25±2)°C has been investigated. Experimental data at typical concentration levels like those used at the uranium plant of Caetité, Brazil, obtained by Alvarenga (2010) were used. Data fitting using the slope analysis method revealed that uranium is preferentially extracted by Alamine 336 as UO_2SO_4 species, but extraction of $\text{UO}_2(\text{SO}_4)_2^{2-}$ species may also occur simultaneously.

Introduction

A number of extractants classified in four main types have been normally used for uranium extraction from acid solutions (Kumar et al., 2011): (i) nitrogen-based extractants, that cover predominantly the amide and amine functional groups containing extractants, such as Alamine 336 (n,n-dioctyloctan-1-amine) and Adogen 363 (tri-octyl methylammonium chloride); (ii) phosphorous-based extractants, including tri-butyl-phosphate (TBP), di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (PC88A), tri-n-octyl-phosphine oxide (TOPO or Cyanex 923), and bis(2,4,4-trimethyl penthyl) phosphinic acid (Cyanex 272); (iii) sulfur-based extractants, mainly sulfoxides and other sulfur-containing extractants; and (iv) other extractants.

Tertiary amines are the most common extractant types used to treat industrial solutions resulting from the sulfuric acid leaching of uranium bearing ores. In Brazil, uranium is produced by INB (Indústrias Nucleares do Brasil S.A.), the state-owned company responsible for uranium extraction and its transformation into nuclear energy. The current production consists of 400 tons of uranium per year. The purification of the sulfate leach liquors is carried out by solvent extraction, using Alamine 336 as an extractant (Morais and Gomiero, 2005). The selectivity order of amines for some ions is (Mackenzie, 1997): $\text{UO}_2(\text{SO}_4)_3^{4-} > \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{Fe}(\text{SO}_4)_2^-$. The extraction of a neutral uranium (VI) sulphate species in an adduct type of mechanism is also plausible (Ritcey, 2006). The degree to which either the extraction of an anionic or neutral uranium species is involved would seem to depend on the uranium species present, which in turn depends on the sulfate concentration and pH of the aqueous phase.

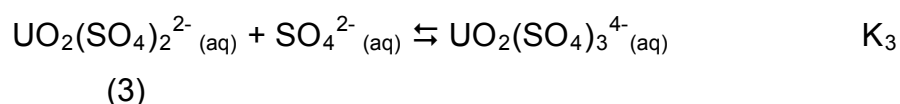
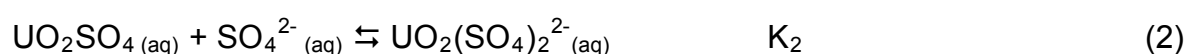
The present study aimed to evaluate the solvent extraction equilibrium of uranium (VI) from sulfate solutions using Alamine 336 at typical operating conditions of the INB plant in Brazil using the slope analysis method. Experimental data used in

^{1*} Corresponding Author, Dept. de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, Brazil, Tel.: +55 (31) 3409-1811, Fax: +55 (31) 3409-1715, E-mail: marcelo.mansur@demet.ufmg.br

the present analysis and methodology were obtained by Alvarenga (2010). The model has been validated to the following conditions: initial concentration of uranium from 2×10^{-3} to 9×10^{-3} M (0.46 to 2.1 g.L $^{-1}$), initial concentration of sulfate from 0.25 to 1.00 M (23 to 95 g.L $^{-1}$), and $0 \leq \text{pH} \leq 0.54$. The initial concentration of Alamine 336 in the organic phase varied from 0.05 to 0.20 M.

Modeling of uranium (VI) sulfate extraction with Alamine 336

Uranium (VI) dissociates in sulfate media according to the following reactions (NEA database, 2004; Vercouter et al., 2008; Vopálka et al., 2010):



The distribution of uranium (VI) species within the studied operating conditions (concentration range limited by vertical gray lines) is shown in Figure 1. Calculations were done using stability constants (K_1 to K_3) from distinct authors portrayed in Table 1. The concentration of HSO_4^- and SO_4^{2-} ions in the aqueous phase were determined assuming dissociation of sulfuric acid according to:

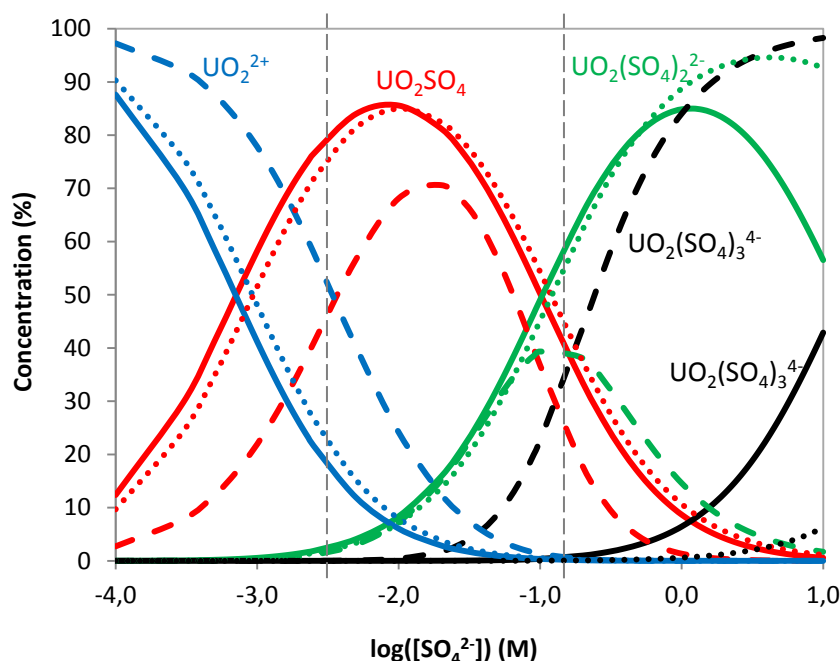


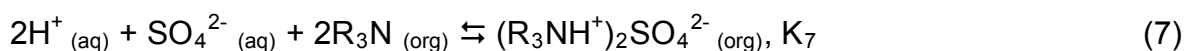
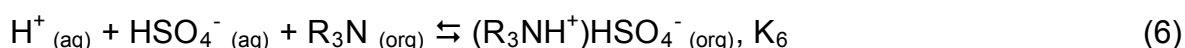
Figure 1. Speciation diagram of uranium (VI) sulfate: NEA database (2004) – continuous curves; Vopálka et al. (2010) – dotted curves; Vercouter et al. (2008) – dashed curves ($[U]_{total} = 0.01 \text{ M}$; $T = 25^\circ\text{C}$; stability constants listed in Table 1).

Table 1. Stability constants of uranium (VI) sulfate in the aqueous phase ($I = 0$; $T = 25^\circ\text{C}$).

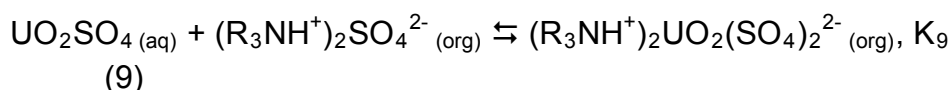
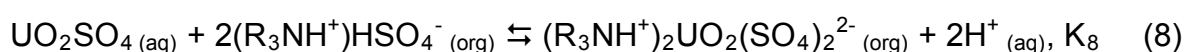
	NEA ^[11]	Vopálka et al. ^[12]	Vercouter et al. ^[13]
log(K₁)	3.15 ± 0.02	3.03 ± 0.31	2.45 ± 0.05
log(K₂)	0.99 ± 0.07	0.92 ± 0.25	1.03 ± 0.04
log(K₃)	-1.12 ± 0.38	-2.17 ± 0.25	0.76 ± 0.20

According to Figure 1, the predominance of species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_3^{2-}$ is expected. The occurrence of $\text{UO}_2(\text{SO}_4)_3^{4-}$ is significant only when the concentration of SO_4^{2-} is higher than 1.5M, according to Vercouter et al. (2008). Therefore, neutral and anionic species may preferentially compete to be extracted by Alamine 336, given that it is a water insoluble extractant that is capable of forming oil soluble salts of anionic species at a low pH (www.cognis.com). Species HSO_4^- and SO_4^{2-} also predominate in the aqueous phase at $0 \leq \text{pH} \leq 0.54$.

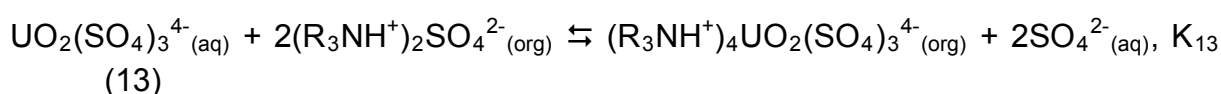
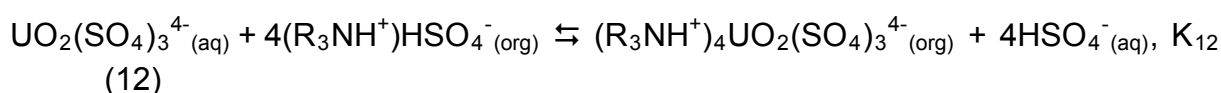
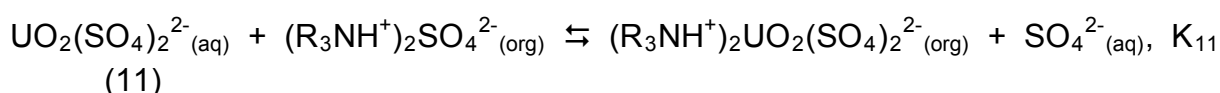
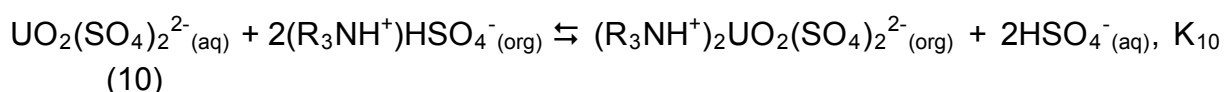
- Protonation of Alamine 336 with HSO_4^- and SO_4^{2-}



- Reactions between the protonated amine species with neutral species of uranium (VI) sulfate



- Reactions between the protonated amine species with anionic species of uranium (VI) sulfate



The distribution coefficient of uranium (D_U) is given by the following equation:

$$D_U = \frac{[(R_3NH^+)_2UO_2(SO_4)_2^{2-}] + [(R_3NH^+)_4UO_2(SO_4)_3^{4-}]}{[UO_2^{2+}] + [UO_2SO_4] + [UO_2(SO_4)_2^{2-}] + [UO_2(SO_4)_3^{4-}]} \quad (14)$$

Equations (9) and (11) are not independent and can be derived by combining them with Eq. (2). Substituting Eqs. (1)-(13), and Eq. (14):

$$D_U = \frac{K_a[R_3N]^2[H^+]^p + K_b[R_3N]^4[H^+]^4[SO_4^{2-}]}{\frac{1}{K_1K_2[SO_4^{2-}]^2} + \frac{1}{K_2[SO_4^{2-}]} + 1 + K_3[SO_4^{2-}]} \quad (15)$$

where (i) $p = 1$ and $K_a = K_6^2K_8/(K_2K_5)$ if equilibrium is governed by Eq. (8), (ii) $p = 2$ and $K_a = K_7K_9/K_2$ if equilibrium is governed by Eq. (9) or Eq. (11), (iii) $p = 2$ and $K_a = K_6^2K_{10}$ if equilibrium is governed by Eq. (10), (iv) $p = 2$ and $K_a = K_7K_{11}$ if equilibrium is governed by Eq. (11), (v) $K_b = K_3K_6^4K_{12}$ if equilibrium is governed by Eq. (12), and (vi) $K_b = K_3K_7^2K_{13}$ if equilibrium is governed by Eq. (13). Equation (15) depends on the concentration of the extractant, protons, and sulfate ions in the equilibrium. Stability constants K_1 to K_3 are given by NEA database^[11] values shown in Table 1, while K_a and K_b are parameters to be determined by data fitting. No activity coefficient was considered and the model does not presume the aggregation of amine salts in the organic phase.

The concentration of free extractant in the organic phase is proportional to the mass balance of total uranium extracted from the aqueous phase given by:

$$[R_3N] = [R_3N]_{\text{initial}} - m ([U]_{\text{initial}} - [U]) \quad (16)$$

where $m = 1, 2$ or 4 corresponds to the stoichiometric coefficient of extractant in Eqs. (8) to (13). To identify the predominant species involved in the extraction of uranium using Alamine 336, Eq. (15) was fitted in parts, i.e., it was assumed that equilibrium occurs with only one species in the organic phase and one species in the aqueous phase. In this manner, 20 distinct equations can be derived from Eqs. (15) and (16). Taking the logarithms in those equations, fitting was carried out by data plotting as $\log(D_U)$ versus $\log([R_3N]^2[H^+]^p[SO_4^{2-}]^n)$ if species $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ are predominant in the organic phase according to (i) Eq. (8) ($p = 1, m = 2$), or (ii) Eq. (9) or Eq. (11) ($p = 2, m = 1$), or (iii) Eq. (10) ($p = 2, m = 2$), or as $\log(D_U)$ versus $\log([R_3N]^4[H^+]^4[SO_4^{2-}]^{n+2})$ if species $(R_3NH^+)_4UO_2(SO_4)_3^{4-}$ are predominant in the organic phase according to (iv) Eq. (12) ($m = 4$), or (v) Eq. (13) ($m = 2$). In those fittings, $n = 2$ if equilibrium occurs with species UO_2^{2+} in the aqueous phase, $n = 1$ if it occurs with UO_2SO_4 species, $n = 0$ if it occurs with $UO_2(SO_4)_2^{2-}$ species, or $n = -1$ if the $UO_2(SO_4)_3^{4-}$ species predominates in the aqueous phase.

Fitting results shown in Figure 2(a) reveal that equilibrium may occur predominantly between the $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ and aqueous species $UO_2(SO_4)_2^{2-}$, given that, in this case, only a straight line with an angular coefficient relatively near unity and satisfactory R^2 coefficient was obtained with blue data fitting. Extraction is also satisfactorily described by Eqs. (9) to (11), however a better fitting is obtained

when aqueous species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ are considered, despite the lower R^2 coefficient, see Figure 2(b). Perhaps all these reactions may occur simultaneously at changing extents depending on the operating condition. Therefore, based on the present analysis, uranium (VI) could be extracted by Alamine 336 as UO_2SO_4 and/or as $\text{UO}_2(\text{SO}_4)_2^{2-}$. According yet to data fitting, however, equilibrium may not occur with the species $(\text{R}_3\text{NH}^+)_4\text{UO}_2(\text{SO}_4)_3^{4-}$ and reactions given by Eqs. (12)-(13) for the operating conditions studied, because angular coefficient below 0.5 was obtained in all fitting attempts. This result is inconsistent with previously published literature (Sato, 1963; Shmidt, 1971) and mechanism may depend on acidity. In addition, fluorescence measurements done by Vercouter et al. (2008) indicated that species $\text{UO}_2(\text{SO}_4)_3^{4-}$ occurs solely when the concentration of sulfate is equal or higher than 1.5 M. Too scatter data (low R^2 coefficient) was obtained with $n = 2$ (equilibrium with aqueous species UO_2^{2+}) and these data were not displayed in Figure 2.

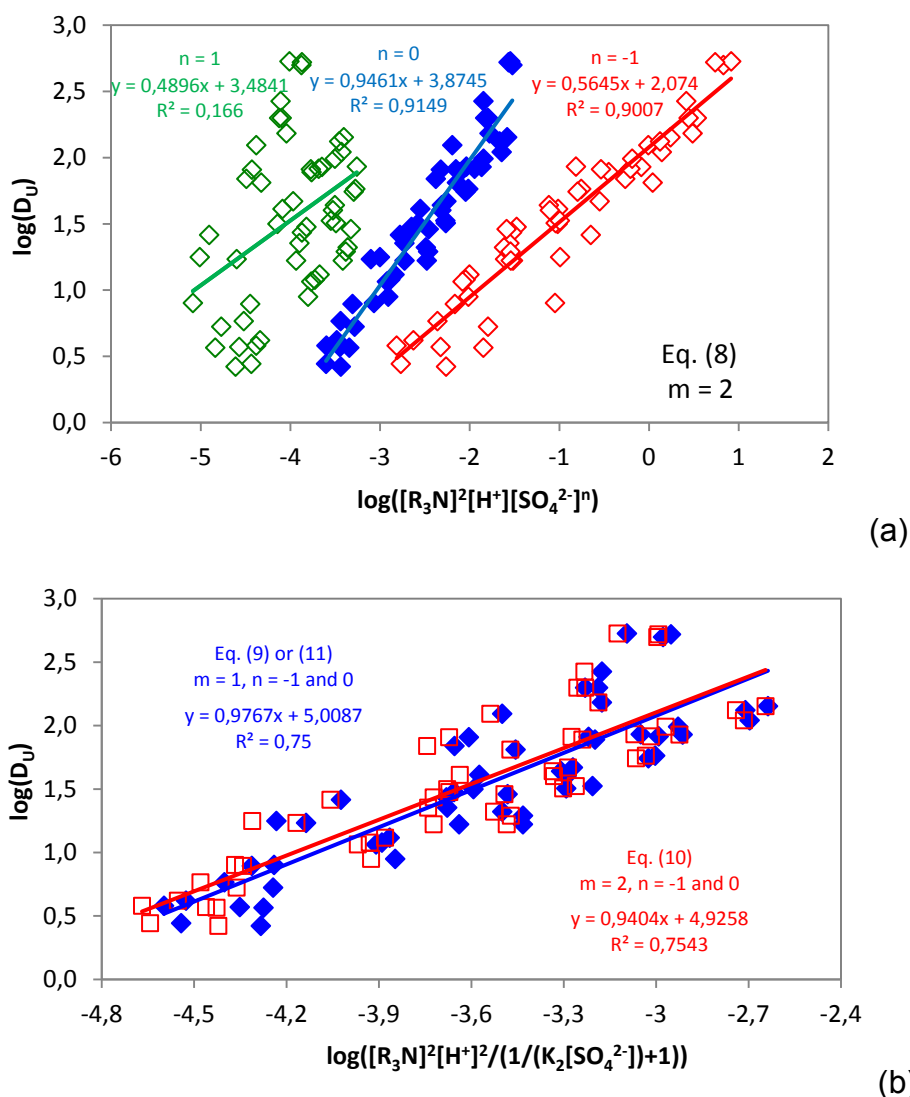


Figure 2. Data fitting: (a) Equilibrium between $(\text{R}_3\text{NH}^+)_2\text{UO}_2(\text{SO}_4)_2^{2-}$ and UO_2SO_4 ($n = 1$, green) or $\text{UO}_2(\text{SO}_4)_2^{2-}$ ($n = 0$, blue) or $\text{UO}_2(\text{SO}_4)_3^{4-}$ ($n = -1$, red) given by Eq. (8) with $m = 2$, and (b) Equilibrium between $(\text{R}_3\text{NH}^+)_2\text{UO}_2(\text{SO}_4)_2^{2-}$ in the organic phase and aqueous species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ ($0 \leq \text{pH} \leq 0.54$; $T = 25^\circ\text{C}$).

Alamine 336 is expected to be fully protonated in $0 \leq \text{pH} \leq 0.54$. Equation (6) leads to the extraction of HSO_4^- ions, favoring the consumption of SO_4^{2-} ions; such consumption is also expected by the protonation of Alamine 336 given by Eq. (7). Consequently, Eq. (3) most likely occurs from the right to the left, as long as UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ species are extracted by Alamine 336.

Conclusions

- Species distribution calculations in the aqueous phase revealed that concentrations of UO_2^{2+} are negligible within the evaluated condition ($[\text{U}]_{\text{total}} = 0.01 \text{ M}$; $0 \leq \text{pH} \leq 0.54$; $T = 25^\circ\text{C}$). Species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ predominate within operating conditions ($-2.5 \leq \log([\text{SO}_4^{2-}]) \leq -0.8 \text{ M}$);
- Uranium (VI) is preferentially extracted by Alamine 336 as UO_2SO_4 , according to Eq. (8). Species $\text{UO}_2(\text{SO}_4)_2^{2-}$ may also be extracted simultaneously, according to Eqs. (10)-(11). The extraction of species $\text{UO}_2(\text{SO}_4)_3^{4-}$ seems improbable for the operating conditions investigated;

Acknowledgments

Authors acknowledge Brazilian agencies FAPEMIG (PRONEM 16/2010, APQ-04026-10), CNPq, CAPES and INCT Acqua (www.acqua-inct.org) for the financial support, Prof. Carlos Antônio Moraes and Eng. Carlos Leon Alvarenga for cooperation, as well as Indústrias Nucleares do Brasil S.A. (INB) (www.inb.gov.br).

References

- Alvarenga, C.L.G., Estudo da extração líquido-líquido de urânio com Alamine 336 a partir de meio sulfúrico na ausência e na presença de íons cloreto. Master Thesis, CDTN, Belo Horizonte, Brazil, 2010, p. 71.
- Kumar, J.R.; Kim, J.-S.; Lee, J.-Y.; Yoon, H.-S. A brief review on solvent extraction of uranium from acidic solutions. *Sep. Purific. Rev.*, 2011, 40, 77-125.
- Mackenzie, J.M.W. Uranium solvent extraction using ternary amines. Uranium Ore Yellow Cake Seminar, Melbourne, Australia, 1997.
- Moraes, C.A.; Gomiero, L.A. Uranium stripping from tertiary amine loaded solution by ammonium sulfate. *Minerals Eng.*, 2005, 18, 1277-1281.
- NEA (Nuclear Energy Agency). Chemical thermodynamics of uranium. OECD, France, 2004, p.735.
- Ritcey, G.M. Solvent extraction – Principles and applications to process metallurgy. Vol. I, Ottawa, CA, 2nd Ed. Revised, 2006.
- Sato, T., The extraction of uranium (VI) from sulfuric acid solutions by tri-n-octylamine. *J. Inorg. Nucl. Chem.*, 1963, 25, 441-446.
- Shmidt, V.S. Amine extraction; Keter Press: Israel, 1971.
- Vopálka, D., Stamberg, K., Motl, A., Drtinová, B. The study of the speciation of uranyl-sulphate complexes by UV-Vis absorption spectra decomposition. *J. Radioanal. Nucl. Chem.*, 2010, 286, 681-686.
- Vercouter, T., Vitorge, P., Amekraz, B., Moulin, C. Stoichiometries and thermodynamic stabilities for aqueous sulfate complexes of U(VI). *Inorganic Chem.*, 2008, 47, 2180-2189.

Separation of Fe (III) from chloride solution by solvent extraction method and Tri-n-butyl phosphate (TBP)

Nima Sadeghi¹, Eskandar Keshavarz Alamdari^{1*}

Summary

Nowadays, hydrometallurgical process was proposed for most metal production. But dissolution of disturbing elements in addition to target metal is the main trouble. Hence, leach liquors must be purified by Solvent extraction technic. Our past studies are shown TBP can extract some precious Metals from Chloride media. Fe ions are main impurities of the system. A comparative study on Fe (III) extraction from synthesized chloric solution of Iron defined concentration has been carried out using TBP in distilled kerosene. Studies was carried out very low concentration (0.05-0.75 M) of extractant and continued until the remarkable Iron extraction. The Iron extraction was negligible at low concentration (0.1 M) of TBP. Overall condition is changed with increasing extractant level so that Fe extraction percent is more than %85 at 0.75M TBP and 3M HCl. An increase in the level of HCl leads to a higher extraction percent in compared to that of at higher value of TBP. The effect of TBP H^+ and Cl^- concentration on distribution ratio was studied that $HFeCl_4 \cdot 2TBP$ is suggested as extracted organic macromolecule. Also, for separation of iron from chloride solution by low concentration of TBP (<0.25M) is suitable but increasing extractant concentration decrease selective extraction if iron was consider as impurity.

Key words: separation, iron, chloride media, solvent extraction

1. Introduction

Purification of product was done in several methods that solvent extraction is one of them. Tri-butyl phosphate, known commonly as TBP, is relatively inexpensive with low solubility in water and appropriate extraction performance that was purpose for different metallic ions extraction from chloride, sulphate or nitrate solution. TBP usually used for anionic species extraction from chloride media while was proposed for gold (Sadeghi et al., 2013), iron (... , 2011), palladium (... ,2012) Selenium (... , 1984), tin and in chloride solution. So if Separation of these elements be considered, extraction condition should be evaluated, individually.

Namely, when gold minerals is leached in chloride media, such as aqua regia, Au dissolved with Fe, Cu, Zn, Ni, Se, Te and etc. if TBP was selected for concentration and purification processes, Au and Fe may be extracted, simultaneity. Hence, changing applicable parameter, such as temperature, acid and extractant concentration, for purification process could be useful.

Iron is one of the main impurities in hydrometallurgical process which is important. Hence, studing on purification of iron from aqueous solution is critics. Mishra et al. (2011) reported Fe(III) from chloride leach liquor using TBP and extraction efficiency was compared with Cyanex 921 and Cyanex. Cl^- concentration has tangible effect on

¹ Department of mining and metallurgical Eng., Amirkabir University of Technology, Tehran, IRAN

* Corresponding Author, Email: alamdari@aut.ac.ir, Telephone: +98 21 6454 2971

Fe extraction by TBP, unlike Cyanex921 and 923. H^+ , TBP and Cl^- concentration effect on Fe extraction was investigated and Conditions were determined to increase extraction performance.

Present study, the condition for iron extraction and extracted macromolecules by TBP is investigated. Also, TBP uses for Au and Fe extraction for chloride media and Separation terms For Au and Fe is studied in extraction stage. For more purification different compositions are Evaluate for Fe scrubbing from chloride media.

2. Material and methods

$FeCl_3$ (Merck, chemical company, Germany) was used for iron source in aqueous solution. Chloric acid and nitric acid was purchase Dr. Mojalalli labrator company (iran). Organic phase provide by mixing kerosene(Isfahan refinery co.) and TBP((FLUKA, Switzerland)) Batch experiments were conducted in a flask containing equal volumes (20 mL) of aqueous, mixture of hydrochloric acid and definite initial concentration of Fe and organic phases. The mixture was mechanically agitated (400 rpm) for 30 min. The mixtures were then separated by a decanting funnel for 15 min to allow complete separation. The metal content of the aqueous phase was determined by atomic absorption spectroscopy (Varian, A240) and then the organic phase was estimated by mass balance calculations. pH of aqueas solution determined by metller- Toledo (F430) pH meter.

3. Results and discussion

3.1 Effect of $[HCl]$ on extraction of iron

To study the effect of HCl concentration on extraction of iron, the concentration of HCl in the feed solution was varied in the range 0.05 to 6 M. The solution with a constant concentration of Fe(III) but different concentrations of HCl was prepared by adding different volumes of concentrated HCl and distilled water. The above solution was equilibrated with an equal volume of 0.1 and 0.5 M TBP for 30 min. It was observed that extraction of iron increased from 0.05 to 13.5 % and 0.4 to 99.2, respectively (fig1.).

3.2 Effect of hydrogen and chloride ion concentration on extraction of iron

As be seen in Fig. 1, Hcl concentration changes increases changes Fe extraction, considerably and H^+ or Cl^- influence on Fe extraction. So, effect of added ions concentration should be checked. To study the effect of $[Cl^-]$ on extraction of iron, the $[Cl^-]$ in the feed was varied within 2.5 to 5 M by adding NaCl while keeping the HCl concentration constant at 3 M (Fig. 2). The extraction of iron increased from 3.1% to 21% and 4% to 82.2% with 0.1 and 0.5 M TBP, respectively. Comparing Fig.

1 and Fig. 2 appears to be Cl^- the main factor to increase the extraction of iron. There are two state for iron in aqueous solution, Fe II and Fe III. Fe III is stable in chloride media. According to pourbaix of $\text{H}_2\text{O}-\text{Fe}-\text{Cl}$, Fe was react Cl^- and form chloride complexes FeCl^{2+} , FeCl_2^+ , FeCl_3 , respectively. FeCl_3 is stable in high concentration of Cl^- , thermodynamically. FeCl_3 extract by TBP with Cl^- and H^+ so Cl^- . Hence, TBP considerably extract Fe in high concentration of Cl^- . Also, extraction reaction can be suggested in eq(1):



3.3 Effect of pH and log[Extractant] on extraction of iron

The plot of log D vs. pH for 0.1M and 0.5M TBP are straight lines with slopes of 1.09 and 1.13 (Fig. 3), respectively indicating the association of 1 mol of H^+ ion with the extracted macromolecule. So, n in eq (2) is 1. Also, Based on Charge balancing l value is one.

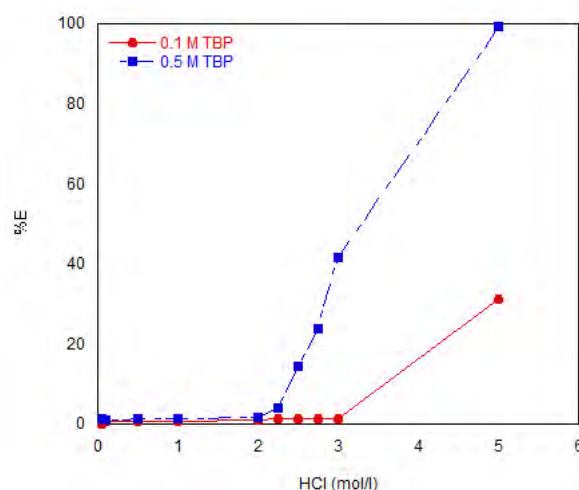


Fig. 1: Effect of [HCl] on extraction of iron with different concentration of extractant in kerosene

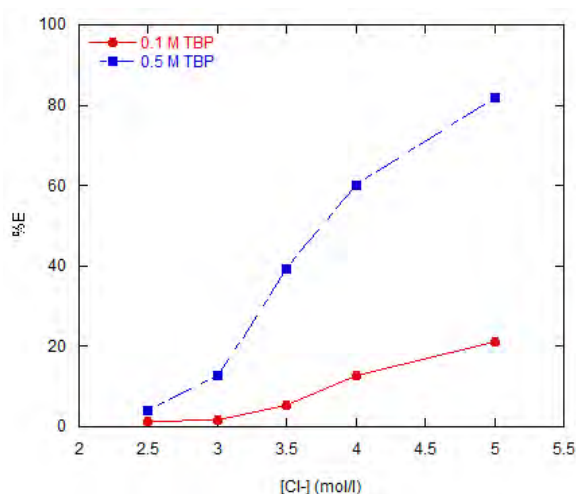


Fig. 2: Effect of $[\text{Cl}^-]$ on extraction of iron using TBP in kerosene.

To study the effect of extractant concentration on extraction of iron from the aqueous solution bearing 1 g/L Fe and 2.5 M HCl, the concentration were varied within the range 0.05-0.75 M in kerosene. The plot of $\log D$ vs. $\log [TBP]$ was straight lines with slope values of 2.01 and 2.03 for 3 and 3.6 M HCl, respectively (Fig. 4). So 2 TBP molecules with 1 H^+ ions and $FeCl_4^-$ formed extract macromolecule and extracted species is suggested $HFeCl_4 \cdot 2TBP$, while Mishra and et al. (2011) suggested $HFeCl_4 \cdot TBP$.

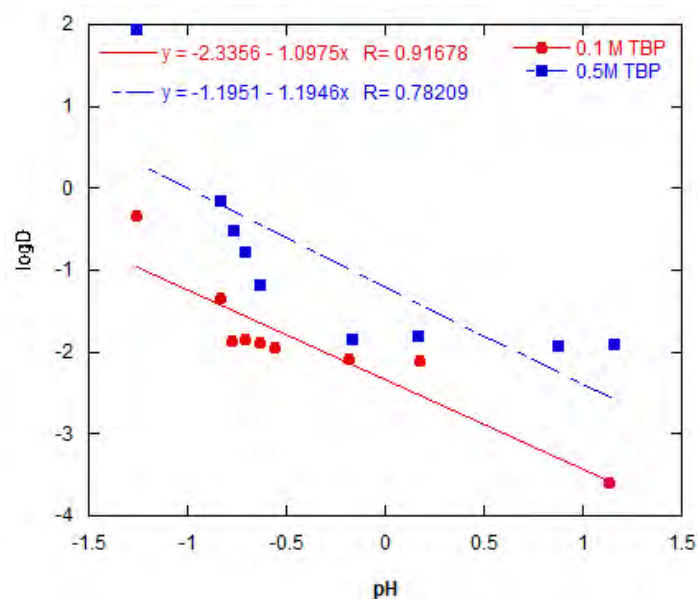


Fig. 3: Effect of pH on extraction of Fe(III) using 0.1 and 0.5 M TBP in kerosene.

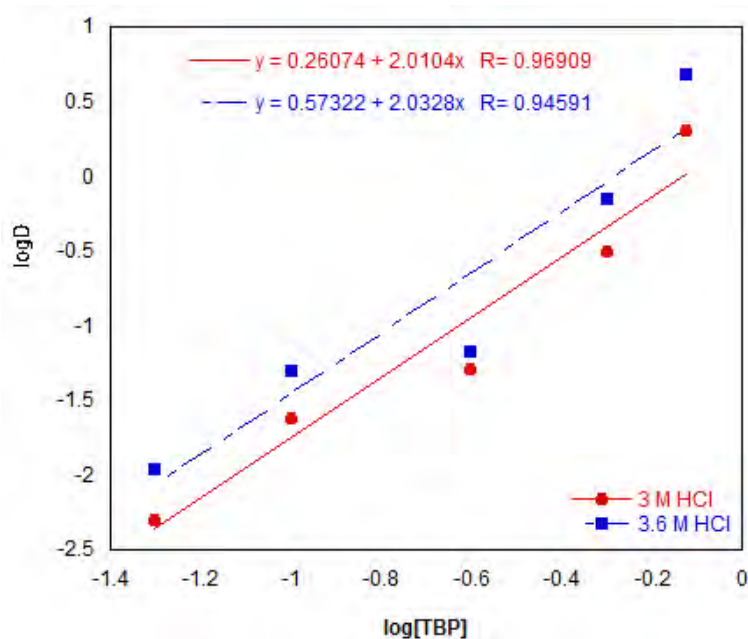


Fig. 4 Plot of $\log D_{Fe}$ vs. $\log [TBP]$

3.3 determine separation condition from other metals

Also Au extraction from chloride solution was reported (Sadeghi et al., 2013) previously. Hence, determination the condition for separation Au and Fe can be useful. In other words, studies should be conducted to find out where that gold extracted and iron remain in aqueous solution or vice versa. Acid and extractant concentration is two main practical parameters for solvent extraction process. So, by depicting gold and iron extraction in various extractant and acid concentration the optimum condition can be obtained. Initial Au and Fe concentration was spotted 0.5 and 1 g/l, respectively.

In Fig. 5(a), Au extraction was proper in long range of acid concentration. Au extraction percent change 64% to 98% at 0.5-10 M HCl whereas Fe extraction change 0 to 34% at 0-6 M HCl. In Fig. 5 (b), TBP concentration increased and Au and Fe extraction change 83% to 99.4% and 0 to 90%, respectively. So, medium HCl concentration, 2-4M HCl, is suggested for efficient extraction and purification. If leach liquor has high concentration of HCl, e.g $C_{HCl} > 3$ M HCl, should use other purification method in solvent extraction process. Scrubbing and stripping stage can be used purification of chloride solution.

3.4 scrubbing of organic phase

Base on Fig. 1 and Fig. 5, iron can be extracted in high acid concentration, substantially. a scrubbing stage for impurities elimination from organic phase can be spotted. Hence, various compositions were examined for organic phase scrubbing. The TBP loaded organic contained 1 g/L Fe. To scrub out the iron values from the loaded organic, the scrubbing studies were carried out with distilled water, chloric acid and sodium hydroxide. All of this composition cant strip Au from chloride solution

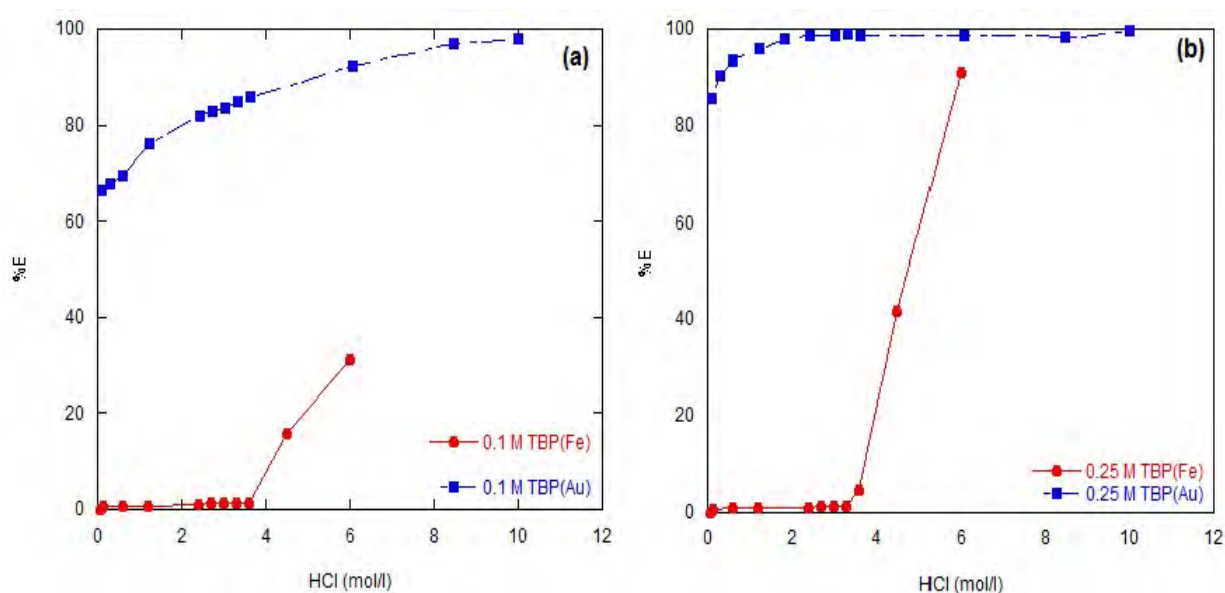


Fig. 5: Comparing between Au and Fe extraction from chloride solution by (a) 0.1 and (b) 0.25 M TBP

Table 1: various composition for Fe scrubbing from organic solution

	%Scrubbing		
	0.1 M	0.25 M	0.75 M
Distill water		98.24	
HCl	12.54	7.54	2.52
NaOH	6.5	17.25	32.5

(Sadeghi et al., 2013). Equal volumes of distilled water and the Fe-loaded TBP were equilibrated. Distilled water can scrubs satisfactory but other composition scrubbing is not proper.

4. Conclusion

- Fe could be extracted by TBP from chloride solution, considerably.
- Extracted macromolecule was $\text{HFeCl}_4 \cdot 2\text{TBP}$
- Fe must be converted to chloride complexes for extraction
- Increasing the chlorine ion concentration is desirable effect on Fe extraction
- Increasing extractant concentration decrease selective extraction if iron was considered as impurity.
- In lower acid concentration, TBP can separate Au and Fe in extraction stage
- To remove iron, the organic phase is scrubbed by distilled water.

Reference:

Hoh, Y. C., Chang. C. C., Cheng W. L., Shaw.I.S., The separation of selenium from tellurium in hydro chloric acid media by solvent extraction with tri-butyl phosphate, *Hydrometallurgy* 9, 1983, 381—392

Jae Woo Ahn, Jae Chun Lee, Separation of Sn, Sb, Bi, As, Cu, Pb and Zn from Hydrochloric Acid Solution by Solvent Extraction Process Using TBP (tri-n-Butyl phosphate) as an Extractant, *Materials Transactions*, 52, 2011, 2228 -2232

Lee J. Y., Raju. B., Kumar. B.N., Kumar. J. R., Park. H. K. , Reddy. B. R., Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst, *Separation and Purification Technology* 73, 2010, 213–218

Mishra, R. K., Rout P.C., Sarangi. P.C., Nathsarma. K.C. A comparative study on extraction of Fe (III) from chloride leach liquor using TBP,Cyanex 921 and Cyanex 923, / *Hydrometallurgy* 104, 2010, 298–303

Sadeghi N., Alamdari E.K., Fatmehsari D. H., Darvishi D., Alamdari A. K., kafash Rafsanjani A. B., Solvent Extraction of Gold from Chloride Solution by Tri-Butyl Phosphate (TBP), 23rd International Mining Congress & Exhibition of Turkey, 16-19 April 2013

Evidence for a predictable difference between nitrate and sulphate anions in the solvent extraction of base metals by acidic extractants

*Hutton-Ashkenny M.^{*1}, Ibana D.², Barnard K.R.³*

Solvent extraction for the recovery of base metals from nitric acid leaching of nickel laterite ores has become of interest as the Direct Nickel nitric acid leaching process nears commercialisation. Due to the dominance of sulphate hydrometallurgy, there has been limited research into solvent extraction of base metals from nitrate liquors and how this may differ from sulphate. Very few studies have specifically investigated the effects of the anion in base metal solvent extraction. This lack of data makes assessing the potential application of solvent extraction to nitrate liquors difficult. The present paper presents the extraction of seven different metals using eight different reagent systems under otherwise identical conditions in both sulphate and nitrate matrices. Comparison of the resulting pH₅₀ values revealed a predictable difference between the pH₅₀ of extraction in the two matrices, with extraction occurring at lower pH from the nitrate matrix. This outcome provides a guide for extrapolating existing data from sulphate systems to estimate probable behaviour in nitrate systems.

Introduction

There are three major alternatives for solution treatment of nickel laterite acid leach solutions. Two of these options, mixed sulphide precipitation (MSP) and mixed hydroxide precipitation (MHP), require precipitation of intermediate products. This in turn requires re-leaching before further processing to recover the metal values can be undertaken. MSP production uses toxic hydrogen sulphide gas [1] whereas MHP is less selective for nickel and cobalt and has a higher moisture content than MSP, increasing transport costs [2]. The third processing option is direct solvent extraction (DSX), which can produce separate nickel and cobalt products at higher purity than the MHP or MSP intermediates.

Direct Nickel Ltd. is developing a process for nitric acid leaching of nickel laterite ores with a staged MHP nickel and cobalt recovery operation [3]. DSX from the nitric acid leach is a potential avenue for generating higher value products and is therefore of interest. It is not known, however, whether extrapolation of the extensive information available from commercial base metal sulphate systems is relevant to a nitric acid-based solvent extraction (SX) system.

Differences in the pH of metal extraction have been noted previously between aqueous sulphate and nitrate matrices, although there are limited studies with this particular focus [4-7]. In these cases, small decreases in the pH required for extraction in a nitrate matrix are observed. Chromium extraction by the phosphinic acid Cyanex[®]272 occurs at 0.4 pH units lower in a 0.1 M nitrate solution compared to a 0.1 M sulphate solution [5]. The extraction of copper by Cyanex[®]301 (the mono-thio

^{*1} WA School of Mines, Curtin University and Direct Nickel Ltd., Australia – huttonashkenny@gmail.com

² WA School of Mines, Curtin University, Australia

³ CSIRO Process Science and Engineering / CSIRO Minerals Down Under National Research Flagship, Australia; keith.barnard@csiro.au

analogue of Cyanex 272) from 0.1 M nitrate and sulphate solutions also occurs at 0.4 pH units lower in the nitrate matrix [4]. In these two studies, the anion concentration was kept constant at 0.1 M, but the ionic strength would be greater in the sulphate solutions due to the higher charge on the sulphate anion. Investigations by Du Preez and Preston [6] show that at the same ionic strength (1 M), the extraction of all lanthanide metals by the carboxylic acid Versatic 10 occurs at 0.5 pH units lower in the nitrate matrix (1 M) than the sulphate matrix (0.33 M). The extraction of nickel by a synergistic combination of 4-(5-nonyl)pyridine and Versatic 10 also occurred 0.5 pH units lower in a nitrate matrix (1 M) than a sulphate matrix (0.33 M) [7].

These few studies indicate a trend of decreasing pH required for metal extraction from a nitrate matrix relative to a sulphate matrix. This trend appears to persist when examining studies in either nitrate or sulphate matrices in the wider literature but direct comparisons of different studies are more problematic due to variations in operating conditions such as metal concentration, aqueous ionic strength, reagent concentration, temperature, and aqueous to organic ratios. The present study therefore aimed to systematically investigate the equilibrium extraction of moderate concentrations of metals of interest in a typical nickel laterite DSX feed liquor by acidic (cation exchange) solvent extraction reagents from both nitrate and sulphate aqueous matrices at constant ionic strength under otherwise equivalent operating conditions. Comparisons between metal extractions were made via the pH_{50} values, the pH at which 50% of metal extraction occurs, for each metal in each system.

Experimental

Aqueous and organic solution preparation

A bulk nitrate mixed metal solution containing metal nitrate salts each at 0.01 M was prepared with analytical grade calcium, cobalt, manganese, nickel, and zinc nitrate and reagent grade copper and magnesium nitrate in 1 M reagent grade sodium nitrate. This solution was adjusted to pH 1 with analytical grade concentrated nitric acid. A bulk sulphate solution containing metal sulphate salts each at 0.01 M was prepared with analytical grade copper, manganese, nickel, and zinc sulphate and reagent grade calcium, cobalt, and magnesium sulphate in 0.33 M analytical grade sodium sulphate to achieve the same calculated ionic strength as 1 M sodium nitrate, assuming complete dissociation. This solution was adjusted to pH 1 with analytical grade concentrated sulphuric acid.

Organic solutions were prepared using technical grade solvent extraction reagents diluted to 0.5 M in Shellsol D70 (Shell Chemicals). Extractants used were: D2EHPA (di-2-ethylhexyl phosphoric acid, 98%, Chemorex), HEH(EHP) (phosphonic acid (2-ethylhexyl)-mono (2-ethylhexyl) ester, 97%, SNF FloMin), Cyanex[®]272 (*bis*-2,4,4-trimethylpentyl phosphinic acid, 85%, Cytec), Versatic 10 (*iso*-decanoic acid, 99%, Shell Chemicals), LIX[®]63 (5,8-diethyl-7-hydroxy-dodecan-6-oxime, 70%, BASF), LIX[®]860-NIC (5-nonylsalicylaldoxime, 82.6%, BASF), LIX[®]84-I (2-hydroxy-5-nonylacetophenone oxime, 50%, BASF), and nonyl-4PC (nonyl-4-

pyridinecarboxylate, 95%, China Central South University). The reagents were used as supplied and the quoted purities were obtained from either the MSDS or the manufacturer. The following solutions of reagents and reagent combinations were prepared: D2EHPA, HEH(EHP), Cyanex 272, Versatic 10, LIX 63, LIX 63 and Versatic 10, LIX 860 and D2EHPA, LIX 84 and D2EHPA, and nonyl-4PC and Versatic 10.

Extraction pH isotherm procedure

Each of the nine reagent or reagent combinations was separately mixed with both the mixed metal nitrate and sulphate aqueous solutions at an aqueous to organic ratio (A:O) of 1:1 at 23°C using an overhead mixer (65 mm diameter impeller) at 1300 rpm (tip speed 4.42 m/s) in a stainless steel mixing box (9 × 9 × 14 cm). The emulsion pH was measured using a pH probe (Ionode, IJ44-A) and samples of the emulsion were taken at 0.5 pH unit intervals with a glass syringe and immediately filtered through Whatman 1PS paper. The pH was adjusted using either 100 g/L sodium hydroxide, or 550 g/L sodium hydroxide for sulphate isotherms below pH 3, over a pH range dependant on the organic reagents being used. Sampled organic phases were stripped (3 M nitric acid, A:O 3:1, 60°C) for 1 hour in a shaker-incubator operating at 250 rpm. The aqueous raffinate and loaded strip liquors were analysed with atomic absorption spectroscopy (AAS) using an Agilent 240 FS spectrophotometer.

Thermodynamic modelling

Thermodynamic modelling using PHREEQC (pH Redox Equilibrium modelling software in the C programming language, United States Geological Service) using a modified version of the mintek.v4 database was carried out to predict any difference in metal hydroxide precipitation, as an analogue to solvent extraction, from 1M ionic strength nitrate or sulphate solutions. The species added to the database were: $\text{Ni}(\text{NO}_3)_2(\text{aq})$ $\log K = -0.60$ [8], $\text{Co}(\text{NO}_3)_2(\text{aq})$ $\log K = 0.66$ [9], and $\text{Ca}(\text{NO}_3)_2(\text{aq})$ $\log K = 0.65$ [10]. No aqueous magnesium nitrate species were present in the modified database. The model equilibrated an initial solution of 0.01 M of the same metal ions used to generate the pH isotherms in a 1 M ionic strength sodium nitrate or sulphate matrix at pH 1 with atmospheric oxygen and carbon dioxide. The oxidation reduction potential (ORP) was calculated from the subsequent dissolved oxygen redox couple (O^0/O^{2-}). Charge balances were maintained with the relevant anion. The pH was raised by addition of NaOH to the solution and the model was allowed to equilibrate with the least soluble form of the metal hydroxide at 0.5 pH intervals from pH 1 to 14. It is important to note that the modelling results use hydroxide precipitation as an analogue to solvent extraction behaviour and are only relevant to specific conditions under thermodynamic equilibrium. Further, results are based on the Debye-Huckel model for aqueous activity, which may not be appropriate at ionic strengths as high as 1 M and so results must be treated with caution.

Results and Discussion

Confirmation of matrix effect on base metal extraction

To determine the accuracy of the experimental method, several cobalt nitrate ($n = 5$) and cobalt sulphate ($n = 4$) Cyanex 272 extraction isotherms were generated. These yielded 95% confidence intervals around the mean (95% CI) and standard deviations (s) of 95% CI = 3.58 ± 0.16 and $s = 0.13$ for nitrate, and 95% CI = 4.05 ± 0.15 and $s = 0.09$ for sulphate. As the two confidence intervals do not overlap the difference between the mean nitrate pH_{50} and mean sulphate pH_{50} is statistically significant. This was further confirmed using Student's t test ($p < 0.00043$) with an assumption of common variance validated using the F -test. The difference in pH_{50} when changing from a sulphate to a nitrate matrix $\Delta pH_{50(N-S)}$ was therefore used to assess the matrix effect on extraction of all tested metals by a variety of organic solutions.

Difference of pH_{50} between sulphate and nitrate matrices

The pH_{50} values for all examined systems in a sulphate matrix are listed in Table 1 and the results for a nitrate matrix in Table 2. The matrix-based pH_{50} differences for nitrate minus sulphate, $\Delta pH_{50(N-S)}$, are presented in Table 3. A clear and consistent difference can be seen favouring extraction of all metals from the nitrate matrix by any given reagent system. Interestingly, the extraction of nickel by oxime reagents appeared to be more favourable than other metals or other extractant types from a nitrate matrix. For all examined metals excluding nickel, average $\Delta pH_{50(N-S)}$ values of between -0.45 and -0.54 were obtained.

For nickel extracted by systems not containing oximes a similar $\Delta pH_{50(N-S)}$ with a 95% CI of -0.56 ± 0.11 pH units ($s = 0.09$) was obtained. When either hydroxyoxime or phenolic oxime was present, however, the $\Delta pH_{50(N-S)}$ 95% CI was -0.90 ± 0.26 pH units ($s = 0.16$). Although the two ranges just overlap, a two sample t -test assuming equal variances (validated using an F -test) showed that the $\Delta pH_{50(N-S)}$ for nickel extraction by oximes was significantly different to the $\Delta pH_{50(N-S)}$ for nickel extraction by other acidic reagents ($p < 0.0052$). Excluding the results for nickel extraction by oximes, the 95% CI for the mean of all $\Delta pH_{50(N-S)}$ values was -0.51 ± 0.03 pH units ($s = 0.11$). The observed increased extraction from nitrate over sulphate matrices, and the magnitude of this difference, is consistent with the outcomes obtained from studies previously discussed [4-7]. It would therefore appear reasonable to expect a shift in pH_{50} moving from moderate ionic strength sulphate solutions to comparable nitrate solutions of approximately -0.5 units for any metal extracted by any acidic extractant with the exception of nickel extraction by oximes where the $\Delta pH_{50(N-S)}$ is -0.9 units.

Table 1: pH_{50} values for metals extracted by different reagents from a 0.33 M sodium sulphate matrix

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	Versatic 10 + LIX 63	LIX860 NI + D2EHPA	LIX84 + D2EHPA	nonyl-4PC + Versatic 10
Co	3.7	4.0	4.4	6.8	5.3	3.2	2.3	3.0	5.6
Cu	2.8	3.3	3.8	4.4	<3	<3	<1	1.1	<3.5
Ni	4.2	5.2	6.3	6.6	5.4	4.1	2.3	2.7	5
Zn	1.4	1.6	2.2	6.1	6.3	3.9	1.5	1.8	5.4
Ca	1.8	3.1	5.2	7.1	>8	6.7	2.2	2.1	6.7
Mg	3.3	4.4	5.3	8.5	>8	8.1	3.1	3.3	8.2
Mn	2.3	3.2	4.1	7.0	8.1	5.4	2.2	2.4	6.5

Table 2: pH_{50} values for metals extracted by different reagents from a 1 M sodium nitrate matrix

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	Versatic 10 + LIX 63	LIX860 NI + D2EHPA	LIX84 + D2EHPA	nonyl-4PC + Versatic 10
Co	3.1	3.5	3.9	6.3	5.0	2.7	1.7	2.4	5.2
Cu	2.2	2.7	3.4	<4	<3	<2	<1	<1	2.9
Ni	3.5	4.7	5.8	6.1	4.3	3.2	1.4	2.0	4.4
Zn	<1	<2	1.7	5.6	5.9	3.5	1.1	1.2	4.8
Ca	1.3	2.8	4.6	6.6	>8	6.4	1.7	1.7	6.2
Mg	2.7	3.9	4.9	7.9	>8	>7	2.4	2.6	7.9
Mn	1.7	2.6	3.6	6.4	7.8	4.9	1.5	1.9	6.1

Table 3: pH_{50} difference between nitrate and sulphate aqueous matrix for a given metal extracted by a given solvent extraction reagent system*

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	Versatic 10 + LIX 63	LIX860 NI + D2EHPA	LIX84 + D2EHPA	nonyl-4PC + Versatic 10
Co	-0.6	-0.5	-0.5	-0.5	-0.3	-0.5	-0.6	-0.6	-0.4
Cu	-0.6	-0.6	-0.4						
Ni	-0.7	-0.5	-0.5	-0.5	-1.1	-0.9	-0.9	-0.7	-0.6
Zn			-0.5	-0.5	-0.4	-0.4	-0.4	-0.6	-0.6
Ca	-0.5	-0.3	-0.6	-0.5		-0.3	-0.5	-0.4	-0.5
Mg	-0.6	-0.5	-0.4	-0.6			-0.7	-0.7	-0.3
Mn	-0.6	-0.6	-0.5	-0.6	-0.3	-0.5	-0.7	-0.5	-0.4

* Blank cells were not calculated as the pH_{50} for at least one isotherm was out of the tested pH range

Comparison with thermodynamic modelling data

Thermodynamic modelling showed a preference for precipitation of metal hydroxides from a nitrate matrix over a sulphate matrix, supporting the results of extraction pH isotherms. The model, however, predicted varying differences between hydroxide solubility from the two matrices depending on the metal ion in question, contrary to data in Table 3. The largest differences between hydroxide solubility in both matrices were predicted for nickel and zinc. It is well known that nickel, due to a d^8 electron configuration, has increased stability when in an octahedral field over other first row transition metals as a result of increased ligand field stabilization energy (LFSE); zinc with a d^{10} configuration has no increased stability [11]. The combination of decreased solubility of nickel with respect to hydroxide formation in a nitrate matrix and the ready adoption of octahedral or square planer (a distortion limit for an octahedral field) configuration by oxime-metal complexes may be a cause for preferential nickel extraction over other metals by these reagents from a nitrate matrix.

Conclusions

Extraction of cobalt, copper, zinc, calcium, magnesium, and manganese from nitrate and sulphate matrices by acidic solvent extraction reagents consistently produced a $\Delta\text{pH}_{50(\text{N-S})}$ of -0.5 units. Nickel extraction also gave a $\Delta\text{pH}_{50(\text{N-S})}$ of -0.5 units except when extracted by oxime-containing systems, where a larger $\Delta\text{pH}_{50(\text{N-S})}$ of -0.9 units was calculated. This generalisation provides a guide for useful extrapolation of base metal extraction from sulphate matrices to comparable nitrate matrices.

Acknowledgement

The support of the Minerals Down Under National Research Flagship, Direct Nickel, and the International Postgraduate Research Scholarship is gratefully acknowledged.

References

1. Molina, N., *Nickel and Cobalt Sulphide Precipitation a Proven Method of Selective Metal Precipitation in Laterite Process Flowsheets*. in *Hydrometallurgy of Nickel and Cobalt 2009*. 2009. Sudbury, Canada: CIM.
2. Willis, B., *Trends in PAL downstream recovery options*. in *ALTA 2008 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum*: Perth, WA.
3. McCarthy, F. and G. Brock, *The Direct Nickel Process continued progress on the pathway to commercialisation*, in *ALTA 2011 Nickel/Cobalt/Copper Conference*: Perth, WA.
4. El-Hefny, N.E. and J.A. Daoud, *Extraction of Copper(II) by Cyanex 302 in kerosene from different aqueous media*. *Solvent Extraction and Ion Exchange*, 2007. **25**(6): p. 831-843.
5. Lanagan, M.D. and D.C. Ibana, *The solvent extraction and stripping of chromium with Cyanex (R) 272*. *Minerals Engineering*, 2003. **16**(3): p. 237-245.
6. Du Preez, A.C. and J.S. Preston, *The solvent extraction of rare earth metals by carboxylic acids*. *Solvent Extraction and Ion Exchange*, 1992. **10**(2): p. 207-230.
7. Preston, J.S. and A.C. Du Preez, *Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines*. *Hydrometallurgy*, 2000. **58**(3): p. 239-250.
8. Duro, L., M. Grivé, E. Cera, C. Domenech, and J. Bruno, *Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment*, 2006, Swedish Nuclear Fuel and Waste Management Co: Stockholm, Sweden.
9. O'Day, P.A., G.E. Brown, and G.A. Parks, *X-Ray Absorption Spectroscopy of cobalt(II) multinuclear surface complexes and surface precipitates on kaolinite*. *Journal of Colloid and Interface Science*, 1994. **165**: p. 269-289.
10. Högfeld, E., *Stability constants of metal-ion complexes Part A Inorganic Ligands*. 1982, Stockholm, Sweden.
11. Cotton, F.A. and G. Wilkinson, *Advanced Inorganic Chemistry* 4th Edition ed. 1980: John Wiley and Sons.

Partial inhibition of LIX®860-cobalt(III) formation by organic acids

*Hutton-Ashkenny M.*¹, Barnard K.R.², Ibane D.³*

Phenolic oximes show good selectivity for nickel and cobalt over impurity metals found in typical acidic laterite leach solutions. Unfortunately, oximes suffer from cobalt(III) poisoning and slow nickel loading and stripping kinetics. Previous authors found that the addition of the phosphoric acid D2EHPA to the phenolic aldoxime LIX®860 resulted in synergistic extraction of nickel and cobalt, faster extraction and stripping kinetics for nickel, and found that quantitative stripping of cobalt after a single contact could be achieved. In the present work, the ability of phosphoric, phosphonic, phosphinic, and carboxylic acids to reduce cobalt poisoning of LIX 860 loaded from a nitrate aqueous feed was assessed. The phosphoric acid D2EHPA was the only acid to enable near-quantitative cobalt stripping. A LIX 860/D2EHPA organic solution was therefore subjected to multiple cobalt load-strip cycles to assess ongoing cobalt recovery as would be necessary in a commercial system. Although the majority of cobalt was stripped, cobalt slowly accumulated in the organic phase, suggesting that this reagent combination may not be suitable for the commercial extraction of cobalt from a nitrate matrix.

Introduction

There is currently no standard method for the recovery of metal values from acidic nickel laterite leach solutions. Two options, which produce intermediate products requiring further processing, are mixed sulphide precipitation (MSP) and mixed hydroxide precipitation (MHP). MSP requires toxic hydrogen sulphide gas, while MHP is less selective against impurities [1]. The major alternative to these options, direct solvent extraction (DSX), bypasses an intermediate precipitation step and produces higher value products than the intermediates [1]. Direct Nickel Ltd. is currently developing a process for nitric acid leaching of nickel laterite ores with a staged MHP nickel and cobalt recovery operation [2]. DSX is a potential avenue for generating higher value products from this process and is therefore of commercial interest.

Phenolic oximes are selective for nickel(II) and cobalt(II) over common nickel laterite impurities after iron and aluminium hydrolysis, although they suffer from poor nickel extraction kinetics [3] and, more importantly, cobalt poisoning [4], where cobalt cannot be stripped by conventional means. Cobalt poisoning is thought to occur via oxidation of square planar Co(II)-oxime₂ to octahedral Co(III)-oxime₃ in the organic phase via a Co(II)-oxime₂-(O₂) intermediate [5]. This complex can only be stripped via a reductive strip such as with zinc powder or by photochemical stripping [5]. This complicates the stripping process, as is experienced at the Queensland Nickel Yabulu ammoniacal solvent extraction refinery, where a bleed stream of the stripped organic must be treated to remove cobalt(III) and regenerate the oxime [6].

Synergistic solvent extraction (SSX) seeks to exploit the combination of solvent extraction (SX) reagents to provide better separation of target metals and impurities

*¹ WA School of Mines, Curtin University and Direct Nickel Ltd., Australia – huttonashkenny@gmail.com

² CSIRO Process Science and Engineering / CSIRO Minerals Down Under National Research Flagship, Australia – keith.barnard@csiro.au

³ WA School of Mines, Curtin University, Australia

than either of the two individual reagents. As a result, SSX using existing commercial reagents is an active area of research in the nickel laterite processing industry [7].

SSX of nickel and cobalt by the combination of phenolic oximes 5-nonylsalicylaldoxime (LIX[®]860-NI, ACORGA[®]M5640) or 2-hydroxy-5-nonyl-acetophenone oxime (LIX[®]84-I) with di-2-ethylhexylphosphoric acid (D2EHPA) shows promise for enhanced extraction of nickel and cobalt [3, 8]. D2EHPA also significantly increases the rate of nickel extraction over LIX 84 alone, even at catalytic concentrations [3]. Furthermore, the addition of D2EHPA to an organic phase containing LIX 860 in single batch extractions of cobalt from sulphate solutions results in complete cobalt stripping [9, 10]. These benefits increase the potential for nickel-cobalt extraction from acidic solutions using phenolic oxime-based SSX. This paper presents an investigation into the effect of different organic acids on cobalt poisoning of LIX 860, and the effect of sequential load-strip cycles on stripping of cobalt loaded from a nitrate aqueous matrix. The study was undertaken to assess the commercial application of phenolic oximes to DSX from a nitric acid leach solution relevant to the Direct Nickel process.

Materials and Methods

Aqueous and organic solution preparation

Cobalt solutions (0.01 M) were made up in a NaNO₃ matrix (1 M) using analytical grade Co(NO₃)₂ and reagent grade NaNO₃. The pH of the aqueous phase was adjusted with analytical grade NaOH (100 g/L). Loaded organic samples were stripped with analytical grade H₂SO₄ (350 g/L).

Organic solutions were prepared using technical grade solvent extraction reagents diluted in Shellsol D70 (Shell Chemicals). Extractants used were LIX[®]860-NIC (5-nonylsalicylaldoxime, 82.6%, BASF), D2EHPA (di-2-ethylhexyl phosphoric acid, 98%, Chemorex), HEH(EHP) (phosphonic acid (2-ethylhexyl)-mono (2-ethylhexyl) ester, 97%, SNF FloMin), Cyanex[®]272 (*bis*-2,4,4-trimethylpentyl phosphinic acid, 85%, Cytec), and Versatic 10 (*iso*-decanoic acid, 99%, Shell Chemicals). The reagents were used as supplied and according to the purity quoted by the manufacturer. The following five organic solutions were prepared: LIX 860, LIX 860 and D2EHPA, LIX 860 and HEH(EHP), LIX 860 and Cyanex 272, LIX 860 and Versatic 10.

Timed poisoning studies

Cobalt was loaded into an organic phases containing LIX 860 (0.05 M) and an organic acid (0.05 M) by contacting the phases at aqueous to organic ratio (A:O) of 1:1 using a magnetic stirrer for 15 minutes at a pH dependent upon the organic acid used. The phases were immediately separated through Whatman 1PS paper. The aqueous feed and raffinate solutions were analysed with atomic absorption spectroscopy (AAS) using an Agilent 240 FS instrument to determine the organic phase cobalt concentration by difference. The loaded organic was stored in a glass jar with a loosely fitting lid at room temperature. Organic samples were taken after 1,

4, 8, 24, 48, 96, and 192 hours and stripped at A:O of 3:1 and 50°C for 40 minutes with H₂SO₄ (350 g/L). The cobalt concentration of the loaded strip liquor was determined with AAS to calculate the percentage of cobalt stripped.

Sequential load-strip studies

An organic phase containing LIX 860 (0.5 M) and D2EHPA (0.5 M) was loaded with cobalt in a stainless steel mixer box using a magnetic stirrer at A:O of 1:1 and 23°C for 10 minutes at pH 4.5. The phases were separated and the raffinate analysed for cobalt with AAS. The loaded organic was stripped with H₂SO₄ (350 g/L) at A:O of 1:1 and 50°C for 40 minutes using an overhead stirrer. The phases were separated and the loaded strip liquor analysed with AAS. A sample of the stripped organic was washed with 100 g/L H₂SO₄ at A:O of 3:1 and dried over analytical grade anhydrous Na₂SO₄. The visible spectrum of the dried organic sample was obtained using a Varian Cary 1C spectrophotometer. The cobalt concentration of these samples was measured with AAS using standards made up by loading LIX 860 in Shellsol D70 with a cobalt aqueous analytical standard at A:O of exactly 1 at pH 4.5. The raffinate was analysed by AAS to ensure complete loading. The load-strip-analysis process was repeated ten times using fresh aqueous feed and the same organic solution.

Results and Discussion

Organic acid influence on synergistic behaviour and cobalt stripping with LIX 860

Initial work investigated the synergism exhibited when organic acids were combined with phenolic oximes. The use of the more acidic phosphoric or phosphonic acids resulted in synergism for nickel and cobalt extraction, but the use of less acidic phosphinic or carboxylic acids did not. These results will be described more fully in a future publication. Despite this absence of synergistic behaviour, the potential for these acids to inhibit cobalt oxidation remained of interest.

Stronger organic acids combined with LIX 860 resulted in higher stripping of cobalt than weaker organic acids after standing for one hour (Table 1); each acid tested increased cobalt stripping above that of LIX 860 alone. Near quantitative cobalt stripping was observed only for LIX 860/D2EHPA. The loading pH had very little effect on cobalt stripping for LIX 860/D2EHPA and LIX 860/Versatic 10. For LIX 860 with Cyanex 272 a higher loading pH increased cobalt stripping. This is potentially due to the higher pH favouring formation of a cobalt-Cyanex 272 complex over a LIX 860 or mixed ligand complex. For Versatic 10 the pH may not have been high enough to allow coordination with the organic acid, causing cobalt to favour coordination with LIX 860 instead. For D2EHPA near quantitative stripping was achieved in all cases.

In the case of LIX 860/D2EHPA, the loaded organic phase was brown with a slight pink hue, the latter suggesting octahedral coordination of cobalt. Narita *et al.* [3] show from X-ray absorption fine structure analysis that nickel in a LIX 84/D2EHPA solution is six-coordinate. Inter-ligand hydrogen bonding causes square planar configuration

to be adopted by various transition metal–phenolic oxime complexes [11]. Alteration to the octahedral configuration by D2EHPA addition in the nickel system is hypothesised to occur via axial coordination of two D2EHPA molecules. If, as suggested by the colour of the loaded organic, cobalt adopts the same configuration in the LIX 860/D2EHPA system, then the axial sites required for dioxygen binding in the cobalt oxidation-poisoning mechanism discussed by Nishihama *et al.* [5] would be occupied in the LIX 860/D2EHPA solution. Assuming a highly stable complex is formed, this would hinder dioxygen binding and in turn inhibit oxidation of cobalt(II) to cobalt(III) and subsequent cobalt poisoning.

Effect of standing time on the extent of cobalt stripping

Sampling time only had a small effect on ultimate cobalt stripping for the more acidic phosphorus-based acids, with cobalt stripping decreasing by less than 10% for D2EHPA, HEH(EHP), and Cyanex 272 loaded at pH 5.9. Cobalt stripping from LIX 860/Versatic10, however, was considerably higher than LIX 860 alone at the start of the trial and decreased to the same level as LIX 860 after 192 hours, suggesting ongoing oxidation not found in the presence of stronger organic acids.

Quantitative stripping of cobalt from a loaded organic phase of LIX 860/D2EHPA has been reported previously [8-10]. Cerpa and Alguacil [10] found that quantitative stripping of cobalt from AcorgaM5640/D2EHPA remained possible after storing the organic phase for one month. In contrast, the effect of organic acids other than D2EHPA on cobalt stripping from phenolic oximes has not been previously reported. Organic acids are known to hinder cobalt poisoning of 7-decyl-8-hydroxyquinoline (Kelex 100) dissolved in toluene and there is a clear relationship between slower cobalt oxidation on Kelex 100 with stronger organic acids [12]. This general trend was also noted in the present study.

Table 1: Extent of cobalt stripping from 0.05 M LIX 860 and 0.05 M organic acid over time

Organic Solution	Extraction pH	% Co loaded	% Cobalt Stripped after:		
			1 h	48 h	192 h
LIX 860 only	6.1	91%	56%	44%	41%
LIX 860/D2EHPA	3.4	79%	97%	95%	95%
LIX 860/D2EHPA	4.1	97%	95%	95%	97%
LIX 860/HEH(EHP)	5.4	99%	90%	86%	83%
LIX 860/Cyanex 272	4.5	52%	89%	81%	73%
LIX 860/Cyanex 272	5.9	99%	93%	86%	84%
LIX 860/Versatic 10	4.5	48%	75%	53%	37%
LIX 860/Versatic 10	6.8	100%	77%	57%	40%

Cobalt stripping behaviour over several load-strip cycles

The sequential load-strip tests with LIX 860/D2EHPA were performed at higher reagent concentrations and at higher extraction pH than required. Excursions to high pH would be expected under commercial operating conditions and these parameters were chosen to mimic such excursions. Given the results in Table 1, it was not expected that the chosen pH would significantly affect the level of cobalt poisoning.

The visible spectra from the stripped LIX 860/D2EHPA organic after successive cobalt loading stages showed a gradually increasing absorbance which correlated with a darkening brown tint in the stripped organic. The residual cobalt concentration of the stripped organic also increased slightly after each load-strip stage (Figure 1), showing that not all loaded cobalt stripped fully after each stage.

As cobalt poisoning did not increase over time, this result suggests that oxidation of Co(II) to Co(III) occurs primarily during loading, stripping, or both for this system. In systems where a weak octahedral complex is formed with a weaker donor ligand, then equilibrium with a species containing dioxygen substituting an axial donor ligand may allow ongoing oxidation. That cobalt can slowly accumulate in an organic phase containing LIX 860/D2EHPA under the nitrate-based load-strip conditions used indicates that any commercial application would require the use of a remedial step, such as a reductive strip bleed stream. Although not assessed, it is expected that similar behaviour would be observed at lower pH and also in sulphate-based systems. Further investigation of the LIX 860/D2EHPA cobalt complex is warranted to better understand the role of the two extractants in this system, although it should be noted that the ability for D2EHPA to extract many metals in its own right at low pH makes this particular system unsuitable for the selective recovery of nickel and cobalt.

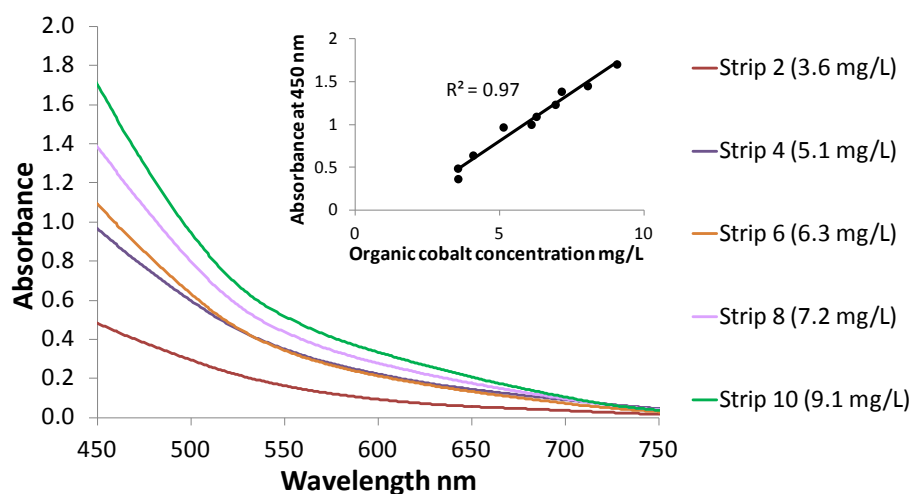


Figure 1: Visible spectra of organic phase after every second strip (baseline of fresh organic manually subtracted), organic phase cobalt concentration, determined using AAS, in brackets. Inset: A plot of visible absorbance at 450 nm versus residual organic cobalt concentration.

Conclusions

The addition of all tested organic acids to LIX 860 hindered cobalt poisoning of the phenolic oxime. Stronger organic acids were more effective at hindering cobalt poisoning than weaker organic acids; D2EHPA > Cyanex 272 $\approx$ HEH(EHP) > Versatic10. Cobalt stripping from LIX 860/D2EHPA was near quantitative after a single load, but after 10 load-strip cycles cobalt slowly accumulated in the organic phase. A stable octahedral LIX 860/D2EHPA/cobalt(II) complex may form during loading, subsequently hindering cobalt poisoning. Constant accumulation of cobalt

would be unacceptable in a commercial operation and the combination of LIX 860/D2EHPA would possibly require a reductive strip bleed stream to be commercially viable.

Acknowledgement

The support of the Minerals Down Under National Research Flagship, Direct Nickel, and the International Postgraduate Research Scholarship is gratefully acknowledged.

References

1. Willis, B. *Trends in PAL downstream recovery options*. in *ALTA 2008 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum*. Perth, WA.
2. McCarthy, F. and G. Brock. *The Direct Nickel Process continued progress on the pathway to commercialisation*. in *ALTA 2011 Nickel/Cobalt/Copper Conference*. Perth, WA.
3. Narita, H., M. Tanaka, Y. Sato, T. Yaita, and Y. Okamoto, *Structure of the Extracted Complex in the Ni(II)-LIX84I System and the Effect of D2EHPA Addition*. *Solvent Extraction and Ion Exchange*, 2006. **24**(5): p. 693-702.
4. Guesnet, P. and D. Bauer, *Solvent-extraction of cobalt by LIX-65-N - oxidation of cobalt(II) chelates in organic phase*. *Analisis*, 1981. **9**(4): p. 129-134.
5. Nishihama, S., N. Sakaguchi, T. Hirai, and I. Komasaawa, *Photoreductive stripping of cobalt loaded on hydroxyoxime extractant in a liquid-liquid extraction system*. *Ind. Eng. Chem. Res.*, 2000. **39**(12): p. 4986-4990.
6. Skepper, I.G. and J.E. Fittock. *Nickel cobalt separation by ammonical solvent extraction: The operating experience*. in *Value Adding Through Solvent Extraction, Proc. ISEC 1996*. 1996. Melbourne, Australia.
7. Cheng, C.Y., K.R. Barnard, W. Zhang, and D.J. Robinson, *Synergistic solvent extraction of nickel and cobalt: A review of recent developments*. *Solvent Extraction and Ion Exchange*, 2011. **29**: p. 719-754.
8. Alguacil, F.J., *Solvent extraction with DP-8R/LIX 860 mixtures for the selective separation of cobalt and nickel*. *Revista De Metalurgia*, 2002. **38**(3)
9. Zhang, P., T. Yokoyama, T.M. Suzuki, and K. Inoue, *The synergistic extraction of nickel and cobalt with a mixture of di(2-ethylhexyl) phosphoric acid and 5-dodecylsalicylaldoxime*. *Hydrometallurgy*, 2001. **61**(3): p. 223-227.
10. Cerpa, A. and F.J. Alguacil, *Separation of cobalt and nickel from acidic sulfate solutions using mixtures of di(2-ethylhexyl)phosphoric acid (DP-8R) and hydroxyoxime (ACORGA M5640)*. *Journal of Chemical Technology and Biotechnology*, 2004. **79**(5): p. 455-460.
11. Keeny, M.E. and K. Osseo-Asare, *Transition metal hydroxyoxime complexes*. *Coordination Chemistry Reviews*, 1984. **59**: p. 141-201.
12. Guesnet, P., J.L. Sabot, and D. Bauer, *Kinetics of cobalt oxidation in solvent extraction by 8-quinolinol and Kelex 100*. *Journal of Inorganic and Nuclear Chemistry*, 1980. **42**(10): p. 1459-1469.

Study of separation of metals from HEV Li-ion batteries using AKUFVE

Part1: From nitrate leach liquor

*Sravya Kosaraju^{*1}, Christian Ekberg¹, Stefan Allard¹*

Summary

Li-ion batteries are now used in electric vehicles (EV's), plug-in hybrid vehicles (PHEV's) and, hybrid electric vehicles (HEV). In addition to Li, other metals of value such as Co, Ni, Mn, Al, and, Cu are present in these batteries. Recycling Li-ion batteries, especially those of vehicle scale will be necessary in the near future due to the growing numbers of Li-ion battery run vehicles. Recycling these batteries will also help solve the problem of improper disposal of end of life batteries. Recycling, when done with the focus to recover pure streams of the involved metals, might even reduce the environmental effects of virgin metal extractions. Solvent extraction was chosen to achieve separation and recovery of metals with higher purity from Li-ion leachate.

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II), Co(II), Fe(III) from nitrate leachate using both acidic and solvating extractants was made. Metal ion separation studies with acidic extractant were made with respect to pH and extractant concentration and studies with solvating extractant were made with respect to nitrate concentration and extractant concentration.

Introduction

Recycling of vehicle scale Li-ion batteries will soon become necessary with market projections of battery run vehicles (HEVs, PHEVs and EVs) show increasing sales from as early as 2015 [Al-Alawi & Bradley, 2013]. The battery powered vehicles require batteries with high specific volumetric and gravimetric energy densities. Therefore, dismantling and recycling are challenging. Many popular Li-ion battery chemistries contain metals such as Ni, Mn, Co, Li, Cu, and Al [Ritchie & Howard, 2006]. Some of these metals are of economic importance while there some which strategic importance. Recycling Li-ion batteries focusing on recovery of pure metals might reduce atleast by a fraction of virgin metal extraction and emissions related to not just mining but also transportation. For this particular reason the technique solvent extraction is chosen

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II), Co(II), Fe(III) from nitrate leachate using Cynex 272 (acidic extractant) and cyanex 923 (solvating extractant), separately was made. The separation studies with Cynex 272 were made with respect to pH and extractant concentration while studies

¹ Contact: sravya@chalmers.se

with Cyanex 923 were made with respect to nitrate concentration and extractant concentration.

A vehicle scale Li-ion battery pack has about 30-120 prismatic Li-ion batteries stacked depending on the power needed for the vehicle. Each battery, within it has many Li-ion cells (cathode/separator-electrolyte/anode). The batteries tested for the purpose of this article had carbon as anode and for the same reason will be left out of the present discussion. After heat treatment, mechanical dismantling and, crushing steps, the black-mass- or the metal containing fraction of the battery which also is the electrochemically active substance was leached with 1M HNO₃ solution. The present studies are made on stock solutions prepared with the same relative ratios of the metal-ions in the leachate.

Experimental

Reagents

Li-ion batteries for this study were provided by ETC Battery and Fuel cells Sweden AB. The extractants Cyanex 272 (bis-(2,4,4-trimethylpentyl)phosphinic acid) and Cyanex 923(a mixture of four tri-alkyl oxides) were procured from Cytec. HNO₃(65%) from Sigma Aldrich. Nitrate salts of Li, Mn, Ni, Fe, Co and Sodium perchlorate were all from Merck, Proanalysis.

AKUFVE

The AKUFVE apparatus was used for the present separation studies. The physical description and its working are described clearly elsewhere [Rydberg, 1969, Albinsson, 1988, Ekberg et al, 2006]. This apparatus gives good control of a small scale extraction with regard to temperature, pH, centrifuging for separation of phases and automatic sampling reducing the huge uncertainties that can come from human handling and subsequent organic phase entrenchment upon the aqueous phase.

Chemical system used and experimental procedure

Two different systems were investigated,

1. Separation of metals with Cyanex 272 at concentrations 0.1, 0.5 and 1M in solvent 70 diluent, at increasing pH.
2. Separation of metals with Cyanex 923 at concentration 0.1, 0.5 and 1M in solvent 70 and separation with varying concentrations of nitrate.

For the pH increase 3-0.5M NaOH was used. For the effect of nitrate the ionic strength was kept close to 2, although for few points to the highest concentration of nitrate the ionic strength goes up to 2.4. In the same study (effect of nitrate the aqueous solution was made with 10⁻⁵M metal concentrations in 1M HClO₄ to keep the start [H⁺]concentration the same as the leachate and 1MNaClO₄. The D-values of the metals was checked before adding any nitrate, to make sure that the metals are

not extracted due to complexes formed with chlorate. Nitrate additions were made using 10.3M NaNO₃

Aqueous samples that were taken from the solvent extraction experiments were diluted using 1M HNO₃ and measured using an inductively coupled plasma emission spectrometer (ICP-OES). The distribution ratios (D_M) were calculated by

$$D_M = \frac{[M_{org,tot}]}{[M_{aq,tot}]}$$

The concentration of metal –ions in the organic phase $[M_{org,tot}]$, was calculated as the difference between the starting aqueous phase metal concentration and remnant metal concentration extraction in to the organic phase.

Results and Discussion

Separation of metals with Cyanex 272

Figures 1-3, show the separation of metals with respect to pH with Cyanex 272 concentrations 0.1, 0.5 and, 1M respectively. Iron is strongly extracted at a very high acidic range and remains with organic phase even at pH7 for all three extractant concentrations. In 0.1M Cyanex 272 system, manganese and cobalt are extracted after pH 5.5. In 0.5M and 1M Cyanex 272 systems manganese and cobalt are extracted at pH4, at higher acidity range than in 0.1M Cyanex 272. There is also better separation of manganese and cobalt in the 1M Cyanex 272. Nickel is only after pH6 in 0.1M extractant, however starts being extracted after pH5.5 in 1M extractant. Li remains in the aqueous solution the studies pH range for all the three concentrations of extractants.

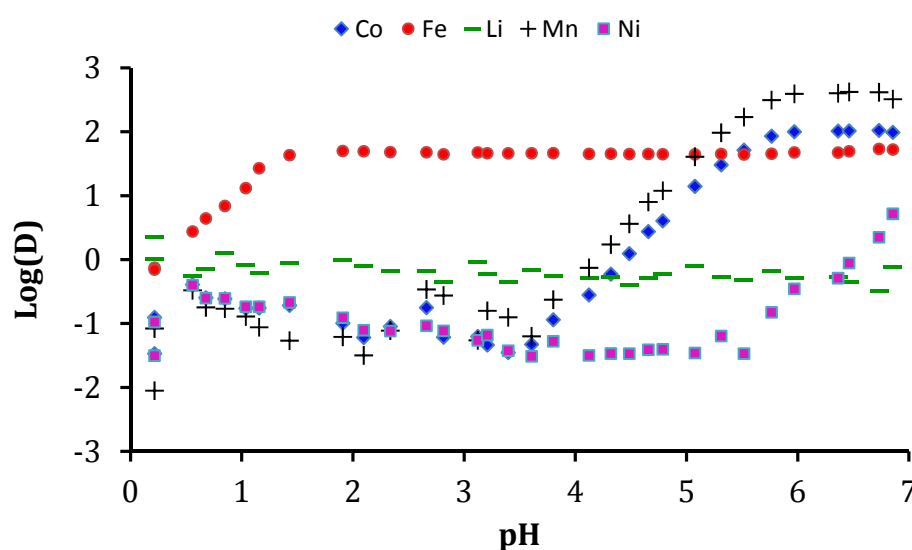


Figure 1 :Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 1M HNO₃, 21°C, two experiments

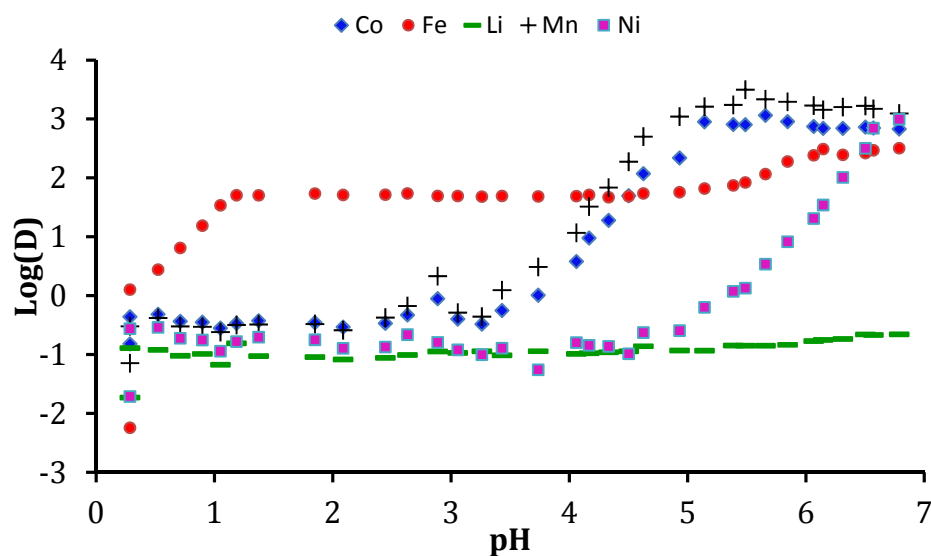


Figure 2: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.5M Cyanex 272 in solvent 70, aqueous phase: 1M HNO₃, 21°C, two experiments

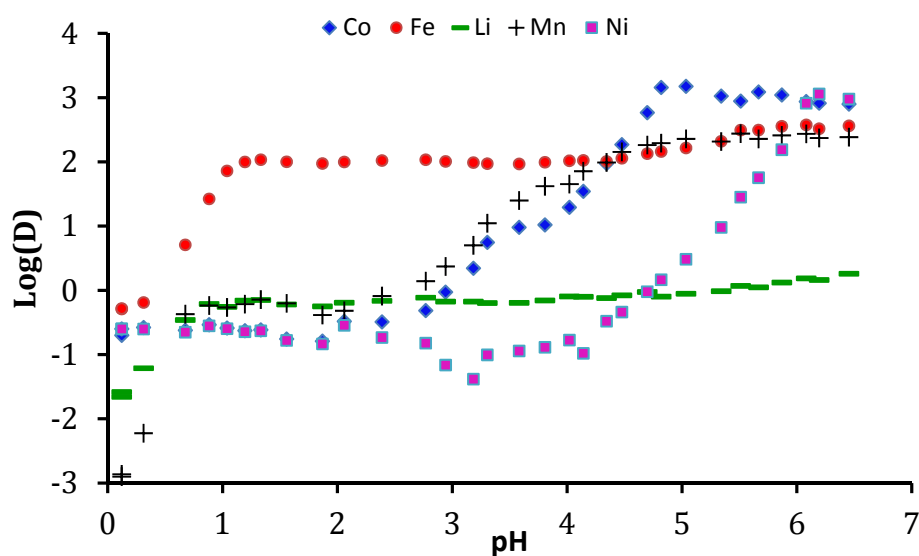


Figure 3: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 1M Cyanex 272 in solvent 70, aqueous phase: 1M HNO₃, 21°C, two experiments

Separation of metals with Cyanex 923

Figure 4 shows the effect of Cyanex 923 concentration on the separation of the metal ions. There is no significant increase in the extraction, however this could be due to

the fact that the nitrate concentration that is needed for the metal-ions to make the neutral complexes so they can be extracted needs to be higher.

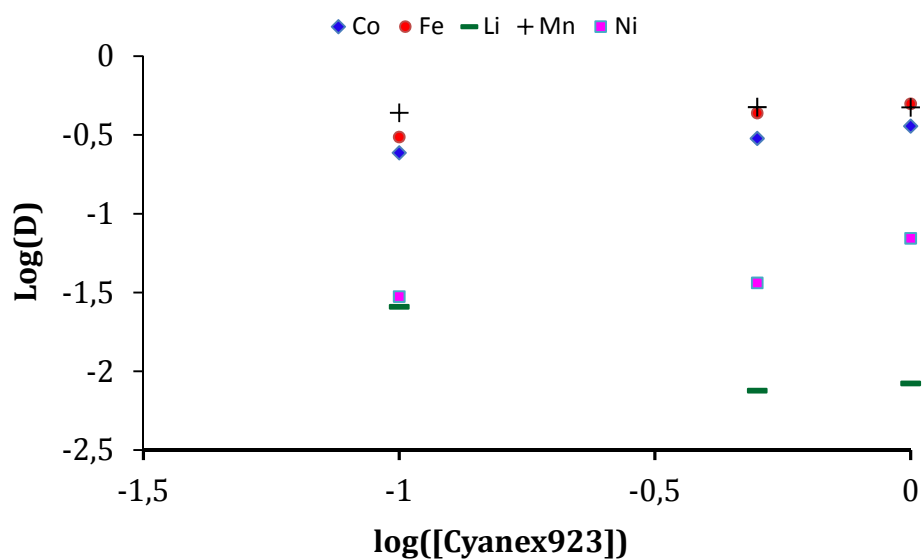


Figure 4 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1, 0.5 and 1M Cyanex 923 in solvent 70, aqueous phase: 1M HNO₃, 21°C, three experiments

Effect of nitrate on extraction with Cyanex 923

Figure 5, shows the effect of nitrate concentration on the extraction of metal ions in to the organic phase. Increase in D-values is observed only after 3M concentration of nitrate.

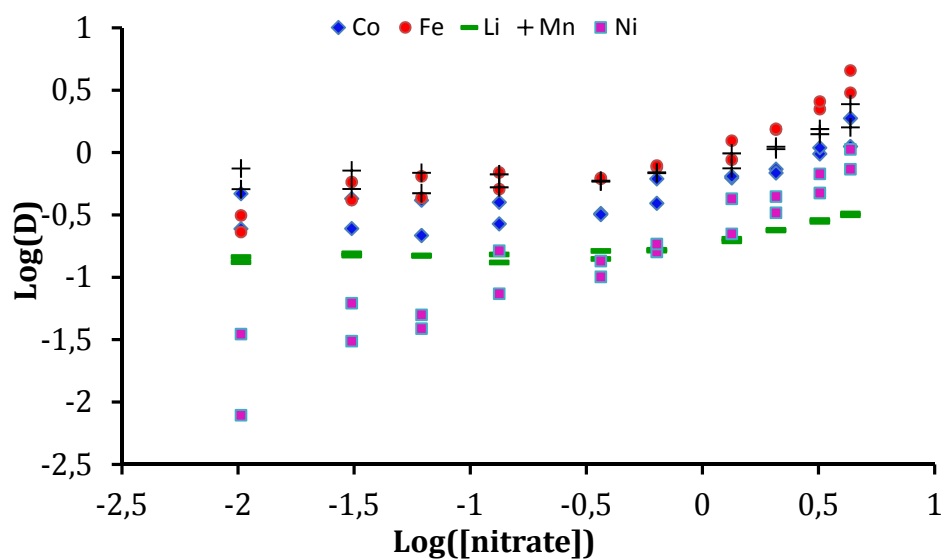


Figure 5 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 1M HClO₄ and 1M NaClO₄, 21°C, two experiments

Conclusion

Separation of Li-ion battery metals is possible using both Cyanex 272 and 923. In the Cyanex 272 system, higher extractant concentration gave higher D-values for all metals and good separation. Li extraction was not affected by the concentration of the Cyanex 272.

In the Cynex923 system, the extraction of metals was only improved slightly by extractant concentration, however it was more dependent on the nitrate concentration

References

1. Al-Alawi, Bradley.(2013) Review of hybrid, plug-in hybrid, and electric vehicle market modeling Studies. *Renewable and Sustainable Energy Reviews* 21: 190-203.
2. Albinsson. (1988) *Development of the AKUFVE-LISOL technique. In Solvent extraction studies of lanthanide acetylacetonates* PhD-Thesis thesis. CTH, S-412 96, Gothenburg, Sweden
3. Ekberg, Persson, Ödegaard-Jensen, Albinsson, Andersson.(2006) Redox control in solvent extraction studies using a PEEK AKUFVE unit. *Solvent Extraction and Ion Exchange* 24: 1-7.
4. Ritchie, Howard.(2006) Recent developments and likely advances in lithium-ion batteries. *Journal of Power Sources* 162: 809-12.
5. Rydberg.(1969) Solvent extraction studies by the AKUFVE method. *Acta Chemica Scandinavica* 23

Study of separation of metals from HEV Li-ion batteries using AKUFVE

Part2: From sulphate leach liquor

*Sravya Kosaraju^{*1}, Christian Ekberg¹, Stefan Allard¹*

Summary

Li-ion batteries are one of the popular choices for their use in electric vehicles (EV's), plug-in hybrid vehicles (PHEV's) and, hybrid electric vehicles (HEV). In addition to Li, other metals of value such as Co, Ni, Mn, Al, and, Cu-are present in these batteries. Recycling vehicle scale Li-ion batteries soon will be necessary due to the growing trend in battery run automobile market. A plan for safe and economically rewarding disposal should be in place before the end of life batteries get collected in large volume and landfilled. Instead with proper recycling not only is the improper disposal problem tackled, but also the environmental effects of virgin metal extractions can mitigated, if the end aim is to recover pure streams of the involved metals. Solvent extraction was chosen to achieve good separation and recovery of metals with higher purity from Li-ion sulphate leachate.

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II),Co(II), Fe(III) from sulphate leachate using both acidic and solvating extractants was made. Metal ion separation studies with acidic extractant were made with respect to pH and extractant concentration and studies with solvating extractant were made with respect to sulphate concentration and extractant concentration.

Introduction

Recycling vehicle scale Li-ion batteries soon will be necessary due to the growing trend in battery run automobile market from as early as 2015 [Al-Alawi & Bradley, 2013]. The battery powered vehicles require batteries with properties such as high specific volumetric and gravimetric energy densities. Recycling these batteries also presents challenges due to the same properties. However, recycling Li-ion batteries focusing on recovery of pure metal streams will help tackle the problem of improper disposal of end of life batteries, along with giving economic and environmental benefits by recovery of metals such as Ni, Mn, Co, Li, Cu, and Al, which are often found in these batteries [Ritchie & Howard, 2006]. For this particular reason the technique solvent extraction is chosen

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II),Co(II), Fe(III) from sulphate leachate using Cynex 272 (acidic extractant) and cyanex 923(solvating extractant), separately was made. The separation studies with Cynex 272 were made with respect to pH and extractant concentration while studies

¹ Contact: sravya@chalmers.se

with Cyanex 923 were made with respect to sulphate concentration and extractant concentration.

Each battery, has about 40-60 Li-ion cells (cathode/separator-electrolyte/anode) stacked one after the other. The batteries tested for the purpose of this article had carbon as anode and for the same reason are left out of the present discussion. After heat treatment, mechanical dismantling and, crushing steps, the black-mass- or the electrochemically active substance, was leached with 1M H₂SO₄ solution to dissolve the constituent metals. The present studies are made on stock solutions prepared with the same relative ratios of the metal-ions found in the leachate.

Experimental

Reagents

Li-ion batteries for this study were provided by ETC Battery and Fuel cells Sweden AB. The extractants Cyanex 272 (bis-(2,4,4-trimethylpentyl)phosphinic acid) and Cyanex 923(a mixture of four tri-alkyl oxides) were procured from Cytec. HNO₃(65%) from Sigma Aldrich. Sulphate salts of Li, Mn, Ni, Fe, Co and Sodium perchlorate were all from Merck, Proanalysis.

AKUFVE

The AKUFVE apparatus was used for current separation studies. The apparatus is described clearly elsewhere [Rydberg, 1969, Albinsson, 1988, Ekberg et al, 2006]. This apparatus gives good control of a small scale extraction with regard to temperature, pH, centrifuging for separation of phases and automatic sampling reducing the huge uncertainties that can come from human handling and subsequent organic phase entrenchment upon the aqueous phase.

Chemical system used and experimental procedure

Two different systems were investigated,

1. Separation of metals with Cyanex 272 at concentrations 0.1, 0.5 and 1M in solvent 70 diluent, at increasing pH.
2. Separation of metals with Cyanex 923 at concentration 0.1, 0.5 and 1M in solvent 70 and separation with varying concentrations of sulphate.

For the pH increase 3-0.5M NaOH was used. For the effect of sulphate the ionic strength was kept close to 2. In the same study (effect of sulphate the aqueous solution was made with 10⁻⁵M metal concentrations in 1M HClO₄ to keep the start [H⁺]concentration the same as the leachate and 1MNaClO₄. The D-values of the metals was checked before adding any sulphate, to make sure that the metals are not extracted due to complexes formed with chlorate. Sulphate additions were made using 1.3M Na₂SO₄.

Aqueous samples that were taken from the solvent extraction experiments were diluted using 1M HNO₃ and measured using an inductively coupled plasma emission spectrometer (ICP-OES). The distribution ratios (D_M) were calculated by

$$D_M = \frac{[M_{org,tot}]}{[M_{aq,tot}]}$$

The concentration of metal –ions in the organic phase $[M_{org,tot}]$, was calculated as the difference between the starting aqueous phase metal concentration and remnant metal concentration in aqueous phase after extraction in to the organic phase.

Results and Discussion

Separation of metals with Cyanex 272

Figures 1-3, show the separation of metals with respect to pH with Cyanex 272 concentrations 0.1, 0.5 and, 1M respectively. Iron is strongly extracted and remains with organic phase even at pH7 for all three extractant concentrations. The D_M increase considerable to large number (>100) for all metal ions except Li when the concentration of the extractant is increased. In 0.1M Cyanex 272 system, manganese and cobalt are extracted after pH4. In 0.5M and 1M Cyanex 272 systems manganese and cobalt are extracted at pH 2.5, at higher acidity range than in 0.1M Cyanex 272. There is also better separation of manganese and cobalt in both 0.5M and 1M Cyanex 272. Nickel is separated after pH6 in 0.1M extractant, however starts being extracted after pH 4.5 in 1M extractant. Li remains in the aqueous solution for the studied pH range in 0.1M extractant system while is extracted to about 50% in 0.5 and 1M extractant systems

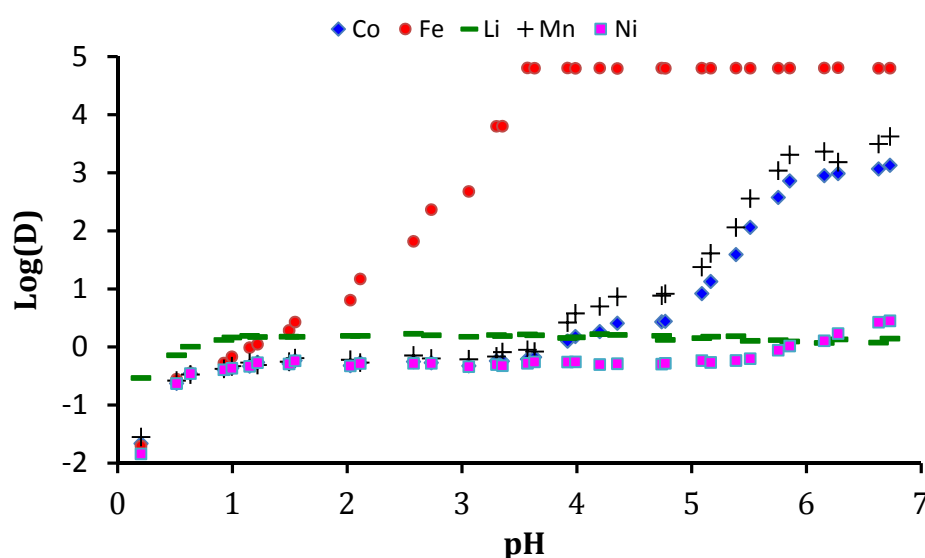


Figure 1 :Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 0.1M H₂SO₄, 21°C, two experiments

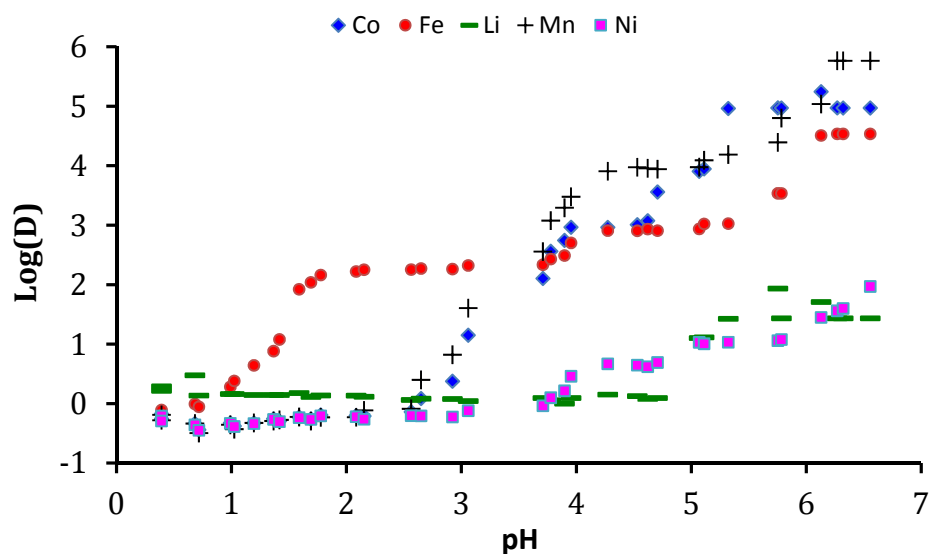


Figure 2: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.5M Cyanex 272 in solvent 70, aqueous phase: 0.5M H_2SO_4 , 21°C, two experiments

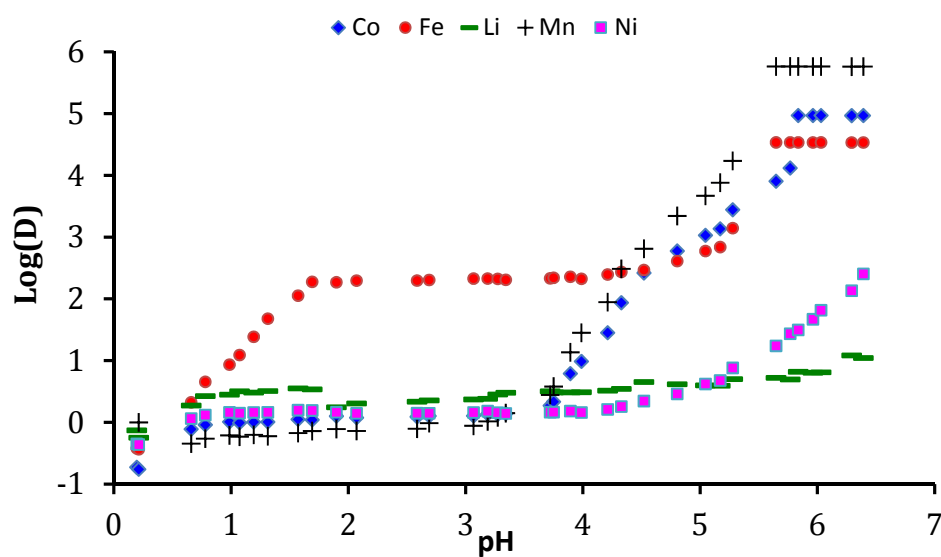


Figure 3: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 1M Cyanex 272 in solvent 70, aqueous phase: 1M H_2SO_4 , 21°C, two experiments

Separation of metals with Cyanex 923

Figure 4 shows the effect of Cyanex 923 concentration on the separation of the metal ions. There is slight increase in the extraction of all metals except nickel, at 1M extractant concentration.

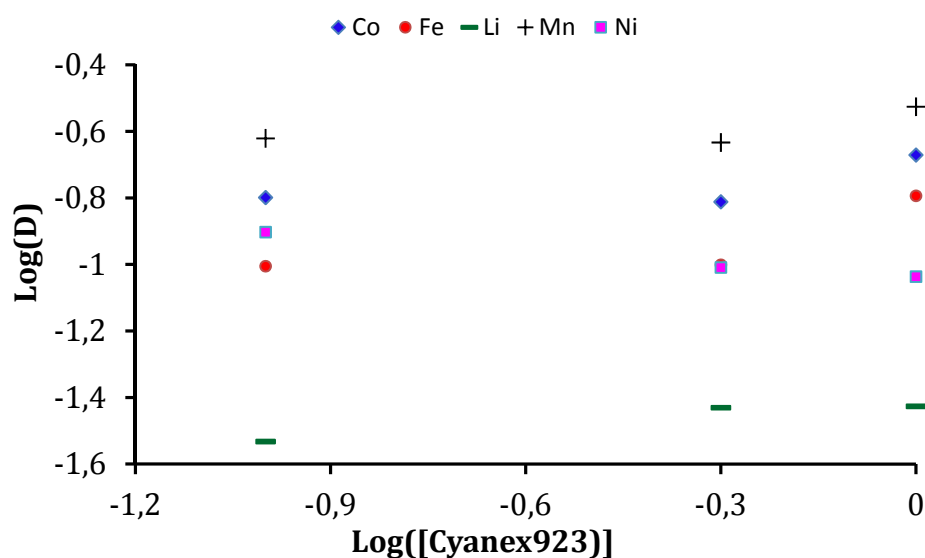


Figure 4 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1, 0.5 and 1M Cyanex 923 in solvent 70, aqueous phase: 1M H_2SO_4 , 21°C, three experiments

Effect of sulphate on extraction with Cyanex 923

Figure 5, shows the effect of sulphate concentration on the extraction of metal ions in to the organic phase. Increase in D-values is observed from 0.1M concentration of sulphate.

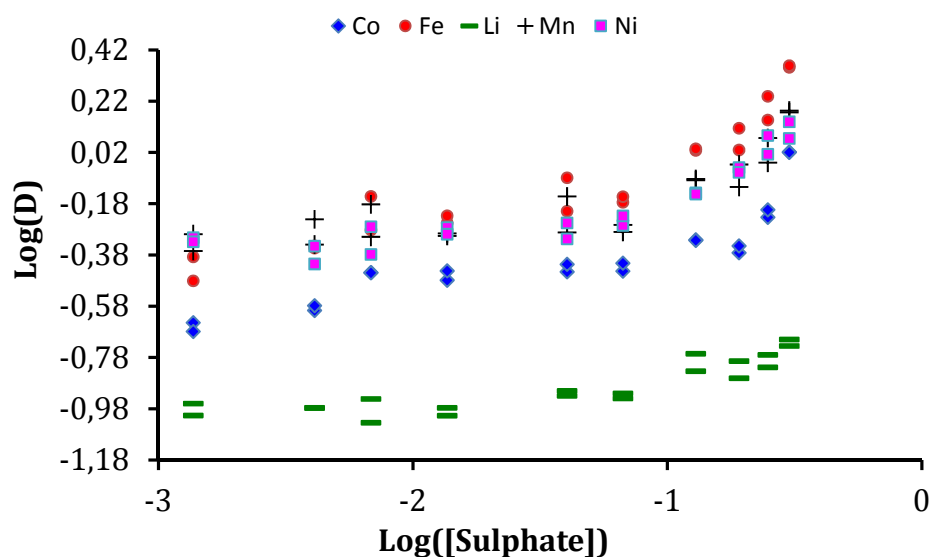


Figure 5 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 1M $HClO_4$ and 1M $NaClO_4$, 21°C, two experiments

Conclusion

Separation of Li-ion battery metals is possible using both Cyanex 272 and 923. The sulphate aqueous system works better not only for separation but also has higher D-values as compared to the nitrate system (Part1).

In the Cynex923 system, like in the case of nitrate system, the extraction of metals was improved by extractant concentration, however it was more dependent on the sulphate concentration.

References

- Al-Alawi, Bradley.(2013) Review of hybrid, plug-in hybrid, and electric vehicle market modeling Studies. *Renewable and Sustainable Energy Reviews* 21: 190-203.
- Albinsson. (1988) *Development of the AKUFVE-LISOL technique. In Solvent extraction studies of lanthanide acetylacetonates* PhD-Thesis thesis. CTH, S-412 96, Gothenburg, Sweden
- Ekberg, Persson, Ödegaard-Jensen, Albinsson, Andersson.(2006) Redox control in solvent extraction studies using a PEEK AKUFVE unit. *Solvent Extraction and Ion Exchange* 24: 1-7.
- Ritchie, Howard.(2006) Recent developments and likely advances in lithium-ion batteries. *Journal of Power Sources* 162: 809-12.
- Rydberg.(1969) Solvent extraction studies by the AKUFVE method. *Acta Chemica Scandinavica* 23

Study of separation of metals from HEV Li-ion batteries using AKUFVE

Part3: From chloride leach liquor

*Sravya Kosaraju^{*1}, Christian Ekberg¹, Stefan Allard¹*

Summary

Li-ion batteries of various chemistries are one of the popular choices for their use in electric vehicles (EV's), plug-in hybrid vehicles (PHEV's) and, hybrid electric vehicles (HEV). Typical vehicular batteries have metals such as Co, Ni, Mn, Al, and, Cu in addition to Li. As the number of battery run vehicles increase in numbers, it becomes important in the near future to plan the collection and waste management processes for the end of life batteries. In this context recycling Li-ion batteries, especially those of vehicle scale, plays an important role. Recycling Li-ion batteries has multiple fold advantages such as remediating improper disposal of end of life batteries, reducing economic and environmental impacts caused due to virgin metal extractions, at least to some extent and ensures raw material resource availability. Solvent extraction technique can produce very pure streams of metals which can again be used in the production of new batteries or other product manufacturing. The process is very similar to separation of metals from naturally occurring minerals, except in this case the starting material is Li-ion battery waste.

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II), Co(II), Fe(III) from various leachates using both acidic and solvating extractants was made. Part1 deals with separation from nitrate aqueous media, Part2 with sulphate and and the current article, Part3 deals with Chloride aqueous media. Metal ion separation studies with acidic extractant were made with respect to pH and extractant concentration and studies with solvating extractant were made with respect to chloride concentration and extractant concentration.

Introduction

Market projections of battery run vehicles (HEVs, PHEVs and EVs) show an increasing trend from as early as 2015[Al-Alawi & Bradley, 2013]. The battery powered vehicles require batteries with high specific volumetric and gravimetric energy densities. Typical vehicular batteries have metals such as Co, Ni, Mn, Al, and, Cu in addition to Li. As the number of battery run vehicles increase in numbers, it becomes important in the near future to plan the collection and waste management processes for the end of life batteries. In this context recycling Li-ion batteries, especially those of vehicle scale, plays an important role. Recycling Li-ion batteries has multiple fold advantages such as remediating improper disposal of end of life batteries, reducing economic and environmental impacts caused due to virgin metal extractions, at least to some extent and ensures raw material resource availability. In order to obtain pure streams of metal, solvent extraction technique is chosen

¹ Contact: sravya@chalmers.se

In the scope of the present work, an investigation of separation of Li(I), Ni(II), Mn(II), Co(II), Fe(III) from chloride leachate using Cynex 272 (acidic extractant) and Cyanex 923 (solvating extractant), separately was made. The separation studies with Cynex 272 were made with respect to pH and extractant concentration while studies with Cyanex 923 were made with respect to chloride concentration and extractant concentration.

A prismatic Li-ion battery has many Li-ion cells (cathode/separator-electrolyte/anode) stacked next to each other. A battery pack of size which is used in commercial vehicles has about 30- 200 batteries with in it, depending on the vehicles power requirements. The batteries investigated for the purpose of this article had carbon as anode and for the same reason is not discussed in the scope of this work.

After an initial heat-treatment to remove the adhesive PVDF, followed by mechanical dismantling and, crushing and sieving, the black-mass- or the metal containing fraction of the battery which also is the electrochemically active substance was recovered. This black mass is then leached with 1M HCl solution. The present studies are made with stock solutions prepared with the same relative ratios of the metal-ions in the leachate.

Experimental

Reagents

The materials used in the concerned experiments have already been reported in Part1 and Part2.

AKUFVE

AKUFVE is the acronym for the Swedish name – Anordning för Konuerlig Undersökning av Fördelningsjämvikter vid Vätske-vätske Extraktion. This translates to Apparatus for continuous measurement of partition factors in solvent extraction. The AKUFVE Apparatus facilitates continuous, rapid and accurate measurements of how solute distributes in a two phase liquid mixture as a function of variations in the simultaneously measured or known physical and chemical conditions. The schematic and it's working are accurately described in articles given in the reference [Rydberg, 1969, Albinsson, 1988, Ekberg et al, 2006]. The apparatus mainly consists of a mixing chamber and a specially designed centrifuge, which works both as separator and a pump. The separated aqueous phase flows via a pH electrode, so continuous measurements can be made, before flowing back in to the mixing chamber.

Chemical system used and experimental procedure

Three main investigations have been made,

1. Separation of metals with Cyanex 272 at concentrations 0.1, 0.5 and 1M in solvent 70 diluent, at increasing pH.

2. Separation of metals with Cyanex 923 at concentration 0.1, 0.5 and 1M in solvent 70.
3. and separation with varying concentrations of chloride

For the pH increase 3-0.5M NaOH was used. For the effect of chloride the ionic strength was kept close to 2, although for few points to the highest concentration of chloride the ionic strength goes up to 2.1. In the same study (effect of chloride the aqueous solution was made with an aqueous phase containing 10^{-5} M metal concentrations in 1M HClO₄ to keep the starting [H⁺] concentration the same as the leachate and 1MNaClO₄. It was previously checked if chlorate contributes to the extraction and D-values indicated that to be negligible. Chloride additions were made using 6.5M NaCl in MQ water.

Aqueous samples that were taken from the solvent extraction experiments were diluted using 1M HNO₃ and measured using an inductively coupled plasma emission spectrometer (ICP-OES). The distribution ratios (D_M) were calculated by

$$D_M = \frac{[M_{org,tot}]}{[M_{aq,tot}]}$$

[$M_{org,tot}$] : Metal concentration in organic phase

[$M_{aq,tot}$] : Metal concentration in aqueous phase

the concentration of metal –ions in the organic phase [$M_{org,tot}$], was calculated as the difference between the starting aqueous phase metal concentration and remnant metal concentration extraction in to the organic phase.

Results and Discussion

Separation of metals with Cyanex 272

Figures 1-3, show the separation of metals with respect to pH with Cyanex 272 concentrations 0.1, 0.5 and, 1M respectively. All the metal-ions have very high D-values even for the 0.1M Cyanex272 system. Iron is strongly extracted at a very high pH remains with organic phase even at pH7 for all three extractant concentrations. In 0.1M Cyanex 272 system, manganese can be separated from cobalt before pH 3.5, while for 0.5 and 1M it can be done before pH 2.5. Nickel separation from lithium is the best in chloride media as compared to nitrate and sulphate media (presented in Part1 and 2).

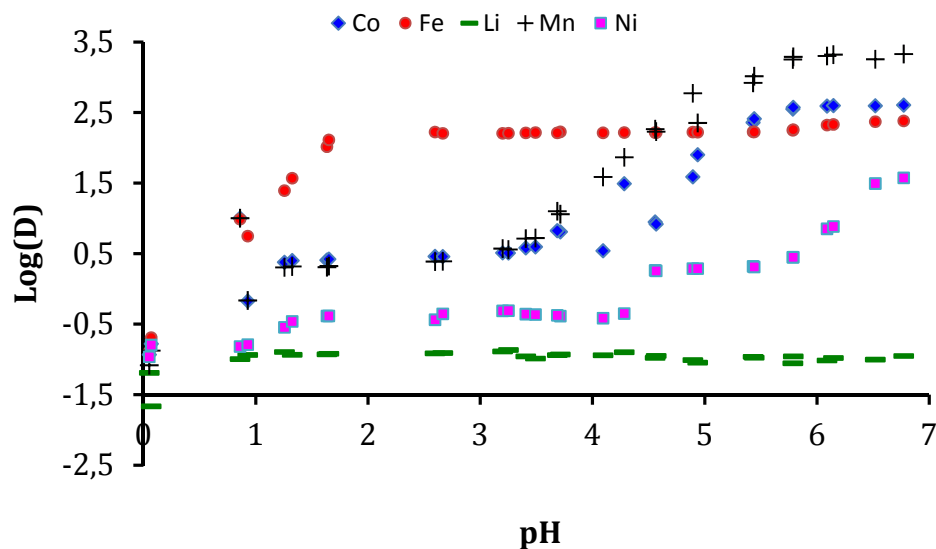


Figure 1 :Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 1M HCl, 21°C, two experiments

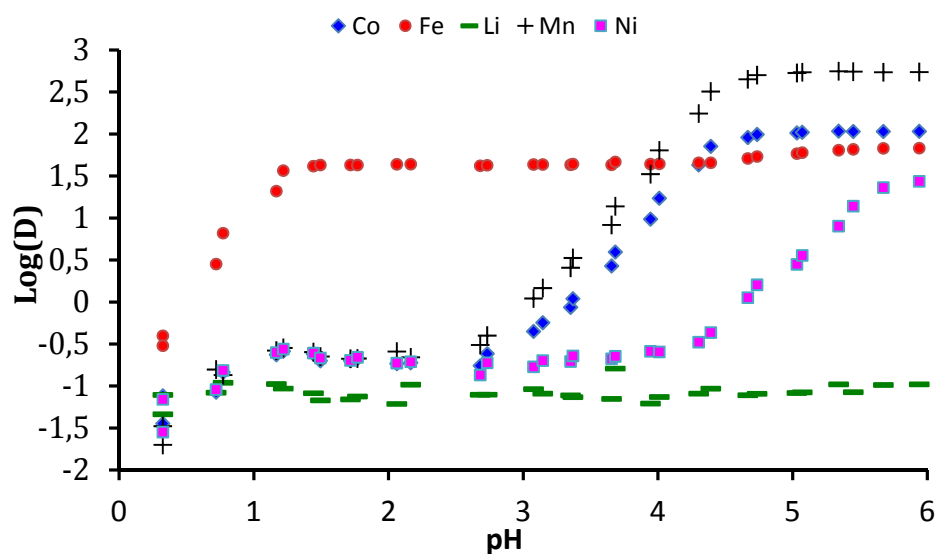


Figure 2: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.5M Cyanex 272 in solvent 70, aqueous phase: 1M HCl, 21°C, two experiments

Separation of metals with Cyanex 923

Figure 4 shows the effect of Cyanex 923 concentration on the separation of the metal ions. The D-values for iron become significantly large when concentration of extractant is increased, however cobalt, manganese and nickel are not affected. Li extraction slightly decreases with extractant concentration.

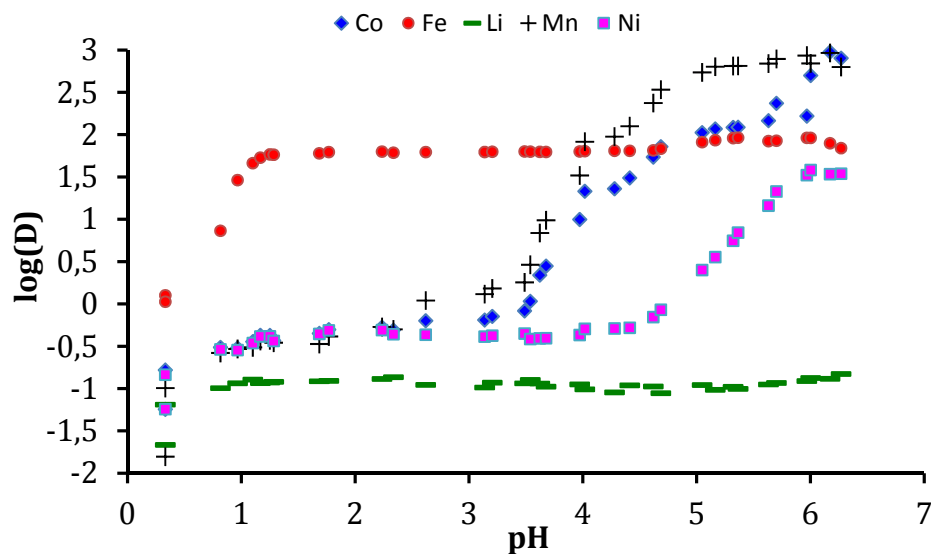


Figure 3: Extraction curves for cobalt, iron, lithium, manganese and nickel in the 1M Cyanex 272 in solvent 70, aqueous phase: 1M HCl, 21°C, two experiments

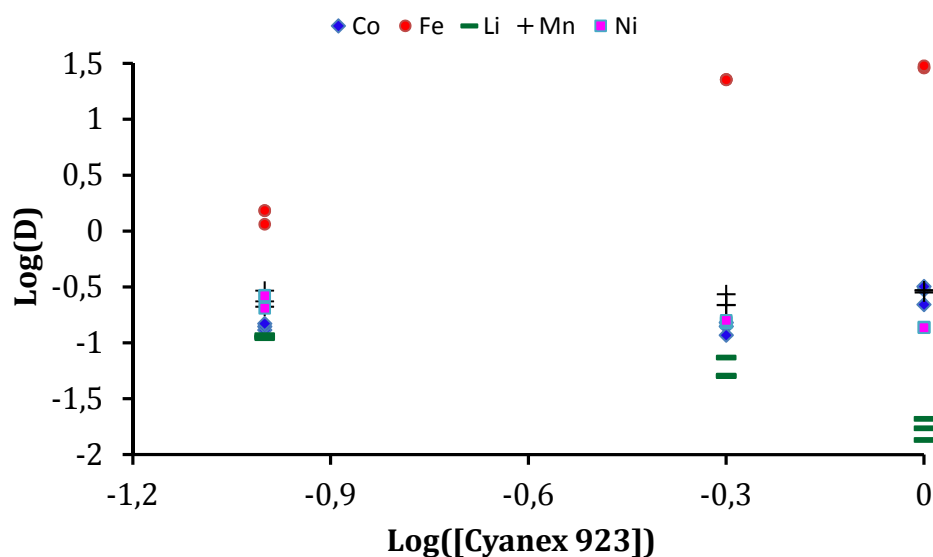


Figure 4 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1, 0.5 and 1M Cyanex 923 in solvent 70, aqueous phase: 1M HCl, 21°C, three experiments

Effect of chloride on extraction with Cyanex 923

Figure 5, shows the effect of chloride concentration on the extraction of metal ions in to the organic phase. D-values for lithium showed a little increase, however for the rest of the metals it significantly increased after the addition of 0.1M chloride.

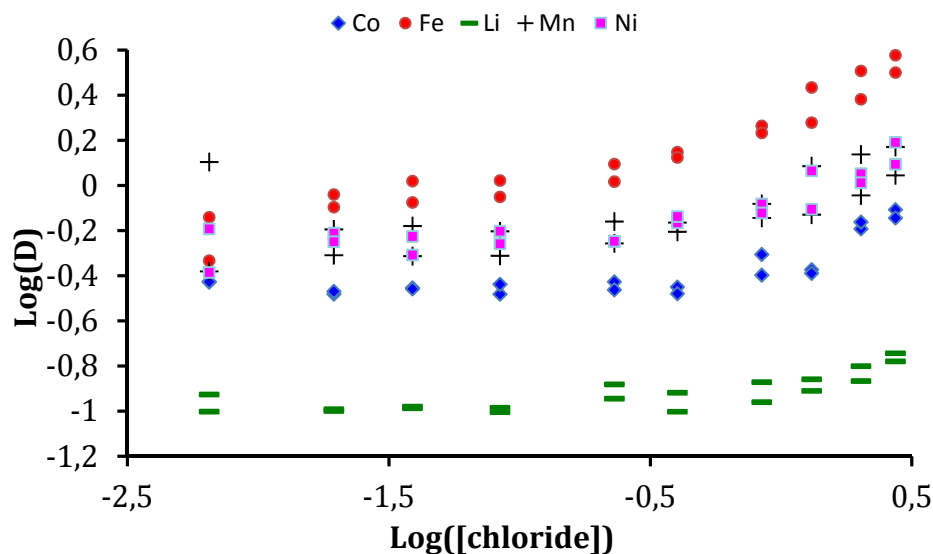


Figure 5 Extraction curves for cobalt, iron, lithium, manganese and nickel in the 0.1M Cyanex 272 in solvent 70, aqueous phase: 1M HClO_4 and 1M NaClO_4 , 21°C, two experiments

Conclusion

Separation of Li-ion battery metals is possible using both Cyanex 272 and 923. In the Cyanex 272 system, higher extractant concentration gave higher D-values for all metals and good separation. Li extraction was not affected by the concentration of the Cyanex 272.

In the Cyanex923 system, the extraction of metals was only improved slightly by extractant concentration, however it was more dependent on the chloride concentration

References

1. Al-Alawi, Bradley.(2013) Review of hybrid, plug-in hybrid, and electric vehicle market modeling Studies. *Renewable and Sustainable Energy Reviews* 21: 190-203.
2. Albinsson. (1988) *Development of the AKUFVE-LISOL technique*. In *Solvent extraction studies of lanthanide acetylacetonates* PhD-Thesis thesis. CTH, S-412 96, Gothenburg, Sweden
3. Ekberg, Persson, Ödegaard-Jensen, Albinsson, Andersson.(2006) Redox control in solvent extraction studies using a PEEK AKUFVE unit. *Solvent Extraction and Ion Exchange* 24: 1-7.
4. Ritchie, Howard.(2006) Recent developments and likely advances in lithium-ion batteries. *Journal of Power Sources* 162: 809-12.
5. Rydberg.(1969) Solvent extraction studies by the AKUFVE method. *Acta Chemica Scandinavica* 23

Separation of copper(II), zinc(II) and nickel(II) from chloride solutions with pyridinecarboxamides

Paulina Budziszewska, Iwona Mądrzak-Litwa, Karolina Wieszczycka, Aleksandra Borowiak-Resterna, Institute of Chemical Technology and Engineering, Poznań University of Technology, Poznań, Poland

For solvent extraction of heavy metals from chloride aqueous solutions hydrophobic esters and amides of pyridinecarboxylic acids can be used. Commercial representative of this class of compounds is Acorga CLX 50, which was used in hydrometallurgical CUPREX process for the recovery of copper from concentrated chloride solutions. In this extractant, as the active component, diisodecyl pyridine-3,5-dicarboxylate was used. The extraction process of copper, zinc, cadmium, and palladium from acidic chloride solutions with mono- and diamides of pyridinecarboxylic acids was extensively described in our previous works. To date there are no studies on the extraction of metal ions from multicomponent solutions with hydrophobic pyridinecarboxamides that would confirm the ability of these compounds to the selective separation of metal ions from aqueous solutions.

The current paper presents the results of equilibrium studies of copper(II), zinc(II), and nickel(II) extraction from chloride media by two hydrophobic pyridine derivatives, N,N-dihexylpyridine-3-carboxamide and N,N,N',N'-tetrahexylpyridine-3,5-dicarboxamide. The influence of the composition of the aqueous phase on selective separation of these metal ions was investigated in the range of 0.1-4 M chloride ions. The results of extraction equilibrium show that both studied amides extract stronger copper than zinc in the whole studied range of chloride concentration. Extraction of nickel at chloride ions concentration ≤ 2 M, practically does not occur. At $[\text{Cl}^-] \geq 3$ M nickel(II) concentration in organic phase does not exceed 0.04 g/L and 0.02 g/L for monoamide and diamide, respectively. The monoamide, being stronger base than the diamide, has higher non-ferrous metals extraction ability in all studies. At constant water activity, the difference between metal ions extraction ability of both amides decreases with increasing chloride concentration.

Rare earth elements recovery from used NdFeB magnets by leaching and solvent extraction

V. Haquin^a, M. Miquirditchian^a, R. Laucournet^b, E. Billy^b

^a CEA Marcoule – Nuclear Energy Division, Radiochemistry & Process Department,
LEPS - Bat 399 - BP 17171, F-30207 Bagnols-sur-Cèze France

^b CEA Grenoble, Technological Research Division, LITEN, LPCE, 17 rue des
Martyrs, F-38054 Grenoble, France

The emerging technologies for energy (wind and hydro power generation, electricity storage with batteries, ...) to tackle climate change and the transition to a green economy are drastically changing the availability of raw materials in the world. Due to a growing demand, most of raw materials involved in these technologies are exposed to a shortage and are considered as critical raw materials. During the last decade, countries or organizations have paid attention to take specific actions, such as strategic stockpiling, substitution or recycling in order to protect themselves against a lack of critical materials availability. According to the European Union by the European Raw Materials initiative and to the U.S. Department of Energy, the rare earth elements are considered as the most critical raw materials due to their supply risk and their economic importance in the emerging technologies.^[1,2] Among the rare earth elements, dysprosium (Dy) is one of the most critical elements. Indeed, dysprosium is required for instance by the industry to manufacture high performing permanent magnets which corresponds to 95 % of the whole dysprosium demand.^[3]

In this context, a hydrometallurgical process is under development in order to recover the rare earth elements from used NdFeB magnets by leaching and solvent extraction. After a thermal treatment, grinding, mechanical and dissolution steps of the magnets, experiments are performed from a solution containing high concentrations of iron and neodymium and lower amounts of boron, praseodymium and dysprosium. The present work is mainly focused on the selective recovery of dysprosium from iron, neodymium and praseodymium in solution. In this way, several extracting systems could be proposed and assessed for rare earth separation.

¹ European Commission, July 2010, Critical raw materials for the EU, Report of the ad-hoc working group on defining critical raw materials

² U.S. Department of energy, December 2011, Critical materials strategy

³ Hoenderdaal S. et al., 2013, Energy, 49, 344

Alkyl Derivatives of 2,2'-Bibenzimidazole as Extractants of *d*-Electron Metal Ions

*Iwona Mądrzak-Litwa, Karolina Wieszczycka, Aleksandra Borowiak-Resterna,
Institute of Chemical Technology and Engineering, Poznań University of Technology,
pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland*

Commercial reagent ACORGA ZNX50, based on dimethyl 1-mono- and 1,1'-bis(tridecyloxycarbonyl)-2,2'-bibenzimidazole, is proposed for the recovery of zinc from chloride solutions by ZENECA Specialities. It was found that ACORGA ZNX50 selectively extracts zinc over iron (particularly, from solutions where ferric chloride has been used as leachant) also in the presence of high concentration of free hydrochloric acid.

The aim of our work was to replace the substituents in the molecule of 2,2'-bibenzimidazole by the alkyl groups with various chain lengths. Investigation of the influence of the number and structure of substituents in 2,2'-bibenzimidazole molecule on the extraction selectivity of zinc(II) and copper(II) in a wide range of concentrations of chloride ions, enable an evaluation of the suitability of the new group of compounds in the separation processes of transition metal ions from water solutions. These results enable the planning of the most optimal structure of organic ligands belonging to the bibenzimidazole group, having specific complexing and extractive properties in relation to the selected *d*-electron metal ions. We have obtained 2,2'-bibenzimidazole by two new, simple methods. In further steps we synthesized 1-alkyl- and 1,1'-dialkyl-2,2'-bibenzimidazole.

Studies, about extraction process for zinc and copper at different concentrations of chloride ion and various concentrations of received extractants, were conducted. In this paper we present the influence of extractants and chloride ion concentrations on the extraction equilibrium and also the correlation between the extraction efficiency and hydrophobicity of used extractant.

Zinc extraction from sulfate-chloride solutions with mixtures of a trialkyl amine and carboxylic acids

*I.Yu. Fleitlikh¹, G.L. Pashkov², N.A. Grigorieva³, O.A. Logutenko^{*4}, A.M. Kopanyov⁵*

In this work, zinc extraction from sulfate-chloride solutions containing iron using mixtures of a C₇-C₉ fraction trialkyl amine (TAA) and monocarboxylic acids (HA) was studied. Caprylic acid and the C₁₁-C₁₉ higher fractions of iso-acids (HIA) were used as the monocarboxylic acids. The main process parameters providing high zinc recovery (~ 99%) and its separation from iron, in particular, the TAA, HIA, and chloride ion concentrations, the aqueous-to-organic phase ratio (A:O) etc., were determined. An extraction flowsheet for zinc recovery from sulfate-chloride solutions as zinc chloride followed by its conversion to zinc sulfate is proposed. The flowsheet includes zinc extraction with the TAA and HIA mixture, washing of the extract with water to remove impurities, chloride ion stripping with an alkaline solution (NaOH), zinc stripping with a sulfuric acid solution, resulting in the extractant regeneration.

The data obtained for synthetic solutions were confirmed for leach liquors of a sulfide concentrate from the Zimneye deposit (Russia). Zinc extraction was carried out from solutions containing (g/L) 10-12 Zn, 2-4 Cu, 12-15 Fe(III), 40-50 Fe(II), 0.7-0.8 Pb, 80-85 Cl, 20-80 H₂SO₄. The composition of the zinc sulfate obtained by the proposed technology was of the best quality in accordance with the State Standard of Russia.

Introduction

Oxidative leaching of polymetallic zinc sulfide ores results in solutions containing, in addition to zinc, large amounts of various impurities (Fe, Cu, Pb, etc.). Extraction processes are most efficient for zinc recovery from such solutions. Tri-*n*-butyl phosphate (TBP), trialkyl phosphine oxide (TAPO, CYANEX 923), alkyl phosphonates of various structures (di-*n*-pentylpentyl phosphonate, DPPP, and di-*n*-butylbutyl phosphonate, DBBP), as well as organic amines (secondary amine, Amberlite LA-2, tertiary amine, Alamine 336, and a C₇-C₉ fraction trialkyl amine, TAA) can be used as extractants.

It should be noted that the use of TBP for the solutions with a high zinc content (10–20 g/L) is problematic due to poor zinc extraction into the organic phase. Unlike TBP, CYANEX 923 extracts zinc very efficiently; however zinc stripping is very difficult in this system [1]. In the Zinclor process, di-*n*-pentylpentyl phosphonate or di-*n*-butylbutyl phosphonate were used for zinc extraction from the liquors deriving from leaching of zinc concentrates with ferric chloride [2]. Zinc stripping was carried out with hot water and resulted in an electrolyte containing ~ 65 g/L of Zn. The Zincex process is of special interest [3]. In this process, an initial chloride solution for extraction contains 20–30 g/L Zn as well as the impurities Fe, Cd, Cu, Pb, and As.

¹ Institute of Chemistry and Chemical Technology, SB RAS, Krasnoyarsk, Russia

² Institute of Chemistry and Chemical Technology, SB RAS, Krasnoyarsk, Russia

³ Institute of Chemistry and Chemical Technology, SB RAS, Krasnoyarsk, Russia

^{*4} Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk, Russia, tel. +79137408074, e-mail: ologutenko@solid.nsc.ru

⁵ Khimpolitekh Ltd., Novosibirsk, Russia

Zinc is extracted with a secondary amine (Amberlite LA-2) as an anion complex $[\text{ZnCl}_4]^{2-}$. The loaded extract is washed with dilute acid to remove the impurities and then zinc is stripped from the organic phase with water. The strip liquor, containing some other cations as well as zinc, is purified by removing the impurities by solvent extraction with D2EHPA. From the washed extract, zinc is stripped with spent zinc sulfate electrolyte resulting in a solution with a high zinc content (80–90 g/L) and containing practically no impurities. To remove iron(III) from D2EHPA, the extractant was treated with concentrated hydrochloric acid solutions. A disadvantage of this technology is the large number of operations and, accordingly, extraction stages ($n > 20$), which leads to great investment costs.

It is obvious that, for zinc extraction, not only secondary but also tertiary amines, such as trioctyl amine, trialkyl amine, Alamine 336 and others can be used. Their extractability decreases in the series quaternary ammonium salts > tertiary > secondary > primary amines > HR+TAA [4].

It should be added that new efficient extractants for zinc recovery are constantly sought. For example amide-amines, demonstrate high selectivity towards zinc in comparison with iron(III) [5].

The purpose of this study was to develop a process for zinc recovery from sulfate-chloride solutions with a high zinc content deriving from leaching of sulfide minerals and to obtain high purity zinc sulfate as a final product. Mixtures of a trialkyl amine and carboxylic acids, which earlier showed a high efficiency for the extraction of cadmium and chloride ion from zinc sulfate solutions [6], were used as the extractants.

Experimental

Reagents

The mixtures of a C_7 – C_9 fraction trialkyl amine (TAA, R_3N) of 81.5% purity and monocarboxylic acids (HA) were used as extractants. Caprylic acid and C_{11} – C_{19} higher fractions of iso-acids (HIA) of 90% purity were used as the monocarboxylic acids. Before extraction, trialkyl amine was converted to the sulfate form by treatment with a stoichiometric amount of sulfuric acid. Dearomatized kerosene ($\text{C}_{10}\text{H}_{22}$) was used as a diluent and 2-ethylhexanol of pure grade as a modifier. The reagents described above were products of domestic production. The mineral salts, alkalis and acids used were also of chemically pure or analytical grades.

Procedure

The liquid–liquid extraction testwork was carried out by mechanical mixing of the phases in test-tubes or in separatory funnels at 22–25°C. The aqueous phase acidity was varied by adding appropriate amounts of sulfuric acid. The chloride ion content in the aqueous phase was varied by adding appropriate amounts of hydrochloric acid or sodium chloride. The time of contact of the phases during extraction and stripping was 15 min.

The pH values of the aqueous phases were determined by potentiometric titration with a glass electrode using pH meters, pH-673 and Akvilon pH-410.

The aqueous phases were analyzed for metal cations. Their contents in the organic phases were calculated from the mass balances. In several cases, to ensure accurate results, the metal-containing organic phases were completely stripped using sulfuric acid solutions. The re-extracts so obtained were analyzed for their metals content. The metal cation concentrations in the aqueous phases (initial aqueous solutions, raffinates and re-extracts) were determined by atomic absorption spectrophotometry.

The concentration of chloride ion in the solutions was determined by potentiometric titration with silver nitrate.

Results and Discussion

The dependences of zinc and iron(III) extraction with the mixtures of TAA and monocarboxylic acids upon the chloride ion concentration in the aqueous phase are presented in Fig. 1.

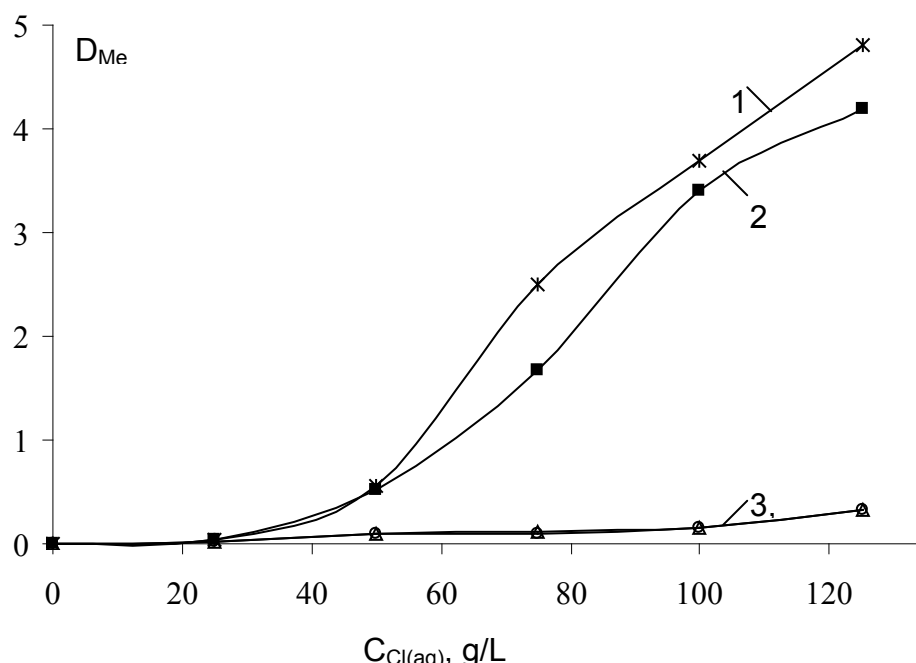


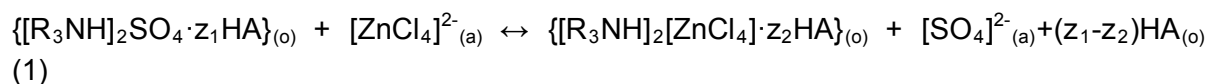
Figure 1. Dependence of zinc and iron extraction with the mixtures of TAA and monocarboxylic acids of various structures upon the chloride ion concentration in the aqueous phase. Aqueous phase composition, g/L: Zn – 10; Fe(III) – 15; H_2SO_4 – 20; Cl^- – 25–125. Organic phase composition: 0.6 mol/L TAA + 0.6 mol/L HA in kerosene + 10% 2-ethylhexanol. O:A = 1:1. 1,3 – TAA+ HIA; 2,4 – TAA+ caprylic acid; 1,2 – D_{Zn} ; 3,4 – D_{Fe} .

It is known that zinc is extracted from chloride solutions with tertiary amines as anion complexes, such as $[ZnCl_4]^{2-}$ [4] and $[ZnCl_3]^-$ [7], and iron is extracted as $FeCl_4^-$ [4]. As seen from Figure 1, an increase in the chloride ion concentration in the aqueous

phase results in an increase in metals extraction, which is obviously due to an increase in the fraction of the extracted complexes in the aqueous phase and, accordingly, in the organic phase. The nature of the carboxylic acids (branched (HIA) or straight (caprylic acid) chain) has little effect on zinc recovery from the solutions (curves 1 and 2). However, it should be noted that, in the presence of caprylic acid, zinc extraction is slightly lower (curve 2) than in the presence of HIA (curve 1).

The concentration range of 75–100 g/L can be considered as an optimum chloride concentration. Below 75 g/L, zinc distribution coefficients decrease (Fig. 1, curves 1 and 2), above the concentrations the separation between zinc and the main impurity iron noticeably becomes worse ($\beta_{\text{Zn/Fe}} \leq 25$). Only the TAA and HIA mixtures were subsequently studied.

The effect of the monocarboxylic acid on zinc and iron(III) extraction with the TAA and HIA mixture is presented in Fig. 2. It is known that extraction with amine salts in the presence of proton donor additives is accompanied by the solvation of the salt anions [8]. Accordingly, taking into account the solvation of the initial extractant and the reaction products with the monocarboxylic acid, zinc extraction, for example, in the form of the $[\text{ZnCl}_4]^{2-}$ complex can be described by equation (1).



Iron(III) extraction can be described analogously to equation (1).

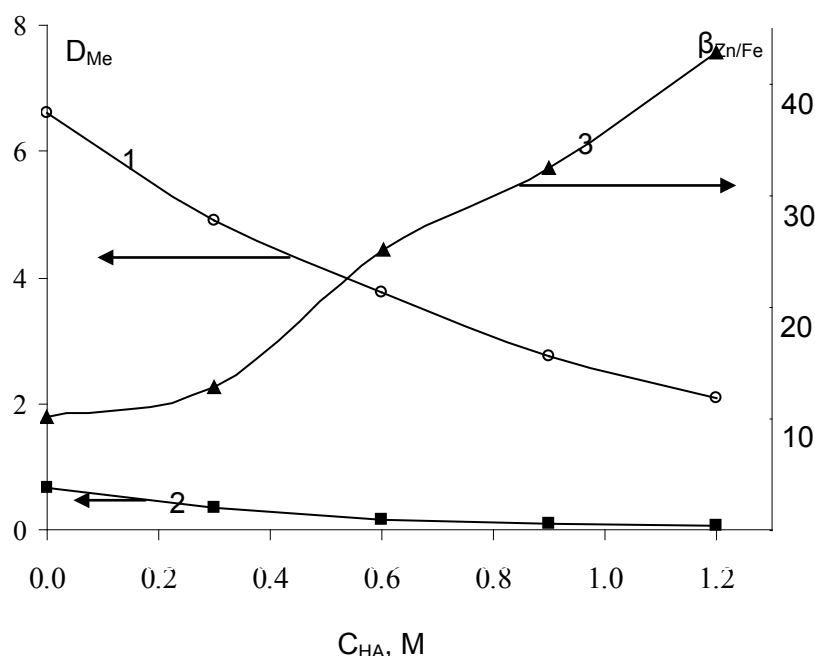


Figure 2. Effect of monocarboxylic acids on zinc and iron(III) extraction with the TAA and HIA mixture. Aqueous phase composition, g/L: Zn – 10; Fe(III) – 15; H_2SO_4 – 20; Cl^- – 100. Organic phase composition: TAA + HA in kerosene + 10% 2-ethylhexanol. TAA = 0.6 mol/L; HIA (HA) = 0.0–1.2 mol/L; O:A = 1:1. 1 – D_{Zn} ; 2 – D_{Fe} ; 3 – $\beta_{\text{Zn/Fe}}$

As seen from the figure, an increase in the monocarboxylic acid content in the organic phase results in a decrease in metals extraction (curves 1, 2). That is

obviously caused by the fact that HA forms more stable solvates with the initial extractant than with the final products of extraction. Accordingly, the reaction equilibrium (1) shifts to the left and metals extraction decreases. An increase in the zinc/iron(III) separation factors when increasing the fraction of HA in the organic phase, is probably caused by stronger solvation of the extracted zinc chloride complexes, when compared to that of the iron chloride complexes (curve 3), with HA.

Based on the data obtained for zinc extraction from sulfate-chloride solutions and its separation from impurities, the following composition of the extractant was chosen: 0.6 mol/L TAA + 0.6 mol/L HA in kerosene + 10% 2-ethylhexanol. In this case, rather high zinc distribution coefficients ($D_{\text{Zn}} = 3.76$) and high zinc/iron(III) separation factors ($\beta_{\text{Zn/Fe}} = 25.2$) are achieved. At lower HA contents in the mixture, $\beta_{\text{Zn/Fe}}$ decreases, at higher HA contents, zinc extraction decreases.

The extraction isotherm for zinc is given in Fig. 3. It is seen that, for the given extractant composition, when the zinc content in the initial solution is 10 g/L and when zinc is almost completely recovered (99%), 3.3 theoretical or 4 practical stages are required.

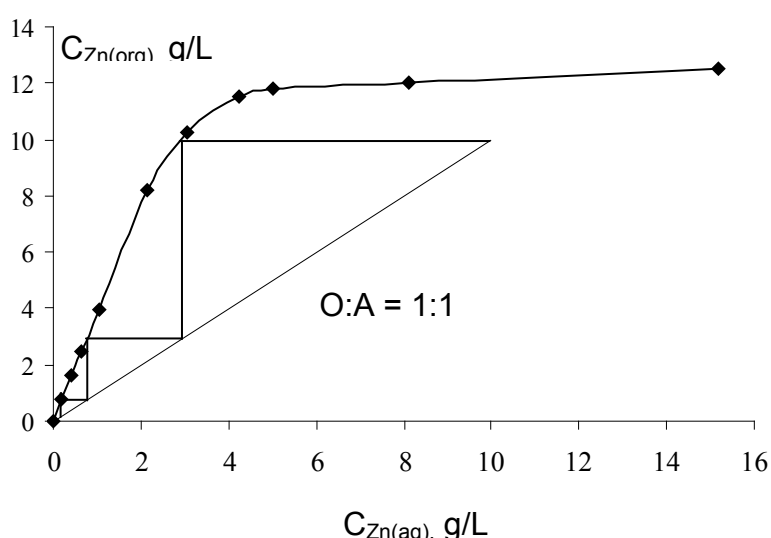
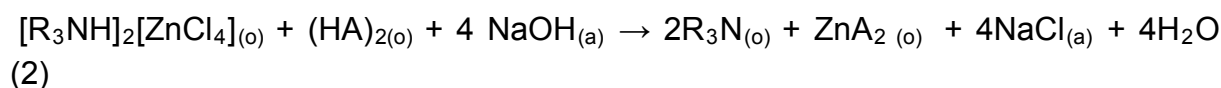


Figure 3. Extraction isotherm for zinc extraction with the TAA and HIA mixture from iron-contained solutions. Aqueous phase composition, g/L: Zn – 0–30; Fe(III) – 15; H_2SO_4 – 20; Cl^- – 100. Organic phase composition: 0.6 mol/L TAA + 0.6 mol/L HA in kerosene + 10% 2-ethylhexanol. O:A = 1:1.

Washing of the zinc extract from iron(III) (~1.5–1.8 g/L) is quite easily carried out with water. At O:A = 5:1, iron is stripped almost completely in three stages. Under these conditions, the percentage of zinc washing from the extract is ~5%.

The washed extract is treated with alkaline solutions (NaOH or NH_4OH) resulting in the separation of chloride ions from zinc: chloride ions pass into the strip liquor as NaCl or NH_4Cl and zinc remains in the organic phase forming zinc carboxylates (Eq. 2). (The subsequent reaction equations for the process, for simplicity, are written without taking into account the solvation of the initial and final products with the monocarboxylic acid in the organic phase).



The data on chloride ion stripping with the NaOH solution are presented in Table 1. As seen from the table, at a final pH range of the strip liquors of 6–8, chloride ions almost completely pass into the aqueous phase, while zinc remains in the organic phase.

Based on the data obtained, it was recommended to strip chloride ion with the stoichiometric amount of a ~5.0 mol/L sodium hydroxide or ammonium hydroxide solution to the final pH range of the strip liquors of 6.0–8.0 in two stages at an O:A ratio of 4:1. This results in obtaining a quite concentrated chloride ion strip liquor (110–120 g/L).

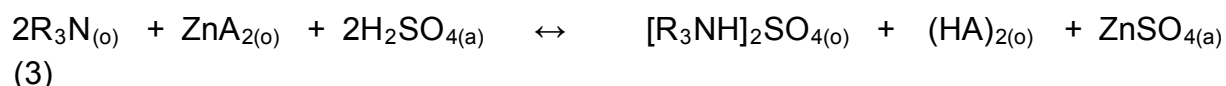
Table 1

Chloride ions stripping with sodium hydroxide solutions

O:A	Final pH values of the strip liquors	Strip liquors	
		Zinc content, g/L	Chloride ion content, g/L
1:1	6.0	0.8	33.8
1:1	7.0	0.1	35.0
1:1	8.0	0.06	34.2
1:1	8.5	0.06	35.1
2:1	7.0	0.12	67.0
3:1	7.0	0.32	103.0
5:1	7.0	0.52	170.0
6:1	7.0	0.82	202.0

Organic phase composition: 0.6 mol/L TAA + 0.6 mol/L HA in kerosene + 10% v/v 2-ethylhexanol. O:A = 1:1. Extract composition, g/L: Zn – 10; Cl⁻ – 35.

Further treatment of the organic phase with a sulfuric acid solution results in zinc stripping and, at the same time, in regeneration of the extractant which is returned to the extraction cycle in the sulfate form (Eq. 3).



As tests showed, at pH ~ 2, zinc is almost completely stripped so increasing the acidity is not necessary as it would result in an unacceptably high consumption of sulfuric acid.

The data obtained for the synthetic solutions were verified and confirmed for leach liquors of a sulfide concentrate from the Zimneye deposit (Russia). Compositions of

the main components of the solutions, organic and aqueous phases as well as process parameters are shown in Table 2.

Table 2*Zinc extraction with the TAA and HIA mixture from leach liquors*

Operations	O:A	Components content in the phases, g/L											
		Aqueous phase composition						Organic phase composition					
		Zn	Fe	Cl ⁻	Cu	As	Pb	Zn	Fe	Cl ⁻	Cu	As	Pb
Extraction	1:1	1.75	64	45.5	1.9	1.78	0.87	8.8	1.32	37	0.11	0.015	0.027
Washing from impurities	5:1	1.8	4.5	–	–	–	–	8.6	0.06	–	not detected	not detected	0.014
Chloride ion stripping	3:1	0.2	–	106	–	–	–	8.4	0.02	–	not detected	not detected	0.01
Zinc stripping	10:1	85	0.017	0.1	not detected	not detected	not detected	0.1	0.01	0.5	not detected	not detected	0.005

Initial solution composition, g/L: Zn – 10; Cu – 2.2; Fe(II) – 54; Fe(III) – 12; As – 1.8; Pb – 0.9; Cl⁻ – 82.3; H₂SO₄ – 82.

Organic phase composition: 0.6 mol/L TAA + 0.6 mol/L HIA in kerosene + 10% v/v 2-ethylhexanol.

Stripping solutions: Water (washing of the extract from impurities); 5% ammonium hydroxide solution, a final pH value of the strip liquors is 7.0 (chloride ion stripping); 550 g/L H₂SO₄ solution, a final pH value of the strip liquors is 2.2 (zinc stripping).

The number of stages (n) for each operation is 1, except the washing operation where n = 2.

Chemical composition of the tin-polymetallic concentrates of the Zimneye deposit (Russia), %: 6.38 Pb, 6.89 Zn, 1.7 Cu, 20.5 Fe, 2.0 As, 1.25 Sn.

Conditions for zinc leaching from concentrates (the product was 80% ground to the particle size of 0.074 mm): 100 g/L H₂SO₄, 50–60 g/L Fe (FeCl₃), t = 90°C, solid:liquid = 1:5, τ = 3 h.

The degree of recovery into the solution, %: Zn – 83–90, Cu – 80–85.

Composition of the zinc sulfate ($\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$) obtained from leach liquors using the proposed technology was of the best quality according to the Russian State Standard GOST 8723-82 (Table 3).

Table 3

Composition of zinc sulfate obtained using extraction with TAA and HIA

Element	Zn	Fe	Cl	Pb	Ca+ Mg	Mn	As	Cu
The sample obtained	40.0	0.0065	0.1	not detected	–	not detected	not detected	not detected
GOST 8723-82, premium grade	40.3	0.02	0.26	0.002	0.2	0.024	-	0.001

The results obtained allow us to recommend the following sequence of operations for zinc recovery and concentration from the solutions:

- Zinc extraction is carried out in 3–4 stages at an O:A ratio of 1:1 (the ratio can be changed depending on the zinc content in the initial leach liquor).
- Washing of impurities from the extract is carried out with water at an O:A ratio of 1:5 in 3 stages.
- Chloride ion stripping is carried out with a stoichiometric amount of sodium hydroxide or ammonium hydroxide with a concentration of ~5.0 mol/L to a final pH range in the strip liquors of 6.0–8.0 in 2 stages at an O:A ratio of 4:1. This results in the production of quite concentrated chloride ion strip liquors (~120 g/L). These solutions can be returned to the leaching stage or can be used for the production of sodium hypochlorite.
- Zinc stripping is carried out with a stoichiometric amount of sulfuric acid with a concentration of ~5.5 mol/L to a final pH value of 2.0-2.2 in 2 stages at an O:A ratio of 9–10:1 resulting in the production of zinc solutions (80–90 g/L Zn) which are suitable for the production of zinc sulfate or electrolytic zinc.

Conclusions

The possibility of zinc extraction from sulfate-chloride solutions with mixtures of a trialkyl amine and monocarboxylic acids has been demonstrated. A process for zinc recovery using the mixtures containing TAA and higher isocarboxylic acids (HIA) was developed. A high degree of zinc recovery (~98.5–99%) is achieved in a small number of stages ($n = 11\text{--}13$) resulting in the production of a high-quality final product

– zinc sulfate. The process developed can be used for efficient zinc recovery from chloride and chloride-sulfate leach liquors of zinc ores.

Acknowledgments

Appreciation for valuable remarks is extended to Dr. D. S. Flett.

References

1. Gangazhe, T., Sole, K.C., Petersen, J. (2011), *Proceedings of the 19th International Solvent Extraction Conference, ISEC'2011*, 3-7 October 2011, Santiago, Chile, p.50 (on CD, chapter 2, № 50, p.1-8).
2. Nogueira, E.D., Suarez-Infanson, L.A., Cosmen, P. (1983), *Proceedings 13th Annual Hydrometallurgy Conference, Canadian Institute of Mining, Metallurgy and Petroleum*, Montreal, pp. 1-23.
3. Nogueira, E.D., Regife, J.M., Blythe, P.M. (1980), *Chemistry and Industry*, vol. 2 (19), pp. 63-67.
4. Schmidt V.S. (1980) Amine extraction. Elsevier "Atomizdat", Moscow. 264 pp.
5. Ellis, R.J., Chartes J., Tasker, P.A., Sole, K.C. (2011), *Solvent Extraction and Ion Exchange*, vol. 27, pp. 657-672.
6. Pashkov, G.L., Kholkin, A.I., Srgeyeva, V.V., Dokuchaev, V.N. (1986), *Non-Ferrous Metals* (Russ. J.), vol. 2, pp. 29-30.
7. Lee, M. S. Nam, S.O. (2009), *Bull. Korean Chem. Soc.* Vol. 30 (7), pp. 1526-1530.
8. Kholopova, G.D., Protasova, N.V., Kuz'min, V.I., Bondarenko, V.S. (1981), *Journal of General Chemistry* (Russ. J.), vol. 53 (5), pp. 1285-1289.

Solvent extraction studies for the separation of rare earth elements using neutral and acidic organophosphorus extractants

Sanela Omanovic, Giuseppe Modolo, Fabian Sadowski, Dirk Bosbach

Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Corresponding author: Sanela Omanovic, s.omanovic@fz-juelich.de

Abstract

Solvent extraction technology for the separation of rare earth elements (REE) remains the uncontested method of choice for the commercial separation of REE into rare earth products. It is generally known that the difficulties encountered in the separation and recovery of adjacent (neighboring) rare earth elements represents a challenging task, due to their similar physical and chemical properties. Hence, currently used industrial solvent extraction processes have relatively low separation factors and a large number of cycles is needed to obtain a product of very high purity [1].

In this investigation, we studied the rare earth intragroup separation (Y, Sc, La-Lu, except Pm) with various organophosphorus extractants from aqueous solutions of hydrochloric acids (0.001-1 mol/L HCl). Eight neutral and acidic extractants were examined. We established literature [2] separation procedure for rare earth elements extracted with HDEHP. Our results show for rare earths, in comparison to the literature distribution ratios, a better extraction of heavier rare earths by an order of magnitude.

Furthermore, the commercial extractants P350, PC88A and HDEHP were compared with five of their derivatives. The extraction of f-elements, using dimethylheptyl-phenyl-phosphonate as an aromatic derivative of P350, yielded a significant increase in the distribution ratio for all rare earths, but it lost selectivity between neighboring elements. 1-Methylheptyl-methyl-phosphonic acid extracts all rare earths better than PC88A and shows a slightly better selectivity for the heavier lanthanides. Diphenylphosphoric acid and HDEHP show similar distribution ratios for all rare earths. However, the other tested extractants do not show significant improvements in the separation of neighboring elements.

Acknowledgement

Financial support for this research was provided by BASF.

Literature

- [1] C. K. Gupta, N. Krishnamurthy, Extractive metallurgy of rare earths, CRC Press, Boca Raton, Florida, 2005.
- [2] T. Sato, Hydrometallurgy 1989, 22, 121-140.

¹Direct extraction of molybdenum from high acid leach solutions of Ni-Mo ore using an oxime extractant of HBL101

Li Zeng , Xiaoli Liao , Liansheng Xiao , Yahui Sun*

Abstract: An oxime extractant of HBL101 was used to extract molybdenum(VI) directly from a strong acid leach solution of Ni-Mo ore calcine. The organic system was optimised in terms of organic composition and conditions of extraction and stripping and further characterised in terms of extraction and stripping kinetics and distribution isotherms and phase separation. More than 99.8% of molybdenum was extracted in two-stage counter current extraction using an organic system of 10%HBL101+5%TBP+70%sulfonated kerosene and a feed containing 14.7g/L Mo and 4mol/L H⁺ with an A/O ratio of 1:1.5 at 30 °C for 5 min. The loaded organic was stripped using ammonia solution after scrubbing with de-ionized water. The stripping of molybdenum was complete in three-stage counter current stripping using 6 mol/L NH₃·H₂O with an A/O ratio of 1:4 at 30 °C for 20 min, realizing the separation of Mo over Ni, Fe, Ca, Mg, Al, Cu and Zn as well as the enrichment and transformation of molybdenum(VI). The concentration of Mo in the strip liquor of pure (NH₄)₂MoO₄ solutions reached 33.4g/L and increased to 143.7g/L after reflux stripping for two times. The extractant of HBL101 exhibited a good performance and stability for reuse.

Key Words : Ni-Mo ore; Acid leach solution; Molybdenum; Recovery; Solvent extraction

1. Introduction

The Ni-Mo ore from the lower Cambrian black shale is a unique low grade multiple metal resource, which is located in the sedimentary polymetallic Ni-Mo-V mineral deposit and ore forming zone of precious and rare earth metals mineralisation with gross reserve of 9.37 million tonnes and widely distributed in southern Provinces of China^[1]. The extraction of molybdenum and nickel from Ni-Mo ore has been widely investigated^[2-6], mainly including oxidative roasting-caustic leaching for extraction of molybdenum, and acidic oxidative leaching for direct extraction of both molybdenum and nickel. For the process of acidic oxidative leaching, the leachings of molybdenum and nickel could reach 99% and 90%, respectively, but the impurities such as Fe, Ca, Mg, P and As are also dissolved into the leach solutions. The current methods on extraction of molybdenum from acid leach solutions include chemical precipitation, ion exchange and solvent extraction. For the method of precipitation, the product is mixture of Mo-P-As with high content of calcium and low economical value. The large consumption of base and without separation of Mo over P and As limits the wide application of ion exchange method.

Solvent extraction has taken an important role in the extraction of molybdenum from acid leach solutions. Although the good separation of molybdenum and nickel from acid solutions using amine extractant of N235 was reported^[7,8], but the leach solution has to be neutralised to pH 2~3 and molybdenum cannot be separated from P and As. This paper investigated the direct extraction of molybdenum from acid leach solutions containing 4 mol/L H⁺ of Ni-Mo ore calcine without neutralisation using an oxime extractant of HBL101.

2. Experimental

2.1 Materials

Reagent of HBL101(HL) was provided by Hunan Hongbang New Materials Company, which is an oxime chelating extractant. The compositions of strong acid

*Corresponding author, School of Metallurgy and Environment, Central South University, Changsha 410083, China; National Engineering Laboratory for Efficient Utilization of Refractory Non-ferrous Metals Resources, Central South University. Email: yuanzhenxia_1104@aliyun.com

leach solutions as feed are shown in Table 1.

Table 1 Compositions of the strong acid leach solution of Ni-Mo ore calcine

Element	Mo	Ni	Fe	Ca	Mg	Al	Cu	Zn	P	As	H ⁺
Concentration(g/L)	~14.7	4.84	14.1	0.55	2.27	3.57	0.37	0.58	4.31	2.91	4mol/L

2.2 Methods

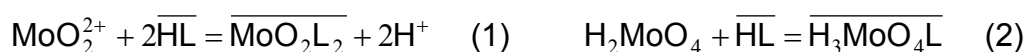
The shakeout tests were carried out in a 125 mL separating funnel immersed in a temperature controlled water bath. To determine the metal extraction distribution isotherms, the organic system containing 10%HBL101 and 5%TBP in sulfonated kerosene was mixed with the acid leach solution at A/O ratios of 1:4, 1:3, 1:2, 1:1.5, 1:1, 3:1 and 30°C.

Samples were collected and analyzed to determine the concentrations of metals. Molybdenum was determined with ammonium thiocyanate colorimetry by spectrophotometer, nickel was titrated with dimethylglyoxime. The aqueous samples were assayed for other metals using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

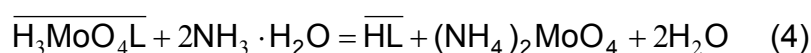
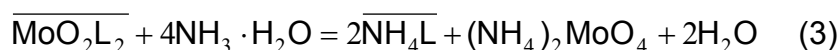
2.3 Experimental fundamental

The acid leach solution of Ni-Mo ore calcine contains 4 mol/L H⁺, in which P and As exists as anions without the formation of heteropolyacid with molybdenum. According to the distribution of molybdenum species in the Mo-H₂O system as a function of pH^[9], molybdenum mainly exists as cations or molecule such as MoO₂²⁺, H₃MoO₄⁺, H₆Mo₂O₈²⁺ or H₂MoO₄ when pH<1, while other metals exist as Ni²⁺, Fe²⁺, Al³⁺, Ca²⁺ and Mg²⁺.

The separation of metal cations over P and As can be achieved using the oxime chelating extractant of HBL101 since the anions of P and As cannot be extracted by the extractant. Because of the larger ionic radius of cationic molybdenum species than those of other metal cations, resulting in the preferential extraction of molybdenum using the extractant, the separation of molybdenum over other metals can thus be achieved. The reactions could be expressed as follows(based on MoO₂²⁺ and H₂MoO₄):



The loaded organic can be stripped using ammonia and the stripping reactions are listed below:



3. Results and discussion

3.1 Extraction

3.1.1 Effect of HBL101 and TBP concentration on molybdenum extraction

It can be seen from Fig. 1 that the extraction of molybdenum sharply increased from 46% to 98% with the increase of HBL101 concentration from 5%(v/v) to 20%(v/v). Given consideration of the cost of extractant and about 80% extraction of molybdenum with 10%(v/v) HBL101, more than 98% of molybdenum can be extracted by three counter current extraction. It was also noted that a slight emulsion

was observed during extraction. Therefore, the modifier of TBP was added in the organic solution to improve the phase separation. It was observed that not only the phase separation was significantly improved with the addition of TBP, but also the extraction of molybdenum increased from 75% to 87% with the increase of TBP concentration from 3%(v/v) to 10%(v/v)(Fig. 2), indicating that TBP also played a role in the extraction of molybdenum. It was found that the loaded organic with 3%(v/v) TBP was solidified after stewing for a certain time, which could be due to the low dissolution of Mo-HBL101 complexes in organic solution with low concentration of TBP. The addition of 5%(v/v) or more TBP could ensure good flow state of the organic solution. Therefore, the organic system consisting of 10%(v/v) HBL101+5%(v/v)TBP in sulfonated kerosene was chose.

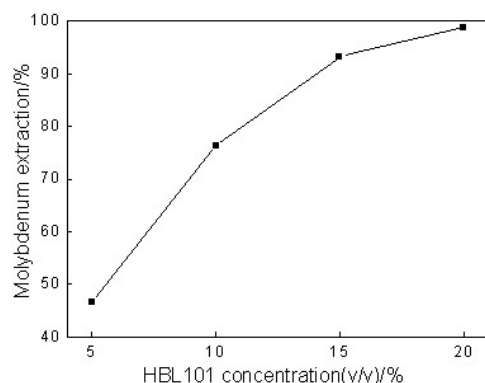


Fig. 1 Effect of HBL101 Conc. on Mo extraction
(O/A=1:1, T=30°C t=5 min)

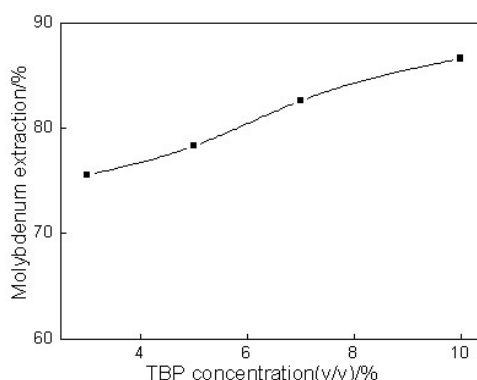


Fig. 2 Effect of TBP Conc. on Mo extraction
(O/A=1:1, T=30°C t=5 min, 10%(v/v) HBL101)

3.1.2 Effect of feed acidity on molybdenum extraction

The effect of feed acidity in the range of 1~4 mol/L H^+ on molybdenum extraction was investigated and the results are shown in Fig. 3. As seen, the extraction of molybdenum sharply increased from 10% to 90% with the increase of feed acidity from 1mol/L H^+ to 4 mol/L H^+ . It was also found that the phase separation became poor when feed acidity decreased to 1 mol/L. Solution acidity is one of key factors affecting the existing form of molybdenum. Molybdenum exists mainly in the form of cations or molecule such as MoO_2^{2+} , $H_3MoO_4^+$, $H_6Mo_2O_8^{2+}$ and H_2MoO_4 when $pH < 1$. But when there are P, As and Si in the solution, they could react with molybdenum to form heteropoly acid such as $PMo_{12}O_{40}^{3-}$, $AsMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{4-}$. The increase of feed acidity from 1mol/L H^+ to 4 mol/L H^+ would be beneficial to the depolymerization of molybdenum heteropoly acid and the stable formation of those molybdenum species of cations or molecule, resulting in the sharp increase of molybdenum extraction. Therefore, the leach solution with acidity of 4 mol/L H^+ can be directly used for the extraction of molybdenum using extractant of HBL101.

3.1.3 Molybdenum extraction distribution isotherms

The molybdenum extraction distribution isotherms with the SX system consisting of 10%(v/v) HBL101+5%TBP in sulfonated kerosene and strong acid leach solutions containing 14.7 g/L Mo at 30°C and its McCabe-Thiele diagram are shown in Fig. 5. It was found that two theoretical extraction stages are needed to reduce molybdenum concentration in the raffinate to less than 5 mg/L at an A/O ratio of 1:1.5. It was suggested that in practice three-stage counter current extraction would be better for circuit stability.

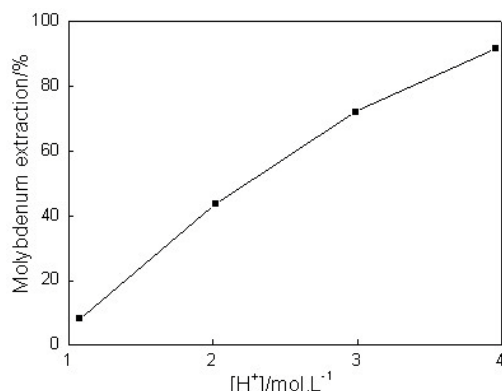


Fig. 3 Effect of solution acidity on molybdenum extraction (O/A=1.5:1, T=30°C t=5 min)

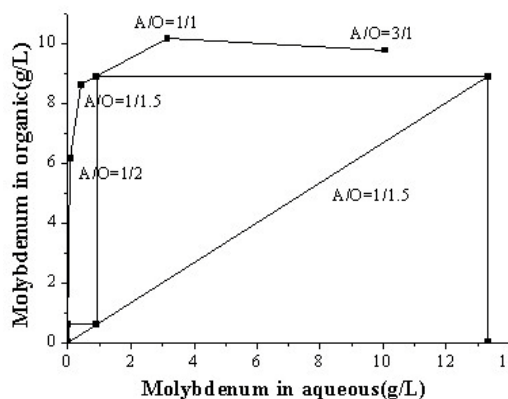


Fig. 4 Molybdenum extraction distribution isotherms

3.2 Scrubbing

Because part of iron and other impurities were entrained into the organic solution during extraction, resulting in formation of a small amounts of precipitates when ammonia solution was used to strip the loaded organic, de-ionized water was used to scrub the loaded organic before Mo stripping. The results are shown in Table 2. As seen, all of iron, calcium, magnesium, copper, zinc and most of aluminium while only 1.75% of molybdenum were scrubbed out. It was observed that there was no precipitate formation during stripping after scrubbing.

Table 2 Results of impurity scrubbing

Element	Mo	Fe	Ca	Mg	Al	Cu	Zn
Concentration in loaded organic (g/L)	8.29	0.06	0.003	0.013	0.018	0.018	0.001
Concentration in scrubbed liquor (g/L)	0.22	0.1	0.005	0.02	0.026	0.04	0.002
Scrubbing (%)	1.75	100	100	100	96.3	100	100

(T=30°C;t=3min ;A/O=1/1.5)

3.3 Stripping

3.3.1 Effect of ammonia concentration on molybdenum stripping

It can be seen from Table 3 that the stripping of molybdenum sharply increased to 91.89% with 6 mol/L ammonia in comparison to that of 40.27% with 2 mol/L ammonia. Further increase of ammonia concentration had little effect on the stripping of molybdenum. It is noted that the phase separation was fast in 50 seconds during stripping with 6 mol/L ammonia. The ammonia concentration of 6 mol/L was then chose as optimum.

Table 3 Effect of ammonia concentration on molybdenum stripping

Concentration(mol/L)	Mo Stripping(%)	Phase separation time(s)
2	40.27	28
4	86.84	30
6	91.89	50
8	93.01	120

(C_{Mo}=8.84 g/L, T=30°C t=20min, A/O =1/4)

3.3.2 Molybdenum stripping kinetics and temperature effect

The stripping kinetics of molybdenum from the loaded HBL101 using a strip solution of 6 mol/L NH₃·H₂O were determined at an A/O ratio of 1/4 and 30°C(Fig. 5). The stripping of molybdenum sharply increased from 50% to 90% with the increase of stripping time from 3min to 20min, indicating that the stripping time was one of important factors affecting the stripping of molybdenum. The effect of temperature on

molybdenum stripping is shown in Fig. 6. As seen, the stripping of molybdenum increased from 65% to 99.5% with the increase of temperature from 20°C to 35°C. Given the consideration of stability of ammonia and organic solutions, stripping temperature of 30°C was chosen as optimum.

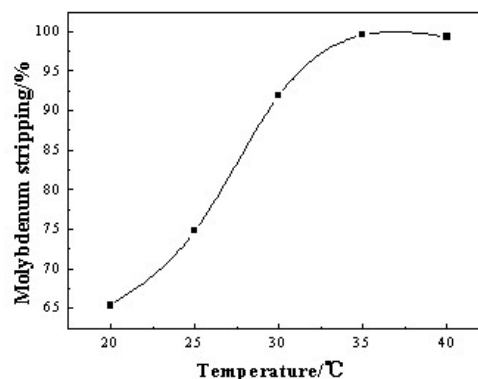
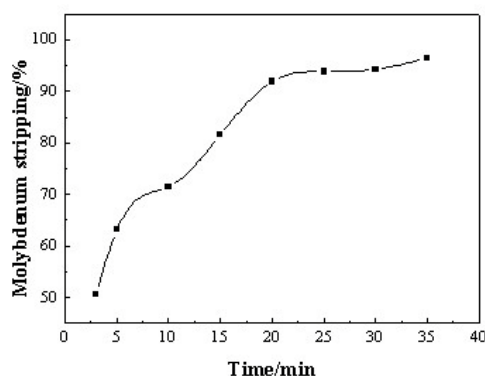


Fig. 5 Effect of time on molybdenum stripping **Fig. 6** Effect of temperature on molybdenum stripping

3.3.3 Molybdenum stripping distribution isotherms

The molybdenum stripping distribution isotherm was determined with the loaded HBL101 system and a strip solution of 6 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ using A/O ratios of 3:1, 1:1, 1:3, 1:4 and 1:5 at 30°C (Fig. 7). Only three theoretical stripping stages are needed to reduce molybdenum concentration in the stripped organic solution to less than 0.1 g/L at an A/O ratio of 1:4.

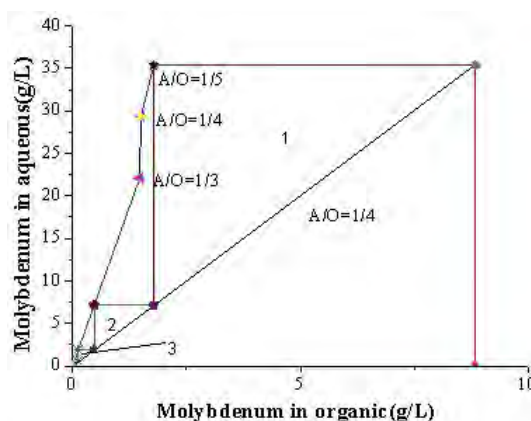


Fig. 7 Molybdenum stripping distribution isotherms with 6 mol/L ammonia at 30°C and its McCabe-Thiele diagram ($C_{\text{Mo}}=8.84\text{g/L}$, $\text{rpm}=200\text{r/min}$, $t=20\text{min}$).

3.3.4 Three-stage counter current stripping

Three-stage counter current stripping test was conducted using a loaded organic solution containing 8.51 g/L Mo and 6 mol/L ammonia at an A/O ratio of 1:4 and 30 °C for 20min. More than 99.9% of molybdenum was stripped using 6 mol/L ammonia by three-stage counter current stripping, leaving 0.004g/L Mo in organic solutions after stripping. The stripped organic solution can be directly reused for the extraction of molybdenum from high acid leach solutions. The concentration of molybdenum in strip liquors reached 33.42g/L and was even up to 143.67 g/L using reflux stripping for two times, which can be directly used to produce ammonium molybdate economically and effectively.

3.4 Further metal extraction and stripping tests

A test was conducted using 10% HBL101 and 5% TBP in sulfonated kerosene at an A/O ratio of 1:1.5 and 30°C to directly extract molybdenum from high acid leach solutions of Ni-Mo ore. After extraction, the loaded organic was scrubbed by deionized water at an A/O ratio of 1:1.5 followed by a solution of 6 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ for stripping in a single contact at an A/O ratios of 1:4. The separation of molybdenum and impurities were investigated and the results are shown in Table 4.

Table 4 Results of separation of molybdenum and impurities

Sample	Concentration (g/L)									
	Mo	Ni	Fe	Ca	Mg	Al	Cu	Zn	P	As
Feed	12.8	4.84	14.05	0.547	2.274	3.567	0.365	0.579	4.31	2.91
Raffinate	0.36	4.94	14.3	0.549	2.332	3.632	0.34	0.598	4.45	2.95
wash water	0.22	0.002	0.10	0.005	0.02	0.03	0.04	0.002	0.007	0.018
Strip liquor	27.6	0.002	0.002	0.002	0.002	0.005	0.002	0.002	0.01	0.009

It can be seen from Table 4 that molybdenum can be highly separated over impurities such as nickel, iron, calcium, magnesium, aluminum, copper, zinc, phosphorus and arsenic.

4. Conclusion

The oxime chelating extractant HBL101 can be used to selectively extract molybdenum directly from high acid leach solutions containing molybdenum, achieving the enrichment of molybdenum and the high effective separation of molybdenum over impurities. The extraction of molybdenum reached 97% using a SX system consisting of 10% HBL101 and 5% TBP in sulfonated kerosene with an A/O ratio of 1/1.5 and 200 rpm at 30°C for 5 min. The saturation capacity of molybdenum on the organic solution was 12.09 g/L. After two counter current extraction, the extraction of molybdenum reached 99.8%, leaving 0.03 g/L Mo in the raffinate. The stripping of molybdenum reached 99.9% using 6 mol/L ammonia with an A/O ratio of 1/4 and 200 rpm at 30°C for 20 min after three counter current stripping, resulting in more than 33 g/L Mo in the strip liquor. The oxime extractant HBL101 exhibited good performance and stability of reuse. Application of HBL101 in industry is expected to make an important impact on the extraction of molybdenum from high acid leach solutions and to deliver good economical benefits.

References:

- [1] Zhao, Z.W., Li, J.T., 2010. Present situation and prospect of Chinese Ni-Mo ore(in Chinese)[J]. China Metal Bulletin, Vol. 29: 38-40.
- [2] Hu, L., Xiao, L.S., Zhang, G.Q., Zeng, L., 2012. Experimental study on leaching molybdenum at high pressure with soda from low-grade molybdenum calcine with high impurities[J]. Mining and Metallurgical Engineering, Vol. 32(6): 66-70.
- [3] Li, Q.G., Xiao, L.S., Zhang, G.Q., Zhang, Q.X., 2007. Process and practice of ammonium molybdate production from Ni-Mo ore by hydrometallurgy(in Chinese)[J]. Chinese Journal of Rare Metals, Vol. 31: 85-89.
- [4] Wang, M.Y., Wang, X.W., 2010. Extraction of molybdenum and nickel from carbonaceous shale by oxidation roasting, sulphation roasting and water leaching[J]. Hydrometallurgy, Vol. 102: 50-54.
- [5] Zhao, Z.W., Li, J.T., Cao, C.F., Huo, G.S., Zhang, G., Li, H.G., 2010. Recovery and purification of molybdenum from Ni-Mo ore by direct air oxidation in alkaline solution[J]. Hydrometallurgy, 2010, 103: 68-73.
- [6] Zeng, L., Xiao, L.S., Xiao, C.L., Gong, B.F., 2013. Study on leaching of molybdenum and nickel from Ni-Mo ore using sodium chlorate[J]. Canadian Metallurgical Quarterly, Vol. 52(4): 335-341.
- [7] Zhu, W., Xiao, L.S., Xiao, C., Gong, B.F., 2010. Molybdenum extraction with N235 from the sulphuric acid leach liquor in Ni-Mo ore(in Chinese)[J]. Rare Metals and Cemented Carbides, Vol. 38(1): 1-4.
- [8] Xiao, C.L., Xiao, L.S., Gong, B.F., 2011. A study of extracting molybdenum from hydrochloric acid leach liquor of Ni-Mo ore using N235(in Chinese)[J]. China Molybdenum Industry, 2011, 35(2): 7-11.

[9] Zeng, L, Cheng, C.Y., 2009. A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts. Part II: Separation and purification[J]. Hydrometallurgy, Vol. 98: 10-20.

Solvent extraction of zinc and nickel by various methods from zinc plant filter cake

*Davood Moradkhani, Faculty of Engineering, University of Zanjan, Zanjan, Iran
; Hossein Kamran Haghighi Department of Mining and Metallurgical Engineering,
Amirkabir University of Technology, Tehran, Iran
; Behzad Sedaghat, Research and Engineering Company for Non-ferrous Metals
(RECO), Zanjan, Iran*

In the present research, various methods of separation and recovery of zinc and nickel from filter cake of zinc plant were investigated. In one of methods, zinc and nickel were simultaneously extracted by 40% of D2EHPA followed by selective stripping of nickel at the pH of 2.8-3. In another method, separation of nickel and zinc was carried out by LIX 984N and D2EHPA and the result showed that at the first step, zinc can be extracted and separated from nickel by 40% of D2EHPA under the following condition: pH of 2.8, A:O of 1:3 in 5 min. Then, remained nickel in solution was extracted by 10% of LIX 984N (at the condition of pH of 5.25, A:O of 1:2 in 5 min.) Solvent extraction of zinc in sodium chloride media was done and as the results, 69.93% of zinc under the condition of 40 ~, 5 min time and pH of 3.6 was extracted. The results of stripping experiments illustrated that 180 g/L of sulfuric acid in organic to aqueous ratio (O:A) of 1:5, 71.35% of zinc stripped.

Keywords: Filter cake; zinc plant residue; solvent extraction; zinc; nickel

High selectivity for cobalt / magnesium separation by solvent extraction in a Pilot Plant

Maria Emília Moraes Castanho de Almeida, André Ribeiro Cotrim

Produquímica Indústria e Comércio S.A

Avenida Jorge Bey Maluf, 2985 Suzano, São Paulo – Brasil – Zip Code 08686-000

Objectives: Recovery of cobalt to produce high grade cobalt sulfate from cobalt concentrate containing 30 to 50% cobalt and main contaminants: 2 to 6% magnesium, 0.1 to 3.5% manganese, 0.1 to 1.5% copper and 0.05 to 0.2% zinc, using a phosphinic acid extractant, Cyanex[®] 272.

New results: Using two scrubbing stages Co/Mg selectivity was between 2000-3000 and with three stages selectivity was greater than 6.000 using a scrub solution of approximately 5g/L of cobalt (pH 4.4 to 4.8). The desired selectivity was reached only when used scrubbing configuration with OA ratio of 10:1. It was also found that is extremely important that the spent scrub solution does not recirculate into the feed tank itself. This spent scrub must be collected in another tank and then added to another PLS. Scrubb solution was prepared from the cobalt stripp, keeping the system self-sustained, but until the desired Co/ Mg ratio is reached, a cobalt sulfate solution of equivalent purity must be used. The leachate prepared by the reaction of cobalt concentrate with sulfuric acid wastreated for iron removal by oxidation/filtration after adjusting pH to 3 with lime and manganese removed by oxidation/filtration with potassium permanganate. The removal of manganese is very important, because manganese contained in the PLS will accumulate in the stripping solution compromising the quality of the purified cobalt sulfate, and increase sludge, which impairs on the operation.

The PLS adjusted to 10g Co/L and pH 4.5 to 5.5, contains typically Mg 2g/L, Fe < 10ppm, Mn < 200ppm, insolubles <100ppm, follows to solvent extraction with 20% Cyanex[®] 272 extractant. The flow of PLS used in the pilot plant was 42L/h. The typical stripp solution contains Co 60g/L, Mg 0.03g/L and is sent to the current process for the production of cobalt sulfate heptahydrate. The cobalt yield of the plant with two extraction steps was 92%, with three steps was 97% and with four steps 99%. The extraction stage used the concept of effect "scrubbing" in a counter-current system. In the first stage of extraction (PLS input) pH must be 4.8 and in the last stage of extraction (raffinate output) pH 5.5 to promote the exchange of magnesium in the organic load by cobalt contained in PLS.

Conclusions: The optimal configuration of the plant was found to have ten stages: four extraction, two scrubbing, two stripping, one regeneration and one neutralization stages. The typical cobalt sulfate has the following composition: Co 20%, Mg < 0,01%, Fe < 5ppm, Mn < 0,01%, Cu < 0,01%, Zn < 0,01%.

Significance of the work: It was possible to determine the optimal configuration of a solvent extraction plant to recover cobalt achieving Co/Mg selectivity greater than 2000 to produce high purity cobalt sulfate from a cobalt concentrate containing high levels of contaminants, especially magnesium. Such high selectivities for Co/Mg were not reported in the literature to the best of our knowledge. Most studies on the recovery of cobalt are intended for the production of cobalt by electrowinning and do not require the removal of magnesium to the levels reached by the current process.

Versatic 10 Acid/NICKSYN™ Synergistic System versus D2EHPA-Cyanex 272 for the Recovery of Cobalt from Typical DRC/Zambian Copper-Cobalt Leach Liquors

*S.J. Archer^{*1}, V. Coetzee², J. Scheepers, A.C. du Preez³, M. H. Kotze⁴,*

Summary

The production of a premium grade cobalt requires stringent control of impurity concentrations in the cobalt advance electrolyte, in order to obtain an electrowon Co with a purity of >99.3%. Typically such a Co refining circuit would, prior to the recovery and upgrading of the Co, entail oxidative precipitation of Fe and Al, Zn, Ca and Mn removal with di-(2-ethylhexyl)phosphoric acid (D₂EHPA) followed by subsequent upgrading and recovery of cobalt with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272).

This paper considers the Versatic acid/Nicksyn™ synergistic system as an alternative to the conventional solvent extraction (SX) unit operations with D₂EHPA and Cyanex 272. This synergistic system provides not only an option for the recovery and efficient separation of Co from Ca and Mg, but also gives the option of selecting the degree of Mn co-extraction.

The technical and commercial aspects of the two refining circuits are compared in a desktop trade-off study, in which estimated cash flow differentials are used to evaluate the two flow sheets. A stochastic economic model was used to estimate the revenue, and operating and capital costs using discounted cash flow techniques.

Introduction

Copper processing circuits on the Copperbelt in Southern Africa require a bleed stream to avoid the build-up of impurities whilst also maintaining the water balance within the leach circuit. This bleed stream is typically the feed to a cobalt purification circuit, provided that cobalt is a targeted by-product.

Several metal species are usually present in such a bleed stream, including Cu, Co, Fe, Al, Mn, Zn, Ni and Mg. The treatment of this bleed stream for the production of a premium grade Co cathode requires stringent control of impurity concentrations in the Co advance electrolyte, in order to obtain an electrowon Co cathode with a purity of >99.3%. Discussions and reviews of some of the successful Co refining circuits are summarised in the literature (Cole & Feather, 2008), (Cole, Sole & Feather, 2006) and (Roux *et al.*, 2007).

Typically such a Co refining circuit would, prior to the recovery and upgrading of Co, entail oxidative precipitation of Fe, precipitation of Al and most of the Cu, Zn, Ca and Mn removal with D₂EHPA, followed by the subsequent recovery and upgrading of Co with Cyanex 272.

^{*1} Corresponding author, DRA Mineral Projects (Pty) Ltd, Sidney.Archer@draglobal.com

² DRA Mineral Projects (Pty) Ltd

³ Mintek

⁴ LANXESS (Pty) Ltd, South Africa

This paper considers, as an alternative to the aforementioned circuit, the use of a synergistic system to replace both the D₂EHPA and Cyanex 272 solvent extraction (SX) unit operations. The SX circuit using the Nicksyn™ reagent in combination with Versatic 10 acid would not only provide for a more effective approach for the recovery and upgrading of Co and its effective separation from Mg and Ca, but also allows control over the degree of Mn co-extraction.

Although the Nicksyn™ extractant would also recover Ni, the Ni content in the Copperbelt ores is typically very low. Any Ni present could be removed from the advance electrolyte via conventional ion exchange (IX) technology.

The comparison outlined in this paper should not to be regarded as definitive, but rather as a general guideline as each operation and application is unique.

Theory

A typical cobalt bleed stream composition (after Fe and Al removal) is shown in Table 1.

Table 1: Bleed stream composition (g/L) post Fe and Al removal.

Average elemental concentrations in g/L									
Element	Co	Mg	Mn	Ca	Ni	Zn	Cu	Fe	Al
Concentration	3 - 8	2 - 3	0.1 – 1.5	0.6	<0.05	<0.05	<0.05	<0.05	<0.05

Selected metal distribution equilibria for pH versus extraction using various organic extractants are shown in Figure 1.

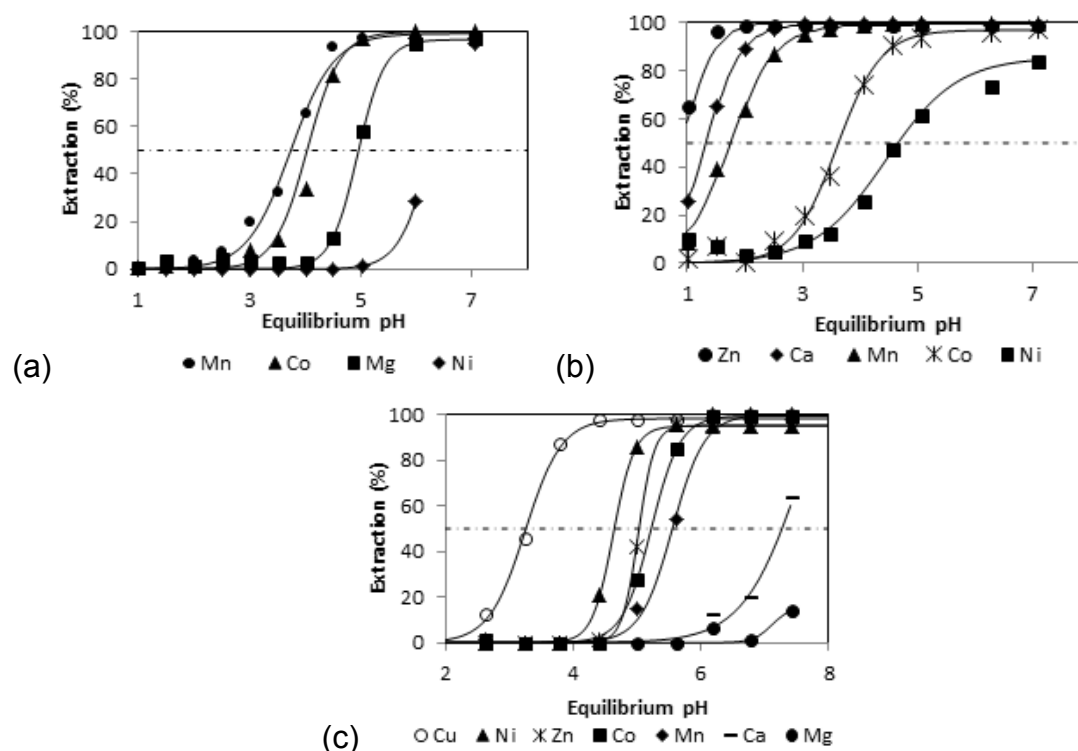


Figure 1 : Typical metal distribution equilibria for the extraction of metals with (a) 15% (v/v) Cyanex 272 (b) 20% (v/v) D₂EHPA (c) 0.5M V10 & 0.5M Nicksyn™

In the case of a phosphinic acid solvent extractant (Cyanex 272), the extraction of manganese prior to cobalt is evident from the order of extraction of the metals shown in Figure 1(a):



When this extractant is used for the recovery and upgrading of cobalt from such a stream, often operating in a closed loop with electrowinning (EW) to produce high grade Co metal, the Mn is quantitatively extracted and reports to the EW circuit. Although some Mn precipitates at the anodes as manganese dioxide (MnO_2), the majority of the Mn has to be bled from the EW circuit and the Co is recovered from this bleed stream via selective precipitation. However, the treatment of this bleed stream for Co recovery is costly, as the Co has to be recycled to the various Co purification circuits and hence additional Co losses are incurred.

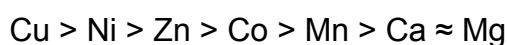
In addition, all the Cu and Zn present in solution would be co-extracted by Cyanex 272 (du Preez *et al.*, 2007) and if optimum Co recovery is targeted, some Mg will be co-extracted (while Ca will be rejected). The Mg co-extraction would have to be either scrubbed from the organic, or bled from the electrowinning circuit.

To cope with the Mn and Zn present in the feed stream, D_2EHPA is employed as an extractant. As indicated by the order of metal extraction depicted in Figure 1(b), these metals are preferentially extracted before Co in the following order:



If relatively efficient Mn extraction is targeted, Ca will co-extract to an even larger extent, and some Co will be co-extracted. This loss of Co would have to be limited via scrubbing of the loaded organic.

In contrast to these two systems, the extraction of metals from a similar stream using a synergistic mixture of 0.5 M Versatic 10 acid (V10) plus 0.5 M Nicksyn™ in Shellsol D70 is illustrated in Figure 1(c). The order of extraction of the metals is as follows:



The synergistic effect of Nicksyn™ when added to V10 acid has been extensively reported in the literature (Du Preez & Kotze, 2013), (Du Preez & Preston, 2004) and (Du Preez *et al.*, 2007) and some of the results are summarised in Figure 2. The $\Delta\text{pH}_{50}^{\text{Ca-Co}}$ increased from 0.56 pH units, when a 0.5 M V10 acid alone is used, to 2.01 units when 0.5 M V10 acid mixed with 0.5 M Nicksyn™ is used. Similarly the $\Delta\text{pH}_{50}^{\text{Mn-Co}}$ increased from 0.05 to 0.35 pH units.

Any Ni present in the feed solution will be co-extracted with the Co, which is extracted in preference to Mn, with the option to reject Ca and Mg almost quantitatively. Although this extractant would also extract all Cu and Zn from the feed stream, these impurities (Cu, Zn and Ni) could be removed from the advance electrolyte via conventional IX technology.

Mn removal is therefore not required via oxidative precipitation in the Fe precipitation step as it is in the conventional system, instead it can be rejected using the synergistic system. Scrubbing of the loaded organic would need to be incorporated to minimise Mn co-extraction.

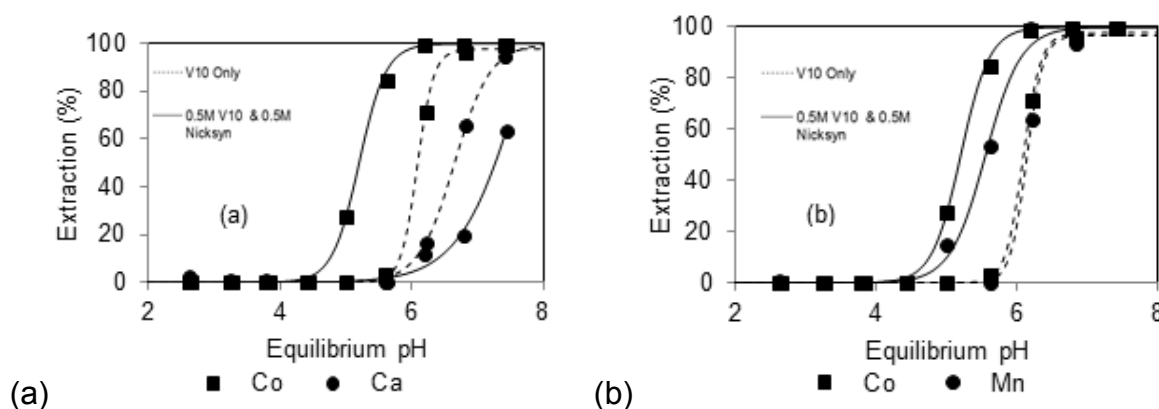


Figure 2: Synergistic effect of Nicksyn™ on the extraction of metals from sulphate solution using 0.5 M V10 acid alone or with 0.5 M Nicksyn™ in Shellsol D70 for (a) Co-Ca and (b) Co-Mn separation

Alternative processing routes considered for Mn removal from the bleed stream prior to Co recovery includes oxidative precipitation of MnO_2 or Mn_2O_3 in the Fe removal circuit using sulphurous acid (Muzadi & Kotze, 2013) followed by the selective precipitation of Co hydroxide. Although these unit operations have been optimised in laboratory test work, they would incur significant capital and operating costs, and cobalt losses could be 1% to 5%.

Basis for trade-off study

For both, the V10/Nicksyn™ synergistic system and the D_2EHPA / Cyanex 272 circuit (Figure 3 and Figure 4 respectively), conceptual process design criteria were developed and cost estimation was completed to determine the likely capital and operating differential costs for these two circuits.

All areas common to both circuits were excluded from the analysis. These plant areas include ore receiving, crushing, milling, classification, leach, Cu-SX, and Fe/Al removal.

Probability distributions were applied to the key system variables used in the model in order to describe the inherent uncertainty associated with them. The difference in Co revenue between the circuits, although not large, was included in the analysis.

D_2EHPA -Cyanex 272 Refining Circuit (Figure 3)

This base-case circuit incorporates Zn, Ca and Mn removal via D_2EHPA followed by the recovery and upgrading of Co with Cyanex 272. The loaded strip liquor/advance electrolyte is subsequently polished with an aminomethylphosphonic acid chelating resin to remove any deleterious impurities (Cu and Zn) which would not be captured by the Cyanex 272. The loaded resin is stripped completely with a strong

acid and the eluate is recycled to the front-end of the circuit. Stripped resin is converted to the Na form prior to loading. The concentrations of Mn, Mg and/or Na are controlled by means of a bleed stream from the spent electrolyte.



Figure 3 : D₂EHPA-Cyanex 272 Refining Circuit Block Flow Diagram

V10/Nicksyn™ Synergistic Refining Circuit (Figure 4)

The proposed circuit configuration, shown in Figure 4, involves replacing both the D₂EHPA and Cyanex 272 solvent extraction unit operations with a V10/Nicksyn™ synergistic system.



Figure 4 : V10/Nicksyn™ Synergistic Refining Circuit Block Flow Diagram

After the oxidative precipitation of Fe and Al, the Co in the bleed stream is recovered and upgraded using a V10/Nicksyn™ synergistic mixture. Owing to the inherent characteristics and selectivity of the synergistic system, the Zn, Cu and Ni are co-extracted into the advanced electrolyte. Similarly to the previous circuit, Cu and Zn are removed with an aminomethylphosphonic acid resin. However, in addition to these elements, Ni is removed with a chelating resin containing the bis-picolylamine functional group. In both instances, the loaded resin is first stripped with a weak acid to recover the majority of the co-loaded Co, followed by a strong acid strip to remove the remaining metals. The weak acid eluate is recycled to the front-end of the circuit, whereas strong acid eluate is routed to neutralisation. The concentrations of Mn, Mg or Na are controlled with a bleed from the advanced electrolyte which also serves to convert the aminophosphonic resin to the Co form after elution.

Financial model results

The financial valuation was done on a bare-bones basis, in real terms and did not consider the effects of taxes, interest, financing models or any escalation. The costs shown are not to be regarded as definitive, but rather differential or incremental cost estimates, since all common items have been excluded from the analysis.

Based on preliminary process flow diagrams and mass balances, equipment lists were produced for both circuits. Capital costs for major equipment items were estimated using a database of recently completed projects or studies. After applying typical factors to estimate the supply and erection costs for the civil, structural, platework, piping, electrical, control and instrumentation disciplines, capital costs were obtained for both circuits.

Operating cost estimates were based on the outcomes of preliminary mass balances. Calculation of reagent consumption rates for both circuits was based on a number of calculations, assumptions, benchmarks, public domain data, vendor data and test work results,. The reagent costs were derived from the estimated rates of consumption for key reagents and using DRA's extensive reagent cost database. The cost for specialised reagents were obtained directly from reagent/chemical suppliers. Power, labour and general maintenance costs were not considered due to the small differential expected between the options.

Based on the expected probability ranges assigned to capital, reagent consumption and reagent supply rate estimates, Figure 5 provides a scatter plot of estimated capital and operating costs for both options. The graph shows the outcomes from Monte Carlo simulations, where each data point represents a simulation outcome. The error bars represent the 90% confidence band.

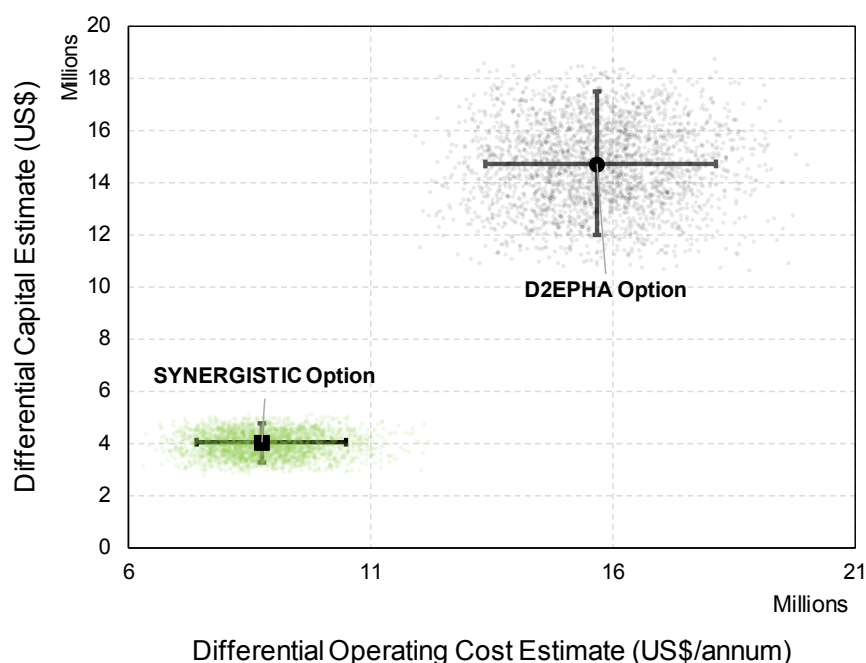


Figure 5: Operating and capital cost differential estimates (bars show the 90% confidence range for simulated outputs)

Figure 6 shows output probability distribution for the differential $NPV_{10\%, \text{real}}$ between the two circuits. The positive number is in favour of the V10/Nicksyn™ option.

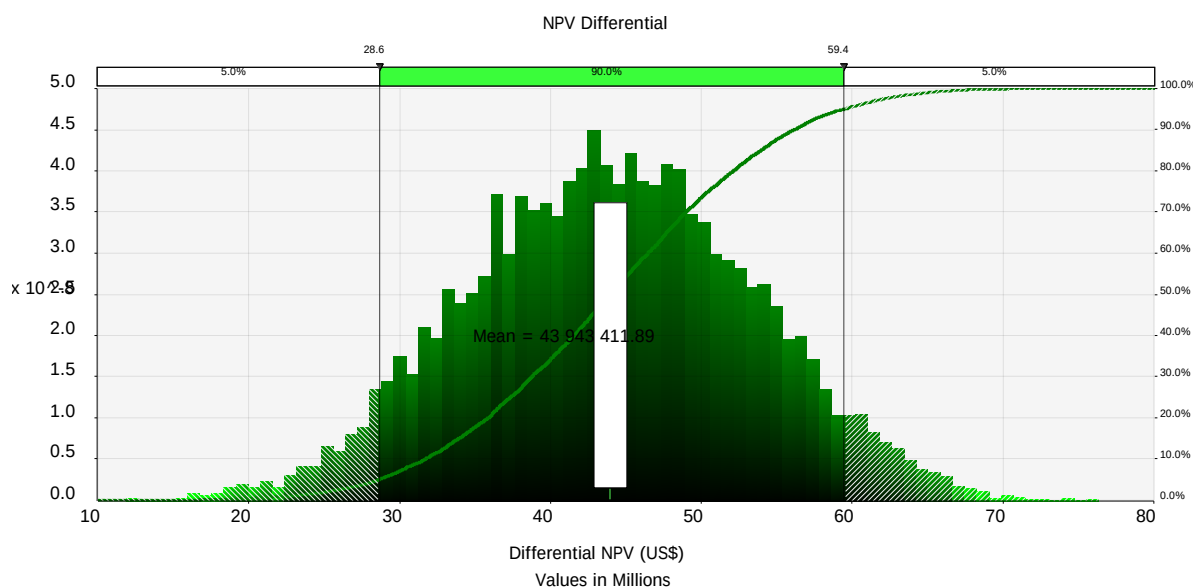


Figure 6: Differential NPV(10%, real) between the two circuits. The positive differential is in favour of the V10/Nicksyn™ option.

Conclusions

Based on the modelling exercise, the use of a V10/Nicksyn™ system to replace both the conventional D₂EHPA and Cyanex 272 solvent extraction (SX) unit operations is expected to provide both capital and operating costs benefits, but may result in a small drop in Co recovery. Despite the marginal reduction in metal output, and based on the design criteria used in the model example, the synergistic circuit is estimated to provide a pre-tax NPV improvement of between US\$20m and US\$70m over a 10 year life of mine.

Acknowledgments

The authors would like to thank Mintek and DRA Mineral Projects for making the necessary resources and information available, needed to complete this study.

References

1. Cole, P. (2002), The Introduction of Solvent Extraction Steps During the Upgrading of a Cobalt Refinery, Hydrometallurgy 64, 69 -77
2. Cole, P., & Feather, A. (2008). Processing of African Copper-Belt Copper-Cobalt Ores: Flow sheet Alternatives and Options. Proceedings of ISEC 2008, I, pp. 131-138.
3. Cole, P., Sole, K., & Feather, A. (2006, April). Solvent Extraction Developments in Southern Africa. Tsinghua Science and Technology, 11(2), 153-159.
4. Du Preez, A.C., Kotze, M.K. (2013) Evaluation of a Versatic 10 acid/Nicksyn™ Synergistic system for the recovery of nickel and cobalt from a typical laterite leach liquor. Base Metals Conference 2013 (pp. 192-208). The Southern African Institute of Mining and Metallurgy.
5. Du Preez, A.C., Preston, J.S. (2004) Separation of nickel and cobalt from calcium, magnesium and manganese by solvent extraction with synergistic mixtures of carboxylic acids. The Journal of The South African Institute of Mining and Metallurgy. 333-338
6. Muzadi, P., Kotze, M.H. 2013. A new development in the oxidative precipitation of Fe and Mn by SO₂/air, Base Metals Conference 2013 (pp. 223-234). The Southern African Institute of Mining and Metallurgy.

7. René du Preez et. al. 2007. Solvent Extraction test work to evaluate a Versatic 10/Nicksyn™ synergistic system for nickel-calcium separation. The Fourth Southern African Conference on Base Metals (pp. 193-210). The Southern African Institute of Mining and Metallurgy.
8. Roux, L., Minaar, E., Cilliers, P., Bellino, M., & Dye, R. (2007). Comparison of Solvent Extraction and Selective Precipitation for the Purification of Cobalt Electrolytes at the Luilu Refinery, DRC. The Fourth Southern African Conference on Base Metals (pp. 343-364). The Southern African Institute of Mining and Metallurgy.

Strong versus Weak Acid Stripping of Loaded D₂EPHA Extractant Containing Calcium

*S.J. Archer^{*1}, V. Coetzee², A.J. du Toit², E.L. Forner² & M.H. Kotze³*

Refining of copper from Cu-Co containing ores in Africa is well understood whereas the purification of cobalt is more challenging due to the impact of deleterious impurities on the electrowon metal. Cobalt in most cases is a secondary product and is co-extracted with copper and other impurities during leaching. Copper is recovered from the Pregnant Leach Solution (PLS) by means of copper Solvent Extraction (SX) and the resultant raffinate is recycled to leach to maximise acid utilisation. The water balance and build-up of impurities, including cobalt, are managed by bleeding the CuSX raffinate. This bleed stream is then further processed to recover cobalt. Numerous process options for the purification of cobalt metal can be considered, each comprising of various processing steps.

One of these processing routes considers SX as a means to purify the bleed stream prior to cobalt Electrowinning (EW). Zinc and manganese are extracted from the bleed stream using D₂EPHA to produce an impurity depleted raffinate which then feeds a cobalt SX circuit interlinked with CoEW. A feed stream to D₂EPHA SX containing 0.15 g/L zinc, ~2 g/L manganese and saturated with calcium, requires a high extractant concentration to remove more than 90% of the manganese with <1% cobalt loss. Targeting manganese removal would result in the co-extraction of calcium when using D₂EPHA as extractant and thus careful consideration is required when stripping the organic specifically with regards to acid consumption, the formation of gypsum and the leakage of Zn into the raffinate. This study focuses on the method of stripping of the loaded extractant and the impact it has on downstream unit operations and equipment. Stripping of loaded organic with strong and weak acid strip liquors are compared in a high level trade-off study in which cost differentials are used to evaluate the various methods of stripping. A stochastic approach is also used to quantify the differential in operating (OPEX) and capital (CAPEX) expenditure between the stripping methods. This has been done by utilising Monte Carlo simulations. A probability distribution has been applied to the key system variables in the simulation in order to describe the inherent uncertainty associated with them.

Introduction

Background

The refining of Cu from Cu-Co ores from the copper belt in Africa is well understood whereas that of Co is more intricate due to the deleterious impact of impurities on the electrowon metal. A Cu circuit consists typically of crushing, milling, thickening, reductive atmospheric leach, followed by solid-liquid separation and washing of the residue, CuSX and CuEW. The build-up of impurities (Fe, Mn, Al, Zn, Mg) and Co is managed in the Cu circuit using a bleed (typically a low grade SX raffinate bleed, depending on the circuit configuration). This Cu circuit bleed serves as feed to a Co purification circuit. A comprehensive description of some of the successful impurity removal operations and SX implementation for Co refining are summarised in literature (Roux *et al.*, 2007), (Cole, Sole, & Feather, 2006) and (Cole & Feather,

^{*1} Corresponding author, DRA Mineral Projects, sidney.archer@DRAGlobal.com

² DRA Mineral Projects

³ Lanxess

2008). In general, and for this article, SX, ion exchange (IX) and undivided EW are selected as basis for purification. In terms of economics, higher metal tenors reduce the downstream equipment sizing and lower capital expenditure (CAPEX). For this reason, the purification unit operations are applied to a concentrated Co stream. The concentrated Co Stream is produced by precipitation of a dilute Co stream (Cu circuit bleed) with burnt lime which is then redissolved to a higher metal tenor. Table 1 represents a typical Co solution feed composition saturated with calcium.

Table 1 Typical D₂EPHA SX feed solution composition

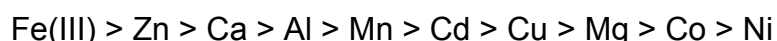
	Cu	Co	Fe	Al	Zn	Mn	Ca
Concentration, mg/L	30	16 903	-	-	146	1 900	688

A purification sequence, as considered for this article, is shown in Figure 1 which includes Zn/Mn SX using D₂EPHA as the extractant.



Figure 1 A cobalt stream purification sequence as considered for this paper

The typical D₂EPHA selectivity is shown below (Nicol, Fleming, & Preston, 1987) and (Sole, 2006):



The D₂EPHA SX circuit's primary function is to remove Mn and Zn in order to limit the build-up of Mn in the subsequent CoSX-EW circuit and to prevent the contamination of cathodes with Zn. It should be noted that allowing Mn to accumulate in the Co electrolyte could result in the formation of permanganate which may deleteriously oxidise the CoSX extractant (Krönighofer, Archer, & Bradford, 2009). Targeting Mn removal with D₂EPHA results in the co-extraction of Fe(III), Zn, Ca and Al as shown above in the selectivity sequence. Ferric loads strongly onto D₂EPHA and requires a HCl restrip to manage its build-up on the organic. Zn, Ca and Mn are stripped from the organic when using H₂SO₄. However, careful consideration is required when considering the strength of H₂SO₄ and its impact on acid utilisation, limestone/lime consumption and the possible leakage of Zn into the raffinate (i.e. CoSX feed).

To avoid gypsum precipitation in the strip circuit, the strip liquor (SL) flowrate must either be equal to or greater than the feed stream to Zn/Mn SX to prevent saturation of calcium. In doing so, the SL acid concentration needs to be as low as possible in order to reduce operating expenditure because the loaded strip liquor (LSL) is sent to neutralisation to precipitate impurities. Neutralisation of LSL is essential to prevent the build-up of Zn in the processing facility and thus cannot be recycled to leach. Reducing the acid tenor, however, impacts largely on the stripping efficiency of Zn, thus allowing Zn build-up on the organic. This build-up could impact on the extraction efficiency resulting in >2 mg/L Zn deporting to the raffinate. To avoid this, the

proposed upfront IX circuit is repositioned in the Zn/Mn SX raffinate stream and appropriately sized to remove both Cu and residual Zn.

An alternative to dilute acid stripping would be to induce gypsum precipitation in the strip circuit by means of a strong acid strip with a much lower flowrate in order to minimise operating expenditure with regards to acid consumption and downstream neutralisation costs. Gypsum precipitation in SX is avoided in most cases, however the concept of precipitation during stripping has been applied for tantalum purification (Cole, Sole, & Feather, 2006). The main difference between these operations is gypsum scaling. Piloting test work conducted at Mintek showed the formation of a competent uniform gypsum precipitate, which settled rapidly to the bottom of the settler, see Figure 2. Scaling was observed to be an issue specifically at surfaces where high flows were encountered such as in the pump mixer (specifically the impeller) and overflow weirs. This can, however, be overcome by allowing for standby mixer-settlers and engineering the equipment/piping for easy maintenance and precipitate (crud) removal.



Figure 2 Settled gypsum precipitate in a D₂EPHA strong acid strip circuit

Furthermore, a third stripping configuration can also be considered in which selective stripping is employed using a combination of both weak and strong acid to improve the Zn stripping efficiency and to prevent gypsum precipitation.

Data and parameters

The extraction behaviour as a function of pH is selected for a 20% (v/v) D₂EPHA extractant, in Shellsol 2325 (~25% aromaticity) diluent. This is shown in Figure 3 together with an extraction isotherm, showing a McCabe-Thiele construction at a pH of ~2.2 and caters for a 95% stage efficiency.

The equilibrium strip isotherms were generated experimentally by contacting a maximum loaded 20% D₂EPHA sample with 15 g/L H₂SO₄ at various O:A ratios (refer to Figure 4.)

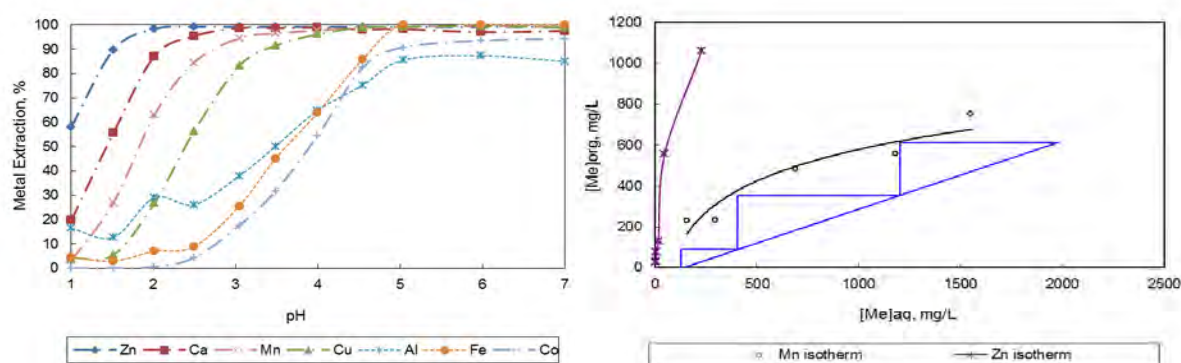


Figure 3 a) Extraction as a function of pH for 20% D₂EPHA b) Extraction isotherm at pH ~2.2

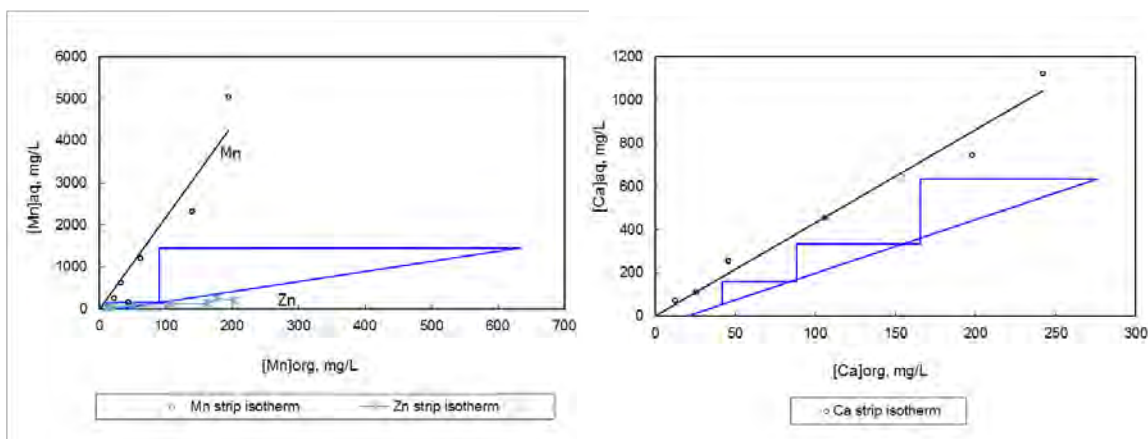


Figure 4 Stripping isotherms generated for 20% maximum loaded D₂EPHA with 15 g/L H₂SO₄ at various O:A ratios for a) Mn & Zn b) Ca

The Zn strip isotherm using a dilute SL (15 g/L H₂SO₄) is located below the Mn operating line (see Figure 4) demonstrating that a limited amount of Zn stripping occurs under the conditions chosen for constructing the strip isotherm. Zn extraction is dependent on the residual Zn concentration of the stripped organic, therefore more stringent stripping conditions have to be applied to enable Zn extraction to low zinc tenors (< 2 mg/L) in the raffinate.

Description of options

The pH profile selected across D₂EPHA SX ranges from ~2.0 to 2.5. The D₂EPHA LSL stream is neutralised for impurity control by means of precipitation to prevent impurity build-up in the production facility. This will impact on the reagent consumption and operating cost of the circuit. Therefore, three options are evaluated for the stripping of loaded D₂EPHA organic:

1. A concentrated (or strong) acid solution (150 g/L H₂SO₄), where gypsum formation in the mixer-settlers will be inevitable due to the O:A ratios required (Extraction O:A of 3 and a Strip O:A of 62);
2. A dilute (or weak) acid solution (15 g/L H₂SO₄), operated below calcium saturation in the strip circuit to prevent gypsum formation (Extraction O:A of 3 and a Strip O:A of 2.44);

3. A selective strip circuit, initially stripping with a dilute acid solution (10 g/L H_2SO_4 at an O:A of 2.6) followed by a final strip using a concentrated acid solution as SL (62 g/L H_2SO_4 at an O:A of 10). The operating parameters were optimised to prevent gypsum formation and to minimise overall reagent consumption.

It was identified that a dilute strip could result in Zn reporting to the raffinate and high lime consumption for neutralisation of the free acid in the LSL. The dilute strip option would require the IX unit operation to be repositioned to the D₂EPHA SX raffinate stream and sized accordingly for the removal of both Cu and Zn.

The strong acid strip option will generate crud (gypsum precipitate) and scaling, which results in more frequent maintenance requirements. Some of these risks can be mitigated with the use of anti-scaling agents (effect on extraction to be confirmed), and carefully engineered equipment.

In addition, gypsum formation in the concentrated strip circuit can be mitigated by moving the D₂EPHA SX into the Co electrolyte stream, as calcium is rejected during CoSX when employing CYANEX 272. This configuration mitigates the need for increasing the IX sizing for Zn, and an optimum acid concentration of the strip liquor can be determined. It is expected that this circuit configuration will result in higher Co losses. The viability of this option will be evaluated in a subsequent study.

Techno-financial evaluation

Basis for comparison

The techno-financial evaluation assumes three typical SX, IX and undivided EW based Co processing flow sheets. The analysis was done on a bare-bones basis, in real terms and does not consider the effects of taxes, interest, financing models or any escalation. Note that the costs shown are not to be regarded as definitive, but rather differential costs. Any common items between the various options have been discarded from the analysis.

CAPEX basis

An extensive spread sheet based analysis model was developed for this evaluation. All equipment is of standard supply apart from a redesigned, specialised settler that can handle the formation and removal of gypsum solids. A standby piping, pump-mixer and specialised settler arrangement is included to assist with maintenance requirements for the concentrated acid strip option. It is assumed that a normal centrifuge crud system will be able to handle the removal of the gypsum solids from the specialised settler's underflow. The crud system includes a centrifuge with an option to incorporate diluent addition as a means to recover entrained extractant.

The D₂EPHA SX strip and IX circuit configurations for the different options evaluated are listed in Table 2.

Table 2 Option configuration and equipment considerations

Units	Concentrated acid strip	Dilute acid Strip	Selective acid strip
Pump mixer – settler	0	2	4 (3x dilute 1x concentrated strip)
Pump mixer – specialised settler	3*	0	0
IX position	SX feed	SX raffinate	SX feed
IX sized for	Cu	Zn	Cu

* Two operational and one standby unit.

The main CAPEX considerations include:

- Differences in major mechanical equipment;
- A typical design criteria for each flow sheet in support of mass balancing and equipment sizing;
- Mechanical equipment costs determined from recently executed studies as well as DRA's internal database;
- Internal DRA factors applied for civils, structural (supply and erection), platework (supply and erection), mechanical erection, piping (supply and installation), electrical, control and instrumentation (supply and installation), transport, project services and P&G's.

OPEX basis

The major OPEX considerations include:

- Reagent costs estimated from DRA's recently updated (2013) reagent supply database;
- Reagent consumptions determined from high level mass balances, and include: Sulphuric acid for SX strip and IX elution; NaOH for pH control of SX, pH adjustment prior to IX, and IX resin regeneration; S950 resin in bi-Na form for Cu and Zn removal; burnt lime for LSL neutralisation (impurity control); solvent losses due to organic entrainment in LSL, raffinate, and gypsum solids; and resin losses;
- Power, labour and general maintenance costs were found to have a negligible effect on the differential OPEX.

Results and uncertainty

Based on the expected ranges and uncertainties assigned for key reagent consumption and supply rates, Figure 4a shows a scatter plot (differential CAPEX vs OPEX) of the various options that summarises the uncertainty scatters. Figure 4b shows a box-plot of the differential Net Present Cost for each option relative to the strong acid strip option.

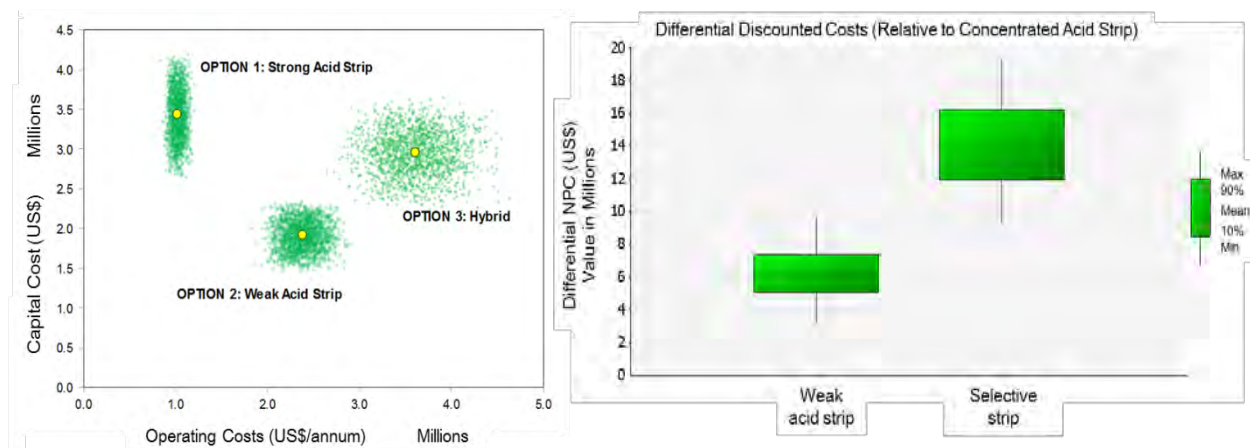


Figure 5 Financial analysis: Differential a) CAPEX vs OPEX b) Discounted costs (relative to strong acid strip)

These figures show that both weak acid and selective strip are characterised as higher cost options over the life of mine (assumed 10 years), despite the requirement for lower CAPEX.

The main contributors to uncertainty were evaluated for each option. In general the lime supply cost and consumption uncertainty, followed by acid supply cost, contributed the most to the overall uncertainty. Nonetheless, despite the uncertainty relating to lime (\$300-\$450/t) and sulphuric acid (\$80-\$130/t) supply cost, it was found that the strong acid strip option returns the best value proposition.

Conclusion

A stochastic approach was used to quantify the differential in OPEX and CAPEX between the stripping methods and positioning of the IX unit operation. This has been done by utilising Monte Carlo simulations. A probability distribution has been applied to the key system variables to be used in the simulation in order to describe the inherent uncertainty associated with them. The analysis showed an OPEX saving over life of mine if a strong acid strip is adopted. It was estimated that the discounted cash flow benefit is between US\$4m and US\$10m, on a pre-tax basis. It was found that the selective strip option is expected to have the highest life cycle cost of all the options considered. Moreover, despite the uncertainties identified, the strong acid strip option returns the best value proposition. Furthermore, the technical risks associated with the strong acid strip can be mitigated with: anti-scaling agents (to be confirmed); the design of a specialised mixer-settler that includes a standby unit (also included in the techno-financial evaluation); with careful engineering to improve

maintenance requirements; and procedures for reducing fire risks.

Acknowledgment

Thank you to Mintek for making test work data and information available, thus allowing us to present this paper.

References

1. Cole, P., & Feather, A. (2008). Processing of African Copper-Belt Copper-Cobalt Ores: Flowsheet Alternatives and Options. *Proceedings of ISEC 2008, I*, pp. 131-138.
2. Cole, P., Sole, K., & Feather, A. (2006, April). Solvent Extraction Developments in Southern Africa. *Tsinghua Science and Technology*, 11(2), 153-159.
3. Krönighofer, T., Archer, S., & Bradford, L. (2009). A cobalt solvent extraction investigation in Africa's Copper Belt. *Hydrometallurgy Conference 2009* (pp. 329-340). South Africa: Southern African Institute of Mining and Metallurgy.
4. Nicol, M., Fleming, C., & Preston, J. (1987). Application to Extractive Metallurgy. In G. Wilkinson, R. Gilard, & J. McCleverty (Eds.), *Comprehensive Coordination Chemistry* (pp. 779-842). Oxford: Pergamon.
5. Roux, L., Minaar, E., Cilliers, P., Bellino, M., & Dye, R. (2007). Comparison of Solvent Extraction and Selective Precipitation for the Purification of Cobalt Electrolytes at the Luilu Refinery, DRC. *The Fourth Southern African Conference on Base Metals* (pp. 343-364). South Africa: The Southern African Institute of Mining and Metallurgy.
6. Sole, K. (2006). *Solvent Extraction and Ion Exchange: Short Course*. Johannesburg: Anglo Research (Project No. S200601535, Report No. 1).

Experimental design for solvent extraction of rare earth light and medium elements in hydrochloric acid media using D2EHPA in isoparaffin

*Clenilson da Silva Sousa Junior^{*1}, Marisa Nascimento², Carolina Bogéa da Costa³*

ABSTRACT

Modeling and simulation assists in developing procedures for the separation and purification of elements or compounds with high purity minerals. The technical design of experiments already has wide application in mathematical modeling of hydrometallurgical processes. According to the literature, several factors may influence the solvent extraction of rare earths in hydrochloric acid solutions by D2EHPA, such as: aqueous metallic solution, organic solution, aqueous/organic (A/O) ratio, time of contact and pH.

Rare earths constitute a group of elements belonging to the lanthanide transition elements with atomic numbers 57-71. They are often classified into two groups according to their atomic number with the light rare earths including La (57) to Eu (63) and the heavy rare earths including Gd (64) to Lu (71). The light rare earths often include element number 39, yttrium (Y).

The objective was to study the effect of 4 variables on the solvent extraction of Sm^{3+} and Nd^{3+} : D2EHPA extractant concentration, total rare earth concentration, aqueous solution pH, and the A/O ratio. The investigation was carried out using “cube + star” experimental design with center points thereby requiring $2^4 + 10 = 26$ experiments being conducted. A mathematical model was constructed from the resulting data using non-linear regression. It describes the results within the ranges studied with statistical satisfaction.

Keywords: rare earth; D2EHPA; modeling.

Introduction

Rare earths (RE) are a group of elements that belong to the group of transition elements metals (old group III-B). These metals can be classified according to their atomic number thereby causing a separation into groups classified into heavy (Gd-Lu), also known with the group of yttrium, and light (La-Eu), also known as the group of Cerium. Some authors still consider some elements classified as medium [1]. Many minerals are rich in these elements, and currently there are about 200 minerals TR distributed in a variety of classes such as halides, carbonates, oxides, phosphates, silicates and other [2].

Some minerals have shown commercial interest as: gadolinite, euxenite, apatite, monazite, bastnaesite and xenotime [3]. The largest bastnaesite reserves are in China and the United States. In Brazil, India, South Africa, Thailand and Sri Lanka occur in monazite sands and heavy minerals. Regarded as the giant market of RE, 57.7% of the global reserves of rare earths, in 2008, were in China, followed by the Russia and the USA. According to Andrade [4], in 2008, rare earths were not mined

^{1*} clenilson.sousa@ifrj.edu.br; Department of Chemistry, Federal Institute of Rio de Janeiro, IFRJ, Brazil.

² Service Clean Technologies/CPMA, Center for Mineral Technology, Brazil.

³ Service Clean Technologies/CPMA, Center for Mineral Technology, Brazil.

in the U.S.A., however, concentrates previously produced rare earths in Mountain Pass, CA, were processed to obtain a concentrate of lanthanum as well as neodymium with 25% praseodymium. In 2010, China had only 37% of known reserves of RE, however, even with the reduction of reserves China is responsible today for 97% of world production. Besides China, USA and the Russia, other major powers also have RE reserves: Australia, India, Brazil and Malaysia [2,5] as shown in Table 1.

Table 1 World Reserves of Rare Earth, in 2009 [6].

Countries	Reserves (tonnes)
China	36,000,000
Russia	19,000,000
USA	13,000,000
Australia	5,400,000
India	3,100,000
Brazil	48,000
Malaysia	30,000
Other countries	22,000,000
Total	99,000,000

Among the physic-chemical properties of these elements can give prominence to the atomic number, where the REE (rare earth elements) with atomic number pair are more abundant than those with odd number due to higher nuclear stability associated to with even number of protons. The presence of Thorium and Uranium is fairly common in TR containing minerals, especially monazite [6].

Some of the characteristics of these elements as magnetism, luminescence and fluorescence make the interest in these metals grow in the international market every year, mainly regarding the supermagnetics industry, production of LED lamps, fiber optics and other applications. Due to the great demand in the domestic and international RE, numerous research works have been developed to extract, separate and purify these elements of great commercial importance [6].

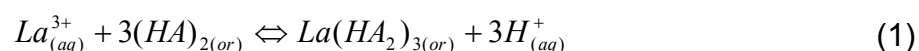
Theoretical

Solvent extraction is a technique which has been widely applied for the recovery of metals on the industrial scale, particularly the rare earth metals. This technique has the advantages of a high extraction capacity, fast kinetics and good separation and currently one of the main techniques of separation, purification and recovery of metallic components. Solvent extraction permits the efficient and selective transfer of

ionic species present in an aqueous solution to an organic phase. The process consists in adding an organic solution containing an organic solvent (extractant) capable of extracting the metal of interest of an aqueous solution containing different metals [7,8].

There is then a reaction between the metal and the extractant forming a chemical compound that has a greater affinity for the organic phase. After this process, the re-extraction and the recovery of metal the organic phase to the aqueous solution (containing the same chemical components previously used in preparing the aqueous phase to the extraction). The metal is then recovered into the new aqueous phase to yield the metal in pure form [9]. Organic solvents commonly used in this technique are: ethers, alcohols, amines, phosphorus compounds and carboxylic acids. According Lee [10], the best results occur when the extraction complexes are almost insoluble in water but quite soluble in the organic phase. In this study, tests were conducted using a chelating agent extractant with acid characteristics.

According to Lenz and Smutz [11], a general formulation can be derived from the reaction stoichiometry for the extraction of lanthanides (La) using the extractant D2EHPA, according to Equation 1:



The equilibrium constant for Equation 1 is given as follows:

$$K_M = [La(HA_2)_3]_{(or)} \cdot [H^+]_{(aq)}^3 / [La^{3+}]_{(aq)} \cdot [(HA)_2]_{(or)}^3 \quad (2)$$

According Lee [10], in practice, there are many species that coexist during extraction, as the M^{3+} , MA, MAn, MX, HA, MXA, among others, so it is convenient define as extraction constant (K) according to Equation 3:

$$K'_{ex} = [MA'_n]_{(or)} \cdot [H^+]_{(aq)}^n / [M']_{(aq)} \cdot [HA']_{(or)}^n \quad (3)$$

where $[MA'_n]_{(or)}$ is total metal concentration in the organic phase, regardless of the form, $[M']_{(aq)}$ is total concentration of all forms of metal in aqueous phase, and $[HA']_{(or)}$ is ligand concentration in the overall organic phase.

The most common way of evaluating the efficiency of the extraction process is through the distribution coefficient (D), defined as:

$$D = [M]_{(or)} / [M]_{(aq)} \quad (4)$$

where $[M]_{(or)}$ and $[M]_{(aq)}$ are respectively the total metal concentration in the organic and aqueous phases without regard to how the metal is present. The distribution coefficient is a measure that takes into account if a particular solvent will be able to properly extract a certain metal from an aqueous solution. Despite its limitations, the distribution coefficient is a parameter commonly used in studies of solvent extraction with dimensionless values different for each variable change [12]. According Nathsarma and Devi [13], the value of D depends on various factors such as the ratio between the aqueous and organic phase's ratio (A/O), extractant solution concentration, temperature, pH, and others. The two selective extraction of metals contained in the same liquor can be expressed using the separation factor (α), which can be defined as the ratio between distribution coefficients of the respective metals. A high value of the separation factor indicates the possibility of performing a selective extraction of metals. However, the distribution coefficient does not provide the ease of extraction of the metal from the aqueous phase as well as the required number of stages in the continuous process.

Methodology

The rare earth oxides used in this study were supplied by Stanford Materials Corporation Company with a purity of 99.9%. The organic extractant solutions were prepared by dissolving the acid bis (2-ethylhexyl) phosphoric acid of the Sigma Aldrich, with purity 99.9%, in isoparaffin (17/21), obtained from Ipiranga Company without any preliminary purification.

Stock solutions were prepared of 5.0 liters of synthetic liquor of the $RECl_3$, similar to a liquor produced from leaching Monazite, based on the percentage values of oxides reported by Nuclemon⁴ (without Cerium) and therefore with a total concentration of rare earths being 50 g L^{-1} as shown in Table 2. A total of 3 moles of rare earths need 9 moles of HCl to have total conversion to chlorides which can be accomplished with 1 L of concentrated HCl, the equivalent of 12 moles.

The extraction tests were performed by adding aliquots of 25.00 mL of aqueous solution (liquor TR) to 125 mL Erlenmeyer flasks with the addition of HCl per vial under constant agitation, in order to achieve the pH of the experimental design. Following stabilization of aqueous solution, 25.00 mL of organic solution were added to the flask. Tests were conducted at different ratios between the aqueous and organic phases (A/O). Erlenmeyer flasks were placed on a shaker orbital at 250 rpm for 15 minutes at room temperature.

⁴ Is a Brazilian company in the field of extractive metallurgy, working in research and technical work.

Afterwards the mixtures were transferred to a separator funnel, allowed to disengage for 40 minutes, and separated. Chemical analyzes of the initial aqueous solutions and the solutions after contact tests were performed by optical emission spectrometry with inductively coupled plasma (ICP-OES). The ionic concentrations in the organic phases were calculated by the difference between input data and output to their respective ratios A/O.

The design of experiments is an alternative way to determine how variables affect a particular response in a series of tests. The variables or input factors are first identified, and then systematically changed to assess the effects on the response via the generation of mathematical models of the process. It is a statistical tool used to determine the variables that most influence the response of the process with a goal of identifying what value the the variables should be in order to optimize the process [14]. The solvent extraction tests were conducted using the design experiments type "star + cube" with two the center points under varying conditions of the independent variables that may influence the extraction of neodymium and samarium: concentration, A/O ratio, the concentration of the organic extractant, and pH as presented in Table 3. Factors such as temperature and contact time were not considered in this study. The experimental results were statistically analyzed using the software STATISTICA ® 7.0 [15]. In total 26 tests were performed, with 4 levels for the variables in order to obtain a representative model for the process, as represented by Equation 5, which covers mainly the linear effects and the quadratic effects as well as the second order interactions for set of variables and levels below:

$$Y = a_0 + \sum b_i X_i + \sum c_i X_i^2 + \sum d_i X_i X_{i+1} \quad (5)$$

Table 2 Composition of Rare Earth oxides present in Monazite.

Components	Molecular weight	Mass added of oxide (g)	Mass of oxide (%)	Moles total
La ₂ O ₃	325.82	210.2	42.02	1.29
Pr ₆ O ₁₁	1021.4	48.7	9.74	0.29
Nd ₂ O ₃	336.48	174.7	34.93	1.04
Sm ₂ O ₃	348.70	24.2	4.84	0.14
Eu ₂ O ₃	352.00	3.2	0.64	0.02
Gd ₂ O ₃	362.60	15.2	3.04	0.08
Tb ₄ O ₇	747.60	3.7	0.74	0.01
Dy ₂ O ₃	373.00	4.7	0.94	0.02
Ho ₂ O ₃	377.80	2.2	0.44	0.01
Er ₂ O ₃	382.60	2.2	0.44	0.01
Y ₂ O ₃	225.81	11.2	2.24	0.10
Totals	-	500.2	100	3.01

Table 3 Levels of the variables of design of experiments for the solvent extraction of rare earths.

Level	-1	0	+1
[D2EHPA] (% v/v)	10	15	20
A/O	1/1.5	1/2	1/2.5
pH	0.5	0.75	1.0
[RE] total (g L ⁻¹)	30	40	50

Results and Discussion

From the analytical data, it was possible to calculate distribution coefficients (D) for Sm and Nd. It was observed that the values of D for Sm³⁺ exhibit higher values (between 8.00 and 58.67) than for Nd³⁺ (between 0.06 and 0.65) under the same experimental conditions. Based on these results we can say the extraction of samarium was more selective. From these experimental results, it was possible to develop a mathematical model using the Statistica® software using separation factors ($F = D_{Sm}/D_{Nd}$) as the response (dependent factor). The values of $F = D_{Sm}/D_{Nd}$ to all modeled points showed good fit, compared with the values generated experimentally and may be seen based on the residual values shown in Table 4.

To extract samarium from neodymium with maximum selectivity, the conditions yielding the largest separation factor should be selected which occurred with Test 13.

Based on the coefficients generated, it was possible to obtain an equation which represents the value of the ratio between the coefficients of two extraction of trivalent metals (Equation 6). However, a reduced equation can be derived which considers only the variables that have greater significance to influence the response (Equation 7).

$$\begin{aligned}
 F (D_{Sm}/D_{Nd}) = & 6,00472 - 0,99938.[D2EHPA] - 0,34406.[D2EHPA]^2 - \\
 & 0,07123.A/O - 0,07577.A/O^2 + 1,70306.pH - 0,58842.pH^2 - 0,27754.[TR] - \\
 & 0,18991.[TR]^2 - 0,56058.[D2EHPA].A/O - 2,85740.[D2EHPA].pH + \\
 & 1,85512.[D2EHPA].[TR] + 1,30754.A/O.pH - 0,34214.A/O.[TR] - \\
 & 0,03470.pH.[TR]
 \end{aligned} \quad (6)$$

$$\begin{aligned}
 F (D_{Sm}/D_{Nd}) = & 6,00472 + 1,70306.pH - 2,85740.[D2EHPA].pH + \\
 & 1,85512.[D2EHPA].[TR] + 1,30754.A/O.pH
 \end{aligned} \quad (7)$$

as indicated by the Pareto chart (Figure 1) from the observation of *p* values that are below 0.05. It was found that the product of the concentration of D2EHPA concentration and RE ([D2EHPA] x [RE]_{total}) is the variable that has the greatest influence on the ratio of the distribution coefficients of metals, followed by the concentration of total Rare Earths, the product of the ratio A/O and pH, concentration

of D2EHPA quadratic, quadratic pH, concentration of D2EHPA linear and ultimately the product of the ratio A/O and the total concentration of Rare Earths.

Of the four variables in Equation 7 that affect the response the greatest, three contribute positively such that, when their values get larger, the separation factor, F, gets higher. However, the other variable has a negative influence such that the lower its value, the greater the separation factor becomes.

Table 4 Values of distribution coefficients (D) to extraction of Neodymium and Samarium, and separation factor experimental and modelled.

Tests	DNd experimental	DSm experimental	F experimental	F modelled	Differences
1	0.06	0.28	4.76	4.73	0.03
2	0.12	0.33	2.75	2.78	0.03
3	0.21	1.33	6.31	6.52	0.21
4	0.12	0.67	5.50	5.04	0.46
5	0.12	0.60	5.12	5.14	0.02
6	0.07	0.34	4.65	4.80	0.15
7	0.24	1.33	5.57	5.29	0.29
8	0.12	0.62	5.15	5.43	0.28
9	0.33	1.66	4.98	4.21	0.78
10	0.12	1.00	8.25	8.68	0.43
11	0.65	3.01	4.63	4.92	0.28
12	0.24	0.91	3.84	4.71	0.87
13	0.12	1.36	11.33	10.80	0.54
14	0.57	2.46	4.33	3.78	0.55
15	0.25	2.55	10.21	10.35	0.14
16	0.15	0.90	6.02	6.11	0.08
17	0.15	0.87	5.78	6.23	0.45
18	0.07	0.46	6.80	6.82	0.02
19	0.27	1.54	5.73	5.35	0.38
20	0.27	1.66	6.27	6.30	0.03
21	0.13	0.67	5.33	5.42	0.08
22	0.10	0.73	7.12	7.18	0.06
23	0.26	2.11	8.18	8.31	0.14
24	0.22	1.73	8.00	7.75	0.25
25	0.15	0.73	4.86	4.50	0.36
26	0.18	0.27	1.50	1.86	0.36

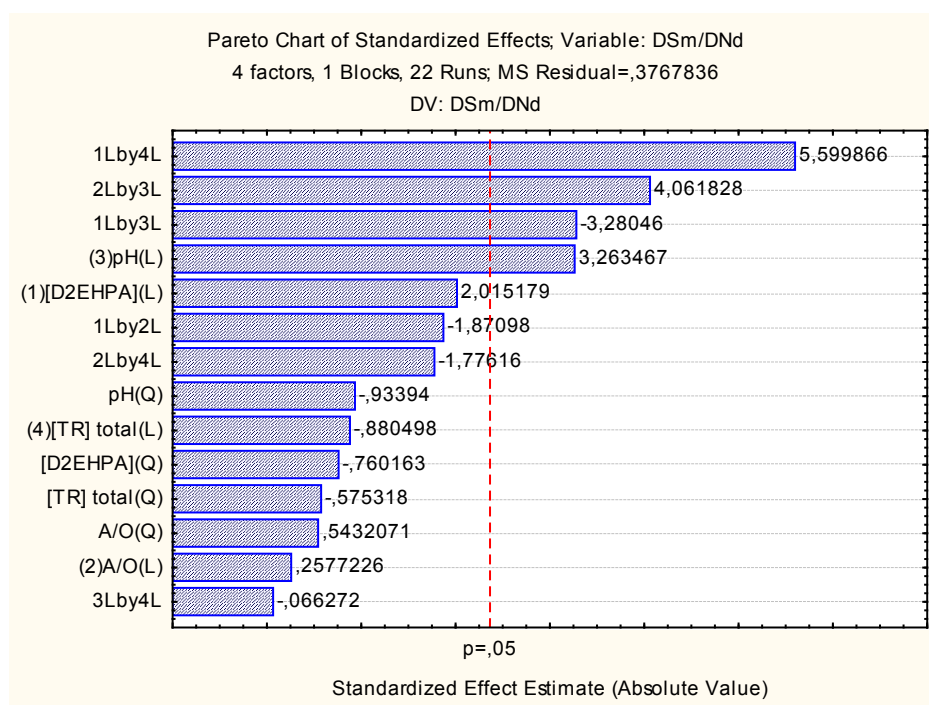


Figure 1 Pareto chart for representing the relationship between the extraction coefficients of Sm^{3+} and extraction coefficients Nd^{3+} .

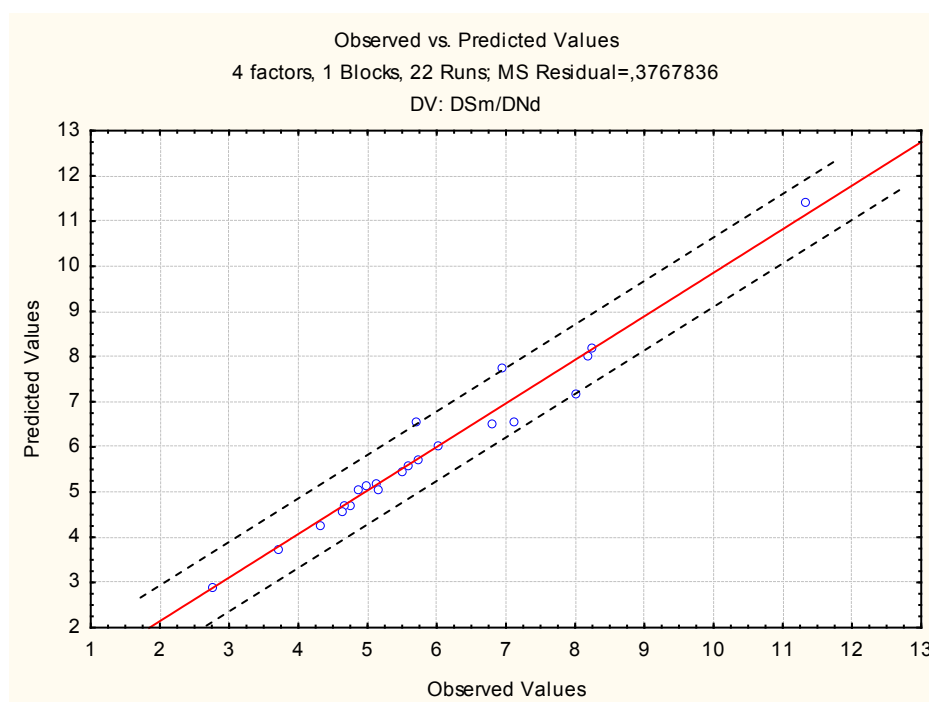


Figure 2 Normal probability chart waste to the relationship between the coefficients extraction of Sm (III) and the coefficients of extraction of Nd (III).

The distribution coefficient ratios from the tests are compared to the calculated values from the model in Figure 2. From the graph one can observe that the model has a good fit compared with the experimental data yielding a confidence level of 95% with most data points being close to baseline within the limits confidence.

The coefficients of the equation are displayed in a coded form depending on the levels of the variables (-1, 0 and 1) needing to be processed when the desire is to use their actual values. Table 4 shows the optimum values for obtaining higher values of F, present in chloride solution, according to the model.

Table 4 Levels of the variables of design of experiments for the solvent extraction of rare earths.

Variable	Variable minimum	Critical value	Variable maximum
[D2EHPA] (% v/v)	4.7	13.7	25.3
A/O	1:4.5	1:1.55	1:1
pH	0.25	0.93	1.4
[RE] total (g L ⁻¹)	19.4	32.3	50

Conclusion

This method, if applied beforehand to hydrometallurgical processes, can help advance solvent extraction of metals from aqueous solutions because it can show optimum conditions for extracting metals, decreasing reagent costs, decreasing operations time, and increasing extraction efficiency. It can be seen that the model has validity when compared to the values of extraction percentages determined by experimental techniques. In this regard, it is even possible to predict the behavior of liquor before conducting solvent extraction tests.

References

1. Vieira, E.V., Lins, F.F. *Concentração de minérios de terras-raras: uma revisão*. Rio de Janeiro, *Série Tecnológica Mineral* 73, pp. 51-62, 1997.
2. Kanazawa, Y.; Kamitani, M. *Rare earth minerals and resources in the world*. *Journal of Alloys and Compounds* 408, pp.1339–1343, 2006.
3. Abrão, A. (1994) *Química e tecnologia de terras-raras*. Rio de Janeiro: Centro de Tecnologia Mineral, *Série Tecnológica Mineral* 66, pp. 212-219, 1994.
4. Andrade, R.H.P. *Sumário Mineral 2009*. DNPM, pp.88-89p., 2001.
5. Costa, N. *Os índios e a “guerra dos elementos”*, 2010.
6. Salazaca, K., Mcnut, M.K. *Mineral Commodity Summaries* U.S. Geological Survey, pp. 129-141, 2010.
7. Yin, S., Wu, W., Zhang B., Zhang, F., Luo, Y., Li, S., Bian, X. *Study on separation technology of Pr and Nd in D2EHPA-HCl-LA coordination extraction system*. *Journal of Rare Earths* 28, pp.111-115, 2010.
8. Hirai, T., Nishihama, S., Komasawai, I. *Advanced liquid-liquid extraction systems for the separation of rare earth ions by combination of conversion of the metal species with chemical reaction*. *Journal of Solid State Chemistry* 171, pp.101-108, 2003.

9. Gupta, C.K., Mukherjee, T.K. *Hydrometallurgy in Extraction Processes*. Flórida: 1ªed, v 1, 1990, pp.27-31, 1990.
10. Lee, M.S.; Ahn, J.G.; Son, S.H. *Modeling of solvent extraction of zinc from sulphate solutions with D2EHPA*. *Materials Transactions* 42, pp. 2248–2552, 2001.
11. Lenz, T.G.; Smutz, M. *A comparison of monomerized and dimerized di(2-ethylhexyl) phosphoric acid as lanthanide extractants: The system $\text{SmCl}_3 \cdot 6\text{H}_2\text{O} / \text{M D2EHPA}$* . *Journal of Inorganic and Nuclear Chemistry* 28, pp. 1119-1120, 1966.
12. Sousa Junior, C.S. *Desenvolvimento de modelos termodinâmicos para processos de separação líquido-líquido de metais divalentes*. Escola de Química, Universidade Federal do Rio de Janeiro, 196p., 2011.
13. Nathsarma; K.C.; Devi, N. *Separation of Zn(II) and Mn(II) from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272*, *Hydrometallurgy* 84, pp.149–154, 2006.
14. Calado, V.; Montgomery, D. *Planejamento de experimentos usando o Statistica*. e-papers, Rio de Janeiro, pp.22-43, 2003.
15. Nascimento, H. T. S.; Freire Filho, F. R.; Rocha, M. M.; Ribeiro, V. Q.; Damasceno-Silva, K. J. *Produção, avanços e desafios para cultura do feijão-caupi no Brasil*. Embrapa Amazônia Oriental, 2009.

Recovery of Zinc from HCl Industrial Effluents

*M. Lurdes F. Gameiro¹, Remígio M. Machado¹, João M.A. Rodrigues¹,
Katarzyna Staszak², Magdalena Regel-Rosocka², Karolina Wieszczycka²,
M. Rosinda C. Ismael¹, M. Teresa A. Reis¹, Jorge M.R. Carvalho^{*1}*

Summary

This article reports on a study of zinc recovery from hydrochloric acid effluents, by solvent extraction (SX). The effluents studied were firstly processed in order to obtain an aqueous solution rich in zinc (5-12 g/L) and with a low content of acid (10-12 g/L), iron (323-550 mg/L) and minor elements such as copper (16-71 mg/L), lead (6-38 mg/L) and nickel, chromium and cadmium (<0.2 mg/L). Subsequently, iron and copper were removed from this solution, before zinc recovery. The latter process, involving the metal extraction with CYANEX 272 sodium salt and TBP (in Shellsol D70), the scrubbing of the organic phase with deionised water and the metal stripping with H₂SO₄ solutions with or without zinc, was highly efficient. A zinc recovery up to 99.8% was obtained.

Introduction

The aim of the pickling baths used in hot-dip galvanizing plants is to remove rust and scales from metallic parts before its galvanization. These baths become exhausted as the dissolved metals content increases and are usually disposed in landfills [1]. However, the zinc, iron and HCl present in the effluents must be recovered on account of economical and environmental reasons.

Several authors proposed different methods for the recovery of zinc, the most valuable component of the waste liquor [1-4]. In the present study, the authors developed a process for zinc recovery from galvanizing industrial effluents, which involved three steps, the first one of zinc enrichment by SX with optimized phase ratios, the second one of iron (III) precipitation and copper cementation, and the third one of zinc solvent extraction.

Methodology

Iron (III) extraction experiments

The organic phases were prepared, dissolving the mixture of extractants and modifier in the aliphatic diluent Shellsol D70, from Drogas Vigo (Portugal), and washed with deionised water to remove the soluble impurities. The mixture tested was the phosphonic acid (2-ethylhexyl)-mono(2-ethylhexyl)ester, IONQUEST 801 20% (v/v), from Albright & Wilson Americas (Tenneco Company) and the primary aliphatic amine PRIMENE JM-T 10% (v/v) from Rohm & Haas. The modifier used was isotridecanol 20% (v/v), provided by Cognis.

The synthetic feed phases were 9.8 g/L zinc, 108-564 mg/L iron and 96-133 mg/L copper (pH 0.15-1.04) aqueous solutions. These phases were prepared using the

^{*1} Corresponding Author, Centre for Chemical Processes (CPQ) / Centre for Natural Resources and the Environment (CERENA), Instituto Superior Técnico, Lisbon, Portugal. E-mail address: jcarv@tecnico.ulisboa.pt

² Institute of Chemical Technology and Engineering, Poznan University of Technology (PUT), Poland

analytical grade reagents ZnCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and HCl . The scrubbing phase was a 5 g/L H_2SO_4 .

The aqueous and the organic phases were put into contact in separating funnels, in an orbital shaker at 120 rpm, with temperature control (25 °C) during at least 1 hour. Aqueous:organic phases volumetric ratios (A:O) of 1:1 and 1:2 were tested in the extraction experiments and 1:3 in the scrubbing experiments.

Precipitation and cementation experiments

In the iron precipitation experiments, real effluents from a hot-dip galvanizing plant were tested. These effluents were subjected to an initial treatment which included iron (III) to iron (II) reduction, extraction of zinc with tributyl phosphate (TBP, from Rhodia) and stripping of the loaded TBP with deionised water.

These experiments were carried out by putting the aqueous solutions in a 1 L batch reactor, equipped with a magnetic stirrer and a pH meter (Metrohm). The media pH was increased to ~4.0-4.5 by adding 150 g/L NaOH.

Copper cementation was accomplished by adding zinc powder p.a. Merck (< 60 μm) to the suspension. Moreover, a flocculating agent was rapidly mixed with a glass rod and then the mixture stood for 5 to 10 minutes. The anionic flocculant Magnafloc 1011, from Allied Colloids Limited, and the cationic Zetag 51 Polymer were tested.

Zinc recovery experiments

Zinc recovery involved the metal extraction, the scrubbing of the organic phase with deionised water and the metal stripping with sulphuric acid aqueous solutions from 100 to 150 g/L with (48.0-48.8 g/L) or without zinc.

In the extraction experiments the organic phase contained 30% of the extractant (15% NaR + 15% HR), 30% of the modifier TBP (volumetric percentages) and the diluent Shellsol D70. The extractant tested was the bis(2,4,4-trimethylpentyl) phosphinic acid, CYANEX 272, which was supplied by CYTEC. The extractant sodium salt was formed by incorporation of 5 M NaOH into the organic phase, at the ratio of A:O=1:10. The predefined volume of the NaOH solution was slowly added, drop by drop, to the stirred organic phase using a burette. After the neutralization, an only homogeneous organic phase was formed. The aqueous phase was the industrial effluent after the treatment mentioned above.

The stripping phases were prepared using H_2SO_4 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

The aqueous and the organic phases were put into contact in separating funnels, in an orbital shaker, as previously referred.

Chemical analyses and pH determination

The metals concentration in the aqueous phases was determined by atomic absorption spectroscopy (Perkin Elmer, AAnalyst 200 model). The metals in the

organic phases were stripped with 200 g/L H_2SO_4 (3 consecutive contacts, A:O=3:1) and analysed by the same method.

The chloride ion concentration in the aqueous phases was determined by ion chromatography through the SMEWW 4110 B procedure [5]. HCl was titrated using KI as Fe(III) reducing agent [6].

The pH of the aqueous phases was measured using a Metrohm 827 pH lab meter with a combined electrode.

Results and Discussion

Iron (III) extraction

The iron (III) removal involved two steps: extraction and scrubbing of the loaded organic phase to recover the co-extracted zinc.

Several experiments were carried out to study the influence of initial pH of the aqueous feed phase, iron initial concentration and A:O ratio on the metals extraction. The experimental results are listed in Table 1.

Table 1: Extraction with IONQUEST 801 and JM-T mixture: concentrations in aqueous phases (mg/L)

Run	A:O	pH _i	pH _f	Zn _i	Zn _f	Fe _i	Fe _f	Cu _i	Cu _f
1	1:2	1.04	1.60	9800	6080	564	1.2	110	110
2		0.16	0.86	9800	7680	552	85	96	97
3		0.15	0.85	9800	7840	108	4.4	133	140
4	1:1	1.04	1.52	9800	7840	564	375	110	108
5		0.16	0.71	9800	8640	552	115	96	94
6		0.15	0.72	9800	8640	108	93	133	134

Table 1 shows that the iron extraction was more efficient for the A:O ratio of 1:2. In fact, extraction percentages from 85% (run 2) to 99.8% (run 1) were obtained. However, zinc co-extraction was also higher in the latter experiment, attaining a value of 38%. The minimum zinc co-extraction obtained was 12% in runs 5 and 6 but, in these experiments, only 79% and 14% of iron was extracted. Copper was not co-extracted. To test different levels of zinc co-extraction, the organic phases resulting from runs 1 and 5 were selected for the scrubbing step. The results are presented in Table 2.

Table 2: Scrubbing with 5 g/L H_2SO_4 : concentrations of metals (mg/L)

Run	A:O	Aqueous phase			Organic phase ¹					
		Zn _f	Fe _f	Cu _f	Zn _i	Zn _f	Fe _i	Fe _f	Cu _i	Cu _f
1	1:3	3920	0.4	0.2	1860	553	281	281	~0	~0
5		2560	1.5	2.7	1160	307	437	436	2.0	1.1

¹The metals concentrations in the organic phase were determined by mass balance.

In the experiments 1 and 5, 70% and 74% of zinc was stripped from the organic phase, respectively, as demonstrated in Table 2. Moreover, iron was not stripped.

Precipitation and cementation

Fe(III) removal was also evaluated by precipitation with NaOH. Copper removal was tested by cementation with zinc powder. Preliminary experiments indicated a difficult filtration due to finely divided precipitates and thus one decided to test 2 flocculants, one of them anionic and the other one cationic. The results are shown in Table 3.

Table 3: Precipitation, cementation and flocculation: concentrations of zinc powder, flocculants and metals in the aqueous phases (mg/L)

Run	Zinc powder	Floc.	pH _i	pH _f	Zn _i	Zn _f	Fe _i	Fe _f	Cu _i	Cu _f	Pb _i	Pb _f
1	266	19.9 ¹	0.57	5.11	9500	9500	550	9.8	16	3.2	38	0.01
2	266	20.0 ²	0.57	5.05	9500	9500	550	27	16	1.2	38	0.05
3	270	19.7 ¹	0.57	4.81	9500	9500	550	17	16	0.2	38	0.05
4	224	19.4 ¹	0.61	5.82	11600	10600	323	1.5	71	35	5.8	0.25
5	240	19.3 ¹	0.61	4.80	11600	10200	323	23	71	40	5.8	0.46

Flocculant: ¹Cationic; ²Anionic.

Minor elements (mg/L): Cr_i=0.05, Cr_f~0; Ni_i=Ni_f~0; Cd_i=Cd_f~0 (Runs 1-3);

Cr_i=0.2, Cr_f~0; Ni_i=Ni_f=0.1; Cd_i=0.2, Cd_f=0.1 (Runs 4-5).

Iron removal percentages of 93% to 99.5% were attained, without co-precipitation of zinc. Moreover, it was possible to remove 80% to 99.1% of copper by cementation (runs 1-3). The results were similar for both flocculants, but slightly better for the cationic one (runs 1-2). Therefore this agent was used in subsequent experiments.

Zinc recovery

The process of zinc recovery, after iron (III) precipitation and copper cementation, included extraction, scrubbing (to remove sodium and chloride, avoiding contamination of the zinc electrolysis) and metal stripping from the organic phase. In some experiments, the organic phase, after the stripping step, was recycled to the extraction step, after new formation of the CYANEX 272 sodium salt. The results are presented in Tables 4-6.

Table 4: Extraction with CYANEX 272 salt: concentrations of metals in the aqueous phases (mg/L)

Run	A:O	pH _i	pH _f	Zn _i	Zn _f	Fe _i	Fe _f	Cu _i	Cu _f	Pb _i	Pb _f	Ni _i	Ni _f		
1 <i>F</i>	3:1	4.00	4.53	4800	12.4	3.6	~0	26	8.7	0.1	0.08	0.04	0.04		
2 <i>F</i>		4.38	4.76	5100	1.8	0.2		5.6	1.8	~0	0.14	0.05			
3 <i>F</i>		5.11	3.10	9500	2400	9.8		2.5	3.2	3.1	0.01	0.02		0.04	0.02
4 <i>F</i>		5.05	3.11			27		7.0	1.2	1.0	0.05	0.21			0.03
5 <i>F</i>	2:1	5.82	3.50	10600	525	1.5	0.6	35	26	0.25	0.13	0.11	0.11		
5 <i>R</i>			2.98		1720		0.5		34		0.18		0.15		
6 <i>F</i>			3.50		525		0.6		26		0.13		0.11		
6 <i>R</i>			2.90		1920		0.5		34		0.27		0.12		

Organic phase: F: fresh; R: recycled. Other minor elements (mg/L): Cr_i=Cr_f~0; Cd_i=Cd_f~0.

Table 4 shows that it was possible to extract 95% of zinc using the fresh organic phase (runs 5-6). In the experiments carried out with the recycled organic phase, the zinc extraction percentage was lowered to 84% (run 5) and 82% (run 6).

Table 5: Scrubbing with deionised water: concentrations in the aqueous phases (mg/L)

Run	A:O	pH _i	pH _f	Zn _f	Fe _f	Cu _f	Pb _f	Cr _f	Ni _f	Cd _f	Cl _f	Na _i	Na _f
1 F	1:1	5.74	3.46	130	~0	44	0.05	~0	~0	not analysed (n.a.)			
2 F			3.58			6.0							
3 F	2:1	5.80	3.13	1680	0.04	0.04		0.01	0.01				
4 F					0.15	~0							
5 F	2:1	5.60	3.23	960	~0	1.1	~0	0.03	0.09	0.01	1300	0.02	51.6
5 R			3.04	1280	0.24	0.56		0.05	0.12	0.02	1700		74.5
6 F			3.23	960	~0	1.1		0.03	0.09	0.01	1300		51.6
6 R			2.93	1520	0.26	0.65		0.05	0.08		2000		n.a.

Table 6: Stripping: concentrations in the aqueous and organic (grey background) phases (mg/L)

Run	A:O	Zn _i	Zn _f	Fe _i	Fe _f	Cu _i	Cu _f	Pb _i	Pb _f	Cr _i	Cr _f	Na _i	Na _f	Cl _f
1 F^2	1:10	0	88000	0	0.75	0	76	0	0.45	0	~0	0	<i>not analysed</i>	
2 F^1			62400		1.2		13		0.38					
3 F^2		48000	104000		2.0		0.05		~0					
4 F^2			99200		6.0		0.03		0.03					
5 F^2	5:1	48800	49600	1.0	0.02	0.08	0.03	0	0.04	0	0.23	194		
5 R^2			46400	1.2	~0	0.18					0.88	239		
6 F^2	3:1		52800	2.2	0.01	0.07	0.04		0.46		285			
6 R^2			51200	0.6	~0	0.09	0.03		3.3		406			
5 F	5:1	18720	56.4	21	13	~0	~0	~0	0.36	0.99	0.90	<i>not analysed</i>		
5 R		15840	1060	11	4.0	0.27		0.45	~0	0.63	0.81			
6 F	3:1	18720	42.0	21	4.1	~0		~0	0.63	0.99	0.90			
6 R		15840	1490	5.7	4.7				~0	~0	0.72			

H₂SO₄ (g/L): ¹100; ²150. Minor elements (mg/L): Ni_{i,o}=Ni_{f,o}=Ni_{f,a}~0; Cd_{f,a}~0, Cd_{i,o}=0-0.1, Cd_{f,o}=0-0.2.

Zinc recoveries of 99.7% and 99.8% were obtained in runs 5 and 6, respectively, using the fresh organic phase in the metal extraction. These percentages were reduced to 93.3% and 90.6% when using the recycled organic phase. The impurities content in the stripping phase, to be used in the electrolysis, was lower in run 5. The diagram of the developed flowsheet is presented in Figure 1.

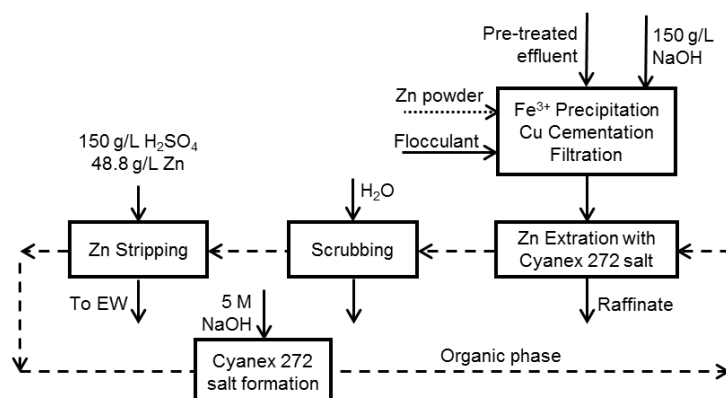


Figure 1: Flowsheet of the proposed zinc recovery process.

Conclusions

The iron removal was tested by SX with the mixture IONQUEST 801 20%, PRIMENE JM-T 10% and isotridecanol 20%, in Shellsol D70, and by precipitation with NaOH. The results demonstrated that it was possible to extract 99.8% of iron from a solution with initial pH of 1.04 and A:O=1:2. However, the co-extraction of zinc attained 38%. In the case of the precipitation, it was possible to remove 99.5% of iron without co-precipitation of zinc and thus this process was more efficient than SX.

After iron precipitation, it was possible to remove 80% to 99.1% of copper from the solution by cementation with zinc powder.

Zinc recovery involved the metal extraction, the scrubbing of the organic phase with deionised water and the metal stripping with H₂SO₄ solutions with or without zinc. The results obtained showed that the SX process was highly efficient for removing zinc from the solutions, using a sodium salt of CYANEX 272 as the extractant, with a metal extraction up to 95%.

It is worth mentioning that a stripping agent having a typical composition of an electrolytic zinc solution (~50 g/L of zinc, 150 g/L of H₂SO₄) was also tested. Even under this specific experimental condition, it was possible to attain 99.8% of metal recovery. This interesting result highlights the possibility of using an integrated process involving SX and electrolysis for zinc recovery.

Acknowledgements

Financial support for this study by Agência de Inovação (AdI, Portugal), through the project QREN 13626 *B-Galvanização* (Partner: Eurogalva), is gratefully acknowledged. M.L.F. Gameiro would like to thank Fundação para a Ciência e a Tecnologia (FCT, Portugal) for her Post-doctoral grant (SFRH/BPD/47196/2008).

References

1. Lum, K.H., Stevens, G.W., Kentish, S.E. (2014) *Development of a process for the recovery of zinc sulphate from hot-dip galvanizing spent pickling liquor via two solvent extraction steps*, Hydrometallurgy, 142, 108-115.
2. Cierpiszewski, R., Miesiąc, I., Regel-Rosocka, M., Sastre, A.M., Szymanowski, J. (2002) *Removal of Zinc(II) from Spent Hydrochloric Acid Solutions from Zinc Hot Galvanizing Plants*, Ind. Eng. Chem. Res., 41, 598-603.
3. Regel-Rosocka, M. (2010) *A review on methods of regeneration of spent pickling solutions from steel processing*, Journal of Hazardous Materials, 177, 57-69.
4. Regel-Rosocka, M., Nowak, Ł., Wiśniewski, M. (2012) *Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids*, Separation and Purification Technology, 97, 158-163.
5. Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA, AWWA, WEF, Washington.

6. Ismael, M.R.C. **(1999)** *Iron removal by liquid-liquid extraction*, Ph.D. Thesis, Instituto Superior Técnico, Technical University of Lisbon.

Mechanism and thermodynamics of synergistic separation of vanadium and nickel from sulfate media using D2EHPA and Cyanex 272

S.M.M. Noori¹, F. Rashchi^{,1}, A. Babakhani¹, E. Vahidi²*

Summary

In this investigation a model was developed to predict the synergistic effect of Cyanex 272 and D2EHPA on co-extraction and separation of nickel and vanadium from sulfate leach liquors of power plant fly ash with the aim of increasing separation efficiency. The stoichiometric coefficient of vanadium was determined for sole D2EHPA and three different D2EHPA to Cyanex 272 ratios by applying the slope analysis method. The experimental data of vanadium extraction at pH range of 1 – 2.5, temperature of 25, 35, 45, and 55 °C and various proportions of organic solvents (D2EHPA and Cyanex 272) were used to propose correlations of distribution coefficient of vanadium by multiple linear regression. The extraction equilibrium constants, enthalpy change, and entropy change of the extraction reaction were also determined.

Introduction

Due to the wide applications of vanadium and nickel in the steel industry as alloying elements, ceaseless extraction of mineral resources of these two metals are becoming more and more insufficient to answer the rapid growing demands especially in industrialized countries. In recent years, mainly because of depleting in main sources of nickel and vanadium, researchers have been trying to recover and extract these metals from secondary sources such as fly ashes, crude oil, power plant residues, and spent catalysts [1, 2].

Fly ash generated by power plants is categorized as a special waste by US EPA. These residues from fossil fuel combustion are captured by pollution control equipment and disposed in special landfills [3]. In landfills, leaching of heavy metals such as nickel and vanadium from fly ash into ground water, soil, and/or surface water is the main potential environmental concern. Furthermore, due to the limited storage capacity of landfills, safe disposal becomes more and more costly. Based on the investigations by Tsai and Tsai [3] current consumption of heavy oil as fuel in power stations in Taiwan is approximately 15 million m³ per year and the approximate production of fly ashes is 43000 tons per year. Therefore, from economical and environmental viewpoints, it is imperative to develop means of both diverting these types of wastes from the solid waste stream, and also recovering nickel and vanadium as valuable metals from fly ashes.

Amer [4] leached boiler-ash with sulfuric acid to recover vanadium and nickel sulfate at temperature 200 °C, partial oxygen pressure 15 atm, and sulphuric acid concentration 60 g/l. The mentioned process requires high temperature and pressure that is not practical in industrial scale from the economic aspect.

Lai et al studied metals (e.g. Al, Co, Cu, Fe, Mo, Pb, V, and Zn) recovery from spent Hydro Desulfurization Catalysts (HDS) by 2 types of strong acids for a leaching period of 0.5-2 h at 70 °C [5]. After finding the best condition, the metals recovery for Mo, Ni, V were 14, 60, and 65%, respectively which are not appropriate results for recovering those valuable metals. Other scientists have tried to develop processes for extracting

¹ School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, PO Box 11155/4563, Tehran, Iran, (rashchi@ut.ac.ir)

² Department of Civil and Environmental Engineering, University of South Florida, Tampa, FL 33620, USA

and separating both nickel and vanadium from secondary sources, but most of the mentioned processes are expensive and time-consuming and can contaminate ground waters. Furthermore, some of the suggested routes only work out for vanadium although those secondary sources include considerable amount of nickel which should be recovered [3, 6- 7]

In the present study, a novel synergistic extraction system using Cyanex 272 and D2EHPA as extractants has been investigated. In addition, the extraction mechanism and thermodynamic parameters of vanadium were investigated in detail as a comparison between single D2EHPA and mixture of Cyanex272 and D2EHPA as organic solvents in solvent extraction process. Also, by applying RSM method, a model for finding the best condition of extracting nickel and vanadium was generated.

Experimental

Each SX test was performed by mixing 200 mL of the aqueous solution with 200 mL of the organic phase. The aqueous to organic phase ratio (A/O) of 1:1 and temperature 25°C were applied in all tests except those experiments which were done for determination of the best condition of extraction. A pH-meter was used to monitor pH during the experiments.

In order to obtain extraction isotherms, pH was successively changed by adding either sulfuric acid or ammonium hydroxide solution drop wise. The two-phase mixture was agitated by a mechanical shaker for approximately 10 minutes and after pH was stable, the phases were allowed to separate. Then, a sample was taken, transferred to a separatory funnel, and allowed to disengage. The metal ion concentration in the aqueous phase was estimated directly immediately by titration method and the concentration of metal ions in the organic phase was calculated from the difference between concentrations in the aqueous phase before and after extraction by mass balance.

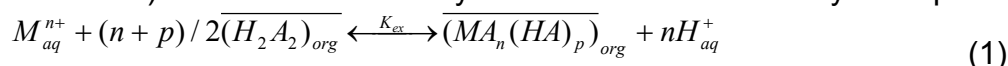
Results and discussions

Influence of Cyanex 272 as Synergist

Figure 1 shows the percentage of vanadium and nickel ions extracted as a function of pH at different D2EHPA to Cyanex 272 ratios at 25 °C. As it can be seen, the figure illustrates significant synergistic shifts of nickel towards vanadium isotherms due to the addition of Cyanex 272 to D2EHPA. Also, by increasing the ratio of Cyanex 272 to D2EHPA, the vanadium extraction curve slightly shifted to the left and that of nickel strongly to the right. In other words, addition of Cyanex 272 to D2EHPA significantly improves the separation of vanadium over nickel.

Extraction mechanism of vanadium by D2EHPA and Cyanex 272

In order to determine the formation of metal–organic complex during extraction of vanadium, a dimer state of D2EHPA and Cyanex 272 has been considered as reported by various authors [11-12]. Thus, the extraction mechanism of the metal ion (in this case vanadium) with D2EHPA and Cyanex 272 in kerosene may be expressed as follows:



Where (H₂A₂) is extractant in dimeric form, M is metal, n is valence of the metal or metal complex ion and p number of molecules of extractant engaged in reaction. The

equilibrium constant of the extraction reaction K_{ex} , can be given as a function of molar concentration, provided that the ionic strength of the aqueous solution is constant.

$$k_{ex} = \frac{[MA_n(HA)_p]_{org} [H^+]_{aq}^n}{[M^{n+}]_{aq} [H_2A_2]_{org}^{(n+p)/2}} \quad (2)$$

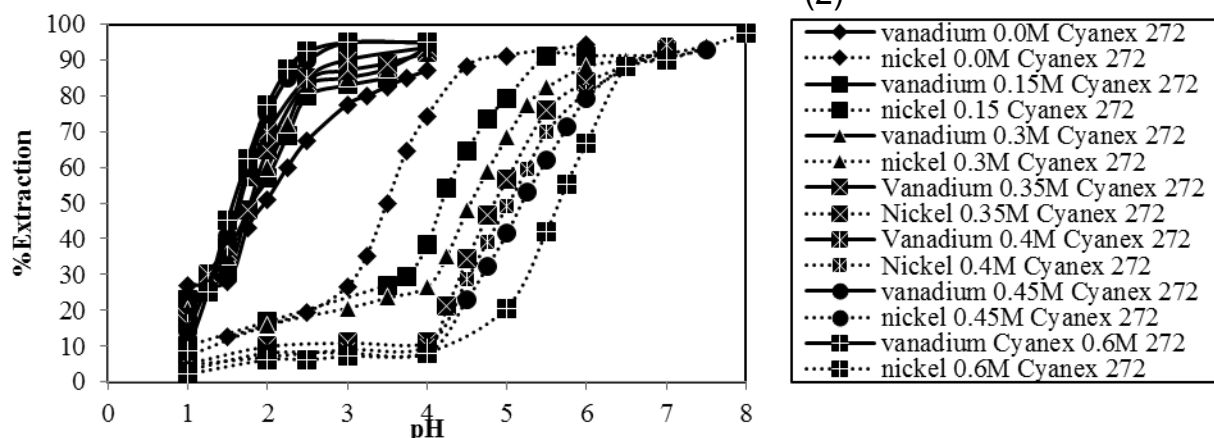


Figure 1. Effect of increasing Cyanex 272 to D2EHPA on extracting nickel and vanadium at 25°C and O/A ratio of 1:1 in kerosene.

The distribution coefficient, D , is defined as the ratio of metal concentration in organic phase to the metal concentration in aqueous phase at reaction equilibrium, and is substituted into the above equation.

$$D = K_{ex} \frac{[H_2A_2]_{org}^{(n+p)/2}}{[H^+]_{aq}^n} \quad (3)$$

By taking the logarithm of the above equation:

$$\log D = \log K_{ex} + (n+p)/2 \log [H_2A_2]_{org} - n \log [H^+] \quad (4)$$

$$\log D = \log K_{ex} + (n+p)/2 \log [H_2A_2]_{org} + npH \quad (5)$$

As shown in Figure 2 plot of $\log D$ vs. equilibrium pH for vanadium gave straight lines with a slope of ca. 2.0 for sole D2EHPA (0.6 M) and also Cyanex 272 (0.6 M), suggesting the totally released protons included two ions of H^+ during extraction (n in equation 1).

As shown in Figure 3 which demonstrates plot of $\log D$ vs. $\log [H_2A_2]_{org}$, concentration of sole D2EHPA and Cyanex 272 was varied in the range of 0.2 – 0.6 (M) in kerosene at both equilibrium pHs of 1.5 and 2. As it can be seen the extraction of vanadium was linearly related to the extractant concentration and the slope value $\{(n+p)/2\}$ was determined to be ca. 1.5 thus the p value becomes 1.

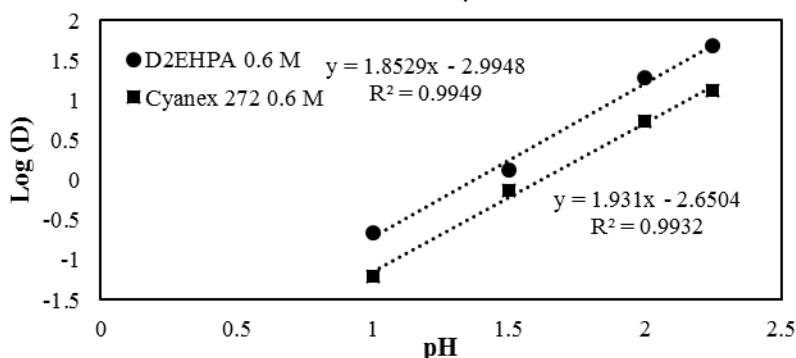


Figure 2. Effect of pH on the extraction of vanadium with sole D2EHPA and Cyanex 272 at concentrations of 0.6M extractant.

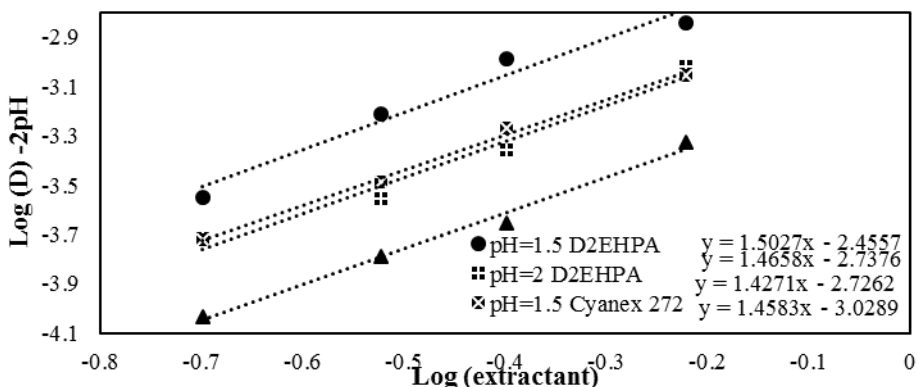
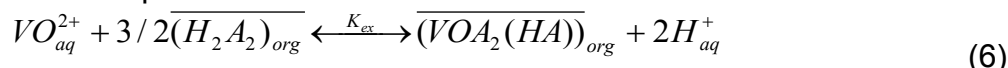


Figure 3. Effect of sole D2EHPA and Cyanex 272 concentrations on the extraction of vanadium.

The extraction mechanism for vanadium extraction by sole D2EHPA and Cyanex 272 can be represented as:



It indicates that vanadium is participated in cationic exchange reaction with 1.5 molecules of dimeric D2EHPA and Cyanex 272 with formation of $\overline{(VOA_2(HA))}_{org}$ complex in the organic phase.

Extraction mechanism of vanadium by mixture of D2EHPA and Cyanex 272

Figure 4 demonstrates plot of log Dm vs. equilibrium pH. Similarly, in order to determine the extracted complexes in the mixed-extractant systems, a series of experiments were carried out and the conventional slope analysis method was used. In this figure, the plots of log Dm vs. pH_e at fixed concentration of Cyanex 272 (0.3 M) and D2EHPA (0.3 M) illustrate a straight line with a slope of ca. 2.0, which suggests that there is 2 released protons in the extraction reaction equation similar to the extraction of vanadium by sole D2EHPA and Cyanex 272. Therefore, the extraction of vanadium by mixture of D2EHPA and Cyanex 272 is in accordance with the equation (6) and vanadium was extracted in the formation of $\overline{(VOA_2(HA))}_{org}$ complex in the organic phase.

In order to determine the participation of each extractant in the extraction mechanism of vanadium, Figures 5 and 6 were plotted which illustrate the Log(Dm) vs. Log(extractant). In Figure 5 it can be seen that by changing D2EHPA concentration (0.2 - 0.4 M) at fixed concentration of Cyanex 272 (0.3 M) the slope of the diagram is ca. 1 which shows participation of one molecule of D2EHPA in the synergism system. Likewise, Figure 6 shows the changing of Cyanex 272 concentration (0.2 - 0.4 M) at fixed D2EHPA (0.3 M). From this figure it can be concluded that 0.5 molecule of Cyanex 272 participates in the extraction of vanadium.

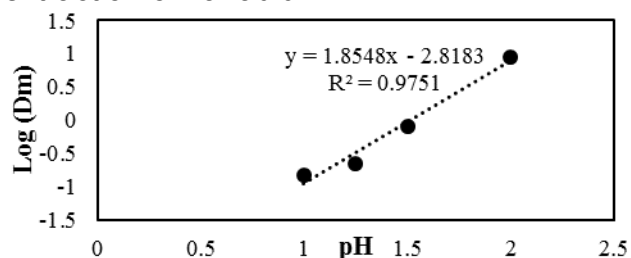


Figure 4. Effect of pH_e on extraction of vanadium with mixture of D2EHPA 0.3M and Cyanex 272 0.3 M.

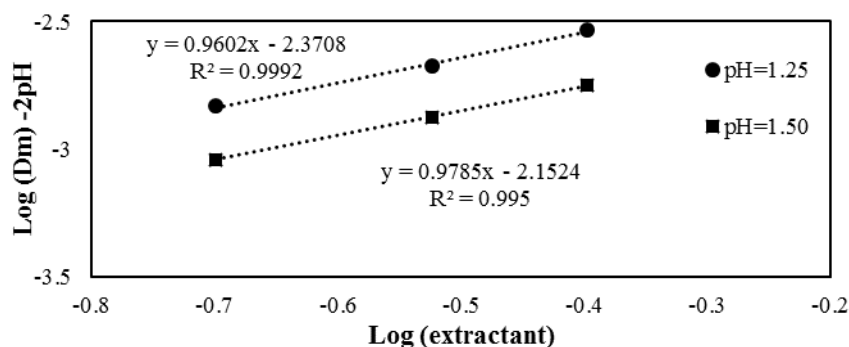


Figure 5. Effect of D2EHPA concentration at fixed Cyanex 272 on the extraction of vanadium.

Thermodynamic study

Experimental temperature plays an important role in a liquid-liquid extraction process. At fixed concentrations of pH=2 and extractants D2EHPA (0.25 M) Cyanex 272 (0.35 M) the influence of temperature has been studied in the present work. If the relationship between the distribution ratio and the temperature is obtained, the change of enthalpy of the reaction, ΔH , can be calculated according to the following equation:

$$\frac{\Delta D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (8)$$

Where R is $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

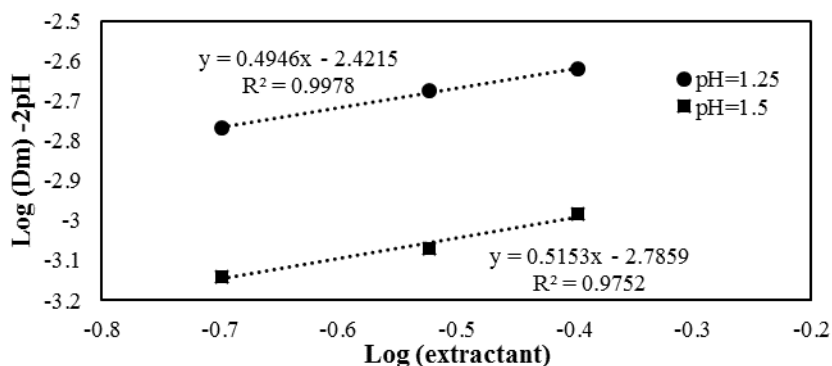


Figure 6. Effect of Cyanex 272 concentration at fixed D2EHPA on the extraction of vanadium.

The change of Gibbs free energy (ΔG) and the change of entropy (ΔS) can thus be obtained as follows:

$$\Delta G = -RT \ln K \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (10)$$

Where ΔG and ΔS are determined when T is 298 K.

Plots of log D versus $[1000/T \text{ (K)}]$ are shown in Figure 7 and the K values, calculated from equation (5). The ΔH , ΔG , and ΔS values were calculated as $12.12 \text{ kJ mol}^{-1}$, 15.2 kJ mol^{-1} , and $-10.35 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. It can be seen that the sign of ΔH is positive, indicating that synergistic extraction processes is endothermically driven.

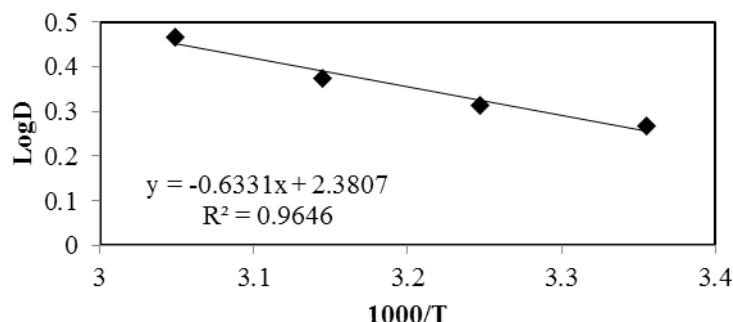


Figure 7. Relationship between distribution coefficient and temperature for vanadium extraction, $pH = 2$.

Conclusions

1. Increasing Cyanex 272 to D2EHPA at fixed total concentration of 0.6 M for extraction of vanadium and nickel from sulfate media resulted in a slight shift to the left on extraction isotherm of vanadium, but a major influence on nickel extraction by shifting isotherm to the right.
2. The extraction mechanism and behavior of vanadium by sole D2EHPA and Cyanex 272 are similar to that of the synergistic extraction by mixtures of D2EHPA and Cyanex 272. From the extraction studies the formation of $(VOA_2(HA))_{org}$ species was predicted with sole D2EHPA, Cyanex 272 and with the mixture of D2EHPA and Cyanex 272.
3. Based on the synergistic studies (D2EHPA (0.3 M) and Cyanex 272 (0.3 M)), one molecule of D2EHPA and 0.5 molecule of Cyanex 272 participate in the extraction of $(VOA_2(HA))_{org}$.
4. Calculation of the thermodynamic parameters, ΔH , ΔG , and ΔS , indicates that synergistic extraction reaction of vanadium is endothermically driven.

References

- [1] A. Ognyanova, A. T. Ozturk, I. De Michelis, F. Ferella, G. Taglieri, A. Akcil, F. Vegliò, *Hydrometallurgy*, Vol. 100, No. 1–2, 2009, pp. 20–28.
- [2] R. Moskalyk, A. Alfantazi, *Minerals Engineering*, Vol. 16, No. 9, 2003, pp. 793–805.
- [3] S. Tsai, M. Tsai, *Resources, Conservation and Recycling*, Vol. 22, 1998, pp. 163–176.
- [4] A. M. Amer, *Waste Management*, Vol. 22, No. 5, 2002, pp. 515–520.
- [5] Y.-C. Lai, W.-J. Lee, K.-L. Huang, C.-M. Wu, *Journal of Hazardous Materials*, Vol. 154, No. 1–3, 2008, pp. 588–94.
- [6] L. Zeng, Q. Li, L. Xiao, *Hydrometallurgy*, Vol. 97, No. 3–4, 2009, pp. 194–197.
- [7] S. Vitolo, M. Seggiani, F. Falaschi, *Hydrometallurgy*, Vol. 62, No. 3, 2001, pp. 145–150.
- [8] X. Li, C. Wei, J. Wu, C. Li, M. Li, Z. Deng, H. Xu, *Transactions Nonferrous Metals Society of China*, Vol. 22, No. 2, 2012, pp. 461–466.
- [9] M. R. Tavakoli, D. B. Dreisinger, *Hydrometallurgy*, Vol. 141, 2014, pp. 17–23.

Liquid surfactant membranes technique for the removal of Cr^{6+} from galvanisation effluents

Tânia L. S. Miranda, Vanesa O. Silva, Adriane Salum, Cibele Konzen,
Estêvão M. R. Araújo, Fabrício E. B. Coelho, Julio C. Balarini
Departamento de Engenharia Química, UFMG
Belo Horizonte, Brazil*

Summary – The present work aimed to evaluate the use of liquid surfactant membranes as a technique for the treatment of effluents from a galvanising industry by removing and reducing the Cr^{6+} concentration in this type of wastewater. Initially, the operating conditions for the extraction of Cr^{6+} from a synthetic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ (353 mg.L^{-1} of Cr) were experimentally determined. Next, the technique was applied to an actual effluent from a galvanising industry containing, among other metals, 77.4 mg.L^{-1} of Cr^{6+} and $1,494 \text{ mg.L}^{-1}$ of Zn^{2+} . The system was composed of 3 phases: external phase - EP (synthetic solution or effluent), membrane phase - MP (Alamine[®] 336, 1-decanol, and ECA 4360 and Escaid[™] 110) and internal phase - IP (KOH solution). Under the determined operating conditions ($[\text{Extr}] = 5\% \text{ w/w}$, $\text{pH}_{\text{EP}} = 1.5$, $T = 25 \text{ }^\circ\text{C}$, permeation time = 5 min and $[\text{KOH}]$ in IP = 0.6 mol.L^{-1}), 98% of the initial Cr^{6+} from the $\text{K}_2\text{Cr}_2\text{O}_7$ solution were extracted in a single stage, leaving 4.99 mg.L^{-1} of Cr^{6+} in the final EP. In 3 stages, 99.1% of the initial Cr^{6+} from the same feed were extracted, with a final concentration of Cr^{6+} of 0.27 mg.L^{-1} in the EP. When the LSM technique was applied to the real effluent, under these same operating conditions and in a single stage, the Cr^{6+} percentage of extraction decreased (84%) and a co-extraction of Zn^{2+} was observed (4%). A sharp effluent pH reduction ($[\text{HCl}]_{\text{initial EP}} = 2.0 \text{ mol.L}^{-1}$) with a simultaneous increase in $[\text{KOH}]$ in IP (1.2 mol.L^{-1}) yielded an extraction of 94.6% of Cr^{6+} and 58.4% of Zn^{2+} in a single stage. With a new IP ($\text{HCl } 5.0 \text{ mol.L}^{-1}$) and at its natural pH (~ 6.0), also in a single stage, the effluent yield an extraction of 94.7% of Cr^{6+} without any Zn^{2+} co-extraction, although the effluent $[\text{Zn}^{2+}]$ concentration was about 20 times higher than that of $[\text{Cr}^{6+}]$. The final Cr^{6+} concentration of the effluent was 3.9 mg.L^{-1} .

Introduction

In the last years, as a result of a mounting concern about environmental issues and in compliance of the limits for the discharge of pollutants into water bodies of the Brazilian legislation, the industries that produce effluents containing heavy metals have massively invested in the development of waste processing and treatment in an effort to avoid producing, recycle, reduce or eliminate substances that have toxic effects on human beings and on the environment. In the industrial galvanising process, which consists in the application of a protective Zn coat resistant to corrosion to iron or steel pieces⁽¹⁾, metals and chemical reagents are used to treat the surface of the pieces. The resulting effluents can have a great impact on the environment and cause major health problems to human beings. The literature⁽²⁻⁴⁾ describes various methods for the removal/recovery of Cr^{6+} from effluents, among which solvent extraction, ionic exchange, adsorption, precipitation/filtration, oxidization/reduction and membrane separation stand out. Among the methods under study, separation by liquid surfactant membranes (LSM) has raised particular interest⁽⁵⁾. LSM usually have a high extraction capacity as a result of their great selectivity, being an alternative for the separation and concentration of solutes, since the extraction and stripping steps are performed in a single stage. LSM allow extraction from low concentration solutions, such as industrial effluents⁽⁶⁾. The main objective of this study was to evaluate the technical potential of LSM in the treatment

of an effluent from a galvanising industry aiming the reduction of the Cr^{6+} concentration in this type of wastewater.

Experimental work

The investigated extraction system had three phases with the following composition: external phase – EP (synthetic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ ($353 \text{ mg.L}^{-1} \text{ Cr}^{6+}$) or actual effluent from a galvanising industry ($77.4 \text{ mg.L}^{-1} \text{ Cr}^{6+}$ and $1,494 \text{ mg.L}^{-1} \text{ Zn}^{2+}$)), membrane phase – MP (surfactant ECA 4360, extractant Alamine[®] 336, aliphatic diluent Escaid[™] 110, modifier 1-decanol), and internal phase – IP (KOH solution). The phases ratio EP:MP:IP was 9:2:1. The primary emulsion was prepared at a stirring speed of 13,000 rpm for 5 min⁽⁷⁾. The multiple emulsion was prepared by adding the primary emulsion to the external phase in a reactor under moderate agitation (150 rpm). After the permeation time, the agitation was interrupted and the loaded primary emulsion was demulsified by electrostatic coalescence (voltage of 1.7 kV and frequency of 5 kHz⁽⁸⁾).

The objective of this study was to reduce the concentration of Cr^{6+} in the final raffinate of the treatment of the effluent from a galvanising industry to its limit values (0.1 mg.L^{-1}) pursuant to the Brazilian legislation⁽⁹⁾. For this purpose, the Cr^{6+} extraction from a synthetic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ containing $353 \text{ mg.L}^{-1} \text{ Cr}^{6+}$ was carried out firstly in one stage according to the variables and conditions presented in Table 1. The experiments were performed by varying the operating conditions of one variable at a time and maintaining the other parameters conditions constant.

Table 1 - Investigated variables and their levels.

Parameters	Levels
External phase pH	0.25 - 0.50 - 0.75 - 1.0 - 1.25 - 1.50 - 1.75 - 2.00 - 2.50 - 3.50
Carrier concentration (% w/w)	2 - 5 - 8 - 11
Permeation time (min)	3 - 5 - 7 - 10 - 15 - 20 - 30
Inner phase KOH concentration (mol.L^{-1})	0.12 - 0.18 - 0.22 - 0.27 - 0.36
Permeation temperature ($^{\circ}\text{C}$)	25 - 35 - 45 - 55

The adopted response variables were the chromium percentage extraction and the chromium percentage stripping (%), which were calculated as follows:

$$\text{Extraction (\%)} = \frac{\text{Cr}^{6+} \text{ mass extracted from the external phase}}{\text{Cr}^{6+} \text{ initial mass in the external phase}} \cdot 100 = \frac{m_i^{EP} - m_f^{EP}}{m_i^{EP}} \cdot 100$$

$$\text{Stripping (\%)} = \frac{\text{Cr}^{6+} \text{ mass stripped from the membrane phase into the internal phase}}{\text{Cr}^{6+} \text{ mass extracted from the external phase}} \cdot 100 = \frac{m_f^{IP}}{m_i^{EP} - m_f^{EP}}$$

In these equations, m is the Cr^{6+} mass, the superscripts IP and EP refer to the internal and the external phases and the subscripts i and f are the initial and final conditions, respectively.

Atomic absorption spectrometry (GBC – model Avanta PM) was used to quantify chromium in the final and initial external and internal phases.

Under the best experimental conditions previously determined, three-stage experiments were carried out, in which the feed of the subsequent stages was the raffinate obtained in the previous stage and a fresh membrane phase was used in each operation cycle (cross-current operation).

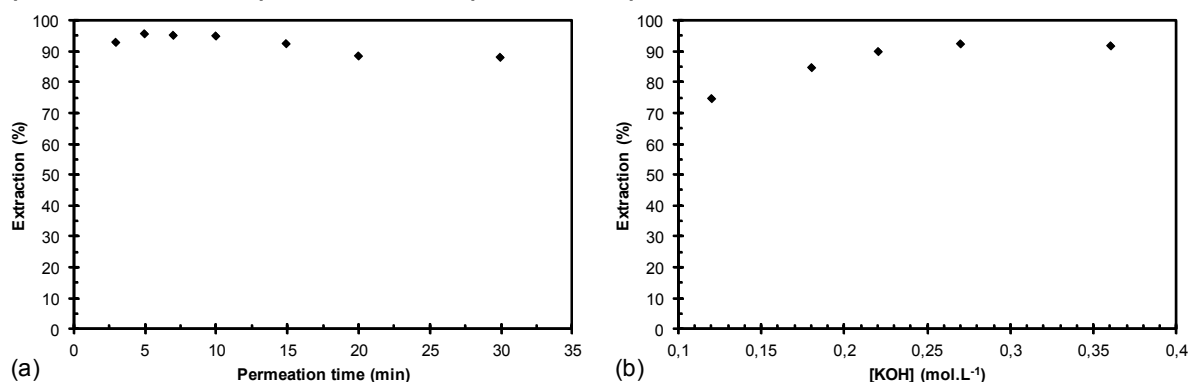
Four additional experiments were performed with the solution of $K_2Cr_2O_7$ ($353 \text{ mg.L}^{-1} \text{ Cr}^{6+}$) using the same pre-established conditions but changing the inner phase KOH concentration (0.27 (used in the previous condition), 0.60, 1.2, 2.4 mol.L^{-1}).

Then, single-stage extraction of Cr^{6+} from an actual galvanising industry effluent was first performed in the best conditions determined for the $K_2Cr_2O_7$ solution. Next six experiments were carried out with the actual effluent but changing the initial pH of the external phase (HCl concentrations of 0.03, 0.3 and 2.0 mol.L^{-1}) and KOH concentrations of the internal phase (0.6 and 1.2 mol.L^{-1}), maintaining the remaining conditions constant. Additionally, another experiment was carried out, promoting the extraction of Cr^{6+} from the effluent at its natural pH (around 6.0) using 5.0 mol.L^{-1} HCl solution as internal phase.

Results and Discussion

Extraction of Cr^{6+} from a $K_2Cr_2O_7$ solution

Figure 1 depicts the experimental results obtained for the extraction of Cr^{6+} from a $K_2Cr_2O_7$ solution ($353 \text{ mg.L}^{-1} \text{ Cr}$) in the experimentally pre-established extraction conditions (Table 1). The concentration of Alamine[®] 336 in the membrane phase, the initial pH in the external phase and the temperature were 2% w/w, 1.25 and 35°C , respectively, except when these parameters were being investigated. The stirring speed used in the permeation step was 150 rpm.



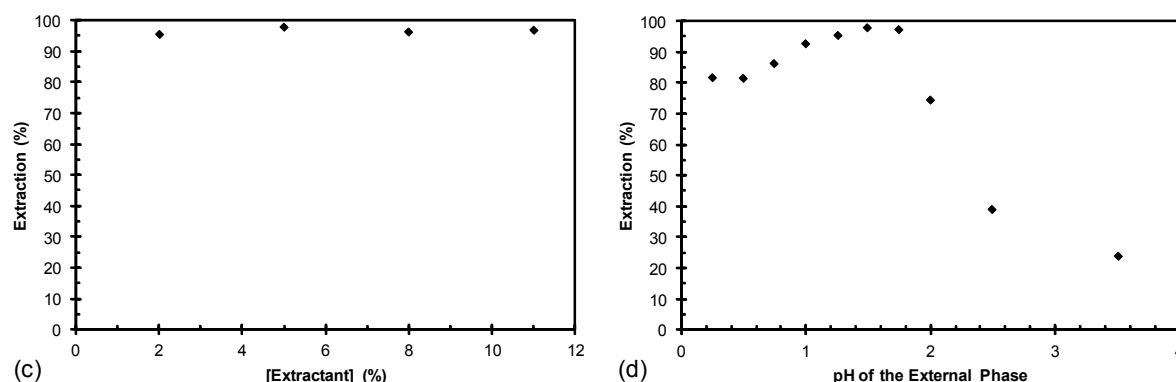


Figure 1 - Effect of different parameters on Cr^{6+} extraction with Alamine® 336 (a) permeation time, (b) $[\text{KOH}]$ in the internal phase, (c) $[\text{Alamine}^{\circledR} 336]$ in the membrane phase and (d) initial pH of the external phase

In general, the percentage of extraction increases significantly with the increase in the permeation time for short time intervals and stabilises for longer time intervals. A high percentage of extraction (over 88%) was obtained for all the investigated permeation times. After 15 min, the percentage of extraction seems to decrease slightly (Figure 1a). Based on these results, all the following experiments were carried out with a permeation time of 5 minutes.

As shown in Figure 1b, the Cr^{6+} extraction increased up to the inner phase KOH concentration of 0.27 mol.L^{-1} . This behaviour can be explained by the increase of the ionic force in this phase. A very high ionic force can result in an uptake of water from the outer phase into the inner phase droplets and in their rupture with consequent reduction in the percentage of extraction, which was not observed in the concentration range investigated.

For all the extractant concentrations studied, the percentage of extraction was over 95%. Usually an increase in the extractant concentration results in a transport of a greater number of solute molecules from the external phase to the internal phase. However, excess of extractant may increase the membrane viscosity and hinder the mass transfer and extraction. In the present operating conditions, an increase in the extractant concentration did not result in a significant variation of the percentage of extraction (Figure 1c).

From the investigation of the initial pH of the external phase, the best results were obtained for a pH ranging from 1.00 to 1.75, at which the Cr^{6+} percentage of extraction was over 92% (Figure 1d). The increase in the initial pH ($\text{pH} > 1.75$) resulted in a decrease in the percentage of extraction. The mass transfer mechanism for the Cr^{6+} extraction with Alamine® 336 is described by a co-transport of H^+ and Cr^{6+} ions from the external phase to the internal phase. This co-transport results in an increase in the pH of the external phase and in a simultaneous decrease in the pH of the internal phase. Tertiary amines need to be activated to react with the $\text{Cr}_2\text{O}_7^{2-}$ ions at the interface of the external/membrane phases to form a solute-extractant complex. When the pH in the outer phase is high, the amine remains in a non-protonated form and therefore the Cr^{6+} percentage of extraction decreases⁽¹⁰⁾.

The results obtained for different temperatures (25, 35, 45 and 55°C) were much similar, with the Cr^{6+} percentage of extraction over 94%.

From the previously presented experiments, the selected conditions were: permeation time = 5 min, $[\text{KOH}]$ in the internal phase = 0.27 mol.L^{-1} ,

[Alamine® 336] = 5% w/w, pH = 1.50, T = 25°C. The Cr^{6+} extraction for this condition was 96.8% with a final external phase containing $9.8 \text{ mg.L}^{-1} \text{ Cr}^{6+}$.

The results obtained in three-stage cross-current extraction with the same conditions mentioned above are shown in Table 2.

Table 2 - Three-stage Cr^{6+} extraction with liquid surfactant membranes.

Stage	Cr^{6+} in $\text{EP}_{\text{initial}}$ (mg)	Cr^{6+} in Raffinate (mg)	$[\text{Cr}]_{\text{Raffinate}}$ (mg.L^{-1})	Cr^{6+} extraction per stage (%)	Total Cr^{6+} extraction(%)
1°	70.85	2.56	11.51	96.4	96.4
2°	2.42	0.11	0.56	95.4	99.8
3°	0.11	0.05	0.27	51.9	99.9

The three-stage extraction provided a total percentage of extraction of 99.9% and a final external phase with a Cr^{6+} concentration of 0.27 mg.L^{-1} . It is noteworthy that the limit stipulated by the Brazilian resolution⁽⁹⁾ to the Cr^{6+} discharge is 0.1 mg.L^{-1} , and an additional stage would probably attain the Brazilian legislation limit. However, this experiment was not performed.

Despite the good results obtained for the Cr^{6+} extraction from the external phase, it was observed that the Cr^{6+} stripping percentage was low and substantial amount of Cr^{6+} was still present in the membrane phase. Then, before studying the extraction in the actual effluent, four additional experiments in a single stage using a synthetic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ were performed with different KOH concentrations in the inner phase ($0.27, 0.60, 1.2, 2.4 \text{ mol.L}^{-1}$). The results are shown in Table 3.

TABLE 3 – Effect of internal phase KOH concentration on the Cr^{6+} extraction and stripping.

$\text{IP}_{\text{initial}} [\text{KOH}]$ (mol.L^{-1})	Cr^{6+} in EP_{final} (mg)	pH in EP_{final}	Cr^{6+} in MP (mg)	Cr^{6+} extraction (%)	Cr^{6+} stripping (%)
0.27	2.10	2.3	21.6	96.8	64.4
0.60	1.10	3.5	0.50	98.4	97.6
1.2	1.10	9.2	11.1	98.4	81.8
2.4	2.90	10	11.6	95.7	78.3

The Cr^{6+} extraction percentage was high for all investigated conditions (over 95%), but depending on the internal phase KOH concentration the Cr^{6+} mass in the membrane phase showed significant differences.

The best result (98.4% of Cr^{6+} extraction, 97.6% of Cr^{6+} stripping and a final external phase containing $4.99 \text{ mg.L}^{-1} \text{ Cr}^{6+}$) was obtained for an internal phase with a KOH

concentration of 0.60 mol.L^{-1} . For the two higher concentrations, an increase in the final pH of the external phase was observed. As previously explained, the raise of the ionic force of the inner phase was caused by the increase of KOH concentration. This probably led a swelling of the inner phase and at the highest KOH concentration may have occurred a rupture of the droplets of this phase with a loss of KOH solution for the external phase. The KOH concentration of 0.60 mol.L^{-1} was used in the subsequent experiments with the actual effluent.

Cr⁶⁺ extraction from an actual galvanising effluent

The Cr⁶⁺ extraction percentage from an actual galvanising effluent (84%) using the experimentally pre-established operating conditions for the K₂Cr₂O₇ solution was lower than the Cr⁶⁺ extraction with the synthetic solution (98%). Since the actual effluent has high Zn²⁺ concentration ($1,494 \text{ mg.L}^{-1}$), nearly 20 times higher than Cr⁶⁺ concentration (77.4 mg.L^{-1}), as well as other metals in lower concentrations, the reduction in the Cr⁶⁺ percentage of extraction may have been due to the co-extraction of Zn²⁺ (4%), which competed with Cr⁶⁺ for the extractant in the formation of the complex.

Because the extraction of Cr⁶⁺ from the actual effluent decreased in relation to the synthetic solution, experiments were performed by varying the HCl concentration in the external phase and the KOH concentration in the internal phase simultaneously. The results are given in Table 4.

Table 4 - Simultaneous extraction of Cr^{6+} and Zn^{2+} from an actual galvanising effluent.

$\text{IP}_{\text{initial}}$ [KOH] (mol.L ⁻¹)	$\text{EP}_{\text{initial}}$ [HCl] (mol.L ⁻¹)	Zn^{2+} in $\text{EP}_{\text{initial}}$ (mg)	EP_{final} Zn^{2+} (mg)	Cr^{6+} in $\text{EP}_{\text{initial}}$ (mg)	Cr^{6+} in EP_{final} (mg)	Cr^{6+} extraction (%)	Zn^{2+} extraction (%)
0.6	0.03	434.9	424.8	18.1	3.1	81.8	2.50
0.6	0.30	430.7	360.5	16.3	1.7	89.6	16.3
0.6	2.00	401.3	265.4	16.1	2.3	85.7	33.6
1.2	2.00	401.2	158.4	16.1	2.2	94.6	58.4

A simultaneous increase in the HCl concentration in the external phase and in the KOH concentration in the internal phase led to an increase in the extraction of Cr^{6+} and Zn^{2+} , which is explained by the increase in the driving force. Thus, the use of 2.0 mol.L⁻¹ HCl and 1.2 mol.L⁻¹ KOH resulted in greater simultaneous percentage extraction of Cr^{6+} (94.6%) and Zn^{2+} (58.4%). On the other hand, the extraction from the actual effluent at its natural pH (around 6.0) in a single stage using 5.0 mol.L⁻¹ HCl as the inner phase yielded a selective extraction of Cr^{6+} (without Zn^{2+} extraction) and a final Cr^{6+} effluent concentration of 3.9 mg.L⁻¹.

CONCLUSIONS

According to the results, probably the application of the LSM technique for the treatment of effluents from a galvanising industry can be economically viable, because there is no need to adjust the initial pH of the effluent, saving reagents; Cr^{6+} was selectively removed in relation to Zn^{2+} , which can provide its reuse in the galvanising process itself, or for other purposes; the use of over 2 or 3 stages would probably suffice to adapt the effluent relative to Cr^{6+} ; adapting the operating conditions, Zn^{2+} could be removed using the same extractant (Alamine® 336) after the removal of Cr^{6+} , which would save reagents for the treatment of the chromium and zinc effluent. The technique conventionally used for the treatment of this effluent (precipitation) provides a simultaneous removal of metals, which complicates the reuse of the obtained precipitate, requiring a proper disposal of the solid residue. Alternatively, the removal of chromium would be performed by liquid-liquid extraction, using Alamine® 336 as extractant. However, as the Cr^{6+} in the wastewater is relatively low, the use of solvents would be too high and many stages for the desired removal would probably be necessary. It should also be noted that, using the LSM technique, the amount of extractant used (9.4 g for treating 1.0 L of wastewater) is very low, which is much lower than would normally be in the liquid-liquid extraction.

REFERENCES

1. CARRERA, J. A. et al. Selective Membrane alternative to recovery of zinc from hot-dip galvanizing effluents. *Journal of Membrane Science*, v.326, p.662-680, 2009.
2. RUBIO, J.; TESSELE, F. *Processos para tratamento de efluentes de mineração*. Capítulo 16. Comunicação Técnica elaborada para a 3ª Edição do Livro Tratamento de Minérios. CETEM. 2002.

3. SILVA, P. Extração do cromo em resíduos sólidos de uma indústria de Galvanoplastia. (Dissertação de mestrado) Departamento de Química Fundamental da Universidade Federal de Pernambuco. Recife, 2002.
4. REIS, M. T. A.; CARVALHO, J. M. R. Recovery of zinc from an industrial effluent by emulsion liquid membranes. *Journal of Membrane Science*, v.84, p.201-211, 1993.
5. LI, N. N. Separation of Hydrocarbons by Liquid Membrane Permeation. *Ind. Eng. Chem. Des. Develop.*, v.10, n.2, p.215-221, 1971.
6. PATNAIK, P. R. Liquid Emulsion Membranes: Principles, problems and application in fermentation processes. *Biotechnology Advances*, v.13, nº2, p.175-208, 1995.
7. SALUM, A. Estudo da Permeação de Cobalto e da Separação Cobalto/Níquel em Meio Sulfúrico, com Cyanex 272, pela Técnica de Membranas Líquidas Sulfatantes. Belo Horizonte: Escola de Engenharia da UFMG, 1998. 258p. (Tese, Doutorado em Engenharia Metalúrgica e de Minas).
8. KONZEN, C. Estudo da técnica de extração por membranas líquidas surfatantes aplicada à separação de ácido cítrico. 169 f. Dissertação (Mestrado em engenharia Química) - Escola de Engenharia, Universidade Federal de Minas Gerais, Belo horizonte, 2000.
9. CONSELHO NACIONAL DO MEIO AMBIENTE - CONAMA. Resolução nº 430, de 13 de maio de 2011. Dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera a Resolução nº 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente - CONAMA. Ministério do Meio Ambiente. 2011. 9 p.
10. CHAUDRY, M. A. et al. Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Management*, v.17, n.4, p.211-218, 1997.

Study of the solvent extraction of the lighter lanthanide metal ions by means of organophosphorus extractants

L. Molina¹, C. Basualto, F. Valenzuela, J. Sapag

Laboratorio de Operaciones Unitarias e Hidrometalurgia, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago/Chile.

Summary

This work aims to contribute to knowledge on the separation of the lighter lanthanide ions, lanthanum, cerium, praseodymium and neodymium, by means of solvent extraction technique using a family of organophosphorus extractants. A study of solvent extraction of lighter lanthanide metal ions with organophosphorus extractants, commercially known as D2EPHA, PC88A, CYANEX 272 and CYANEX 301, was made. In first instance, the acid-base behavior of these four extractants was studied allowing to know their apparent pKa and their ability to react with the rare earth elements (REE) at certain pH. From this knowledge, it was possible to propose the use of an aqueous phase buffered to pH 4. In general, in the extraction experiments of the REE ions, it was found that praseodymium ions were extracted with all the extractants, while in decreasing order neodymium, cerium and lanthanum were extracted less efficiently. Moreover, the D2EHPA and PC88A showed higher extraction efficiencies over the whole pH range used, but they did not allow an effective separation of REE ions. Furthermore, with CYANEX 301 some degree of separation of the metal ions was achieved, but the extraction efficiencies were comparatively lower. However, using the CYANEX 272 extractant, better efficiencies of extraction and selectivities for the four REE were reached. It was determined this last one as the most appropriate extractant to separate the REE. On the other hand, the backextraction experiments showed that the cerium ion had the lowest degree of stripped toward the internal backextraction aqueous phase. All this generated knowledge revealed that the pair Nd-Pr was difficult to separate at the established conditions. For this reason, EDTA was employed like a chelant agent which was added to the feed solution. This solution contained those two ions at identical concentrations (2 mM), getting a maximum selectivity coefficient ($S_{Pr/Nd}$) of 1.7. It is possible to conclude that an appropriate combination of the extractant and working conditions would allow a separation path for lanthanum, cerium, praseodymium and neodymium metal ions contained in a leaching aqueous solution.

Introduction

Group IIIB of the periodic table of the elements is made up of the metallic elements known collectively as rare earths (REE). In general, they present extremely similar chemical and physical properties, and therefore they are very difficult to separate. Within the rare earth group, the elements scandium, yttrium, and lanthanum differ in their atomic structure from the elements cerium to lutetium (the lanthanoids or lanthanides). The rare earth elements always occur in nature in association with one other. Therefore, isolation of the individual elements or groups of them requires costly separation and fractionation processes. In recent years there has been great demand for rare earth metals because of their unique physical and chemical properties as new constituents in electronic, optical and magnetic devices. Commercially available rare earth materials have been used as additives in steels or other alloys, permanent

¹ lorena.molina@gca.uchile.cl

magnets, hydrogen storage materials, magneto-optical storage discs, electro- or cathode ray luminescence, etc. Moreover, they have found some possible applications as semiconductor materials. Electric cars may get to use one kilogram of neodymium in their electric engine and ten kilograms of lanthanum in their nickel metal hydride battery[1]. It has been found that the Yb layer of the Al/Yb/GaAs structure can control the Schottky barrier height[2]. Eu has been used as a material for forming the cladding layer of a double-hetero structure Pb-Eu-Se-Te infrared laser diode[3]. One of the most important applications of the rare earth elements is in supermagnetic and superconductor materials, usually permanent magnets based on gadolinium-cobalt, samarium-cobalt or neodymium-iron-boron, with other metals in smaller proportions. Cobalt alloys offer the highest permanent magnet performance known. Use of these materials continues to grow rapidly[4-8]. The rare earth minerals are widespread and plentiful and we should think about the growing demand that there will be for many years to come. Technology now under development will result in needed cost reductions for many rare earth products and will promote the emergence of many new markets. There are two sources for REE recovery: mineral deposits and the recycling of electric, electronic and other waste materials. Indeed, the accumulation of industrial, electronic and optical wastes has been highlighted as a valuable second source of rare earth metals.

In 2005 Jiang et al. developed a hydrometallurgical process to recover lanthanum, yttrium and gadolinium from spent optical glass[9]. Wider use of REEs will require both lower-cost refining and purification methods and the development of many new applications that have been held back by the purity issue[10]. Solvent extraction has been applied practically for the separation of rare earth metals[11,12]. The family of extractants obtained as byproducts of phosphoric, phosphonic, and phosphinic acids seems to be the most promising in achieving the extraction of rare earth metal ions from aqueous solutions by means of solvent extraction[13-16]. This paper aims to contribute to knowledge on the separation of the lighter lanthanide ions of lanthanum, cerium, praseodymium and neodymium by means of solvent extraction techniques using an organophosphorus family of extractants.

Experimental

The extractants di-2-ethylhexyl phosphoric acid (D2EHPA) Merck Co., 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC 88A) DAIHACHI Chemical, bis(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (CYANEX 301) were used without further purification. CYANEX reagents were provided by CYTEC Chile.

All lanthanide reagents were analytical grade from Merck, and their aqueous solutions were prepared in the concentration range of 0.1-20 mM from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Nd_2O_3 , at different pH values measured by an OAKLON model ION700 pH meter using NaOH or HCl. The organic

solutions were prepared at concentrations of 0.1-120 mM of the respective extractant dissolved in kerosene. The kerosene solvent was provided by Shell Chile and was used without further purification.

The experiments were performed by contacting equal 25 mL volumes of aqueous and organic solutions in an appropriate Erlenmeyer flask, covered and agitated in a shaker for 24 h until equilibrium was reached. Later, the raffinate and loaded organic phases were separated and small samples were taken from the remaining aqueous solution. The analyses of the concentrations of rare earth elements were made by inductively coupled plasma with a mass spectrometry detector Agilent model 700.

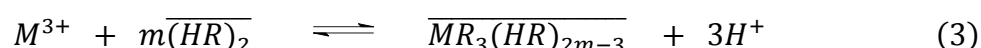
Results and discussion

Theory

The results expressed as the extraction percentage (E%) and the distribution coefficient (DM) were obtained using Equations 1 and 2, respectively.

$$E(\%) = \left(\frac{[M^{3+}]_0 - [M^{3+}]_{eq}}{[M^{3+}]_0} \right) \quad (1) \quad D_M = \left(\frac{[M^{3+}]_0 - [M^{3+}]_{eq}}{[M^{3+}]_{eq}} \right) \quad (2)$$

In both cases, $[M^{3+}]_0$ and $[M^{3+}]_{eq}$ correspond to the concentrations in the feed and raffinate aqueous solutions, respectively. Many authors have reported that the generic reaction stoichiometry for lanthanide elements with organophosphorus extractants (HR) is given by Equation 3.[17,18]



where M^{3+} is the lanthanide metal ion to be extracted from the feed solution, HR is the extractant contained in the organic phase represented as the dimer $(HR)_2$, and $\overline{MR_3(HR)_{2m-3}}$ is the metal complex produced, soluble only in the organic phase. The overline denotes species in the organic phase. Additionally, a measurement parameter which accounts for the effectiveness of a separation process is the separation coefficient " β ", which is based on the distribution coefficients of the individual metal ions, as shown in Equation 4

$$\beta_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (4)$$

- *Extraction of REE by means of organophosphorous extractants*

The optimization of the SX process involves achieving the best extraction conditions in which the uptake of metal ion occurs to the largest extent. To accomplish this goal, this study considered the extraction behavior of the lanthanide elements lanthanum, cerium, praseodymium and neodymium with the organophosphorus extractants D2EHPA, PC88A, CYANEX 272 and CYANEX 301. As extraction measurement

parameter, the metal removal percentage (E%), the metal distribution coefficient (D) and separation factors(β).

In the first instance, the acid-base behavior of the four extractants (D2EHPA, PC-88A, CYANEX 272 and CYANEX 301) were studied allowing to know their apparent pKa and through it the availability to react with the rare earth ions (RE) at certain pH. From this knowledge and the actual such extraction reactions it was possible to propose the use of a buffered feed aqueous phase with 3-cloropropionic acid at pH 4.

A set of experiments was realized to compare the grade of extraction four individual lanthanide ions individually with the four extractants from solutions with pH 4 buffer and without buffer, keeping fixed the other conditions. The organic phase contained each of the four extractants included in this study to a concentration of 40 mM, while the feed phase for each of the four rare earth ions to a concentration of 1 mM. The results are presented in Table 1

Table 1. Extraction percentages with and without buffer

	D2EHPA	PC88A	CYANEX 272	CYANEX 301
La (without buffer)	96,6	66,1	20,1	9,7
La (with buffer)	92,7	94,3	59,3	24,4
Ce (without buffer)	90,7	84,1	37,0	12,1
Ce (with buffer)	93,8	93,7	91,3	20,7
Pr (without buffer)	95,4	91,1	45,5	18,3
Pr (with buffer)	95,5	100,0	95,2	34,9
Nd (without buffer)	94,7	80,8	31,8	7,9
Nd (with buffer)	96,4	94,5	94,3	9,8

The Table 1 shows that the best percentages of extraction were obtained when the feed aqueous phase is buffered. The results showed that D2EHPA extractant have the best extraction performance and in less degree PC 88A, CYANEX 272, and CYANEX 301. However, D2EHPA and PC 88A were not able to discriminate among of REE, while CYANEX 301 discriminated them relatively well, but with a very low extraction extent. Thus, CYANEX 272 extractant performed in the best way under certain pH conditions in order to achieve a possible separation route.

- *Extraction and backextraction of lanthanide metal ions using CYANEX 272 as extractant*

A series of experiments in order to measure the degree of extraction and separation of lanthanide metal ions using CYANEX 272 as extractant were made. The experiments were performed varying extractant concentration in the organic phase in the range of 20 to 120 mM, using aqueous metal ion solutions whose initial concentration was kept constant at values close to 10 mM, with the feed solution at pH 4. The metal distribution coefficients were calculated using equation 2 and the results are plotted in Figure 1. In Figure 1 it is seen that the distribution coefficients

for each metal ion increase to a maximum around a CYANEX 272 concentration of 80 mM in the organic phase. However, it is seen that when the extractant content in the organic phase is increased over that value, the distribution coefficient values of all the metals decrease slightly. This behavior could be explained based on the solubility of the extractant or its complex with the lanthanides ions in the organic phase. In fact, it was observed certain turbidity in the organic phase what indicates that a grade of insolubility of the metal-extractant complex is attained when a higher concentration of extractant was used, affecting and diminishing the extraction distribution coefficient. In order to define a possible separation route of these elements, the separation factors ($\beta_{M1/M2}$) were calculated using equation 4. These separation factor allow make it possible to quantify how much of a metal ion is extracted with respect to another one. Based on the results shown in Figure 1, the calculated values of the separation factors are reported in Figure 2.

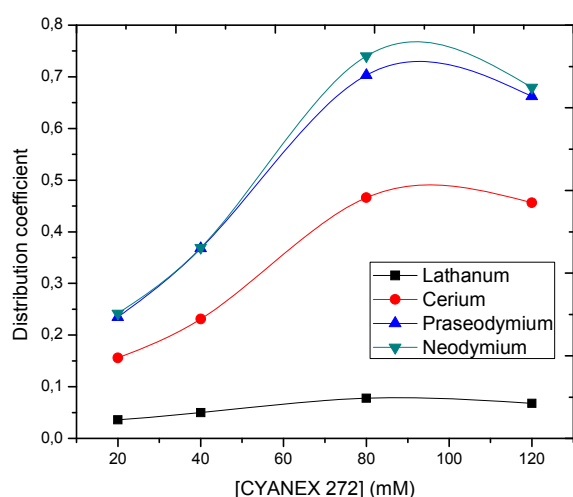


Figure 1. Distribution coefficients of REE as function of CYANEX 272

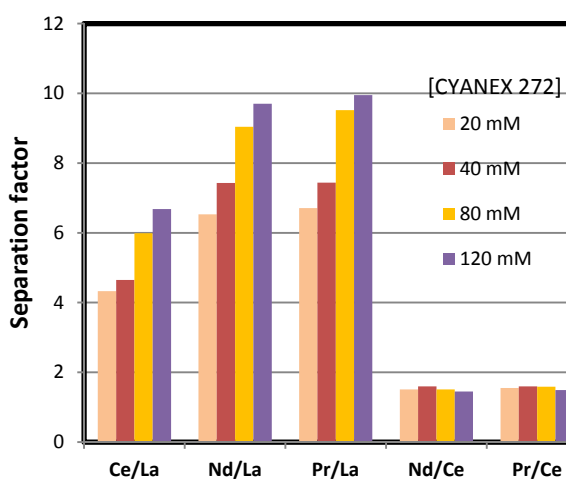


Figure 2. Separation factors of the light lanthanide ions

It is clear that the separation of two or more metal ions will be more feasible as the separation factor β reaches values greater than 1.0. Table 2 shows that based on these separation factors, lanthanum ion is the easiest to separate from the other ions. On the contrary, cerium, praseodymium and neodymium are difficult to separate from one another because their selectivity coefficients are all around 1.0.

Later was performed the backextraction of an organic phase charged with the three elements Ce, Pr, and Nd. It was stripped with a 2 M aqueous solution of hydrochloric acid getting a stripping degree much lower for cerium. The separation factors values in this case were: $\beta_{Pr/Ce}$ 24.8 y $\beta_{Nd/Ce}$ 26.0. Therefore it is possible to think in separating Ce element at this stage.

- *Separation of Nd-Pr pair with EDTA.*

Simultaneous extraction of the Nd-Pr pair is performed by adding different concentrations of EDTA in the feeding phase, keeping constant the concentration of each metal ion at 2 mM, the pH in the feed and concentration of CYANEX 272 in 40 mM. The extraction percentages and selectivity coefficients obtained are shown in Table 2.

Table 2. Extraction percentages and selectivity coefficients

[EDTA] mM	%E		$\beta_{Pr/Nd}$
	Pr	Nd	
1	77,60	67,67	1,66
2	53,08	41,54	1,59
3	22,67	17,50	1,38

Table 2 shows that praseodymium is better extracted than neodymium when EDTA is added in the feed aqueous phase achieving a separation factor of 1.66, as a maximum value.

Conclusions

It is possible to conclude that the separation of La, Ce, Pr, and Nd in aqueous phase by mean the solvent extraction technology may be carried out using the extractant CYANEX 272 controlling the media conditions, by example, the pH, the extractant concentration, the backextraction reaction and the addition of chelating agent to the feed solution.

References

- 1.- R. F. Service, *SCIENCE*, 327, 1596,
- 2.- L. Chang, H. Wang, Y. Cheng, T. Shong, E. Kuang Lin, *J Crystal Growth*, 198/199, 1092,
- 3.- P. Amedzake, E. Brown, U. Hömmerich, S.B. Trivedi, J.M. Zavada, *J Crystal Growth*, 310, 2015,
- 4.- T.Saito, *J Magnetism & Magnetic Mat*, 320,1893-1897
- 5.-W. Kaszuwara, B. Michalski, J. Latuch, M. Leonowicz, *J Magnetism & Magnetic Mat*, 320, 14, e51-e54.
- 6.- W.Y. Zhang, M. Stoica, J. Eckert, P. Yu, J.Z. Jiang, *Intermetallics*, 16, 3, 341.
- 7.- S.B. Han, J.Y. Lv, X.F. Liu, J. Peng, D.F. Chen, J.H. Li, Z.B. Hu, *J Alloys & Comp*, 431, 1-2, 4, 68.
- 8.- H. Fujimoto, H. Shimada, S. Yoshizawa, *Physica C: Superconductivity*, 463-465, 1, 374.
- 9.- Y. Jiang, A. Shibayama, K. Liu, T., Fujita, *Hydrometallurgy*, 76, 1.
- 10.- <http://www.arris-intl.com/customer/Papers/remetalspaper.html> Rare Earth Metals Find Interesting New Uses Despite Lack of Engineering Data.By Roman Lundin and John R. Wilson
- 11.- V. K. Jain, S. G. Pillap, H. C. Mandal, *J Chil Chem Soc*, 52, 2, 1177-1181.
- 12.- B. N. Kokare, A. M. Mandhare, M. A. Anuse, *J Chil Chem Soc*, 55, 4, 431-435.
- 13.- A. A. Abdeltawab, S. Nii, F. Kawaizumi, K. Takahashi, *Sep & Purification Tech*,26, 265.
- 14.- W. Weiwei, W. Xianghan, M. Shulan, L. Hongfei, L. Deqian, *J Rare Earths*, 24, 685.
- 15.- J. Yin, B. Hu, M. He, Z. Jiang, *Analytica Chim Acta*, 594, 1, 61.
- 16.- H. Li, F. Guo, Z. Zhang ,D. Z. Wang Li. *J. &Alloys and Comp.*, 995, 408-412 .
- 17.- H. Kao, P. Yen y R. Juang, *Chem.Eng.J.*119, 167.
- 18.- G. Seop, M. Uchikoshi, K.Mimura, M. Isshiki, *Sep. & Purification Tech.* 67, 79.

Vanadium Recovery by Extraction in Spent Catalyst Used in the Manufacture of Sulphuric Acid

*Maya Ramadianti Musadi**¹

Summary

Vanadium compounds are widely used in the chemical industry. These compounds are effective for catalyzing both organic oxidation and reduction. Vanadium pentoxide (V_2O_5) and ammonium metavanadate (NH_4VO_3) are the common commercial form from of vanadium. V_2O_5 can be used as a dye and color fixer and as a catalyst in the sulfuric acid production. Whereas NH_4VO_3 is used as a corrosive inhibitor in absorption column of CO_2 . Up till now, the vanadium sources are titomagnetite ores and their concentrates. Researches are conducted to utilize vanadium catalysts that have been disposed in the industrial processes. Besides fulfilling the demand for vanadium, the usage of the spent catalysts help to prevent environmental pollution due to the poisonous and dangerous vanadium.

The objective of this research is to recover vanadium compounds from spent catalyst in form NH_4VO_3 . This recovery process consists of two stages, i.e. extraction and crystallization. The result shows that the presence of Fe compound has colored and decreased the purity of the crystal. Consequently, Fe compound should be separated by precipitation. NH_4VO_3 with 60 %-recovery with respect to the spent catalyst and 76%-purity could be obtained by extraction at room temperature using a solution of Na_2CO_3 1,89 M as a solvent. The time of extraction 60 minutes and the ratio of the V_2O_5 weight in the spent catalyst to the solvent volume was 6 gr/l. The process was then continued by the precipitation of Fe compound at pH 12 for two hours and the crystallization of NH_4VO_3 using NH_4Cl 11,2 M for 4 - 5 hours at 60°C.

Introduction

Most chemical processes use catalyst at some stage in production process. The overall catalyst performance is assessed in terms of activity, selectivity and life. Catalyst which is used in the Contact process, conversion of sulphur dioxide in to sulphur trioxide for production sulphuric acid, contents V_2O_5 supported on a special oxide (Fe_2O_3).

Deactivation of this catalyst may result from poisoning, fouling or coking. The rate of catalyst deactivation determining catalyst life. The deactivated catalyst can be regenerated or reused as a catalyst. This method is the most economics solution. It may involve recovery of V_2O_5 from spent catalyst before disposal at a minimize cost and meeting environmental standards.

Vanadium compounds from spent catalysts can be recovered in form NH_4VO_3 . Compared to V_2O_5 , the recovery of NH_4VO_3 is more profitable since the price of vanadate compound in the market is more expensive than V_2O_5 . In addition, to produce NH_4VO_3 one can work in neutral condition while the process of obtaining V_2O_5 should be at low pH (1-3). The process in low pH is often avoided since it requires equipment with strict specification.

The recovery process of vanadium from spent catalyst consists of two stages, i.e. extraction and crystallization. The research focused on the crystallization stage and

* Chemical Engineering Department – National Institute of Technology (ITENAS), Bandung, Indonesia .
Contact :mmusadi@yahoo.com

aimed to find an appropriate condition for obtaining NH_4VO_3 crystal with high purity and high recovery percentage.

The result shows that the presence of Fe compound has colored and decreased the purity of the crystal. Fe compound could be separated by precipitation at pH 12 for two hours and then continued by crystallization of NH_4VO_3 using NH_4Cl 11.215 M for 4 - 5 hours at 60°C .

Experimental Works

Material

The spent vanadium catalyst were supplied by PT Petrokimia Gresik, East Java, Indonesia. Table 1 shows the chemical analysis of spent catalyst sample.

Table 1. Chemical Analysis Data for Spent Catalyst

Compound	%-w
V_2O_5	5.14
Fe_2O_3	1.45
Al_2O_3	1.30
Na_2O	1.85
SiO_2	61.29

Extraction by Na_2CO_3 Solution

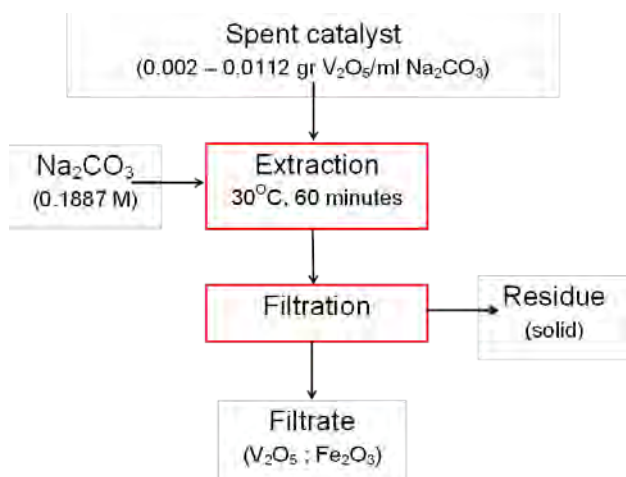


Figure 1. Schematic Diagram for Extraction of Vanadium from Contact Process Spent Catalyst

Preparation of Ammonium Metavanadate

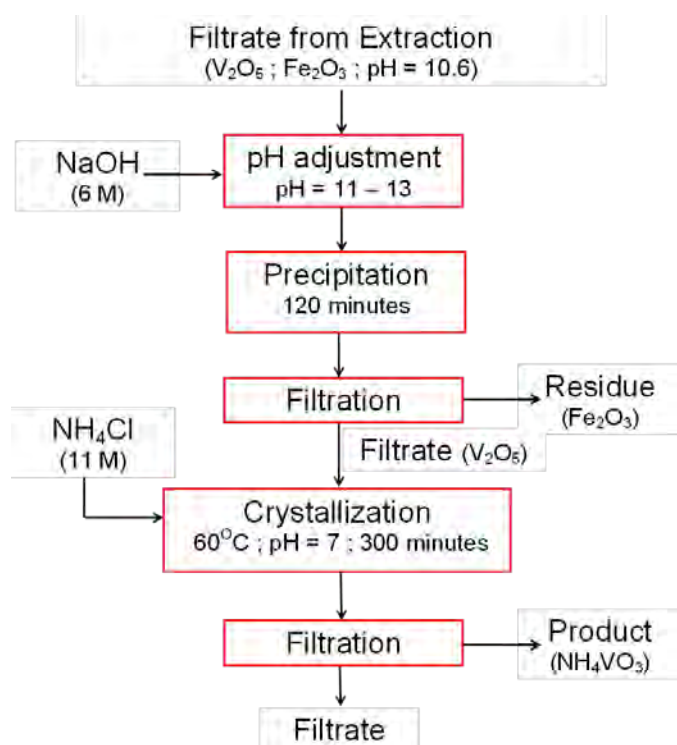


Figure 2. Schematic Diagram for the Preparation of Ammonium Metavanadate (NH_4VO_3)

Analysis Method

The analysis for sample of spent catalyst, extract and filtrate are achieved through the use of gravimetric, titrimetric and atomic absorption spectrophotometric methods.

Results

Extraction

The result of extraction by Na_2CO_3 is shown in Table 2.

Table 2. Chemical Analysis Data for Extraction Product

Compound	Concentration, M	Yield (%)
V_2O_5	0.03000	81.27
Fe_2O_3	0.00500	42.02
Al_2O_3	0.00007	0.42
SiO_2	0.00096	0.07

Effect of pH on precipitation of vanadium and iron

The effect of pH on precipitation was studied using different pH in the range 1 – 4 for 2 hours, the results are shown in Figure 3

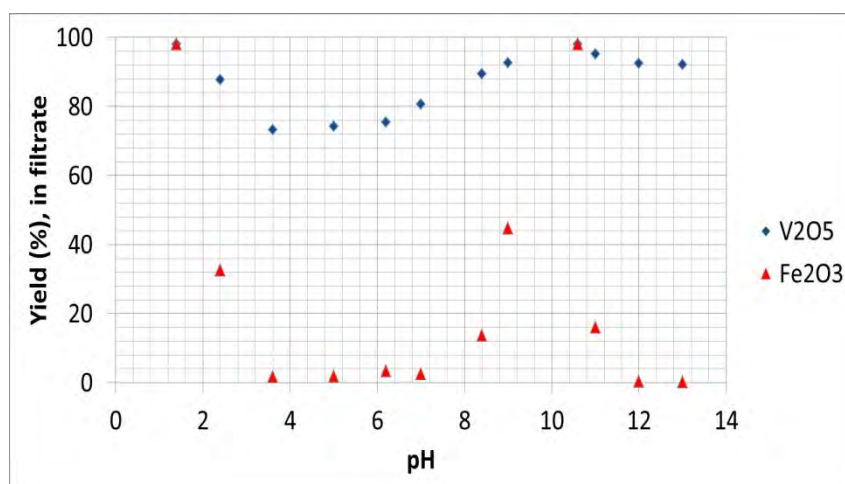


Figure 3. Effect of pH on Precipitation of Vanadium and Iron

Ammonium Metavanadate Preparation

The chemical analysis of precipitation at pH 12 and crystallization at 60°C product indicate that pure ammonium metavanadate was produced. The composition of this product is similar to ammonium metavanadate commercial, see Table 3.

Table 3. Chemical Analysis Data for AMV Product

Compound	Composition, %-w	
	Laboratory	Commercial
V ₂ O ₅	75.48	76.73
Fe ₂ O ₃	0.01	0.01
Al ₂ O ₃	< 0.01	0.01
SiO ₂	< 0.10	0.10

Conclusions

The spent vanadium catalyst could be an alternative resource of vanadium and raw material for ammonium meta-vanadate

The optimum conditions for extraction using Na₂CO₃ solution are :

- 0,006 gram V₂O₅/ml Na₂CO₃ (0.1887 M)
- time of extraction ; 60 minutes

The optimum conditions for ammonium meta-vanadate preparation are :

- pH for Fe precipitation is 12
- temperature crystallization is 60°C

References

1. Abas, F.O., 2005. "Vanadium Oxide Recovery from Spent Catalyst" *Chemical Leaching*, Vol. 26.
2. Baker, R.H., Zimmerman, H., and Maxson, R.N., "Ammonium Metavanadat", *Inorganic Synthesis*, Vol. III, Mc Graw Hill Book Company, Inc., page 117.
3. Charry, I.D., Gonzalez, L.M., and Montes, Consuelo, 2004. "Vanadium Leaching from Spent Catalysts" *Environmental Catalysts Research Group*, Colombia.
4. Enghag, P., 2004. "Encyclopedia of Elements", Chapter 21, Page 543-546, Sweden.
5. Koplis, Gean, 1985. "Transport Process and Unit Operation", Allyn and Bacon, Inc.,.
6. Magnani, J.L., Kachan, G.C., and Ferreira, N.L., 2000. "Vanadium Recovery by Leaching in Spent Catalyst for Sulfuric Acid Production".
7. Mazurek, K., Bialowicz, K., Trypuc, M., 2010. "Recovery of Vanadium, Potassium, and Iron from a Spent Catalyst using Urea Solution".
8. Mousa, K.M., and Kouba, S.K., 2010. "Vanadium Recovery from Spent Catalyst Used in the Manufacture of Sulfuric Acid" *Chemical and Petroleum Engineering*, Vol. 11.
9. Musadi, M.R., 1999. "Vanadium Recovery from Spent Catalyst", Thesis, Chemical Engineering Department ITB, Indonesia.
10. Othmer, K., 1969. "Encyclopedia of Chemical Technology", *Vanadium and Vanadium Alloys*, Vol. 24, Hal. 381-394.
11. Perry, J.H., "Chemical Engineers Handbook", McGraw Hill Book Company, Inc., New York.

Extraction of chromium (VI) by liquid-liquid extraction using Cyphos IL

*Z. Gamiño-Arroyo^{*1}, E.A. Franco-García¹, L.E. Sánchez-Cadena², I. Cano-Rodríguez¹, F.I. Gómez-Castro¹, J. Ramírez-Flores¹, A. R. Uribe-Ramírez¹*

Summary

In this paper we present the results of the separation of chromium (VI) by liquid-liquid extraction using Cyphos IL 101. Chromium is a metal widely used in metal coatings to prevent corrosion. On the other hand, it is a highly toxic metal. Extraction studies were conducted with a synthetic solution of chromium (VI) where the pH, the concentration of extractant and the metal were modified. Those changes allowed us to establish the conditions for adequate extraction. The conditions analyzed were a concentration of metal between 100 to 400 mg/L, pH of 1.9 and a concentration of Cyphos IL 101 of 0.01 mol/L diluted in kerosene. A kinetic study allowed us to determine a contact time of 4 minutes, with those results the extraction isotherm was determined and the number of stages required for the extraction was computed using the McCabe-Thiele method. This strategy showed two stages of extraction for an A/O = 1.05, which allows us to recover 98 % of chromium from the aqueous phase. For stripping, it was used a solution of sodium hydroxide 0.15 mol/L, with a contact time of 40 minutes and an A/O = 2/5. Stripping achieves a yield of 91 % in the continuous process. This work shows that Cyphos IL 101 is an excellent extractant for Chromium (VI) and it may allow recovery of the metal from waste effluents of the metallic coatings industry.

INTRODUCTION

In the chromium electroplating industry, a large amount of waste-containing heavy metals (either diluted or concentrated) are produced. In Mexico there are about 600 of these industries, producing 600 tons of sludge and 300 tons of wastewater per year [1]. The baths of electroplating contain chromic acid (250 g/L), sulfuric acid (2.5 – 4 g/L), boric acid (5 – 10 g/L) and water. Cr(VI) is a stable and highly toxic heavy metal, is considered acutely toxic and mutagenic for most organisms. Its effects in humans are: lung cancer and nasal and sinus cancer; eye, nose and throat irritation; nasal septum ulcerations and gastritis; dermatitis [2]. The permissible limit of Cr(VI) for industrial waste discharges to surface water is 0.5 mg/L [3]. Unfortunately effluents are neutralized and only very few are precipitated, generating large amounts of sludge toxics. Removal of Cr(VI) has been investigated by using: ion-exchange [4], adsorption [5], biosorbents [6] and electrodialysis [7], however these methods are difficult to implement and control. Another technique is the liquid-liquid extraction which is widely used in the separation of metals. In the present work, different commercial extractants were studied. It has been obtained that the best extractant for Cr(VI) from H₂SO₄ medium is trihexyl (tetradecyl) phosphonium chloride (Cyphos IL 101). A number of other metals extracted by this solvent includes: gold [8], palladium [9] and bismuth [10]. However, there is relatively little research on the extraction of Cr(VI) with Cyphos IL 101.

^{*1} Corresponding Author: Departamento de Ingeniería Química, Universidad de Guanajuato, Noria Alta s/n, Guanajuato, Gto. 36050, México. e-mail: gaminoz@ugto.mx

² Author 2: Departamento de Ingeniería Civil, Universidad de Guanajuato, Juárez No. 77, Guanajuato, Gto. 36000, México

EXPERIMENTAL

Reagents and Materials

The extractants Cyphos IL 101, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), tri-n-octylphosphine oxide (Cyanex 921) and a mixture of trialkylphosphine oxides (Cyanex 923), supplied by Cytec Canada Inc., were used without prior purification. Organic phase was prepared with diluted extractant in kerosene (Reasol) or eventually mixed with 10% v/v of n-octanol (Karal). Chromium (VI) stock solution was prepared by dissolving an accurate quantity of analytical grade K_2CrO_4 with distilled water. All other chemical products were of analytical reagent grade.

Experimental procedure

Equal volumes (10-20 mL) of the aqueous and the organic phases were contacted for 30 minutes (sufficient to reach equilibrium) with a magnetic stirrer (600-700 rpm) at $20 \pm 1^\circ C$, pH is adjusted by addition of very small volumes of H_2SO_4 or NaOH, pH measurements were taken using a potentiometer (Hanna). Once equilibrium was attained, the phases were separated and Cr(VI) concentration in the aqueous phase was determined by atomic absorption spectrometry (AAnalyst 200, Perkin Elmer). The concentration of Cr(VI) in the organic phase was calculated by mass balance.

Balance process

Extraction yield or percentage in balance (% Ext) for an aqueous phase relation (A) with respect to organic phase (O) equal to one ($A/O = 1$), where $[Cr]_{aq}$ is the concentration in aqueous phase and $[Cr]_{org}$ is the concentration in organic phase and is defined as:

$$\% \text{ Ext} = \frac{[Cr]_{org}}{[Cr]_{aq} + [Cr]_{org}} 100\% \quad (1)$$

RESULTS AND DISCUSSION

Selection of extractant

A comparative extraction efficiency of Cyphos IL 101, Cyanex 272, Cyanex 921 and Cyanex 923, for the extraction of Cr(VI) was conducted. Results exhibited in figure 1. Cr(VI) extraction efficiency follows the apparent order as: Cyphos IL 101 > Cyanex 921 > Cyanex 923 > Cyanex 272. The advantage is that the Cyphos IL 101 does not form a third phase as the Cyanex 921 or Cyanex 923.

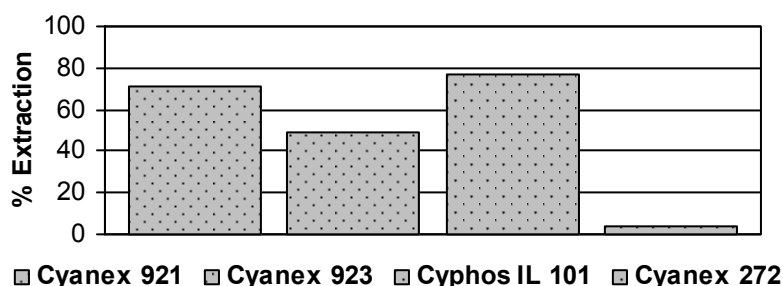


Figure 1. Comparative extractions of Cr(VI) with 0.1 mol/L of different extractants, pH = 5, phase ratio A/O = 1, T = 20°C.

Effect of pH

Figure 2 shows the effect of the pH on the extraction of Cr(VI) with Cyphos IL 101. According to Figure 2, chromium is better extracted under acidic conditions ($\text{pH} = 2$) and extraction efficiency decreases when the pH in equilibrium is increased. Thus, the separation may occur following an anionic exchange mechanism.

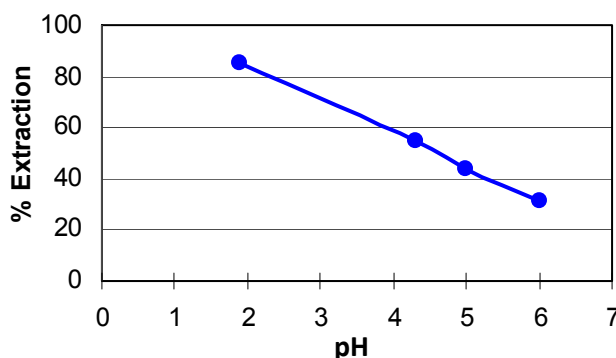


Figure 2. Influence of the pH. Aqueous initial $[\text{Cr(VI)}] = 100 \text{ mg/L}$. $[\text{Cyphos IL 101}] = 0.01 \text{ mol/L}$, phase ratio $A/O = 1$, $T = 20^\circ\text{C}$.

Effect of Cyphos IL 101 concentration

The effect of concentration of Cyphos IL 101 (0.01 – 0.1 mol/L) on Cr(VI) extraction from acidic solutions has been studied and the results are presented in the figure 3. It can be seen that when concentration of Cyphos IL 101 is high (0.1 mol/L), an extraction efficiency of about 99% is achieved. Nevertheless, the most important change on the efficiency occurs in a small range (from 0.01 to 0.02 mol/L). From this point, increasing the extractant concentration will increase only slightly the extraction efficiency.

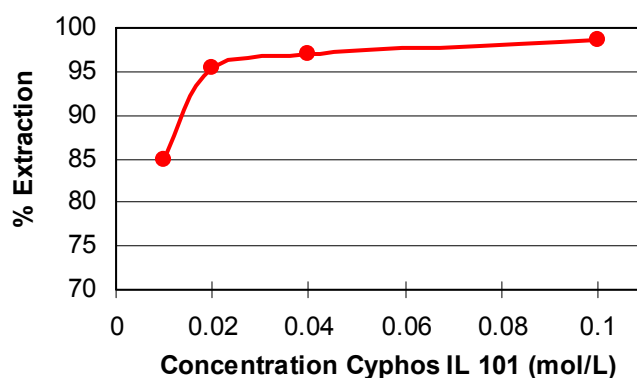


Figure 3. Effect of Cyphos IL 101 concentration. Aqueous initial $[\text{Cr(VI)}] = 100 \text{ mg/L}$. $[\text{Cyphos IL 101}] = 0.01 - 0.1 \text{ mol/L}$, $\text{pH} = 1.9$, phase ratio $A/O = 1$, $T = 20^\circ\text{C}$.

Effect of equilibrium time

Kinetic studies were performed by contact of 50 mL of aqueous solution of Cr(VI) with 50 mL of Cyphos IL 101 extractant, 1 mL of each phase has been taken at different time and concentration of Cr(VI) measured by atomic absorption. For industrial applications, it is important to have knowledge about the time required for the phases to be in contact to achieve a proper separation. Thus, in Figure 4 the effect of the

time on the separation is shown. It can be seen that equilibrium is reached at a very short time (about 2 min) with high extraction efficiency. It can also be noticed that for time higher than 20 minutes, a reduction on the extraction efficiency occurs. Thus, it is not recommended to have high contact times.

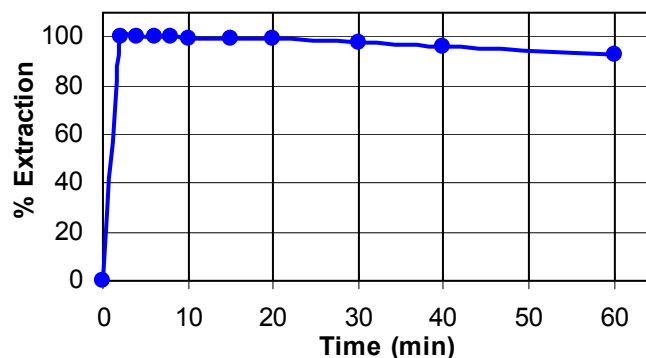


Figure 4. Effect of equilibrium time. Aqueous initial $[Cr(VI)] = 100 \text{ mg/L}$. $[Cyphos \text{ IL } 101] = 0.01 \text{ mol/L}$, $pH = 1.9$, phase ratio $A/O = 1$, $T = 20^\circ\text{C}$.

Calculation of the number of stages for extraction

To compute the number of stages required to perform the separation, the extraction isotherm is first obtained from the experimental results. Then, using the McCabe-Thiele method the number of stages is calculated as two (Figure 5). This result is useful for solutions with a maximum concentration of $Cr(VI)$ of 400 mg/L , $A/O = 1.05$, $pH = 1.9$ and a maximum composition of 1 mg/L on the raffinate. In an experimental continuous system the separation has been performed obtaining a composition of 1.3 mg/L in the raffinate, which is close to the predicted by the model.

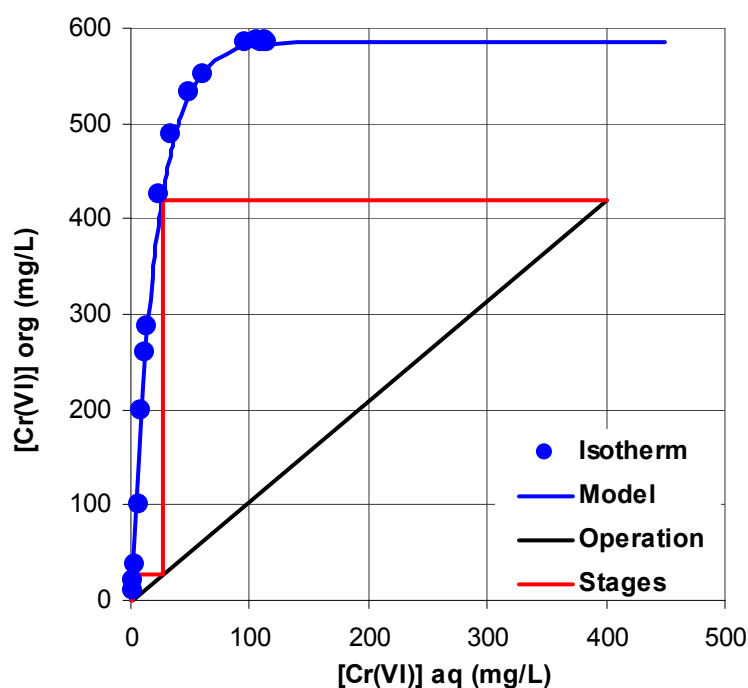


Figure 5. McCabe-Thiele plot for the extraction of $Cr(VI)$ by Cyphos IL 101, $X_o = 400 \text{ mg/L}$; $X_n = 0.96 \text{ mg/L}$, phase ratio $A/O = 1.05$, $T = 20^\circ\text{C}$.

Stripping of the extracted Cr(VI) from the loaded Cyphos IL 101.

Since the extraction occurs following an anionic exchange mechanism, a basic agent must be used for the stripping operation to recover the Cyphos IL 101. It has been observed that NaOH recovers a good quantity of the extractant. In this study, a 0.15 mol/L solution of NaOH has been used and stripping efficiencies of about 80% have been obtained. The loaded solution has a chromium concentration of 98 mg/L, with A/O = 2.5. In Figure 6 the McCabe-Thiele diagram for the stripping process is shown. It can be seen that loaded chrome can be stripped using two extraction stages.

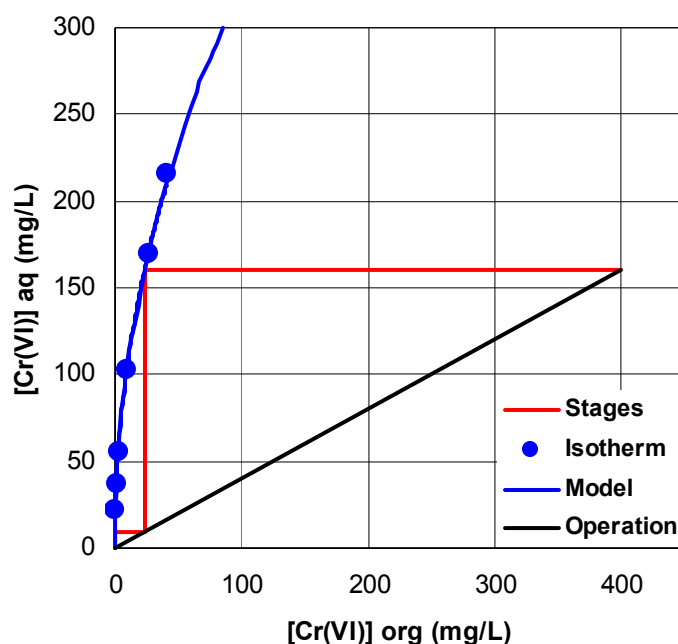


Figure 6. McCabe-Thiele plot for the stripping of loaded Cr(VI) from Cyphos IL 101 by 0.15 mol/L NaOH.

CONCLUSION

In this work the extraction of Cr(VI) with an ionic liquid (Cyphos IL 101) has been studied. It has been shown that the extractant allows the separation of Cr(VI) from aqueous solutions, with a maximum extraction efficiency of 99% with pH = 1.9, A/O = 1 and room temperature. The McCabe-Thiele plot shows that the separation may be performed in a continuous system with two stages for an initial concentration of 400 mg/L of Cr(VI). Furthermore, the extraction agent may be stripped using an NaOH solution (0.15 mol/L) in a system with two stages.

ACKNOWLEDGEMENTS

We thank the University of Guanajuato for the financial support. We also thank CYTEC Canada Inc. for supplying the working samples.

REFERENCES

1. Comisión Ambiental Metropolitana, Concepto de manejo de residuos peligrosos e industriales para el giro de galvanoplastia. Manual de minimización, tratamiento y disposición, 1998.
2. Manuel Repetto Jiménez, Guillermo Repetto Kuhn. Toxicología fundamental. Ediciones Díaz de Santos, 2009.
3. Norma Oficial Mexicana NOM-001-SEMARNAT-1996, Protección Ambiental.- Establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales.
4. Taihong Shi , Zhuochao Wang, Yang Liu, Shiguo Jia , Du Changming. Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion exchange resins. *Journal of hazardous materials* 161(2009) 900-906.
5. E. Álvarez-Ayuso, A. Garcia-Sanchez, X. Querol. Adsorption of Cr (VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide. *Journal of hazardous materials* 142 (2007) 191-198.
6. Ashok V. Bakar, Ameeta R. Kumar, Smita S. Zinjarde. Removal of chromium (VI) ions from aqueous solution by adsorption onto two marine isolates of *Yarrowia lipolytica*. *Journal of hazardous materials* 170 (2009) 487-494.
7. C. Korzenowski, M.A.S. Rodrigues, L. Bresciani, A.M. Bernardes, J.Z. Ferreira. Purification of spent chromium bath by membrane electrolysis. *Journal of hazardous materials* 152 (2008) 960-967.
8. Yu Tong, Hongxiao Yang, Jing Li, Yanzhao Yang. Extraction of Au(III) by ionic liquid from hydrochloric acid medium. *Separation and Purification Technology* 120 (2013) 367-372.
9. Anna Cieszyńska, Magdalena Regel-Rosocka, Maciej Wisniewski. Extraction of Palladium (II) Ions from Chloride Solutions with Phosphonium Ionic Liquid Cyphos IL 101. *Polish Journal of Chemical Technology* 9, 2, 99 – 101, 2007.
10. Luisa Zempoaltecatl, Diana Cholico, Pilar González, Luis Santiago, Imelda Saucedo, Ricardo Navarro, Mario Ávila Rodríguez. Recovery of Bi (III) by liquid-liquid extraction and supported liquid membranes using Cyphos IL 101. 19th International Solvent Extraction Conference, Santiago, Chile, 2011.

Extraction of rhodium(III) and ruthenium(III) ions from chloride solutions with phosphonium ionic liquids as extractants

*Magdalena Regel-Rosocka^{*1}. Martyna Rzelewska¹. Maciej Wiśniewski¹*

Summary

The aim of this work is to investigate rhodium(III) and ruthenium(III) extraction from chloride solutions with phosphonium ionic liquids as extractants. The equilibrium and the influence of time on extraction efficiency are determined. Additionally, the effects of hydrochloric acid and metal ion concentration in the feed phase are studied. Also, rhodium(III) and ruthenium(III) extraction are carried out depending on the type of extractant and its concentration in the organic phase. Co-extraction of protons, chlorides and water are determined. Finally, stripping efficiency with various solutions is studied to find the most efficient strippant and to reuse the organic phase.

Introduction

At present noble metals have a wide range of industrial applications. They are used in electronic, chemical, pharmaceutical and petroleum industries, also in instrument and jewelry making [1]. A demand for these metals has increased in recent years, whereas the natural sources are limited. Both the recovery of noble metals from waste solutions as well as preconcentration techniques, to facilitate their determination at very low levels, are important economical and ecological issues [2]. Liquid-liquid extraction is one of the efficient techniques to separate valuable metal ions from diluted effluents [3].

The aim of this work is to investigate rhodium(III) and ruthenium(III) extraction from chloride solutions with phosphonium ionic liquids as extractants. The equilibrium and the influence of time on extraction efficiency are determined. Additionally, the effects of hydrochloric acid and metal ion concentration in the feed phase are studied. Also, rhodium(III) and ruthenium(III) extraction are carried out depending on the type of extractant and its concentration in the organic phase. **Co-extraction of protons, chlorides and water are determined.** Finally, stripping efficiency with various solutions is studied to find the most efficient strippant and to reuse the organic phase.

Experimental

Reagents

Phosphonium ionic liquids (phosphonium ILs): trihexyltetradecylphosphonium chloride (Cyphos IL 101), trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) supplied by Cytec Industries Inc. (USA) are dissolved in toluene (0.005 M). The structures of the ILs applied are presented in Table 1.

^{*1} e-mail: magdalena.regel-rosocka@put.poznan.pl, Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

The model aqueous solutions contained: 0.0025 M Ru(III) or 0.0025 M Rh(III) in 0.1; 1; 3 or 5 M HCl (the ionic strength was constant: 5 M) and 0.0025 M Ru(III) or 0.0025 M Rh(III) in 0.1 M HCl with 1; 3 or 5 M NaCl.

Table 1. Structures of the extractants used.

Cyphos IL 101. <i>Trihexyltetradecylphosphonium chloride</i>	Cyphos IL 104. <i>Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate</i>

Experimental methods

Extraction has been carried out in a typical way: equimolar aqueous feeds containing metal ions added as chlorides, were mechanically shaken with IL phase (volume ratio w/o = 1) for 20 minutes at 20°C in glass separatory funnels and then allowed to stand for phase separation. For determination of extraction time the studies were carried out in the time range from 1 to 60 min. Stripping of metal ions from loaded organic phases was carried out with 0.5 M NH₄OH and 5 M HCl solutions. The loaded organic phase and stripping phase were shaken at volume ratio w/o=1 for 10 or 20 minutes at 20°C in glass separatory funnels and then allowed to stand for phase separation. Atomic absorption spectrometer Hitachi Z-8200 was used for determination of Rh(III) and Ru(III) in aqueous solutions at 369.2 and 349.9 nm, respectively. Hydrochloric acid and chloride concentrations were determined by potentiometric titration with 0.1 M NaOH or 0.1 M AgNO₃, respectively.

Each experiment was carried out twice and the error has not exceeded 5%.

Results and discussion

Influence of shaking time on extraction

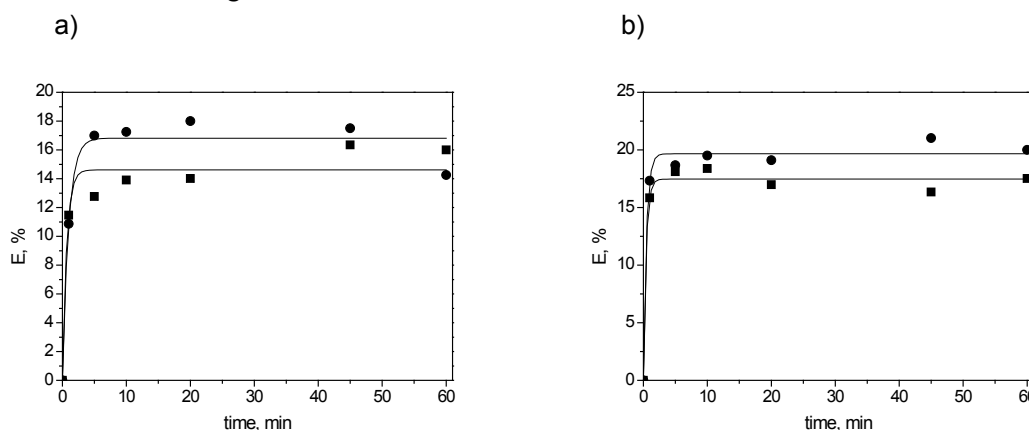


Fig.1. Extraction of Rh(III) from: a) 0.1 M HCl; b) 3 M HCl with (■) IL 101. (●) IL 104 vs. time of shaking.

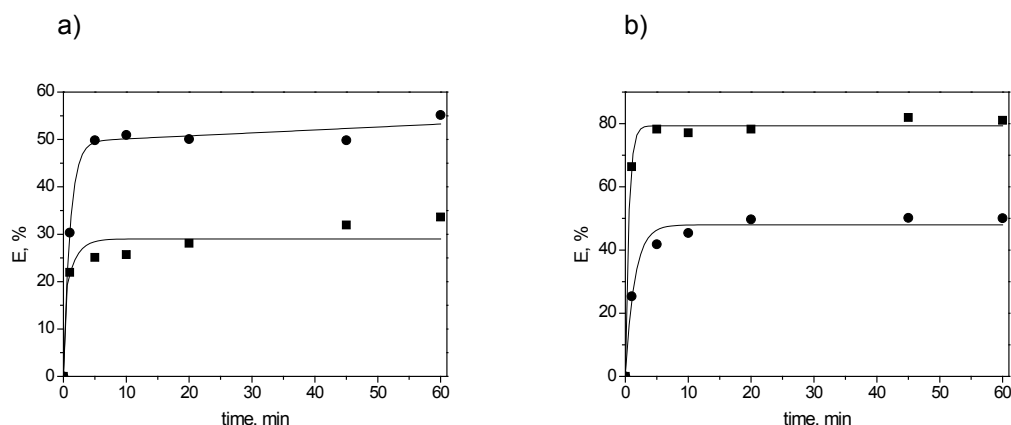


Fig. 2. Extraction of Ru(III) from: a) 0.1 M HCl; b) 3 M HCl with (■) IL 101. (●) IL 104 vs. time of shaking.

Extraction equilibrium state is established quickly; after 5 min of shaking constant values of Rh(III) and Ru(III) extraction are obtained (both from 0.1 and 3 M HCl) (Figs 1 and 2). Unfortunately, extraction efficiency of Rh(III) for both extractants is low. only about 20% Rh(III) is transported to Cyphos IL 104 from 3 M HCl – Fig.1 b. All model aqueous solutions were pale pink before extraction. but after extraction from 0.1 M HCl solutions have changed color to pale yellow/orange. It should be indicated that Ru(III) is much better extracted than Rh(III). The highest efficiency is obtained for the extraction of Ru(III) from 3 M HCl with IL 101 (82%) (Fig.2b). while the lowest – for Rh(III) from 0.1 M HCl with IL 101 (about 25%) (Fig.2a). Extraction of Ru(III) with IL 104 (45-50%) was comparable for both concentrations of HCl in the feed.

Ru(III) and Rh(III) stripping from the organic phase

The results for stripping of Rh(III) and Ru(III) with various stripping phases are presented in Tables 2 and 3.

Table 2. Percentage of Rh(III) stripping.

No.	Rh(III) R. %				
	Cyphos IL 101			Cyphos IL 104	
	0.1 M HCl	0.1 M HCl*	3 M HCl	0.1 M HCl	3 M HCl
1	57.1	29.3	28.7	48.6	34.1
2	49.8	28.6	24.9	36.6	33.4
3	55.7	26.1	27.7	36.8	33.3
4	47.6	23.4	30.4	39.6	30.1
5	43.3	27.7	34.0	33.0	30.8
6	48.2	27.0	26.7	42.2	35.3

* stripping with 5 M HCl

Table 3: Percentage of Ru(III) stripping

No.	Ru(III) R. %			
	Cyphos IL 101		Cyphos IL 104	
	0.1 M HCl	3 M HCl	0.1 M HCl	3 M HCl
1	29.1	8.0	7.3	15.2
2	12.8	7.1	6.0	8.2
3	17.5	5.9	4.5	6.9
4	21.3	6.4	4.5	8.2
5	17.7	5.2	4.4	8.8
6	-	3.8	4.2	7.6

Rh(III) and Ru(III) were stripped with 0.5 M NH_4OH except from the results marked with asterisk in Table 2. In this case, 5 M HCl was used as a strippant. Generally, Rh(III) stripping seems to be more efficient than Ru(III) removal from the organic phases. However, the organic phases after extraction contain less Rh(III) (only up to 20% extracted). Rh(III) stripping with 5 M HCl was twice less than with the ammonia.

The stripping of Ru(III) with 0.5 M NH_4OH is problematic because after 10 minutes of stripping black suspension appears in the aqueous phase. Stripping efficiency of Ru(III) was very low for both extractants.

Influence of HCl concentration

The effect of HCl concentration in the feed on Rh(III) or Ru(III) extraction is shown in Table 4.

Table 4. Influence of HCl concentration in the feed on the efficiency of Rh(III) or Ru(III) extraction (feed: 0.0025 M Rh(III) or Ru(III). 0.1; 1. 3 or 5 M HCl; constant ionic strength; the organic phase: 0.005 M Cyphos IL 101 or 0.005 M Cyphos IL 104).

HCl. M	Rh(III) E. %		Ru(III) E. %	
	Cyphos IL 101	Cyphos IL 104	Cyphos IL 101	Cyphos IL 104
0.1*	14.0	18.0	28.1	50.1
0.1	44.6	50.4	50.1	36.9
1	47.8	38.0	36.6	27.7
3	40.4	31.1	32.1	21.3
5	37.6	14.0	20.1	18.2

* without the addition of salt

Cyphos IL 101 is slightly more effective extractant of both Rh(III) and Ru(III) than Cyphos IL 104. The values of $E_{\text{Rh(III)}}$ from a solution of 0.1 M HCl without NaCl addition for both extractants are low and do not exceed 20%.

Generally, increase in HCl concentration (Table 4) in the feed causes reduction in extraction of ruthenium(III) and rhodium(III) with both phosphonium ILs. The lowest

extraction efficiency of Ru(III) and Rh(III) with Cyphos IL 104 is reported when 5 M acid is present in the feed. Effect of concentration of hydrochloric acid was different for extractant Cyphos IL101.

Determination of acid and chloride concentrations

Hydrochloric acid and chloride concentrations before and after extraction were determined in the aqueous phases by potentiometric titration with 0.1 M NaOH or 0.1 M AgNO₃, respectively. The results are shown in tables 6 and 7.

Table 6. Determination of hydrochloric acid concentration.

HCl [M]	The aqueous phase before extraction [M]		The aqueous phase after extraction with IL101 [M]		The aqueous phase after extraction with IL104 [M]	
	Rh(III)	Ru(III)	Rh(III)	Ru(III)	Rh(III)	Ru(III)
0.1	0.111	0.106	0.100	0.108	0.096	-
1	0.949	0.959	0.890	0.992	0.839	0.980
3	2.726	2.879	2.709	2.918	2.695	2.916
5	4.959	5.063	4.799	4.840	4.802	4.880

Table 7. Determination of chloride concentration.

NaCl [M]	The aqueous phase before extraction [M]		The aqueous phase after extraction with IL101 [M]		The aqueous phase after extraction with IL104 [M]	
	Rh(III)	Ru(III)	Rh(III)	Ru(III)	Rh(III)	Ru(III)
1	1.085	1.020	1.065	1.008	1.082	0.996
3	3.220	3.013	3.120	3.104	3.167	2.987
5	5.226	5.224	5.200	4.972	5.225	5.100

Acid and chlorides have not been extracted into organic phase. Small differences in the measurements are within the limits of measurement error.

Conclusions

Extraction efficiency of Rh(III) and Ru(III) depends on the acidity of the medium and the type of the extractant used. Generally, Rh(III) extraction with both phosphonium ILs studied is inefficient. Ru(III) extraction is very high with increasing HCl concentration but without addition of NaCl to the feed. Further investigations on the conditions of Ru(III) and Rh(III) extraction are necessary to explain the mechanism of reaction.

Acknowledgments

This research was supported with 32/441/14 DS-PB grant.

References

1. C. Hagelüken. *Metall.* 60(1-2) (2006) 31-42.
2. F.L. Bernardis. R.A. Grant. D.C. Sherrington. *React. Funct. Polym.* 65 (2005) 205–217.
3. A. Cieszyńska. M. Regel-Rosocka. M. Wiśniewski. *Przem. Chem.* 90(8) (2011) 1579-1585.

PREPARATION OF THE NOVEL IONIC LIQUIDS FUNCTIONALIZED RESINS WITH TUNABLE STRUCTURE FOR SEPARATION AND RECOVERY OF LUTETIUM(III)

H. M. Cui^{a, b}, and J. Chen^{a,*}

^a *State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.*

^b *University of Chinese Academy of Sciences, Beijing 100049, China.*

Corresponding author email address: jchen@ciac.ac.cn

ABSTRACT

Adsorption of Lu(III) from dilute solutions by novel ionic liquids functionalized resins was investigated. The selectivity studies of the functionalized resins were conducted for Lu(III) and Yb(III) at various pH values, and results showed that both resins displayed excellent affinity and capacity for Lu(III) adsorption at the optimal experiment conditions. The adsorption of Lu(III) on both resins was determined to be ionic strength-dependent in solution, and the data could be fitted to a Freundlich isotherm model. In this work, XPS analysis was also performed to gain a better understanding of adsorption sites for Lu(III) onto the resins.

INTRODUCTION

Rare metals, such as, rare earths(REs), Re(VII) and Mo(VI), and heavy metals, are widely used as key components for electronics, fuel cells, and catalytic converters [1-3]. Along with economic growth is the increasing demand of rare metals. Considering resource sustainability development and environmental improvement, it is a priority and real necessity to develop effective recovery and separation methods for rare metals.

So far, solvent extraction, frequently used for the separation of metals, represents alternative that works well at high concentration [4]. However, drawbacks are associated with solvent extraction for the separation of metals from dilute solutions

[5]: (1) multistage cycles of extraction and back-extraction in order to attain favorable separation, (2) extractant loss owing to its aqueous solubility, (3) third phase formation and usage of volatile diluents. For these reasons, polymer-immobilized ligands have been developed as adsorbents for the separation of metals. Ionic-liquid modified materials have also been prepared and successfully applied as adsorbents in solid-liquid extraction [6]. We have reported the synthesis of varied supported ionic liquids (SILs) including polymer supported ionic liquids (P-SILs) [7-10], silica based material supported ionic liquids (SM-SILs) [11, 12] and membrane supported ionic liquids (M-SILs) [13, 14] for the adsorption of REs(III), Re(VII) and Mo(VI), and heavy metals. Unfortunately, these systems still suffer from the loss of extractant due to the solubility into the aqueous phase. To solve this problem, enhancement of the interaction between the extractant and the support is needed. As a further extension of the above research, an entirely new class of ionic liquids functionalized resins by incorporating Aliquat 336 or P204, Cyanex 272 as cations or anions into chitosan and poly(styrene-divinylbenzene) backbones has been prepared through non-covalent interactions, the chemical structures are shown in Figure 1. Furthermore, [A336][CMCTS] has showed satisfied adsorption ability toward Pb(II) and Y(III) in our studies [15, 16].

In this report, the immobilization of the ligands (P204, Cyanex 272 or acidic organo-phosphoric extractant) by acid-base interaction with polymer matrix produces an interaction, which is far stronger than the usual physical adsorption of the extractant onto the inert polymeric support. In particular, it is easy to envision that tunable resins with metal-binding function can be designed. This is highly desirable property because the target metals can be easily adsorbed by changing their cationic and anionic components. The objectives of this study are to develop a new class of ionic liquids functionalized resins with tunable structure and to evaluate their adsorption behaviors for REs(III), especially for Lu(III) in chloride solutions using batch experiments.

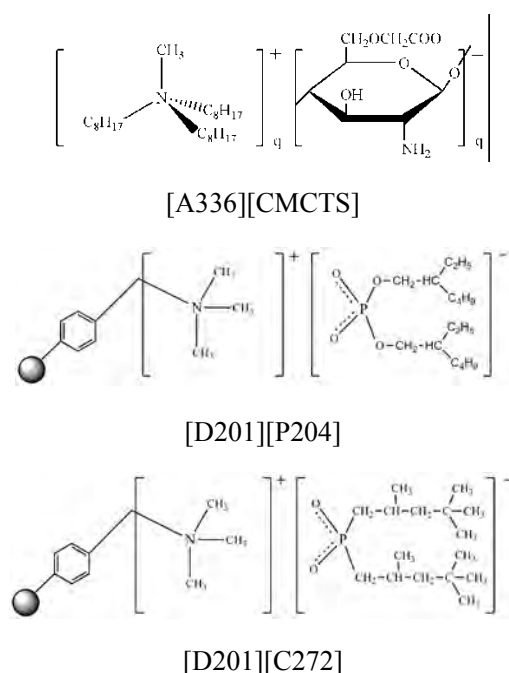


Figure 1. Chemical structures of novel ionic liquids functionalized resins, [A336][CMCTS], [D201][P204] and [D201][C272] (CMCTS: carboxymethylated chitosan; A336: trioctylmonomethylammonium chloride; D201: macroporous strong base anion exchange resin (also Amberlite IRA 900); P204: di-(2-ethylhexyl) phosphoric acid; C272: bis-(2,4,4-trimethylpentyl) phosphinic acid).

EXPERIMENTAL SECTION

Poly(styrene-divinylbenzene) resins are widely used in metal ion separations because of their well-known macroreticular structure and high surface area, as well as their excellent chemical, physical and thermal stability [17]. To exploit the favorable binding properties of these ligands for selective metal separations, functional groups possessing metal binding ability such as phosphoric, amino and carboxyl are introduced into polymeric supports.

D201 resin supplied by Anhui Wandong Chemical Co., Ltd is used as a strong base anion-exchange resin, which has a styrene-divinylbenzene matrix with a quaternary ammonium group. The resin was preconditioned and transferred to the hydroxide form by employing the column method. D201 resin was functionalized with bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), and di-(2-ethylhexyl)

phosphoric acid (P204) by acid-base reaction. The novel ionic liquids functionalized resins were thus obtained.

The as-prepared resins were used as adsorbents for the adsorption of REs(III) from aqueous solutions. Stock standard solutions were prepared by dissolving RE₂O₃ in hydrochloric acid and standardized by EDTA titration using xylenol orange as an indicator. The working standard concentrations of the ions were then obtained by serial dilution. The resins were immersed in metal solutions, in which NaCl was added to give concentration, and continuously shaken to achieve adequate adsorption equilibrium. Then suspensions were filtered, and solutions after adsorption were measured by ICP-AES (Agilent 7500) and UV-visible spectrophotometer (UV mini-1240). The adsorption capacity was calculated from the experimental data using eq 1.

$$q_e = \frac{(C_o - C_e)V}{m} \quad [1]$$

where q_e (mmol/g) is the adsorption capacity; C_o (mM) and C_e (mM) are the initial and equilibrium concentrations of metal ion in the solution, respectively; V (L) is the volume of the solution; and m (g) is the mass of the adsorbent.

The selectivity of the resin against a certain cation was also examined. The selectivity was expressed in terms of the distribution coefficient (D), calculated using the equation below.

$$D = \frac{\text{mmol } M^{n+} / \text{g of adsorbent}}{\text{mmol } M^{n+} \text{ mL of solution}} \quad [2]$$

RESULTS AND DISCUSSION

Selectivity

The selectivity of the resins against REs(III) ions were also examined. Figure 2 gives the distribution coefficients (D) for Yb(III) and Lu(III) as a function of the initial pH, which were determined in single-component systems. These coefficients are frequently used as a measure of the capacity of a adsorbent toward the adsorbates. The results suggests that both resins have strong affinity for heavy rare earths (HREs)

adsorption, but only a trace amount of light rare earths (LREs) is adsorbed. In particular, maximum adsorption percentages for Lu(III) are obtained by [D201][P204] and [D201][C272]. Therefore, it can be expected that the resins can be used for the effective recovery and separation of Lu(III) from dilute solutions.

Previous studies have documented that the pH of solution has a remarkable influence on the adsorption of REs(III) onto adsorbents [18]. We have thus attempted to achieve selective separation of Lu(III) and Yb(III) by changing the pH of solution. As shown in Figure 2, the adsorption of Lu(III) and Yb(III) on both resins are quite complicated. It depends basically on the structural properties of the resins and chemical properties of the metal ions. Figure 2 shows a comparison of D for Lu(III) and Yb(III) on [D201][P204] and [D201][C272]. It is interesting that both resins exhibit preferential adsorption for Lu(III) relative to Yb(III), and the maximum D of [D201][P204] toward Lu(III) is observed at pH 1.65, but the maximum D for [D201][C272] is found at pH 5.16. Clearly, this affinity order holds for most pH values, and the difference of D favors the separation of Lu(III) and Yb(III). The results allow us to reasonably conclude that [D201][P204] and [D201][C272] may be used to separate Lu(III) from the binary Yb(III)-Lu(III) mixtures.

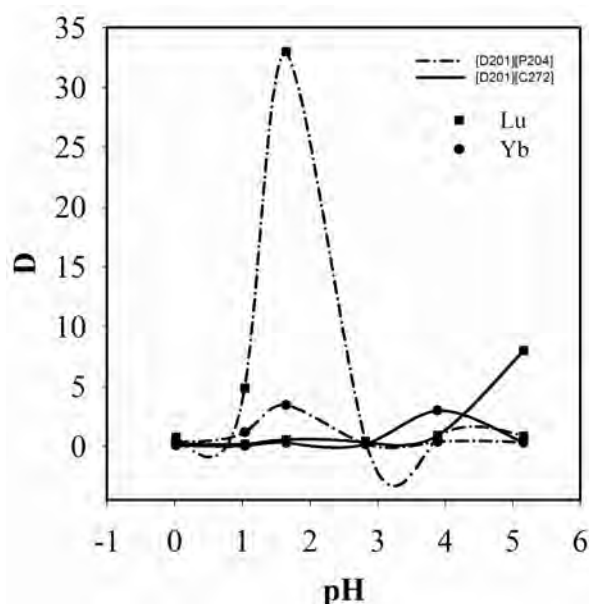


Figure 2. Plot of distribution ratio (D) versus pH; $m = 30$ mg, $V = 10$ mL, $t = 6$ h, $T = 298$ K, $[Lu(III)]$, $[Yb(III)] = 0.5$ mmol L⁻¹, $[NaCl] = 0.5$ mol L⁻¹.

Effect of Ionic Strength

From the preceding discussion, adsorption experiments of Lu(III) were conducted at ionic strengths of 0.01 and 0.5 mol L⁻¹ as a function of equilibrium concentrations. To further elucidate the effect of ionic strength on Lu(III) adsorption, the adsorption behaviors of [D201][P204] and [D201][C272] were studied at different ionic strength, and the increase of the ionic strength was obtained by addition of NaCl. Figure 3 plots the quantity of Lu(III) adsorbed per unit mass of resin and the equilibrium concentration at 0.01 and 0.5 mol L⁻¹ NaCl. The Freundlich isotherm model was also used to fit the adsorption data, and the regressed values of model parameters indicate that the proposed model can predict the Lu(III) adsorption phenomena satisfactorily for both resins. The Freundlich isotherm model is given by

$$q_e = K_f C_e^{1/n} \quad [3]$$

Where q_e is the amount of Lu(III) adsorbed (mmol g⁻¹ of adsorbent); C_e is the equilibrium concentration of Lu(III) (mmol L⁻¹); and K_f (mmol¹⁻ⁿ Lⁿ g⁻¹) and n are the constants that give estimates of the adsorptive capacity and intensity, respectively.

Obviously, Figure 3 illustrates enhanced adsorption of Lu(III) on [D201][P204] and [D201][C272] with increasing ionic strength. The observation of positive influence on the adsorption by the ionic strength can be explained in terms of the desolvation of Lu(III) ions, and electrostatic interactions between sodium chloride and charged surface of the resins. Similar to the results, Aliquat 336 functionalized chitosan adsorbent for Pb(II) adsorption have been reported in our previous study [15]. On the other hand, as shown in Figure 3, a higher adsorption capacity of Lu(III) is obtained by [D201][P204], compared with [D201][C272], but this result does not hold under all conditions studied. For example, at high equilibrium concentration, more significant increase in Lu(III) adsorption is observed for [D201][C272]. The increasing trends observed may be explained that the formation of the Lu(III) complex is favored when deprotonated phosphoryl groups interact with more Lu(III) ions, the presence of nonaccessible cavities are surrounded by Lu(III) ions and, consequently, the formation of the Lu(III) complex is increased.

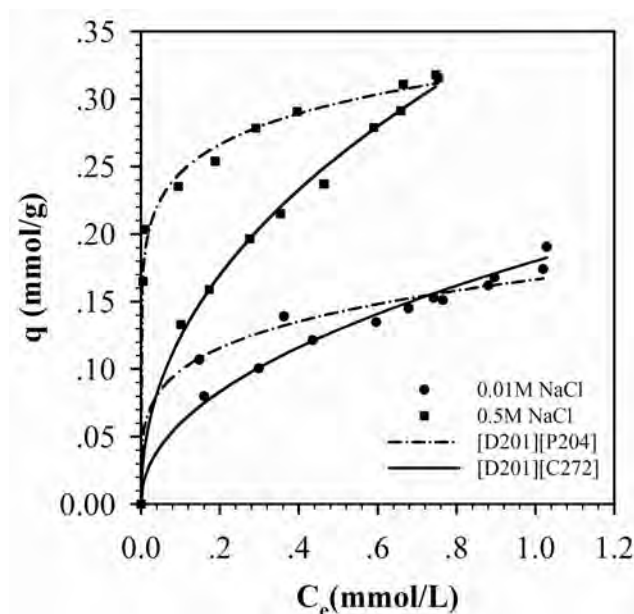


Figure 3. Effect of ionic strength on Lu(III) adsorption and adsorption isotherm; $m = 30$ mg, $V = 10$ mL, $t = 6$ h, $T = 298$ K.

XPS Results

XPS spectra are widely used to distinguish the different forms of the same element and to identify the existence of a particular element in a material. To understand the binding of Lu(III) to the active sites, the as-prepared resins exposed to metal solutions were used for analysis via XPS (Thermo ESCALAB 250, Mono X-ray source, Al Ka 1486.6 eV). Figure 4 shows the typical results of XPS spectra for [D201][P204] and [D201][C272] after Lu(III) adsorption. The lutetium (Lu4d) peaks are observed, which suggest that most of Lu(III) is adsorbed on the surface of both resins. In the case of [D201][P204], after Lu(III) adsorption, the phosphorus peak attributed to phosphate groups is fit into two components: P=O at 134.0 eV, and P-O at 133.2 eV [19], moreover, the two peaks shifts by 0.7 eV and 0.9 eV, respectively (Figure 4a). This indicates that the Lu(III) complex is formed between Lu(III) and phosphate groups, and as a consequence, the electron cloud density of the phosphorus atom is reduced, resulting in a higher BE peak observed. Therefore, the XPS spectra provides evidence that phosphate groups in [D201][P204] coordinate with Lu(III) in the adsorption process. Figure 4b shows binding energies of nitrogen, oxygen, phosphorus and lutetium atoms for [D201][C272] after Lu(III) adsorption. The phosphorus peak can be split into three individual components, similar result that the

presence of Lu(III) shifts the phosphorus binding energies to more-positive ranges is observed, demonstrating that phosphate groups in [D201][C272] also involve in Lu(III) adsorption.

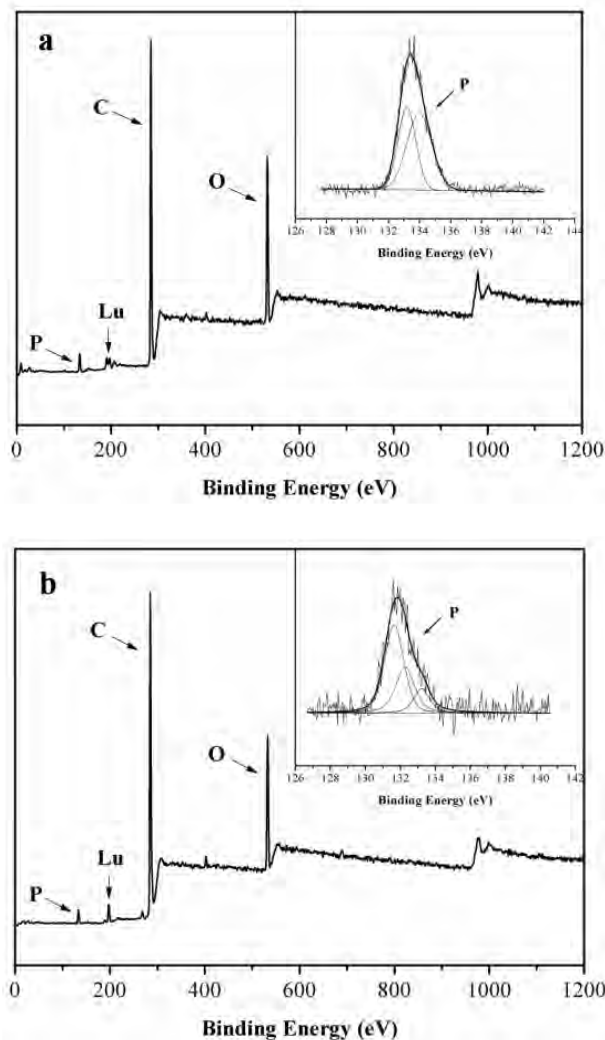


Figure 4. XPS spectra for [D201][P204] after Lu(III) adsorption (a) and [D201][C272] after Lu(III) adsorption (b), the inset indicates the P2p position in [D201][P204] and [D201][C272].

CONCLUSIONS

The novel ionic liquids functionalized resins with tunable structure were synthesized and used to evaluate their adsorption capacities for REs(III). The results of single-component adsorption show that both resins exhibit higher adsorption capacities for Lu(III) compared with Yb(III), demonstrating that these two resins possess the potential for the separation of Lu(III) from the binary Lu(III)-Yb(III)

mixtures. In addition, significant increases in Lu(III) adsorption for [D201][P204] and [D201][C272] are observed as the ionic strength increases in the solution. The XPS analysis carried out in this study indicates strong coordination between Lu(III) and phosphate groups. Indeed, this work shows that these results may provide the basis for the application of the ionic liquids functionalized resins in REs(III) separation and recovery.

ACKNOWLEDGMENTS

This project was supported by the Key Research Program of the Chinese Academy of Sciences (Grant No. KGZD-EW-201-1), the National Basic Research Program of China (Grant No. 2012CBA01202), and the Natural Science Foundation of China (Grant No. 51174184).

REFERENCES

- [1] J. C. Lee, B. D. Pandey, "Bio-processing of solid wastes and secondary resources for metal extraction - A review," *Waste Manag.*, **32**, 3-18 (2012).
- [2] D. Wu, C. Niu, D. Li, Y. Bai, "Solvent extraction of scandium(III), yttrium(III), lanthanum(III) and gadolinium(III) using Cyanex 302 in heptane from hydrochloric acid solutions," *J. Alloy. Compd.*, **374**, 442-446 (2004).
- [3] Y. Xiong, Z. N. Lou, S. A. Yue, J. J. Song, W. J. Shan, G. X. Han, "Kinetics and mechanism of Re(VII) extraction with mixtures of tri-alkylamine and tri-n-butylphosphate," *Hydrometallurgy*, **100**, 110-115 (2010).
- [4] Y. L. Wang, W. P. Liao, D. Q. Li, "A solvent extraction process with mixture of CA12 and Cyanex 272 for the preparation of high purity yttrium oxide from rare earth ores," *Sep. Purif. Technol.*, **82**, 197-201 (2011).
- [5] N. V. Nguyen, J. C. Lee, J. Jeong, B. D. Pandey, "Enhancing the adsorption of chromium(VI) from the acidic chloride media using solvent impregnated resin (SIR)," *Chem. Eng. J.*, **219**, 174-182 (2013).
- [6] L. Vidal, M. L. Riekkola, A. Canals, "Ionic liquid-modified materials for solid-phase extraction and separation: A review," *Anal. Chim. Acta*, **715**, 19-41

(2012).

[7] L. Zhu, Y. Liu, J. Chen, W. Liu, "Extraction of scandium(III) using ionic liquids functionalized solvent impregnated resins," *J. Appl. Polym. Sci.*, **120**, 3284-3290 (2011).

[8] L. Zhu, Y. Liu, J. Chen, "Synthesis of N-methylimidazolium functionalized strongly basic anion exchange resins for adsorption of Cr(VI)," *Ind. Eng. Chem. Res.*, **48**, 3261-3267 (2009).

[9] L. Zhu, Y. Deng, J. Zhang, J. Chen, "Adsorption of phenol from water by N-butylimidazolium functionalized strongly basic anion exchange resin," *J. Colloid Interface Sci.*, **364**, 462-468 (2011).

[10] L. Zhu, J. Chen, "Adsorption of Ce(IV) in nitric acid medium by imidazolium anion exchange resin," *J. Rare Earths*, **29**, 969-973 (2011).

[11] Y. Liu, X. Sun, F. Luo, J. Chen, "The preparation of sol-gel materials doped with ionic liquids and trialkyl phosphine oxides for yttrium(III) uptake," *Anal. Chim. Acta*, **604**, 107-113 (2007).

[12] Y. Liu, L. Guo, L. Zhu, X. Sun, J. Chen, "Removal of Cr(III, VI) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials," *Chem. Eng. J.*, **158**, 108-114 (2010).

[13] L. Guo, Y. Liu, C. Zhang, J. Chen, "Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr(VI) transport," *J. Membr. Sci.*, **372**, 314-321 (2011).

[14] L. Guo, J. Zhang, D. Zhang, Y. Liu, Y. Deng, J. Chen, "Preparation of poly(vinylidene fluoride-co-tetrafluoroethylene)-based polymer inclusion membrane using bifunctional ionic liquid extractant for Cr(VI) transport," *Ind. Eng. Chem. Res.*, **51**, 2714-2722 (2012).

[15] H. Cui, J. Chen, H. Yang, W. Wang, Y. Liu, D. Zou, W. Liu, G. Men, "Preparation and application of Aliquat 336 functionalized chitosan adsorbent for the removal of Pb(II)," *Chem. Eng. J.*, **232**, 372-379 (2013).

[16] H. M. Cui, J. Chen, H. L. Yang, Y. Liu, Y. F. Deng, D. L. Zhang, "Enrichment and separation of Y(III) from dilute solutions using Aliquat 336 functionalized

chelating adsorbent derived from chitosan,” *Chin. J. Anal. Chem.*, DOI: 10. 3724/SP. J. 1096. 2014. 30901.

[17] G. Venkatesh, A. K. Singh, “4-[(2-Hydroxyphenyl) imino] methyl}-1,2-benzenediol (HIMB) anchored Amberlite XAD-16: Preparation and applications as metal extractants,” *Talanta*, **71**, 282-287 (2007).

[18] M. Bouby, J. Lutzenkirchen, K. Dardenne, T. Preocanin, M. A. Denecke, R. Klenze, H. Geckeis, “Sorption of Eu(III) onto titanium dioxide: Measurements and modeling,” *J. Colloid Interface Sci.*, **350**, 551-561 (2010).

[19] B. Zhu, N. Ma, D. Wu, Y. Sun, W. Li, “Synergistic extraction and selective removal of Cu²⁺ from aqueous solution using magnetic nanoparticles coated with mixtures of sodium oleate and saponified 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester,” *Ind. Eng. Chem. Res.*, **50**, 11698-11705 (2011).

Innovation of Solvent Extraction for Metal Separation in Mixed Chloride Media: Case Studies for Different Value Metals

*V.I. Lakshmanan¹, R. Sridhar¹, M.A. Halim^{*1}*

Summary

Solvent extraction is one of the important unit processes in the commercial production of value metals in metallurgical industry. Process Research ORTECH Inc. (PRO) has developed the innovative mixed chloride-solvent extraction processes for the production of value metals from their different sources such as nickel, cobalt and iron from laterite; titanium, vanadium and iron from ilmenite and concentrates; and copper and iron from chalcopyrite. PRO process uses mixed chloride lixiviant ($\text{HCl}+\text{MgCl}_2$) to dissolve these metals in solution. The hydrochloric acid (HCl) leaching media provides the opportunity to regenerate the acid by pyrohydrolysis, while the presence of magnesium chloride (MgCl_2) in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude, making the lixiviant very aggressive and resulting in high recoveries of these metals. The developed process flowsheets are innovative, environmentally friendly and economically attractive.

Introduction

Demand of base metals including iron, titanium, vanadium, cobalt, nickel and copper is tremendously increasing for the development of science and technology in the world. Meanwhile the number of new ore bodies, and the easily exploited ore, are gradually decreasing. Moreover, a rising awareness of environmental protection has lead to more and more difficulty with the smelting process. On the contrary, chloride hydrometallurgy is emerging as an alternative process for the production of base metals [1-4]. Chloride chemistry is complex and quite different from corresponding other systems including sulfate. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. The solubility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is about one fifth that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions [5]. Also, the activity of water is $\ll 1$ in concentrated magnesium chloride solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration [6]. This enhances the leachability of minerals in mixed chloride solutions resulting in increased base metals recovery.

Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy and PRO's patented mixed chloride technology has been applied to the recovery of several value metals including base metals from laterite and sulfide ores, titanium dioxide from ilmenite ores, rare earth elements (REE) from alumino-silicate ores, platinum group metals (PGM) from sulfide ores and gold from refractory ores [7-15]. In this paper, application of PRO's mixed chloride technology for the recovery of iron, cobalt and nickel from laterite ore, iron, titanium and vanadium from ilmenite ore, and iron and copper from sulfide ore is described.

Recovery of Iron, Cobalt and Nickel from Laterite Ores

Lateritic ores are formed by prolonged weathering of ultramafic rocks and its use for production of nickel is gradually increasing [16]. Typical mineralogical profile of nickel laterite ore bodies is as described below [17, 18]:

¹Process Research ORTECH Inc., 2350 Sheridan Park Drive, Mississauga, ON, L5K 2T4, Canada

*Email: halim@processortech.com

- i. Overburden: This zone contains low nickel values ($< 0.8\%$ Ni) and is discarded.
- ii. Limonitic ore zone: This zone contains $\sim 1.2\text{--}1.7\%$ Ni, $\sim 40\%$ Fe and $\sim 1\text{--}4\%$ MgO. Hydrometallurgical processes are used to extract nickel from limonitic ore zone. High pressure acid leach (HPAL) process is used for high iron ($> 35\%$ Fe) limonitic ores.
- iii. Saprolitic ore zone: This zone contains ~ 1.7 to 2.3% Ni and low iron ($< 15\%$ Fe). Pyrometallurgical smelting processes are used to produce ferronickel or matte from saprolitic ores.
- iv. Base rocks: This zone contains $< 0.5\%$ Ni and it is not economic to extract nickel from base rocks.

In some ore bodies, the saprolitic ore profile is either absent or too trace. In ore bodies with rich saprolitic ore zone, the limonitic ores may be stockpiled and stored for later treatment till the higher grade saprolitic ore zone is exhausted.

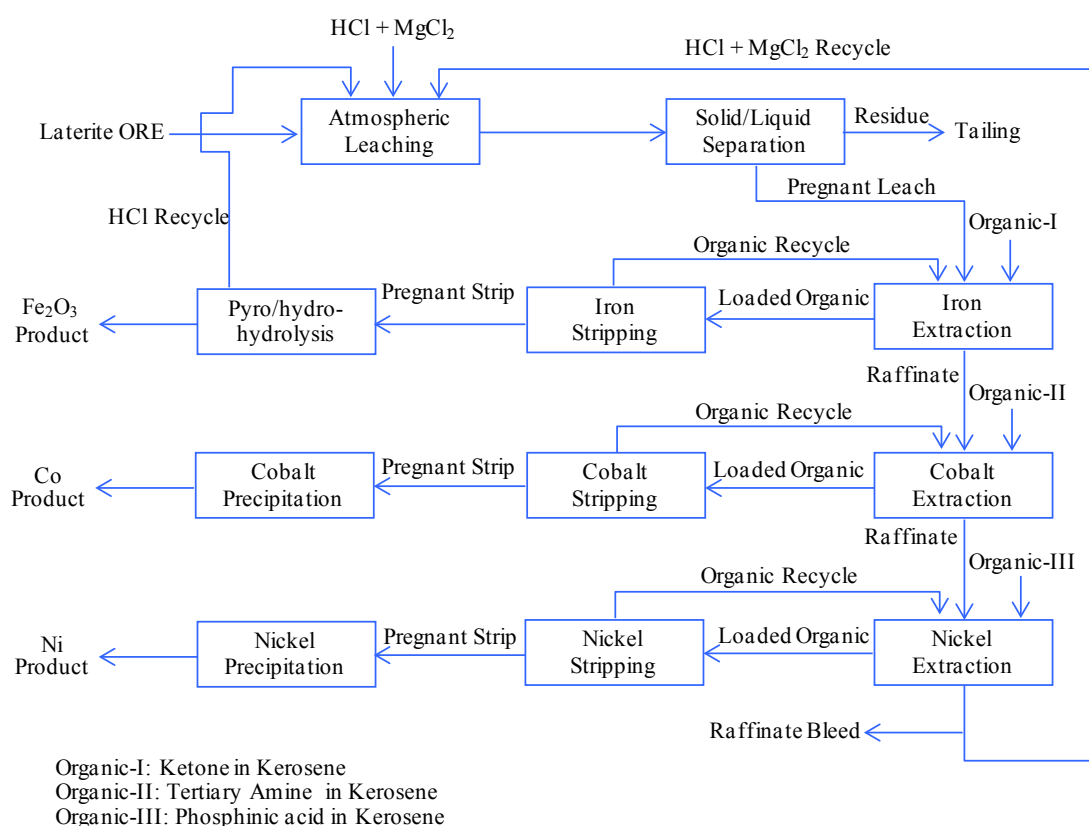


Fig. 1 PRO mixed chloride process flowsheet for the recovery of Fe, Co and Ni from lateritic ores [7].

PRO Laterite Process

Based on chloride hydrometallurgy, an innovative mixed chloride process has been developed by Process Research Ortech Inc. (PRO), which is applicable to both high and low iron laterite ores [7]. The process flowsheet is shown in Fig. 1 [7], which involves novel leaching and solvent extraction separation steps. This process is efficient and environmentally friendly. The salient features of the PRO Laterite Process are as follows:

- i. Leaching: Leaching is conducted in mixed chloride media to dissolve Fe, Ni, Co and Mg in solution.

- ii. Solvent Extraction: Solvent extraction steps are carried out for successive extraction and stripping of Fe, Co and Ni to obtain high purity concentrated pregnant strip solutions of Fe, Co and Ni, respectively.
- iii. Precipitation: Precipitation of Ni and Co from respective high purity concentrated pregnant strip solutions is conducted by the addition of MgO generated by pyrohydrolysis.
- iv. Pyrohydrolysis:
 - a. Fe_2O_3 is produced and HCl is regenerated by the pyrohydrolysis of the iron chloride rich pregnant strip solution.
 - b. MgO is produced and HCl is regenerated by the pyrohydrolysis of the bleed stream from the magnesium chloride containing raffinate of the nickel solvent extraction stage. MgO thus produced can be used for pH control as well as precipitation of Ni and Co from their respective pregnant strip solutions. Excess MgO produced can be sold.
- v. Recycling: HCl and MgCl_2 are recycled to leaching stage.

PRO Testwork

Tests were conducted with a laterite ore having a composition of 0.76% Ni, 0.11% Co and 42.61% Fe. Optimum leach recoveries of Ni, Co and Fe in PRO's proprietary mixed chloride lixiviant were 97.8%, 89.4% and 97.7%, respectively. After solid/liquid separation, the pregnant leach solution went through a series of solvent extraction separation steps to sequentially extract Fe, Co and Ni from the solution using different organic extractants. Loaded organics were stripped using dilute acidic solutions to generate high purity pregnant strip solutions of Fe, Co and Ni individually. The solvent extraction separation steps developed by PRO are highly selective for the target metals, which results in high purity pregnant strip solutions and consequentially high purity Fe, Co and Ni products. Iron oxide and magnesium oxide can be produced from respective solutions by pyrohydrolysis, which will also regenerate the hydrochloric acid. Pyrohydrolysis is a commercially proven process. PRO has developed a novel hydrothermal hydrolysis process that can be used to regenerate the hydrochloric acid and produce high purity iron oxide and magnesium oxide. PRO's hydrothermal hydrolysis process is more economical than pyrohydrolysis process as hydrothermal hydrolysis process runs at a much lower temperature.

Comparison of PRO Laterite Process with Commercial Processes

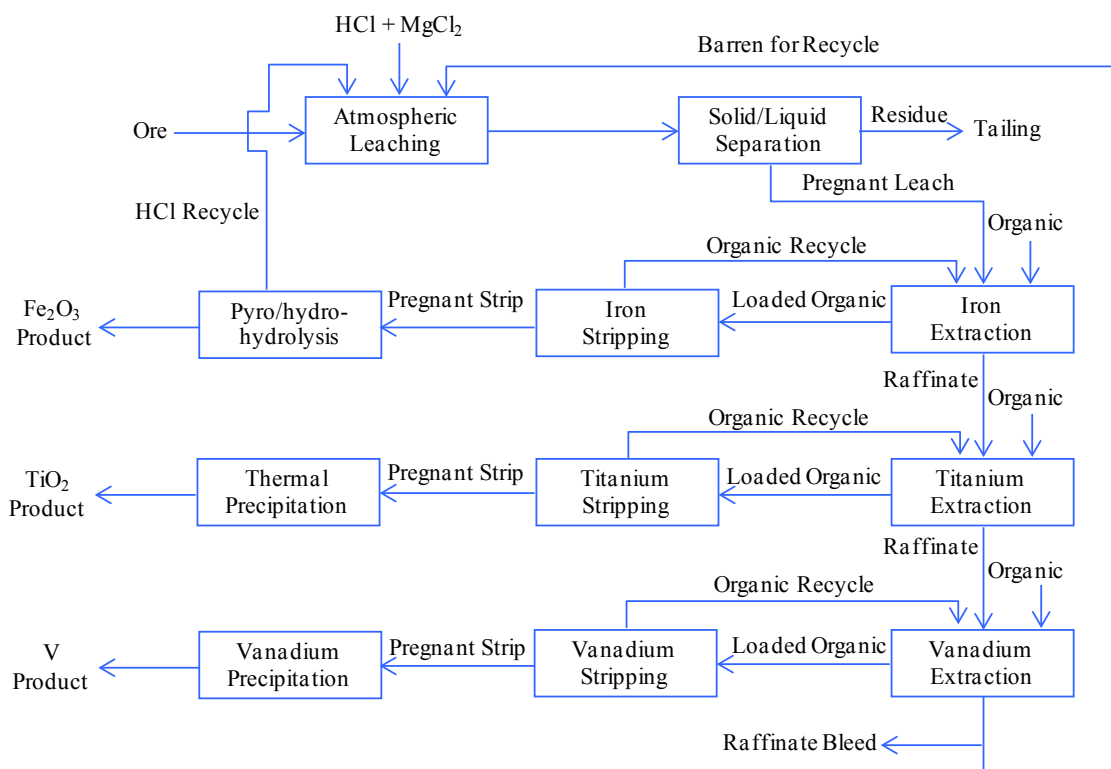
There are three commercial processes for the recovery of nickel from lateritic ores: Pyrometallurgical process, Caron process and High Pressure Acid Leach (HPAL) process [16]. The Pyrometallurgical process involves drying, calcining and smelting of entire ore body at successively higher temperatures and therefore is energy intensive. The Caron process involves ore drying followed by selective reduction of nickel, leaching with ammonia solution and nickel carbonate precipitation from pregnant leach solution. Nickel carbonate is decomposed to produce nickel oxide, which is then reduced to form nickel metal. In contrast, HPAL process involves high pressure leaching with H_2SO_4 followed by counter-current decantation and neutralization. Different options exist for purification of nickel containing solutions and separation of nickel and cobalt with solvent extraction, followed by electrowinning of nickel. A comparison of PRO laterite process with commercial processes is shown in Table 1.

Table 1 A comparison of PRO Laterite Process with commercial processes.

	Pyrometallurgical Process	Caron Process	HPAL Process	PRO Laterite Process
Ores that can be treated	Med-high Ni (1.8-2.5%), low-med Fe (10-20%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Both low Fe and high Fe ores
Ni recovery	~ 95%	~ 75%	~ 95%	> 90%
Co recovery	None	< 50%	~ 95%	> 90%
Fe recovery	No	No	No	Yes
Mg recovery	No	No	No	Yes
Capital cost	High	Medium	High	Low
Operating cost	High	Medium	High	Medium
Energy requirement	High (due to water removal from ore and high temperature processing)	High (due to water removal from ore and high temperature processing)	Low (no water removal from ore and low temperature process)	Medium (no water removal while pyrohydrolysis needed for acid regeneration adds energy cost)
Reagents	Not recycled	Not recycled	Not recycled	Recycled
Residue	High volume	High volume	High volume	Low volume
Environmental	Slag disposal	Residue disposal containing NH_3	Higher residue disposal	Inert residue
Sulphur price	No effect	No effect	Very dependent	No effect
Fuel price	High effect	Medium effect	Lower effect	Medium effect
Byproduct credit	None	None	None	Fe_2O_3 and MgO credit

Recovery of Iron, Titanium and Vanadium from Ilmenite

The main raw material for TiO_2 production is the mineral ilmenite ($\text{FeO} \cdot \text{TiO}_2$), which is commonly found in the mineral sand beaches. It also occurs as hard rock. In the processing of mineral sands, rutile ore is also recovered. Rutile ore is essentially TiO_2 and is used for the production of TiO_2 pigments by the chloride process.

**Fig. 2** The process flowsheet for the production of Fe, Ti and V oxides from ore [12, 15].

PRO Process

PRO has developed a proprietary mixed chloride Canadian Titanium Limited (CTL) process for the recovery of Fe, Ti and V from ilmenite concentrate [12,14, 15]. The process flowsheet is shown in Fig. 2 [12, 15]. This process consists of atmospheric mixed chloride leaching of ilmenite ore to bring Fe, Ti and V in solution. After solid-liquid separation, pregnant liquor is subjected to solvent extraction steps for subsequent extraction of Fe, Ti and V with different organic extractants followed by stripping and precipitation for product recovery.

PRO Testworks

An ilmenite ore containing 22.8 wt.% of Ti, 38 wt.% of Fe, 0.13 wt.% of Cr_2O_3 , 4.69 wt.% of SiO_2 and 2.82 wt.% of MgO with a mesh size of –100 was used as feed material for extraction of iron, titanium and vanadium with a solution of hydrochloric acid and magnesium chloride as a lixiviant under atmospheric pressure at 70-73 °C for 4 hours. The results show that extraction of Fe and Ti was achieved as high as 84.4% and 96.9%, respectively, for a solid loading of 8.8 %, 1.4 times of stoichiometric amount HCl and 300 g/L of MgCl_2 . Then, the slurry was filtered to separate the pregnant leach liquor from residue.

Solvent extraction was carried out for subsequent extraction of Fe, Ti and V with different organic extractants in kerosene from pregnant leach solution. Three different types of extractants namely acidic organophosphorus, neutral and amine extractants could be used to extract titanium followed by vanadium [12, 15]. Detailed explanation of these organics is given in the previous studies [12, 14, 15]. Loaded organics were stripped using acidic solutions to generate high purity pregnant strip solutions of Fe, Ti and V individually (Table 2). Iron oxide can be produced from pregnant strip solution by pyrohydrolysis, which will also regenerate the hydrochloric acid. The titanium pregnant strip was used for thermal precipitation of TiO_2 , while V was precipitated from its pregnant strip solution by increasing pH. The barren solution was used for reagent recovery and the regenerated liquor was recycled.

Table 2 Results of first stage stripping of Fe, Ti and V from their loaded organics with 0.05M HCl, 1M HCl and 1.5M H_2SO_4 , respectively, at the O/A ratio of 1 at room temperature.

Fe			Ti			V		
Concentration		Stripping	Concentration		Stripping	Concentration		Stripping
(g/L)		(%)	(g/L)		(%)	(g/L)		(%)
Organic phase	Pregnant strip		Organic phase	Pregnant strip		Organic phase	Pregnant strip	
37.8	35.6	94	9.8	7.6	78	5.2	4.6	88

Comparison of Titanium Dioxide Production Processes

TiO_2 is currently produced by either the sulphate process or the chloride process. PRO process is compared with the sulfate process and chloride process in Table 3.

Table 3 Comparison between TiO_2 production processes.

	The chloride process	The sulphate process	The CTL process
Raw material (\$/ton of feed)	Higher cost (\$2000 +)	Lower cost Ilmenite (\$300)	Lowest cost Ilmenite (\$250)
TiO_2 product (\$/ton of TiO_2)	High value (\$4500)	Low value (\$3500 +)	High value (\$4500)
Capex	Highest (including front-end)	Medium	Lowest
Opex	Highest (including front-end)	Medium	Lowest
Environmental	Medium challenges	Major challenges	Environmentally friendly
Flexibility in processing raw material	Limitation (Ca, Cr, Mn, Mg, V, size)	Limitation (Cr, V)	Flexible
Process Condition	High Temp. Chlorination (800-1000 °C)	High Temp Leaching (140-180 °C)	Low temp., atmospheric Leaching (70 °C), precipitation (90 °C)
Technology	Old	Old	Patented, New
End to end in one location	Not practiced	Possible	Possible
Pigment production	Rutile	Rutile/Anatase	Rutile/Anatase
Commercially Proven process	In practice	In practice	Innovatively applied, will soon be in practice
Environmental challenges	Disposal of iron and other byproduct chlorides	Disposal of large iron sulphate product and dilute acid	Minimum environmental impact, Iron oxide as byproduct
Safety Requirements	High (chlorine at high temperature)	High (High temperature acid digestion)	Low (no pressurized vessel and lower temperature)
chlorine and carbon/carbon containing chemicals at high temperature	Challenges to handle	N/A	N/A
Energy consumption	High	High	Efficient
Sulfur price	No effect	Substantial effect	No effect

Recovery of Iron and Copper from Sulfide Ores

Copper ore is mainly copper sulfide or copper oxide ore. The chalcopyrite concentrates, which account for about 70% of the world's known copper reserves. In the last 10 years, very few grass roots copper smelter-refinery complexes have been built, due to their very high capital cost. In contrast, there has been a gradual increase in the production of copper by leaching-solvent extraction-electrowinning operation, which is now account for about 30% of world copper production. There are a large number of reasons for looking at process alternatives for the smelter-refinery approach. They are: (i) capital cost; (ii) handling of impurities; (iii) precious metals in copper concentrates; (iv) recovery of valuable by-products; (v) use of existing SX-EW equipment; (vi) mine to market optimization; and (vii) overall economics [19, 20].

PRO Process

Process Research ORTECH (PRO) Inc. has been developed an innovation proprietary mixed chloride leaching technology for the recovery of Fe and Cu from sulfide ores/concentrates [11]. A tentative process flowsheet is shown in Fig. 3. The main features of this flowsheet include leaching of the ores/concentrates at 90-100 °C in recycled mixed chloride ($HCl+MgCl_2$) with an oxidant. In this leaching stage, Fe

and Cu are dissolved and sulphide sulphur is removed as H_2S , which is converted to elemental sulphur in a Claus reactor. Iron and Cu are recovered from leach solution by solvent extraction. Other steps include removal of impurities with lime and production of magnesia and regeneration of HCl by pyrohydrolysis.

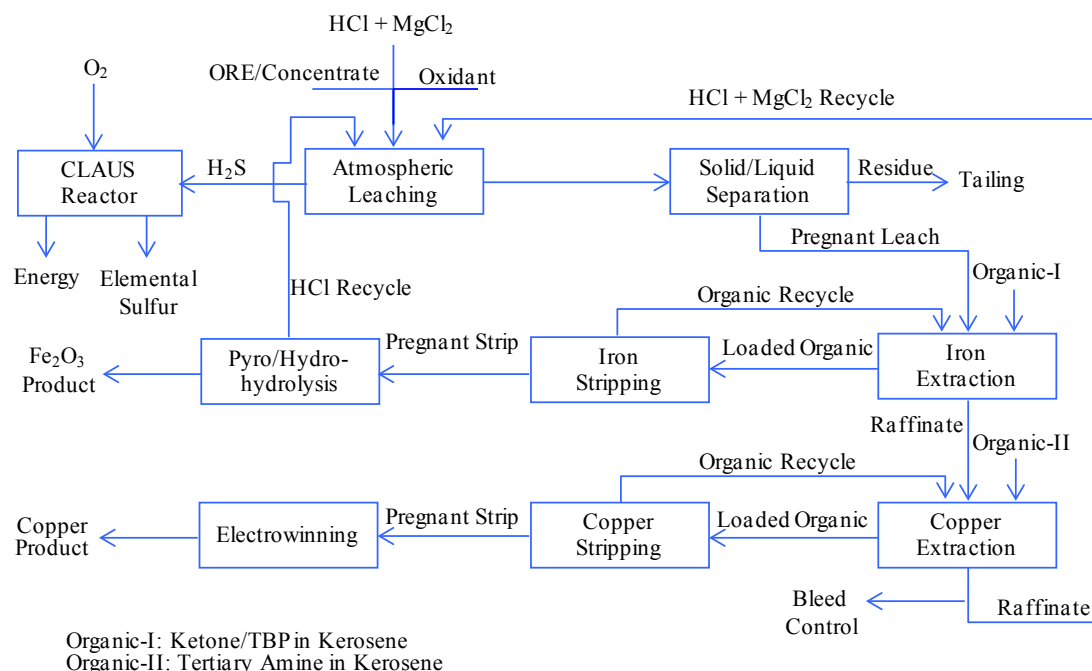


Fig. 3 A tentative process flowsheet for the production of Fe oxide and Cu from their sulfide ores.

PRO Testworks

A series of leaching tests were carried out using a copper ore containing 1.275% Cu, 2.61% Fe and 0.93% S and a leach solution of hydrochloric acid (4N) and magnesium chloride, at a total chloride ion concentration of 400 g/L. The leached solution was subjected to a solid/liquid separation followed by subsequent solvent extraction steps for separation and purification of Fe and Cu.

Iron followed by copper could be selectively separated from pregnant leach solution with a organic solvent contained a ketone/tri-butyl phosphate (TBP) and a tertiary amine in kerosene, respectively. Both of the Fe and Cu could be stripped from their loaded organics with a dilute acid. Barren organics could be recycled to the extraction circuits. The raffinate of the Cu extraction circuit can be treated for removal of impurities with lime followed by pyrohydrolysis to recover magnesia and HCl which can be recycled to the leaching stage. Iron oxide and HCl can be produced from Fe pregnant strip solution by pyrohydrolysis. Copper can be recovered from its pregnant strip solution by electrowinning.

References

1. Moyes, J., Houllis, F., Intec base-metal processes realizing the potential of chloride hydrometallurgy. Chloride Metallurgy 2002, Volume II, E. Peek, G. Van Weert, Eds., Montreal, Canada, October, 2002, 577-592.

2. Leimala, R., Hyvarinen, O., Hamalainen, M., Jyräla, M., The Outokumpu HydroCopper™ Process-design, implementation and operation of a demonstration plant, Copper 2003, 5th International Conference, Vol VI- Hydrometallurgy of Copper (Book 1), P.A. Riveros, D.G. Dixon, D.B. Dreisinger and J.M. Menacho, Eds., Santiago, Chile, 2003, 281-288.
3. Hyvarinen, O., Hamalainen, M., Leimala, R., Outokumpu HydroCopper™ Process-a novel concept in copper production. Chloride 2002, Volume II, E. Peek and G. Van Weert, Eds., Montreal, Canada, 2002, 609-613.
4. Harris, G. B., Lakshmanan, V.I., Magee, T.J., Sridhar, R., Atmospheric chloride leaching of base metal sulfides, Hydro-Sulfides 2004, International colloquium on hydrometallurgical processing of copper sulfides, Santiago, Chile, 2004, 384-398.
5. Lakshmanan, V.I., Sridhar, R., Harris, G.B., Magee, J., The Jaguar Nickel Inc. Sechol Laterite Project atmospheric chloride leach process, International laterite nickel symposium, W.P. Imrie, D.M. Lane, Eds., The Minerals, Metals and Materials Society, Charlotte, North Carolina, USA, March 14-18, 2004, 219-241.
6. Jansz, J.J.C., Estimation of ionic activities in chloride systems at ambient and elevated temperatures, Hydrometallurgy, 11(1), 1983, 13-31.
7. Lakshmanan, V.I., Sridhar, R., Chen, J. Halim, M.A., Separation of iron from value metals in leaching of laterite ores, 2013, U.S. patent application no. US 2013/0149219 A1.
8. Lakshmanan, V.I., Sridhar, R., Halim, M.A., Chloride process for the leaching of gold. 2013, U.S. patent application no. US 2013/0283976 A1.
9. Lakshmanan, V.I., Sridhar, R., Halim, M.A., Process for extraction of rare earth elements. U.S. patent application no US20130283977 A1.
10. Lakshmanan, V.I., Lawson, G.J., Nyholm, P.S., The extraction of copper(II) and iron(III) with Kelex 100 from aqueous media containing chloride ions. ISEC proceedings, 2, 1974, 1169-1183.
11. Harris, G.B., Lakshmanan, V.I., Sridhar, R., Puvvada, G., Process for the recovery of value metals from base metal sulfide ores. 2011, US patent no. US 7968065 B2.
12. Lakshmanan, V.I., Sridhar, R., Sheikhzeinoddin, T., Halim, M.A., Roy, R., Extraction of titanium and vanadium by chloride leach processes. Shijie Wang; John E. Dutrizac; Michael L. Free; James Y. Hwang; Daniel Kim, Eds., T. T. Chen, Honorary Symposium on Hydrometallurgy. Electrometallurgy and Materials Characterization TMS 2012, 295-301.
13. Lakshmanan, V.I., Sridhar, R., Roy, R., Ramachandran, V., Recovery of value metals from ores by mixed chloride extraction. Proceedings of Sixth International Symposium, Hydrometallurgy 2008, Phoenix, Arizona, August 17-20, 2008, 895-902.
14. Lakshmanan, V.I., Sridhar, R., Harris, G.B., Puvvada, G., Process for the recovery of titanium in mixed chloride media. U. S. patent, 2010, No. 7803336B2.
15. Lakshmanan, V.I., Ashok Bhowmick, Halim, M.A., Titanium dioxide: production, properties and application. Titanium Dioxide: Chemical Properties, Applications and Environmental Effects, Jerri Brown, Ed., Nova Science Publishers Inc., Chapter 5, 2014, 75-130.
16. Dalvi, A.D., Bacon, W.G., Osborne, R.C., The past and future of nickel laterites. PDAC 2004 International Convention, March 7-10, 2004, 1-27. Available online: <http://www.pdac.ca/pdac/publications/papers/2004/techprgm-dalvi-bacon.pdf>.
17. Golightly, J.P., Nickeliferous Laterites: a general description, International Laterite Symposium, D.J. Evans, R.S. Shoemaker, H. Veltman, Eds., New Orleans, Louisiana, The Society of Mining Engineers of AIME, New York, 1979, 3-23.
18. Alcock, R.A., The character and resources available to the nickel industry, extractive metallurgy of nickel and cobalt. Proceedings of a Symposium, The Metallurgical Society, C.P. Tyroler and C.A. Landolt Eds., 117th TMS Annual Meeting, Phoenix, Arizona, 1988, 67-89.
19. Dreisinger, D.B., New developments in hydrometallurgical treatment of copper concentrates. Hydro-Sulfides 2004, International Colloquium on Hydrometallurgical Processing of Copper Sulfides, Santiago, Chile, April 2004, 47-73.
20. Dreisinger, D.B., New developments in hydrometallurgical treatment of copper concentrates, Engineering and Mining Journal, 205(4), 2004, 32-35.

Precious metals extraction with sulfur function supported on methylacrylate-styrene copolymer

Minako Iwakuma^{*1}, Shitaro Nakajima¹, Mario Ishikawa¹, Miyakonojo National College of Technology¹, 473-1 Miyakonojo City Miyazaki Prefecture, Japan¹;

Yoshinar Baba², University of Miyazaki², 1-1 Gakuenkibanadai Nishi Miyazaki City, Miyazaki Prefecture, Japan²

Summary;

Newly extractant containing and pyridine sulfur atoms as ligand, methylacrylate- α -o-thiomethylpyridyl-styrene copolymer (ACS1 and ACS2) were synthesized for palladium(II) and gold(III) over base metals. Extraction of metal ions by a batchwise method at 303K from the hydrochloric acid containing 0.1 milli molar metal ions was carried out. Palladium(IV) and gold(III) were selectively extracted in whole concentration of hydrochloric acid with ACS1. These results suggest that ACS1 selectively extracted precious metals from chloride media. The palladium(II) extraction was found to be independent of copper(II) in the solution, even when they are present in 200-fold excess. Extraction equilibria can be achieved within 1h with ACS1.

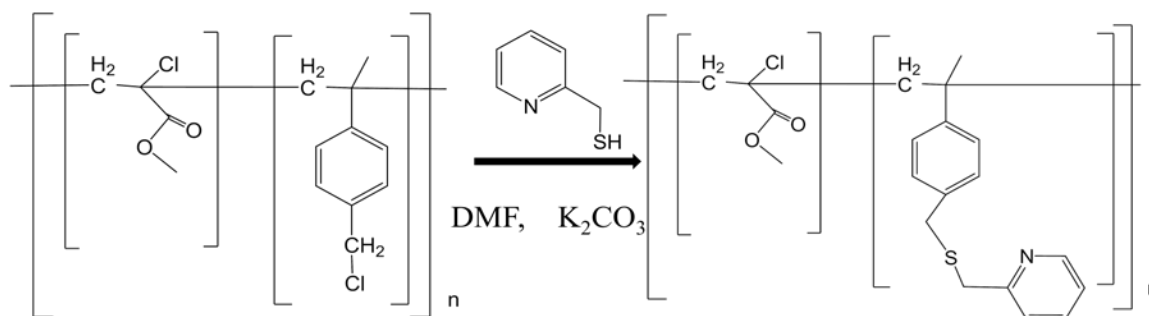
Introduction

Precious metals such as gold (III), palladium (II) and platinum (IV) are important metals in the fields of catalysts and the battery and electronic industries. The selective separation and recovery of precious metals from aqueous solutions are of great importance in hydrometallurgy and wastewater treatment. However, since the separation and purification of these metals are very difficult processes because of their chemical properties and the formation of many chemical species in chloride media, it is very important to develop a more efficient recovery process for their recovery and separation. [1-5] In this study, newly extractant containing pyridine and sulfur atoms as ligands, methylacrylate-(α -o-thiomethylpyridyl)-styrene copolymer (ACS1 and ACS2) was synthesized for precious metals over base metals.

Experimental

Reagent

Methylacrylate- α -(*o*-thiomethylpyridil)-styrene copolymer (ACS) was synthesized from methylacrylchloride-styrene copolymer¹⁾ and thiomethylpyridine according to a conventional method. ACS2 has molecular weight two times as large as ACS1.



Scheme 1 Synthesis of methylacrylate- α -(*o*-thiomethylpyridil)-styrene copolymer.

The reaction mixture was evaporated. Water and chloroform were added to the reaction mixture and then the two phases were separated with a separatory funnel. Chloroform phase was successively washed using 0.1 mol dm⁻³ hydrochloric acid mixed with sodium chloride as a salting out reagent, 1.0 mol dm⁻³ aqueous sodium hydroxide and distilled water. The final product was a viscous brownish liquid. Identification of the purified product was carried out using ¹H-NMR, ¹³C-NMR and FT-IR spectra. The product was identified as ACS and its purity was 97% as measured by gas chromatography.

Extraction of hydrochloric acid with ACS1 and ACS2

To elucidate the distribution behavior of extractant to both the aqueous phase and the organic phase, we examined the distribution of hydrochloric acid to the organic phase. The organic phase was prepared by extractant concentration 0.25wt%. The aqueous phase was prepared by changing the hydrochloric acid concentration from 1.0×10^{-4} to 5.0×10^{-3} mol dm⁻³. Equal volumes of the aqueous and organic phases were placed in Erlenmeyer flask and the combination was

shaken for 3 h. The concentration of hydrochloric acid in the organic phase was determined by acid-base titration with potassium hydroxide dissolved in ethanol.

Selectivity of metal ions with ACS

The aqueous phase was prepared by dissolving metal chloride into hydrochloric acid. The organic phase was prepared by dissolving with chloroform. The initial concentration of each metal was about $1.0 \times 10^{-4} \text{ mol dm}^{-3}$. Equal volumes of aqueous and organic phases were shaken in a flask at extraction operation. Equilibrium was reached within 24 hours at 303K in the extraction of metals from hydrochloric acid. The measurement of extraction equilibrium was carried out by a batchwise method. Equilibrium and initial concentrations of metals were determined by atomic adsorption spectrophotometer. Equilibrium and initial concentrations of hydrochloric acid were determined by an acid-base titration.

Results and Discussion

Table 1 shows the physical properties of ACS1 and ACS2. The weight and mean average molecular weights of ACS1 and ACS2 were measured by size exclusion chromatography (Shimadzu LC-10), respectively. The density of ACS1 and ACS2 were measured by contact angle gauge (KYOWAKAIMEN DropMasters-401).

Table 1 Physical properties of ACS1 and ACS2

	weight average molecule weight	number average molecule weight	Interfacial tension mN/m
ACS 1	3.78×10^4	1.85×10^4	18.5
ACS 2	7.22×10^4	3.63×10^4	16.1

Fig.1 shows the extraction of hydrochloric acid with ACS1 and ACS2, respectively. Saturated amount of hydrochloric acid is $q_{s1} = 1.69 \text{ mmol g}^{-1}$ and equilibrium constant of adsorption is $K_{ad1} = 52.4 \text{ dm}^3 \text{ mol}^{-1}$ with ACS1. Saturated amount of hydrochloric acid is $q_{s2} = 2.08 \text{ mmol g}^{-1}$ and equilibrium constant of adsorption is $K_{ad2} = 21.5 \text{ dm}^3 \text{ mol}^{-1}$ with ACS2. It is indicated that ACS1 are similar character to ACS2. Number and weight molecule weights are not relate to character.

Fig.2 shows the contact time on the extraction percent of palladium(II) with ACS1 and ACS2. Extraction equilibria can be achieved within 15min with ACS1 and ACS2, respectively. The rate of uptake of both ions was quite rapid.

Fig.3 shows the effect of contact time on the extraction percentage of platinum(IV) and gold(III) with ACS1. These results suggest that ACS selectively extracted precious metals from chloride media. Extraction equilibria can be achieved within 1h with ACS1. At equilibrium, 98% of gold(III) and 90% of platinum(IV) were removed from the solution with ACS1.

Fig.4 shows the effect of hydrochloric acid concentration on the extraction percent. Base metals such as copper(II), cobalt(II), nickel(II) and iron(III) were not extracted under these experimental conditions. ACS1 exhibits the high selectivity for gold(III) and palladium(II) over the entire hydrochloric acid concentration range. Platinum(IV) was extracted in the high hydrochloric acid concentration region, while mercury(II) was extracted in the low hydrochloric acid concentration region.

Fig.5 shows the experimental results on the selective adsorption of palladium(II) from the mixture prepared at 1 M containing 200-fold copper(II). As is clear from these results, the adsorption of palladium was independent of the contents of copper even if 200-fold iron

Fig.1 Effect of hydrochloric acid concentration on the extraction percent with ACS1 and ACS2.

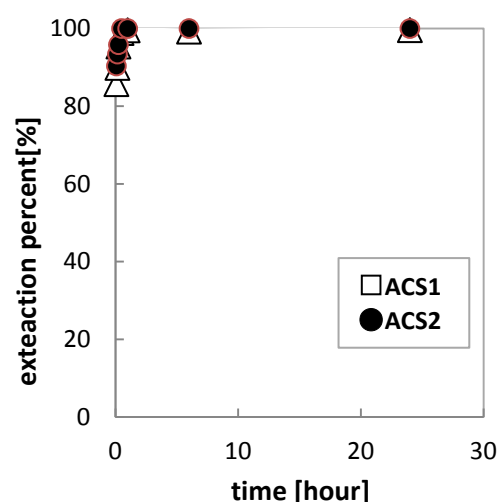


Fig.2 Effect of contact time on the extraction percentage of palladium(II) with ACS1 and ACS2.

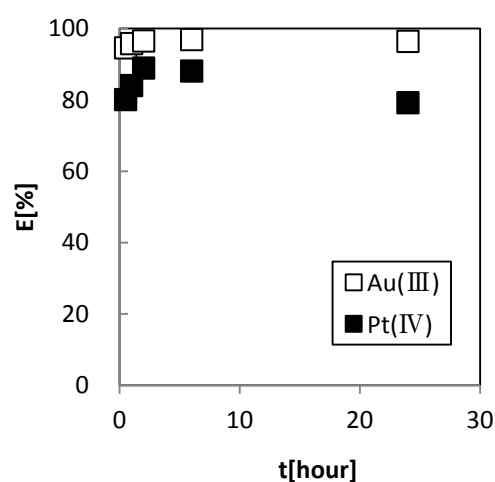


Fig.3 Effect of contact time on the extraction percentage of platinum(IV) and gold(III) with ACS1.

and copper are coexisting in the mixture.

Conclusions

The extraction rate of precious metal with ACS series were the following information was obtained;

(1) Saturated amount of hydrochloric acid is $q_{s1}=1.69\text{mmol g}^{-1}$ and equilibrium constant of adsorption is $K_{ad1}=52.4\text{ dm}^3\text{ mol}^{-1}$

with ACS1. Saturated amount of hydrochloric acid is $q_{s2}=2.08\text{ mmol g}^{-1}$ and equilibrium constant of adsorption is $K_{ad2}=21.5\text{ dm}^3\text{ mol}^{-1}$ with ACS2.

(2) ACS1 selectively extracted precious metals for gold(III), platinum(IV) and palladium(II). Extraction equilibria can be achieved within 1h with ACS1 from chloride media.

(3) ACS1 was a selective extractant for precious metals such as gold(III), palladium(II) and platinum(IV) from hydrochloric acid solution.

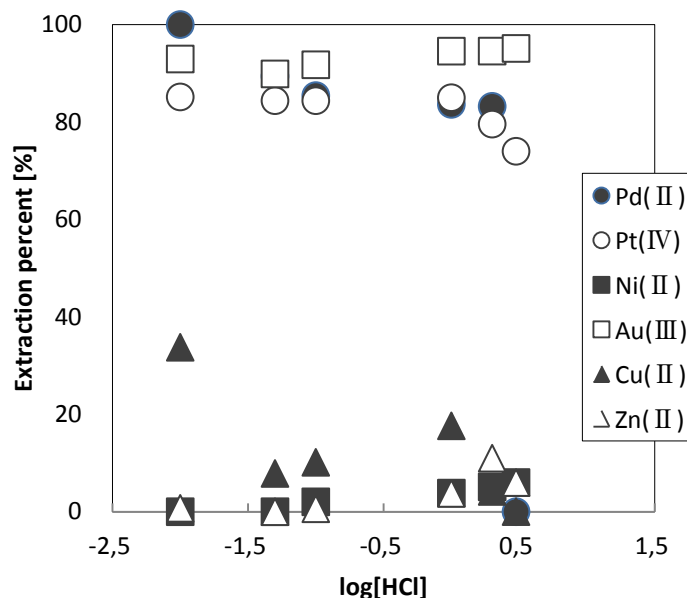


Fig.4 Effect of hydrochloric acid concentration on the extraction percent for various metal ions with ACS1.

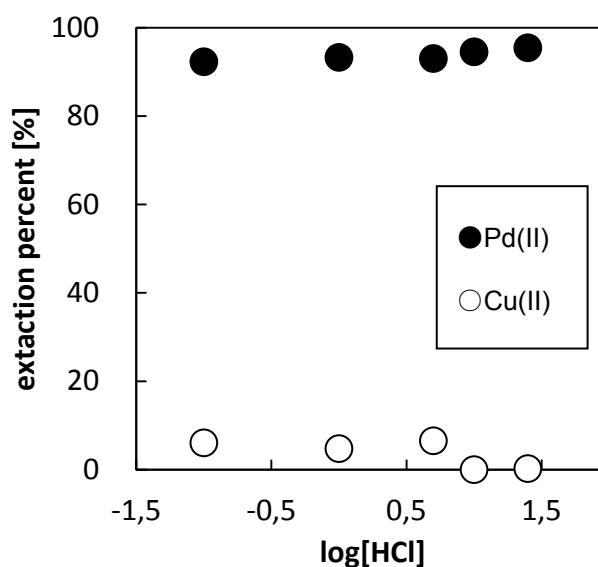


Fig.5 Selectivity of Pd(II) over Cu(II) in the adsorption from the mixture solution of Pd(II) and Cu(III) with ACS1.

References

- 1) K. R. Koch *Coord. Chem. Rev.*, **216 & 217**, 473 (2001)

- 2) D. Cauzzi, M. Costa, N. Cucci. C. Graiff, F. Grandi, G. Predieri, A. Tiripicchico and R. Zanoni, *J. Organometal. Chem.*, **593**, 431 (2000)
- 3) A. Atia, A. M. Donia and A. M. Yousif, *React. Func. Polym.*, **56**, 75 (2003)
- 4) S. Martinez, A. M. Sastre and F. J. Alguacil *Hydrometall.*, **52**, 63 (1999)
- 5) G. V. K. Puvvada and D. S. R. Murthy *Hydrometall.*, **58**, 185 (2000)

A Hydrometallurgy Process For Extracting Cerium(IV) And Thorium (IV) From Bastnasite Using Primary Amine N1923 And Cyanex923

Deqian Li¹ , Jun Lu, Shuzhen Liu, Hongfei Li, Yan Bai, Xiaoqi Sun and Yanliang Wang

State Key Lab of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, P.R.China

ABSTRACT

It is known that half of the amount of the rare earths in bastnasite is cerium. Nowadays cerium is widely used in various fields including catalysts, scintillation material, polishing powder, and ceramic technology. Also Th is one of the most vital elements for nuclear energy programme, its natural sources generally co-exist with REs in monazite or bastnaesite (containing 0.2%–0.3% Th). As a commercially available extractant, N1923 and Cyanex923 have been applied to extract mineral acids and metal ions including Ce(IV) and Th(IV). This paper introduces a simple hydrometallurgy process for separating Ce(IV) and recovering Th(IV) from bastnasite . The simulation test of process has been completed on separatory funnel with 30 mL. Test course adopted fractional extraction method with 5 extraction stages, 5 scrubbing stages(H_2SO_4) and 6 stripping stages($\text{H}_2\text{O}_2 + \text{HNO}_3$) for extracting Ce(IV) and Th(IV) with N1923 as well as 6 extraction stages, 5 scrubbing stages(HNO_3) and 5 stripping stages(H_2SO_4) for recovering Th(IV) from stripping solution containing Ce(III) by Cyanex923. Through simulation test of process, taking H_2SO_4 leaching of roasted bastnasite in air and adding boric acid as feed, we can obtain the CeO_2 products with purity of 99.99% with a yield of >95%, in which $\text{ThO}_2 / \text{CeO}_2 < 10^{-4}$ and the purity of ThO_2 obtained is above 95% with a yield of >99%.

Global Experiences with a Dearomatized Diluent (Escaid™ 110) in SX processes

Dr. Daniel Bien, ExxonMobil Chemical AP, Singapore; Dr. Pierre Yves Guyomar, ExxonMobil Chemical Europe, Brussels, Belgium; Jason Hu, ExxonMobil Asia Pacific Research & Development Co., Ltd, Shanghai, China

Abstract:

Traditionally high flash kerosene cuts have been used as diluent in the SX process. In the recent years more and more a high flash dearomatized cut – Escaid™ 110 is being used. The conversion is driven by technical and environmental performance and availability.

The paper/poster will cover aspects of environmental concerns and industrial hygiene. Show differences in terms of GHS labelling, aquatic toxicity and worker exposure.

A technical comparison between the different diluents in respect to Cu and Ni/Co extraction will be presented, covering aspects like impact of diluent on crud formation and entrainment losses. The paper/poster will also share experiences of SX plants switching from high flash Kerosene to Escaid 110 around the world. There will be references to the Chinese market in particular, where sulfonated kerosene has been predominant.

Extraction and separation of uranium and thorium by di-(2-ethylhexyl) 2-ethylhexyl phosphonate

Yanliang Wang, Changjun Zhao, Wuping Liao^{*} and Deqian Li

State Key Laboratory of Rare Earth Resource Utilization, ERC for the Separation and Purification of REs and Thorium, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China

E-mail: wpliao@ciac.ac.cn

The extraction and separation of uranium(VI) and thorium(IV) from nitrate media by di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP, B) was investigated. The effects of the acidities, salting-out reagents, temperature, the concentrations of metal ions and the extractant have been examined systematically. A possible extraction mechanism for uranium(VI) was proposed as $UO_2^{2+} + 2NO_3^- + 2B_{(o)} = UO_2(NO_3)_2 \cdot 2B_{(o)}$ by the methods of slope analysis. DEHEHP shows a high selectivity towards uranium(VI) over thorium(IV). The separation factor, $\beta_{U(VI)/Th(IV)}$, reaches 150 at 3.5 mol/l HNO_3 . The loaded Uranium can be stripped by distilled water. A countercurrent extraction process (including 3 extraction stages, 2 scrubbing stages, and 4 stripping stages) was designed for the separation of uranium(VI) from a simulated U(VI)-Th(IV)-RE(III) mixture with DEHEHP, which was processed in the separatory funnels. The uranium product was obtained with a purity of 99.9% and a yield of 98%.

Keywords: Solvent extraction; Uranium; Thorium; Neutral phosphorus extractant

Partition of copper and iron ions in aqueous two phase system

*Adriana Jimenez A., Universidad Técnica de Oruro, Oruro, Bolivia; Yecid Jimenez B.,
Universidad de Antofagasta, Antofagasta; Héctor Galleguillos C., Universidad de
Antofagasta, Antofagasta, Chile*

Abstract

Aqueous two-phase system formed by the addition of an inorganic salt to a water-soluble polymer offer many unique advantages when compared to traditional solvent extraction systems for the separation of metal ions. Since both phases are entirely aqueous the use of organic diluents is not necessary to maintain a biphasic system. A variety of non-toxic, inexpensive water-soluble polymers like poly(ethylene glycol) (PEG) can be utilized in combination with a range of relatively innocuous inorganic salts. Also, one of the objectives of the copper solvent extraction is the separation of impurities as iron, thus in this work was tested the possibility of separating copper and iron in ATPS.

The partitioning of copper and iron ions was studied on the ATPSs formed by FeSO_4 + PEG and CuSO_4 + PEG at 25 °C, respectively. The average molar mass of PEG was $4000 \text{ g}\cdot\text{mol}^{-1}$. As of liquid-liquid equilibrium data are planned the ion partition experiences from known compositions of the midpoints of the tie-lines. NaCl, NaNO_3 , KCl and KNO_3 were used as complexing agents to study its effect in the partition stage.

Data on the partition coefficients and percentage extraction of copper and iron ions were obtained, which were analyzed as a function of the concentration of complexing agent. Better results were obtained for the NaCl and KCl complexing agents, reaching extraction percentages up 70%.

Moreover, a partition mechanism was proposed and was found that there is an entropic force driving that cause the ion partition to the top phase.

Solvent extraction recovery of zinc and molybdenum from steelmaking dusts

*Sami Virolainen, Lappeenranta University of Technology, Lappeenranta, Finland;
Tuomo Sainio, Lappeenranta University of Technology, Lappeenranta, Finland.*

In steelmaking, 15-30 kg of different dusts are formed per ton of steel produced. In some cases the dusts may be treated with existing pyrometallurgical processes. Presence of compounds such as Zn may however prevent recycling the dusts back to the pyrometallurgical processes, and presence compounds such as Cr prevents dumping without proper treatment. Hydrometallurgical route, often with solvent extraction, offers a means to recover pure valuable metals and elimination of harmful metals from steelmaking dusts.

In this study, Zn and Mo were identified as most important target compounds and recovered from argon oxygen decarburization (AOD) dusts by leaching and solvent extraction. D2EHPA was successfully used for selective solvent extraction of Zn from H_2SO_4 leachate. Pure Mo was not obtained with any of the studied reagents, but with Aliquat 336 a 100% pure mixture of Mo and Cr was obtained. The additional benefit of Aliquat 336 is that it can function in alkaline conditions. This is significant since lime is often used in the steelmaking process and Mo could be washed from the other studied dust with water to yield a solution with pH 13.7. Also from H_2SO_4 leachate 99% pure Mo/Cr mixture was obtained with Aliquat 336. With LIX 84-I and trioctylamine, Mo and Cr were extracted but only with some impurities. Moreover, these two reagents cannot function in alkaline conditions.

It was found that selectivity of extraction for Mo over Cr could not be significantly improved by altering the reagent concentration. In addition, neither of the metals could be selectively back extracted from the organic phase by the studied methods.

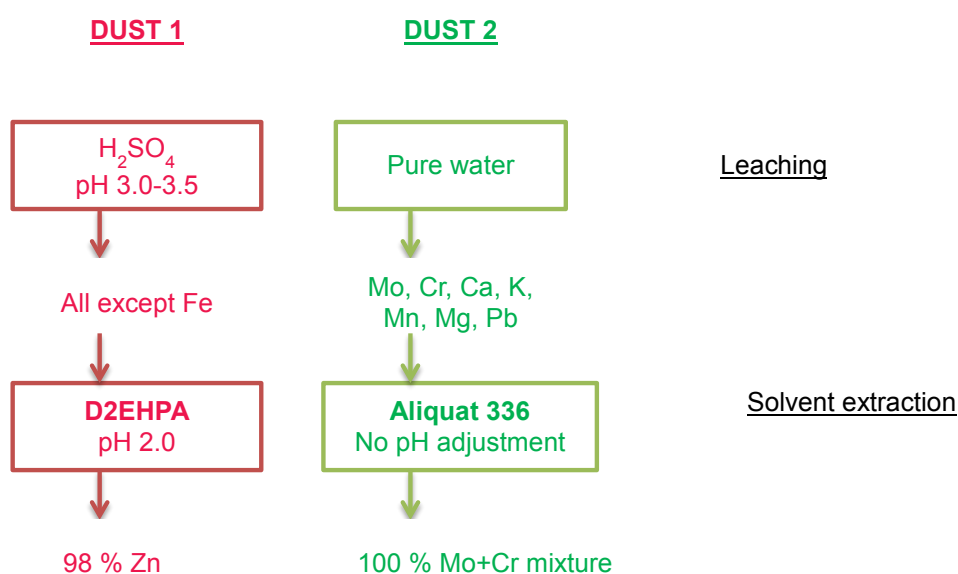


Figure. Suggested processes for recovery of Zn and Mo(+Cr) from argon oxygen decarburization dusts.

Separation of rare earth metal ions by synergistic system with 2-thenoyltrifluoroacetone and TOPO

Fukiko Kubota ^{*1}, *Zhigang Zhao* ¹, *Yuzo Baba* ¹, *Noriho Kamiya* ^{1,2},
Masahiro GOTO ^{1,2}

Summary

The synergistic extraction of rare earth metals by a β -diketone and a phosphine oxide in *n*-dodecane and an ionic liquid was described. A combination of 2-thenoyltrifluoroacetone (HTTA) and tri-*n*-octyl phosphine oxide (TOPO) was found to be effective in synergistically extracting rare earth metals, and the synergistic effect was strongly influenced by the diluent in which the extractants were dissolved. The extraction efficiencies for all the rare earth metal ions were enhanced by the synergistic effect when a conventional organic solvent, *n*-dodecane, was used. However, in the ionic liquid preferentially improved scandium extraction, leading to higher selectivity for scandium than for the other rare earth metals. Slope analysis was conducted to assess each extraction system, and the extraction species of scandium and the other rare earth metals were found to be different in either *n*-dodecane and ionic liquid.

Introduction

There is a great deal of interest in using rare earth elements (REEs) in many industrial fields, but they are generally difficult to separate from each other because of their similar physico-chemical properties. Scandium (Sc), which is categorized into a heavy-group REE, is a very valuable metal because of its low concentrations in known deposits although the abundance in the earth crust is not so low. Scandium has recently been applied in many fields, such as in catalysts, lighting, lasers, titanium and aluminum high-strength alloys, carbon fiber and nanotube materials [1,2]. The extraction and separation of scandium have, therefore, recently become an important research topic [3], however the studies on the separation of Sc are few.

Solvent extraction is a useful method for separating and recovering REEs. The extractant plays a key role in the separation of target metal ions, that is, selecting an appropriate extractant is often critical in determining the success of a solvent extraction process. A highly effective extractant for Sc, however, has not been found to date. Acidic β -diketone is widely used as an extractant for a variety of metal ions. The extraction of REEs with β -diketone such as 2-thenoyltrifluoroacetone (HTTA) has been studied in combination with the synergistic reagents because the extraction efficiency of HTTA for REEs is relatively low. Neutral phosphate derivatives such as tri-butyl phosphate (TBP) or tri-*n*-octyl phosphine oxide (TOPO), which have not been used alone because of its low extraction efficiency, were known to improve the extraction efficiency as a co-extractant [4]. In this study, we examined the synergistic extraction of REEs including Sc with HTTA and TOPO in *n*-dodecane as a model of

^{*1} Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan, f_kubotcm@mail.cstm.kyushu-u.ac.jp

² Center for Future Chemistry, Kyushu University, Fukuoka, Japan

the industrial solvent kerosene. Furthermore, we applied the ionic liquids (ILs) as a diluent.

Ionic liquids (ILs), which are molten salts existing the liquid at around room-temperature, have attracted much attention as “green” alternatives to conventional organic solvents because of their unique properties, including their high thermal stabilities, negligible vapor pressures and less-flammability, and they have been used as novel diluents in liquid–liquid extractions [5-8]. The physico-chemical properties of ILs are tunable, through changing the combination of the constituent ions, which can give distinct improvements in extraction and separation performances. In the IL systems, several extractants, including HTTA, have been used for the extraction of REEs, and the synergistic extraction has been reported using HTTA and a neutral 18-crown-6 [9,10].

In the present study, we examined the extraction behavior of REEs with HTTA and TOPO, both in *n*-dodecane and a hydrophobic IL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₄mim][Tf₂N]), and the synergistic effects on the extraction of these metals were assessed for the separation and recovery of scandium.

Experimental

Reagents

Reagent grade of HTTA and TOPO (Wako Pure Chemical Industries Ltd., Osaka, Japan) were used as extractants.

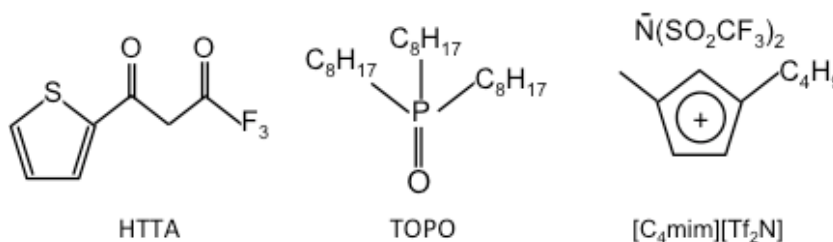


Figure 1 molecular structures of extractants and IL

A hydrophobic IL

[C₄mim][Tf₂N] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Sigma Aldrich, St Louis, MO, USA) and *n*-dodecane were used as solvent. All other reagents were of analytical grade.

Procedure

Extraction equilibrium studies were performed by the conventional extraction method. Aqueous feed phases containing 0.1 mM of each of six rare earth metal ions (Sc, Y, La, Nd, Eu, and Dy) were prepared by dissolving the nitrate salts of the metals in a HNO₃ solution. The pH values, acid concentrations and nitrate ion concentrations of the aqueous phases were adjusted by N-(2-hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid) (HEPES), HNO₃ and NH₄NO₃. Extraction phases were prepared by dissolving a given amount of HTTA and/or TOPO in *n*-dodecane or the IL ([C₄mim][Tf₂N]).

Equal volumes of the extraction and feed phases were mixed in a sealed tube, and after mixing for 60 s in a vibrating mixer, gently shaken at 298K for 12 h to reach equilibrium. After the phase separation, the equilibrium pH of the resulting aqueous phase was measured. The metal concentrations in the aqueous phases were determined using an inductively coupled plasma-atomic emission spectrometer (Optima 5300; Perkin Elmer Co., Waltham, MA, USA). The stripping of metal ions from the extraction phase was also examined using HNO₃ solution. The extraction ratio for the REEs, E [-], was calculated by the Eq. (1),

$$E = ([M]_{aq,0} - [M]_{aq})/[M]_{aq,0} \quad (1)$$

where, $[M]$ represents the concentration of metal ions, subscript aq denotes the aqueous phase, and 0 means the initial state.

Results and discussion

Synergistic extraction with HTTA and TOPO in *n*-dodecane

Synergistic extraction with HTTA and TOPO was examined in *n*-dodecane. As shown in Fig. 2(a), Sc³⁺ was selectively extracted relative to the other REEs with HTTA, and quantitative extraction was achieved at pH >3. Adding TOPO dramatically enhanced the extraction of all the REEs, however the extraction of REEs except Sc³⁺ was more strongly enhanced compared to Sc. (Fig. 2b) We confirmed that the REEs were not extracted using only TOPO under the same experimental conditions, and the improvement in the extraction efficiency of the REE ions was, therefore, attributed to a synergistic effect between the two extractants.

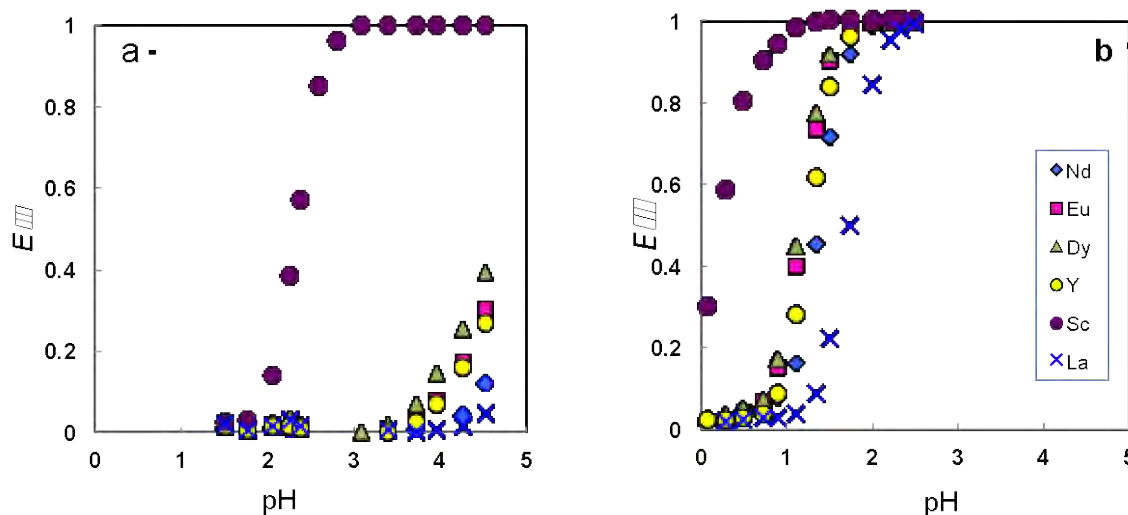


Figure 3 Extraction behavior of rare earth metals with a. HTTA and b. HTTA with TOPO in *n*-dodecane. $[M]=0.1\text{mM}$, a: $[HTTA]=10\text{mM}$, b: $[HTTA]$, $[TOPO]=10\text{mM}$

Synergistic extraction with HTTA and TOPO in the IL [C₄mim][Tf₂N]

The extraction of REEs in the IL [C₄mim][Tf₂N] was also examined (Fig.3). In the IL system, Sc³⁺ was not extracted at the pH range below 3 with HTTA alone, and no selectivity for Sc³⁺ was observed (Fig3.a), in contrast with the extraction behavior

found in the *n*-dodecane system shown in Fig.2a. As shown in Fig.3b, however, the addition of TOPO to HTTA in the IL gave much better REE extraction efficiencies, especially for Sc^{3+} , that is, the magnitude of the improvement for the extraction of Sc^{3+} was significantly larger than that of the other REEs. The REEs are not extracted at all with TOPO alone in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ under the experimental conditions as reported previously [11], and it was confirmed that Sc^{3+} was also rarely extracted at the acid concentration range from 1.5 to 0.2 M where the extraction curve of Sc^{3+} in Fig.3b rose to reach constant. Therefore the combination of the two extractants used in this study must have played an important role in causing the synergistic effect. However, slight differences in the extraction efficiencies of each metal ion using TOPO affected the selectivity in the HTTA–TOPO extraction system.

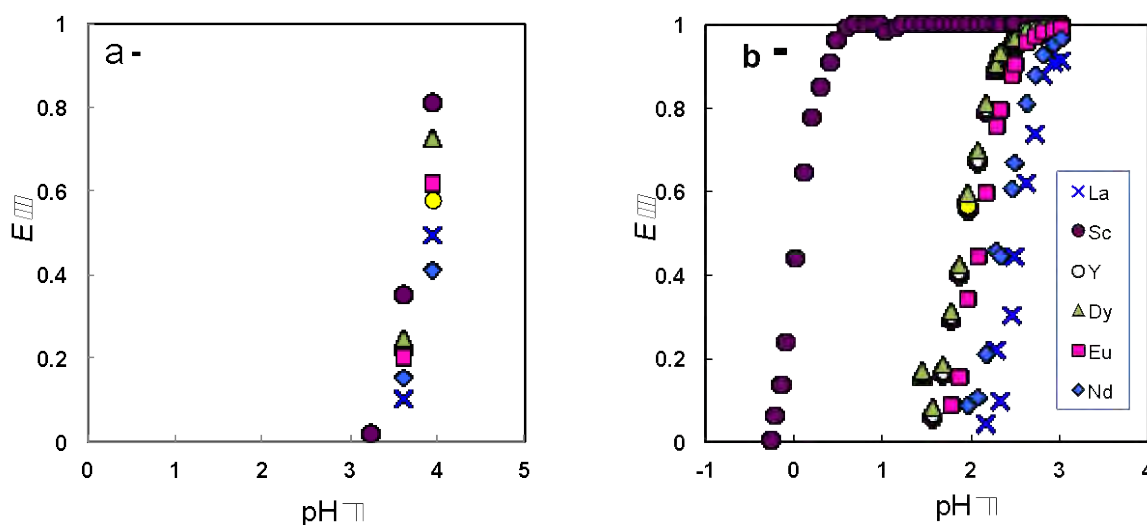
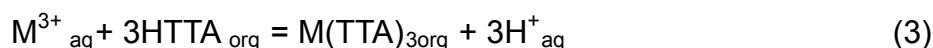


Figure 3 Extraction behavior of rare earth metals with a. HTTA and b. HTTA with TOPO in *n*-dodecane. $[M]=0.1\text{mM}$, a: $[\text{HTTA}]=10\text{mM}$, b: $[\text{HTTA}]$, $[\text{TOPO}]=10\text{mM}$

Extraction mechanism of REEs with synergistic system.

β -Diketones, such as HTTA, are widely used in analyses to extract a variety of metal ions by acting as chelating agents. The mechanism involved in the extraction of trivalent REE ions with HTTA in organic solvents follows Eq. (3) [12].



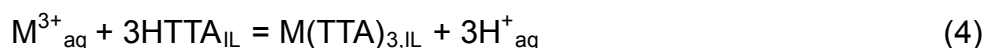
Under the present experimental conditions, the extraction of Sc^{3+} with HTTA in *n*-dodecane was confirmed to follow the Eq.(3) (hereinafter, data not shown).

For the synergistic extraction of REEs with a mixture of HTTA and TOPO, the slope analysis for Sc^{3+} and Eu^{3+} was also conducted to clarify the difference in the extraction behavior between Sc^{3+} and the other REEs. A linear relationship between $\log D$ and the logarithmic $[\text{H}^{+}]$ in the aqueous phase was obtained, with slope 3 for Eu^{3+} and close to 2 for Sc^{3+} . Plots of $\log D$ against $\log [\text{HTTA}]$ at a constant TOPO concentration and of $\log D$ against $\log [\text{TOPO}]$ at a constant HTTA concentration both showed linear correlations, with slopes of 3 and 2, respectively, for Eu^{3+} , and the slopes of 2 were obtained for Sc^{3+} . This suggests that the extracted species in the

synergistic HTTA and TOPO system had a stoichiometry of 3:2:1 (HTTA:TOPO:M, M=Y, La, Nd, Eu, and Dy) and 2:2:1 for Sc^{3+} . As for Sc^{3+} , it was found that a nitrate ion was involved in the extraction reaction.

The ionic radius of Sc^{3+} is much smaller than that of the other REEs, and also the coordination number (6 or 8) was lower than do the other REEs (from 6 to 12). Therefore the complex of Sc^{3+} with HTTA alone, which was coordinatively saturated and sufficiently-hydrophobized, was selectively distributed to the organic phase. In the synergistic system, REEs except Sc^{3+} formed the complex coordinatively saturated with more ligands HTTA than that for Sc^{3+} and two adducts TOPO, and the distribution of the REEs was considered to be enhanced compared to Sc^{3+} .

The extraction of REE ions with HTTA in an IL has previously been studied [9,13], and the following extraction equations were reported.



In the HTTA system, the extraction ability for Sc^{3+} was significantly low, compared to that in the *n*-dodecane. HTTA was solubilized better in the IL than in *n*-dodecane, and the distribution of HTTA to the aqueous phase must be lower in the IL phase than in the *n*-dodecane phase. Furthermore, complex formation of Sc^{3+} with more extractant molecules as expressed by Eq.(5) was considered to be difficult compared to that of Eu^{3+} . Therefore the IL system was considered to be showing lower extraction efficiency than that of the *n*-dodecane system. The addition of TOPO, however, extremely enhanced the extraction efficiency of REEs especially of Sc^{3+} , as above described. The slope analysis was conducted for the synergistic extraction with a mixture of HTTA and TOPO, and the extracted species was estimated to be $\text{Eu}(\text{TTA})_2(\text{TOPO})_3^{+}$ and $\text{Sc}(\text{TTA})(\text{TOPO})_3(\text{NO}_3)^{+}$, respectively under the present experimental conditions. In the synergistic system, the extraction was enhanced especially for Sc^{3+} , and one of the reasons was that the solubility of the Sc complex into the IL phase was considered to be higher than that of the Eu complex, of which size is larger than Sc complex. The release of an imidazolium cation into the aqueous phase was observed and it accelerated the partitioning of the metal complexes.

Stripping

Stripping from the extraction phase was performed by 3 M HNO_3 for both extraction systems. A quantitative stripping was achieved using 3 M HNO_3 in the organic system. The stripping was caused by the undissociation of HTTA and also by the inhibition of the coordination of TOPO brought by the interaction of the coordination site of TOPO with H^{+} in high acidity. In the IL system, the stripping of Sc^{3+} was achieved by 3M HNO_3 however that of the other REEs seemed to be somewhat difficult compared to that of Sc^{3+} despite of their lower extractability. It was considered that the REE complexes might be difficult to be solubilized uniformly into the bulk IL phase in the forward extraction step, compared to the Sc complex.

Conclusions

We investigated the synergistic extraction of REEs using a β -diketone (HTTA) and a phosphine oxide (TOPO), and found that the synergistic effects were different in an IL and in an organic solvent. The extraction efficiencies of the rare earth metals were enhanced by the synergistic effect in the organic solvent, but the effect for Sc^{3+} was smaller than that of the other REEs. However, the synergistic system in IL improved both the extraction efficiencies and the selectivity, in particular for Sc.

Acknowledgement

We thank Sumitomo Metal Mining (SMM) Co., Ltd. for their financial support of this research. This work was partly supported by a Grant-in-Aid for Science Research (No. 25420806) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

Reference

1. J. B. Hedrick, “*Mineral Commodity Summaries 2008: Scandium*” **2008**, U.S. Geological Survey, United States Government Printing Office, Washington: 2008.
2. S. Kobayashi, K. Manabe, *Pure Appl. Chem.*, 2000, **72**, 1373.
3. W. W. Wang, C. Y. Cheng, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 1237.
4. M. Krea, H. Khalaf, *Hydrometallurgy.*, 2000, **58**, 215.
5. F. Kubota, M. Goto, *Solvent Extr. Res. Dev. Jpn.*, 2006, **13**, 23.
6. N. Hirayama, *Solvent Extr. Res. Dev. Jpn.*, 2011, **18**, 1.
7. X. Sun, H. Luo, S. Dai, *Chem. Rev.*, 2012, **112**, 2100
8. F. Kubota, Y. Baba, M. Goto., *Solvent Extr. Res. Dev. Jpn.*, 2012, **19**, 17.
9. N. Hirayama, H. Okamura, K. Kidani, H. Imura, *Anal. Sci.*, 2008, **24**, 697.
10. H. Okamura, N. Hirayama, K. Morita, K. Shimojo, H. Naganawa, H. Imura, *Anal. Sci.*, 2010, **26**, 607.
11. F. Yang, F. Kubota, N. Kamiya and M. Goto, *Solvent Extr. Res. Dev. Jpn.*, 2013, **20**, 225.
12. A. M. Poskanzer, B. M. Foreman, *J. Inorg. Nucl. Chem.*, (1961), **16**, 323-336.
13. M. P. Jensen, J. Neufeind, J. V. Beitz, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466.

Synthesis of novel ditopic ligands for the extraction of transition metal salts

*Robert C. Luckay^{*1}, Hanna-Mari Smuts¹ and Joshua C. Hensberg¹*

Summary

Hydrometallurgical processes are environmentally friendlier than pyrometallurgical processes and include leaching, precipitation, electrolytic reduction, ion exchange, membrane separation and solvent extraction.

We have synthesised two novel ligands for the extraction of transition metal salts. The $[\text{N}_2\text{O}_2]^{2-}$ donor set will bind to the metal ion and the anion will bind with the protonated $-\text{NR}_2$ units. These features create the possibility of separately recovering the metal cation and its anion in one ligand and recycling the ligand.

All ligands were characterised by ^1H and ^{13}C NMR, FTIR, mass spectrometry, m.p. determination (where appropriate) and elemental analysis. Competitive two-phase metal ion solvent extraction experiments were performed. These ligands showed significant selectivity for Cu(II) ions, especially the ligand (with piperidyl groups attached) which extracted > 81% of the Cu(II) ions in a solution of different metal ions at pH 5.09. This selectivity can be explained by the formation of three six-membered chelate rings upon metal complexation which are more selective for smaller metal ions. Competitive transport experiments (water/chloroform/water) were undertaken employing each ligand separately as the ionophore in the membrane (chloroform) phase. The pH of the source phase was 5.09 and that of the receiving phase 1.0. No metal ion transport was observed. Even though a large concentration of Cu(II) was present in the membrane phase, no Cu(II) was present in the receiving phase, indicating that a pH of 1.0 is not the optimum pH conditions for stripping into the receiving phase. A pH isotherm of ligand L2 with Cu(II) was determined from pH 1.0 to 6.0.

This study illustrates that simple ditopic ligands can be used to selectively extract metal salts which provides an advantage over conventional ion exchange reagents which add components to the aqueous stream.

Introduction

In industry, metal recovery and purification from their ores are mainly performed by pyrometallurgical and hydrometallurgical processes. Pyrometallurgical processes have severe environmental implications due to the emission of pollutants and toxic gases. Due to increasingly stricter environmental regulations this is a significant problem as there is an increasing need for “greener” methods. This method is also not cost effective when applied to low-grade ores.¹

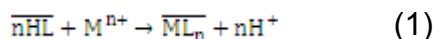
Hydrometallurgical processes differ from pyrometallurgical processes in that the desired metals are separated using techniques that capitalise on electrochemical properties and/or solubility differences while in aqueous solutions. Examples of hydrometallurgical processes include leaching, precipitation, electrolytic reduction, ion exchange, membrane separation and solvent extraction.²

Ion exchange can be used to separate or recover metal ions. This process takes place by means of a mechanism where the desired metal cation replaces another or different metal cation or protons from an anionic group in a complexing agent (Eqn.

1

^{*} Department of Chemistry & Polymer Science, Stellenbosch University, Private Bag X1, Matieland, Stellenbosch, 7602, South Africa.

1). The complexing agents can be deployed on a solid support or in a water immiscible liquid. This does not truly purify the aqueous stream because (i) the number of ions in solution does not change and is often increased; (ii) the pH of the stream may be significantly lowered if there is proton exchange; and (iii) the anions are still in solution.³



A more efficient approach would be to design an extractant that can transport metal salts in a hydrometallurgical solvent extraction process. Salicylaldimine ligands of the H₂salen type bearing NR₂ substituents would function as ditopic ligands, having two separate binding sites to accommodate both the metal cation and its concomitant anion(s). The [N₂O₂]²⁻ donor set of the salen unit will bind to the metal ion and a sulphate, nitrate or chloride anion with the protonated –NR₂ units. These features create the possibility of separately recovering the metal cation and its anion and recycling the ligand. These types of ligands have been pioneered by the Tasker group and they have several examples in the literature.^{1,3,7,8,11} The aldimine functionality is resistant to hydrolysis and can therefore be used in solvent extraction processes because it is able to withstand the relatively strong acidic media required for efficient stripping protocols.⁴

We report herein the synthesis of two novel ditopic ligands and an existing Schiff-base ligand for comparison purposes. We subjected the ligands to competitive metal ion extraction and competitive transport of metal ions as well as competitive extraction of anions. Because ligand **L2** showed such high extraction of Cu(II), we carried out a Cu(II) loading experiment from pH 1 to 6 so as to obtain pH_{1/2}.

Experimental

Reagents, solvents and ICP-OES standards were acquired from Sigma-Aldrich, Merck, Alfa Aesar or SAARChem and used without further purification. Distilled water was obtained from a Milli-Q purification system. Solvents were dried over molecular sieves or distillation before use. NMR spectra were recorded in 5 mm tubes using a variety of deuterated solvents; CDCl₃, DMSO-d₆ and D₂O. ¹H- and ¹³C-NMR spectra were collected on a Bruker AVA 400 NMR spectrometer. Manipulation of spectra was carried out using Mestrec software. Mass spectrometry was performed on a VG Autospec instrument using ionization techniques including electrospray ionization and electron ionization. Elemental analyses were obtained from the University of KwaZulu-Natal. ICP-OES data were gathered on a Perkin Elmer Optima 5300DV and were manipulated using Winlab32 and Microsoft Excel.

Synthesis

Ligands were synthesized according to the literature⁸ and the synthetic scheme is depicted in Figure 1.

Competitive two-phase solvent extraction

Competitive two-phase solvent extraction studies were carried with all three ligands. The metal ions were Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) all at 0.01 mol dm⁻³

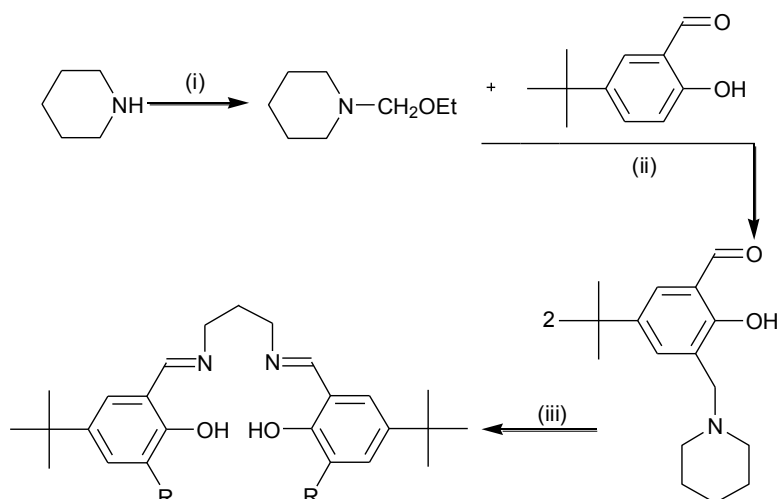


Figure 1. (i) Paraformaldehyde, distillation; (ii) MeCN, N_2 , reflux for 72h; (iii) diaminopropane, Et_2O - $EtOH$ (1:1), room temp. 12 h. Ligands referred to here are **L1**: $R = H$, **L2**: $R = \text{piperidine-CH}_2$, **L3**: $CH_2-N(n-C_6H_{13})_2$.

made up in an acetic acid / acetate buffer at pH 5.09. The ligand concentration was 0.01 mol dm^{-3} and made up in chloroform which has been presaturated with distilled water. 10 ml of the mixed metal ion solution and 10 ml of the ligand solution were placed in polytops (duplicate) and shaken at 220 rpm on a labcon-oscillating shaker.

Competitive transport experiments

Each ligand, at a concentration of 0.01 mol dm^{-3} was used separately as a carrier for the transport of metal ions across a $CHCl_3$ (50 cm^3) bulk liquid membrane. Details of the cell design have been reported elsewhere¹². The source phase consisted of 10 cm^3 of a 0.01 mol dm^{-3} solution of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) metal ions in a CH_3COONa/CH_3COOH buffer at pH 5.09. The receiving phase consisted of 30 cm^3 of 0.1 mol dm^{-3} HNO_3 at pH 1.0. All three phases in the transport cell were stirred at 10 rpm at 25°C . Under these conditions, not only was the stirring process consistent, but also the interface between the organic membrane and the two aqueous phases remained flat and well defined. The cells were covered with slips to prevent any evaporation of solvents over the 24 h period. Samples of the source and receiving phases were taken and used for metal analysis by ICP-OES.

Competitive transport of anions

L2 and **L3**, each at a concentration of 0.01 mol dm^{-3} were used as carriers for the transport of anions across a $CHCl_3$ (50 cm^3) bulk liquid membrane. Details of the cell design have been reported elsewhere¹². The source phase contained 10 cm^3 of a 0.01 mol dm^{-3} solution of 0.01 mol dm^{-3} $CuSO_4$, HNO_3 and HCl at pH 1.91. The receiving phase contained 30 cm^3 NaH_2PO_4/Na_2HPO_4 buffer at pH 6.95. All three phases in the transport cell were stirred at 10 rpm at 25°C . Under these conditions, not only was the stirring process consistent, but also the interface between the organic membrane and the two aqueous phases remained flat and well defined. The cells were covered with slips to prevent any evaporation of solvents over the 24 h period. Samples of the source phase and the receiving phase were taken and used for ion chromatography. The results are quoted as the average value obtained from

duplicate runs in Table 1. Any apparent extraction of a metal ion of less than 2.0% was assumed to be within the experimental error of zero and hence ignored in the treatment of results. In all cases the values between any two duplicate runs did not differ by more than 5 %.

Results and Discussion

All of the ligands were characterised by ^1H and ^{13}C NMR spectroscopy, FTIR spectroscopy, mass spectrometry and melting point determination where solids were obtained. **L1** and **L2** are both yellow solids, having melting points 76.0 – 76.9 °C and 72.0 – 72.9 °C respectively. **L3** is a viscous orange oil, most likely due to the long alkyl chains. The overall yield of **L1** was 96.1 %, **L2** was 25.0% and **L3** was 92.9%. The difference in overall yield between **L2** and **L3** can be attributed to the use of a 30 cm Vigreux column for the distillation steps for **L2** and a Kugelrohr vacuum distillation apparatus for **L3** which produced a much higher yield. Evidence for the



Figure 2: (i) Before and (ii) after images of competitive two-phase metal ion solvent extraction experiments at pH 5.09.

complete formation of products was confirmed by the presence of characteristic resonances for the imine proton at $\delta = 8.3\text{--}8.5$ ppm in the ^1H NMR spectrum and of the imine C centre at $\delta = 165\text{--}166$ ppm in the ^{13}C NMR spectrum, together with the absence of aldehydic C and H centre resonances. The free ligands as well as complexes of the ligands with various metal salts all showed sufficient solubility in CHCl_3 to allow solvent extraction and transport experiments to be carried out.

To investigate the selectivities of the ligands for different metal ions, competitive two-phase metal ion solvent extraction experiments were performed (Fig. 1). All three ligands showed significant selectivity for Cu(II) ions (**L1**-71%, **L3**-73%) especially **L2** which extracted 81 % of the Cu(II) ions in a solution of different metal ions at pH 5.09. This selectivity can be explained by the formation of three six membered chelate rings upon metal complexation which are more selective for smaller metal ions.

Competitive transport experiments (water/chloroform/water) have been undertaken employing **L1**, **L2** and **L3** as the ionophores in the membrane (chloroform) phase. The aqueous source phase contained equimolar concentrations of Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Cd(II). The respective pH values used for the aqueous source (pH 5.09) and receiving (pH 1.0) phases were chosen such that under these conditions it was assumed that the resulting pH gradient across the cell will be favourable for uptake of metal ions from the source phase into the membrane phase while promoting its loss from the membrane phase into the receiving phase. Under the conditions employed, no transport was observed for the six metal ions present in

the source phase. There was however a large amount of copper(II) transported from the source phase into the membrane phase, indicative that a pH of 1.0 is not the optimum pH for stripping into the receiving phase.

Competitive two-phase solvent extraction experiments were also performed using different copper salts in solution to determine the selectivity of ligands **L2** and **L3** for Cl^- , NO_3^- and SO_4^{2-} anions. Both ligands showed a high selectivity for NO_3^- anions, and extracted the least amount of SO_4^{2-} anions, especially **L3** which only extracted < 20 % of the sulphate anions in the solution. Competitive anion transport experiments with the same ligands and anions as above were also studied. The respective pH

*Table 1: Results of transport experiments indicating the percentage of anions present in the source and receiving phases for **L2** and **L3***

Ligand	Phase	Cl^-	NO_3^-	SO_4^{2-}
L2	Source	26.0	0.00	47.4
L2	Receiving	26.9	24.0	0.00
L3	Source	24.3	0.00	81.9
L3	Receiving	22.8	26.6	0.00

values used were pH 1.91 for the aqueous source phase and pH 6.95 for the receiving phase. As indicated in Table 1, both ligands showed selectivity for the NO_3^- anion, and transported all of the NO_3^- anions out of the source phase. The remainder of the anions that were not transported into the receiving phase must be present in the organic membrane phase.

The above mentioned selectivities associated with anion receptors are strongly linked to a phenomenon known as the Hofmeister bias (Fig. 3). The term „Hofmeister bias“ has been suggested to be used in solvent extraction of ionic materials.⁵ This can be used to predict why the NO_3^- and Cl^- anions were extracted in preference to the SO_4^{2-} anions. This is because SO_4^{2-} is much more heavily hydrated than Cl^- and NO_3^- and therefore more hydrophilic and so it prefers to stay in an aqueous environment.

strongly hydrated anions	weakly hydrated anions
Citrate ³⁻ > SO_4^{2-} = tartrate ²⁻ > HPO_4^{2-} > CrO_4^- > acetate ⁻ > HCO_3^- > Cl^- > NO_3^- > ClO_4^-	

Figure 3: The original Hofmeister bias⁵

Metal salt complexes were formed by adding equimolar amounts of nickel, zinc and copper sulfate solutions to the novel ligands in methanol. Colour changes due to complexation were rapid.

Complex formation was confirmed by FTIR of the isolated nickel(II) complex as well as ^1H and ^{13}C NMR spectra of the nickel(II) complex with **L3**. Nickel(II) readily forms low spin diamagnetic planar complexes with H_2salen -type ligands that can be studied by NMR spectroscopy.⁷ Complexation to the nickel(II) complex leads to shifts of the ^1H and ^{13}C NMR signals close to the co-ordination site more downfield compared to those of the metal-free ligands. The ^1H NMR also showed that the phenolic proton signal is lost which is consistent with the metal being incorporated into the $[\text{N}_2\text{O}_2]^{2-}$ donor set.

Copper-only complexes of all three ligands were also formed by adding copper

acetate solutions to the ligands in a chloroform solution. A shift in the imine stretching frequency in the FTIR spectra confirmed complex formation. The isolation of a “metal-only” or metal salt complex depends on the composition of the solvent system as well as the relative basicities of the pendant tertiary amine and the anion.⁸

In hydrometallurgical processes, the strengths of organic acid extractants are often compared by measuring the $\text{pH}_{1/2}$ value, which is the pH associated with 50% loading of the extractant.⁶ The metal content in the organic phase was determined over a pH 1-6 range, to obtain a $\text{pH}_{1/2}$ value. The results of the experiment are indicated in Fig. 4. The $\text{pH}_{1/2}$ value is estimated at pH 2.6. In metal ion extraction, a lower $\text{pH}_{1/2}$ value indicates stronger metal complexation.⁹ A commercial extractant, LIX 84-I has a $\text{pH}_{1/2}$ value at pH 1.¹⁰

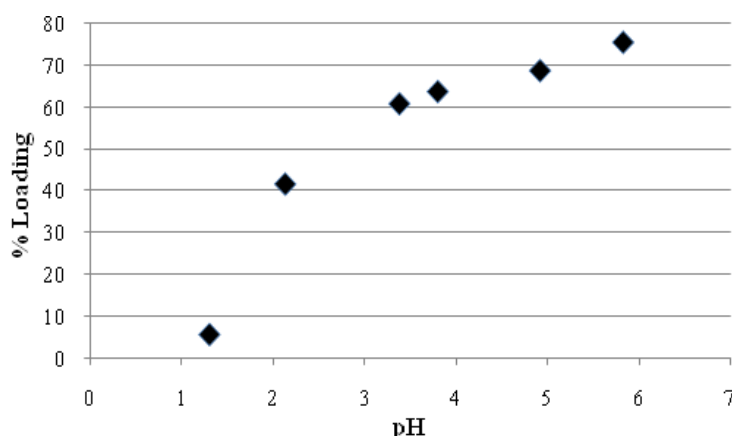


Figure 4: Copper(II) extraction of **L2** as a function of pH.

Conclusion

Relatively simple ditopic ligands related to H_2salen were used to establish selective extraction and transport of copper(II) ions and nitrate anions respectively. The co-extraction of a metal cation with its attendant anion(s) in the form of a metal salt by these types of ligands provide an advantage over conventional ion exchange reagents which have the disadvantage of adding components to the aqueous stream. The NRF and Stellenbosch University is thanked for their financial assistance in this project.

References

1. S.G. Galbraith and P.A. Tasker, *Supramolecular Chemistry*, 2005, 17, 191.
2. International Labour Organisation, *Encyclopaedia of Occupational Health and Safety*, Vol III, 1998, 82.
3. D. J. White, N. Laing, H. Miller, S. Parsons, S. Coles and P. A. Tasker, *Chem. Commun.*, 1999, 2077.
4. J. Szymanowski, in *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, FL, 1993, p. 62.
5. F. Hofmeister, *Arch. Exp. Pathol. Pharmacol.* 1888, 247.
6. P.A Tasker, P.G. Plieger and L.C. West, In *Comprehensive Coordination Chemistry*; J.A McCleverty, T.B. Meyer, Eds.; Vol. 9, Elsevier: Oxford, 2004, p 759.
7. H. A. Miller, N. Laing, S. Parsons, S. Parsons, P. A. Tasker and D. J. White, *Dalton Trans.*, 2000, 3773.

8. R.A. Coxall, L.F. Lindoy, H.A. Miller, A. Parkin, S. Parsons, P.A. Tasker and D.J. White, *Dalton Trans.*, 2002, 55.
9. B.A. Moyer, P.V. Bonnesen, L.H. Delmau, T.J. Haverlock, K. Kavallieratos and T.G. Levitskaia, *International Solvent Extraction Conference Cape Town, South Africa, March 17-21, 2002*, 299.
10. "New Recovery Process Can Yield Both Electrolytic Nickel and Copper", *Engineering and Mining Journal*, January 1972, p. 94-95.
11. S. G. Galbraith, Q. Wang, L. Li, A. J. Blake, C. Wilson, S. R. Collinson, L. F. Lindoy, P. G. Plieger, M. Schroder and P. A. Tasker, *Chem. Eur. J.*, 2007, 13, 6091-6107.
12. P. S. K. Chia, L. F. Lindoy, G. W. Walker, G. W. Everett, *Pure Appl. Chem.*, 1993, 65, 521.

SEPARATION OF INDIUM AND ZINC BY SOLVENT EXTRACTION FROM SULFURIC LIQUOR GENERATED FROM THE LEACHING OF THE COATING DUST OF THE SCRAPPED COMPUTER SCREENS

Carlos A. de Moraes¹, Ana C. Zuccheratte²

^{1,2}Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte/BR,
e-mail: cmorais@cdtn.br¹; acvz@cdtn.br².

ABSTRACT

The computer monitors have as internal coating a compound consisting of oxysulphide, with considerable concentration of indium and zinc, and other metals. This paper describes the study of separation of the metals In and Zn, by solvent extraction, from a sulphuric liquor generated from the leaching of the coating dust of the scrapped computer screens. The parameters investigated were: (1) type and concentration of reagents. (2) Acidity of the aqueous phase. (3) The contact time between the aqueous and organic phases. The best results were obtained with DEHPA and IONQUEST[®]801, however in the case of IONQUEST[®]801, the acidity of the liquor needed to be reduced. The continuous experiment was carried out using DEHPA 1.0 mol.L⁻¹ as the extractant. A loaded organic solution containing 7.5 g.L⁻¹ of In and 0.003 g.L⁻¹ of Zn and a raffinate containing 9.4 g.L⁻¹ of Zn with an In content lower than 0.001 g.L⁻¹ was obtained. The metals content in stripped solution were 26.7 g.L⁻¹ of In and 0.001 g.L⁻¹ of zinc. This process contributes to the reduction and recovery of discarded materials, minimizing the environmental impact, with economic and social return.

KEYWORDS: Solvent extraction; Indium; Zinc; Separation of In/Zn

1. INTRODUCTION

In the last decade, the consumption of electronic devices has grown a lot in the world in general. Two factors are responsible for this in Brazil. First, Brazil has been going through a huge economic transformation; therefore, Brazilian income has increased. Second, new technologies like smartphones, faster computers, and new screen types have become more accessible to a large number of Brazilians. These new devices are replacing the old generation. Consequently, the improper disposal of electronic devices may cause an environmental problem because a lot of them contain toxic substances such as heavy metals with a high potential for pollution. The manipulation or improper disposal of these gadgets can also cause health and environmental problems by contaminating the soil and water bodies.

Electronic garbage usually contains materials that can be recycled and recovered through chemical processes. Although, every device contains a different composition and different kinds of residues, these residues can be separated into six categories: Iron, steel, non-ferrous metals, glass, and plastic. In the case of glass, the largest part comes from the cathode ray tube, (CRT) present in televisions and computers displays. The CRT also contains lead, cadmium, europium, selenium, zinc and yttrium (RESENDE and MORAIS, 2011, 2010).

TV and computers' screens have a coating usually made of a mixture of oxides that contain certain quantities of zinc (~39%), indium (~1,2%) and other elements (RESENDE and MORAIS, 2011, 2010). Indium (In) is an important raw material used in new electronic gadgets (HABASHI, 1997). Zinc (Zn) has many applications: (1) the production of alloys and the galvanizing of steel structures (2) use in batteries and (3) as an essential nutrient for living organisms (AZEVEDO and CHASIN, 2003; DNPM, 2001).

A loaded organic containing 7.5 g.L^{-1} In and 0.003 g.L^{-1} Zn, a raffinate containing 9.4 g.L^{-1} of Zn and less than $0,001 \text{ g.L}^{-1}$ of In and a stripped solution containing 26.7 g.L^{-1} and in 0.001 g.L^{-1} Zn were obtained using a liquor containing 1.49 g.L^{-1} In and 9.8 g.L^{-1} Zn.

2. METHODOLOGY

Reagents and solutions

The liquor used in this study was obtained by the opening of the of the powder coating of CRT screens through sulphuric acid digestion followed by water leaching. The content of the species present in the liquor was: 9.8 g.L^{-1} zinc, 1.49 g.L^{-1} of indium and 102 g.L^{-1} of sulphate containing as impurity 0.016 g.L^{-1} of iron, and acidity of 2.2 mol.L^{-1} (ZUCCHERATTE and MORAIS, 2012).

The commercial extractants investigated were: di-2-ethylhexylphosphoric acid (DEHPA) 97 wt% and 2-ethylhexyl-mono-2-ethylhexylester (IONQUEST[®]801) 99 wt%, supplied by Pecos do Brasil Ltda, and bis-2,4,4-trimethylpentyl-phosphinic acid (CYANEX[®]272) 99 wt%, supplied by Cytec do Brasil Ltda. The solvents were prepared by dissolving the extractant in EXXSOL[®]D100 (mostly aliphatic, aromatic max. of 1.0 wt%) supplied by Exxon Química. The sulphuric and hydrochloric acids used in the stripping experiments were of analytical grade and their solutions were prepared using distilled water.

Experimental procedure

The extraction experiments were carried out through the conventional batch wise method and in a continuous circuit comprised of mixer-settler stages in a counter-current system. The batch experiments were carried out in beakers of 150 mL, under an 800 rpm

mechanical agitation at room temperature (25 °C). Unless specified otherwise, the ratio of aqueous-organic phases (A/O) was 1 (20 mL of each phase). The pH of the aqueous phase was adjusted with the addition of an ammonium hydroxide solution (NH₄OH 6 mol.L⁻¹). The contact time of the aqueous-organic phases was 10 minutes.

The continuous experiment was carried out in a counter-current system using mixer-settlers, with a capacity of 70 mL in the mixer and 250 mL in the settler. The feeding of the aqueous and organic phases was performed using peristaltic pumps. The flow rate of the feed streams and process control were monitored every hour.

The In and Zn content in each phase were determined using an energy-dispersive X-ray spectrometry (Kevex system). The other metals were determined by atomic absorption spectrometry.

3. RESULTS AND DISCUSSION

The parameters investigated in the batch experiments were: extractant agent, pH of the liquor, concentration of the extractant, A/O ratio, and concentration of the scrubbing and stripping acid solution. The main constituents of the sulphuric liquor used in this work are presented in table I.

Table I Composition of the sulphuric liquor used in solvent extraction experiments.

Species	Zn	In ³	SO ₄ ²⁻	Fe ₂ O ₃	H ⁺
Content	9.8	1.49	102	0.02	2.2

3.1. Batch experiments

The influence of three extractants from cationic organophosphorus acid series were tested: (i) DEHPA, (ii) IONQUEST 801 and (iii) CYANEX 272. The concentration of extractants was 1.0 mol.L⁻¹ and the acidity of the liquor was 2.2 mol.L⁻¹ H⁺. The results are shown in table II. Under the conditions in which the experiments were done, the best result was obtained with DEHPA. The lowest percentage of extraction obtained for IONQUEST 801 and CYANEX 272 can be explained by the high acidity of the aqueous phase.

Table II Influence of extractant agent acidity of 2.19 mol.L⁻¹

Extractant	Extraction %		Separation factor
	In	Zn	In/Zn
DEHPA	99.8	5.2	>3,000
IONQUEST 801	33.6	3.7	13
CYANEX 272	13.3	2.4	6

The influence of the acidity of the aqueous phase was investigated in the interval between 2.2 and 0.8 mol.L⁻¹ of H⁺, maintaining the other conditions used in previous experiments. The adjustment of the acidity of the liquor was carried out with addition of ammonium hydroxide (NH₄OH) 6 mol.L⁻¹. The results of these experiments are shown in table III.

Table III Influence of the variation of acidity on the extraction of Indium and zinc

Extractant	Extraction % / Separation factor								
	DEHPA			IONQUEST [®] 801			CYANEX [®] 272		
Acidez	In	Zn	FS	In	Zn	FS	In	Zn	FS
2.2	99.8	5.2	>3,000	33.6	3.7	13	13.3	2.4	6
1.0	99.9	7.1	>3,000	98.2	5.2	>1,000	21.9	3.9	7
0.8	99.9	11.2	>3,000	99.2	7.9	>1,000	25.6	4.2	8

It can be noted that the decrease in acidity of the aqueous phase causes an increase in the extraction of metals, particularly of In, with a consequent increase in the separation factor of metals. The reduction of acidity was most efficient for IONQUEST 801. For CYANEX 272, the reduction of the acidity to the level of 0.8 mol.L^{-1} was not enough to provide a significant increase in the In extraction, and the separation factor remained at a low level.

McCabe - Thiele diagrams

Using lab test results, extraction isotherms were constructed and McCabe–Thiele Diagrams were drawn for both DEHPA and IONQUEST[®]801, in order to determine the theoretical number of stages and the volumetric feed ratio of the liquor and solvent for the continuous experiments. The concentration of the extractants was 1.0 mol.L^{-1} and the liquor acidity was 2.2 mol.L^{-1} when using DEHPA and 0.8 mol.L^{-1} of H^+ IONQUEST 801. The diagrams are shown in Figures 1 and 2. The diagrams show that to load DEHPA with 8.3 g.L^{-1} , 2 stages are required and 3 stages to load IONQUEST[®]801 with 9.0 g.L^{-1} , with a relationship between the aqueous and organic phases of 5.7 and 6.1 respectively.

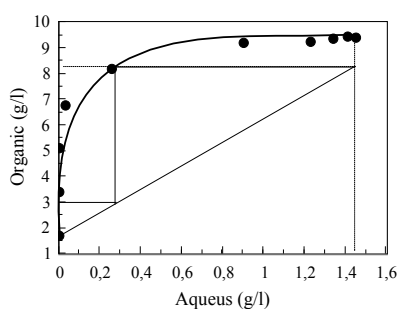


Figure 1 Extraction isotherm of In - McCabe-Thiele diagram for DEHPA 1.0 mol.L^{-1}

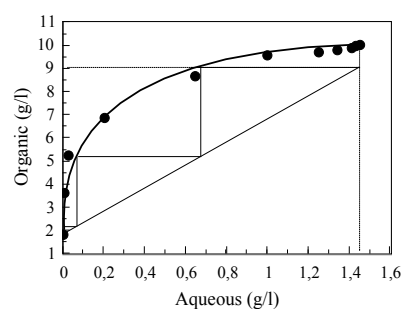


Figure 2 Extraction isotherm of In - McCabe-Thiele diagram for IONQUEST[®]801 1.0 mol.L^{-1}

Scrubbing and stripping

The experiments with H_2SO_4 solution were carried out aimed at the scrubbing of the Zn extracted and the stripping of In. The H_2SO_4 concentration was investigated in the interval between 0.5 and 3.0 mol.L^{-1} . The results indicate that Zn can be easily extracted with this acid. The stripping of Zn from DEHPA was almost 100% over the entire range of acidity investigated. For IONQUEST 801, there was a gradual increase in the extraction of both metals. The results obtained in stripping experiments with H_2SO_4 are shown in Figures 3 and 4.

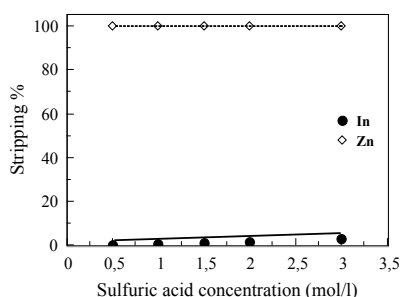


Figure 3 Influence of H_2SO_4 concentration on the stripping of In and Zn from the loaded DEHPA

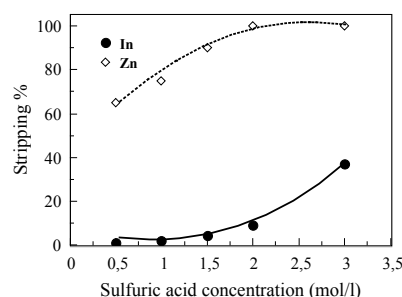


Figure 4 Influence of H_2SO_4 concentration on the stripping of In and Zn from the loaded IONQUEST 801

In the stripping of In from DEHPA the HCl, the concentration was varied from 2.0 mol.L^{-1} to 5.0 mol.L^{-1} while from IONQUEST 801, the HCl concentration was investigated in the range of 1.0 mol.L^{-1} to 3.0 mol.L^{-1} . The results are shown in Figures 5 and 6 below. The stripping of In with HCl is more effective when compared to H_2SO_4 . It can be observed that the stripping from DEHPA can be accomplished with a HCl concentration of 3.0 mol.L^{-1} and from IONQUEST® 801 with HCl concentration of 1.5 to 2.0 mol.L^{-1} .

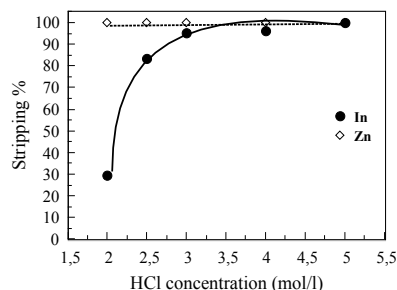


Figure 5 Influence of concentration HCl on the stripping of In from the loaded DEHPA

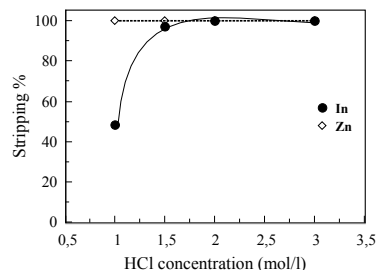


Figure 6 Influence of concentration HCl on stripping of In from the loaded IONQUEST 801

The sequence of the study was performed using DEHPA as the extractant agent and HCl as the stripping agent.

McCabe-Thiele diagram

The stripping isotherm for the indium was constructed according to the successive contact technique using a 3.0 mol.L^{-1} HCl in a volumetric aqueous/organic phase ratio 1 (Figure 7).

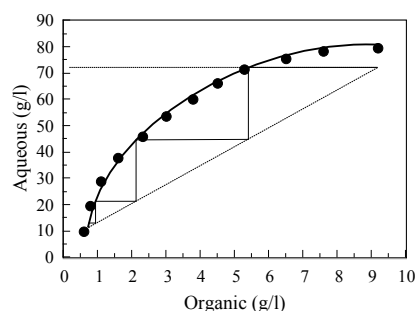


Figure 7 Stripping isotherm for In - McCabe-Thiele diagram

As shown in Figure 7, the loading of the aqueous phase can reach 70 g.L^{-1} using a volumetric ratio of 7.1 in 4 stages.

3.2. Continuous experiment

The continuous experiment consisted only of extraction and scrubbing steps due to the small amount of liquor and aimed at achieving an organic solution loaded with indium and zinc free, without loss of indium. The circuit comprised of mixer/settlers is shown in Fig. 8.

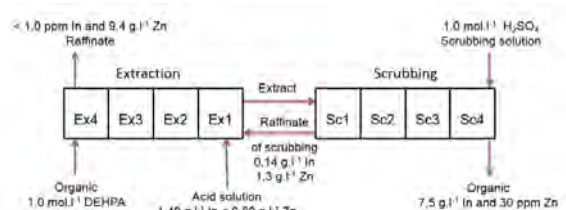


Figure 8 Continuous circuit for the separation of In / Zn.

The extraction step was composed of 4 stages, two more than expected in the McCabe – Thiele diagram (Fig .7). The extraction step was carried out with DEHPA of 1.0 mol.L^{-1} in an A/O volume ratio of 1. In the scrubbing step, the concentration of H_2SO_4 was 1.0 mol.L^{-1} and the O/A volumetric ratio was 4.

After the equilibrium of the system was reached, a loaded organic solution containing 7.5 g.L^{-1} of indium and 0.0003 g.L^{-1} of zinc and a raffinate containing 9.4 g.L^{-1} of Zn, with In content of less than 0.001 g.L^{-1} was obtained.

The stripping of In from the organic loaded solution was carried out with a 3.0 mol.L^{-1} HCl at an O/A ratio of 5. The stripping was done simulating continuous experiments. At the end of the experiment, a stripped solution containing 26.7 g.L^{-1} of In and 0.001 g.L^{-1} of Zn was obtained.

4. CONCLUSION

The internal powder coating of the screens of computer monitors displays contains significant amounts of the metals In and Zn - 1.2% and 39% respectively, and may be considered a secondary source of these metals. The results of this study indicated the technical feasibility of the recovery of In and Zn from the material investigated. The industrial processing of this material indicates the possibility for the recycling of lots of materials with minimal environmental impact during the disposal process.

Among the extractants investigated, DEHPA proved more efficient in the separation of the In/Zn pair. For this extractant, the separation factor was higher than 3,000 for the 3 investigated acidities ($2.2 \text{ mol.L}^{-1} \text{ H}^+$, $0.8 \text{ mol.L}^{-1} \text{ H}^+$ and $1.0 \text{ mol.L}^{-1} \text{ H}^+$). The stripping experiments showed that HCl is more effective in the stripping of In as compared with H_2SO_4 .

Using DEHPA 1.0 mol.L^{-1} as extractant and H_2SO_4 1.0 mol.L^{-1} as scrubbing agent, a loaded organic solution containing 7.5 g.L^{-1} of indium and 0.003 g.L^{-1} of zinc, a raffinate containing 9.4 g.L^{-1} of Zn with a content of less than 0.001 g.L^{-1} was obtained. Using HCl 3.0 mol.L^{-1} as the stripping agent, a stripped solution containing 26.7 g.L^{-1} of In and 0.001 g.L^{-1} Zn was obtained from a liquor containing 1.49 g.L^{-1} In and 9.8 g.L^{-1} Zn.

5. ACKNOWLEDGMENT

Authors are grateful to FAPEMIG, CNPq and CAPES for financial support.

6. REFERENCES

1. HABASHI, F., Handbook of extractive metallurgy. New York: Wiley-VCH, 1997, v1, 488 pp.
2. RESENDE, L. V.; MORAIS, C. A. Study of the recovery of rare earth elements from computer monitor scraps Leaching experiments. Minerals Engineering, 2010. 277-280.
3. RESENDE, L. V.; MORAIS, C. A. Metals recovery from computer monitor scraps. 9th International Conference on Clean Technologies for the Mining Industry, Santiago - Chile, 2011.
4. ZUCCHERATTE, A.C.V., Morais, C. A. Study of leaching of indium from computer monitors scrapped In: XI Jornadas Argentinas de Tratamiento de Minerales - JATRAMI 2012, Neuquén/Argentina, v.1, p.325 – 330, 2012.

Laboratory plant problems on the example of nickel(II) solvent extraction from leaching solution.

Authors: Grzegorz Pietek, Leszek Gotfryd, Zbigniew Szołomicki, Ksawery Becker, Justyna Piwowska

Corresponding author: Grzegorz Pietek e-mail: grzegorz.pietek@imn.gliwice.pl

Affiliation: Instytut Metali Nieżelaznych, Ul. Sowinskiego 5, 44-100 Gliwice, POLAND

Laboratory plant for solvent extraction (figure 1) was built in 2004 by Institute of Non-Ferrous Metals. In last two years solvent extraction of nickel(II) by Versatic 10 from leaching solution was tested on mentioned plant. Solvent extraction plant actually works in 3-3-2 system (3 steps of extraction- 3 steps of washing and 2 steps of stripping). Feed (leach) solution for the mentioned tests was produced by

	Co ²⁺	Si	Mg ²⁺	Ni ²⁺	Mn ²⁺
concentration [g/dm ³]	0.036	0.13	44.7	1.68	0.026

Table 1. Feed solution composition.

laterite ores leaching. Compositions of feed solution (Table 1) and SX plant construction induce many problems in SX plant working. The typical problems of laboratory plant (Figure 1) are:

-The electrodes installation place (Figure 2) is determined by flow level and place of pH controlling reagent addition (NH₃ solution). The electrodes should be placed as close as possible to the mentioned addition place, and electrodes must be organic phase resistant (electrodes with KCl solution outflow). A longer distance between pH electrode and pH regulation agent addition place provokes "floating" pH values in pH



Fig.1. Laboratory solvent extraction plant (IMN Gliwice).

profile registration.

- The unsolved problem is stabilisation time (too high) after working condition changes. The low nickel(II) concentration in feed solution cause low Ni(II) concentration in stripped solution (max 10 g/dm³). This is also consequence of flow rates: feed solution 1.52 dm³/h and 0.25 dm³/h of sulphuric acid(VI) solution(18.7 g/dm³). Typical capacity of acid solution in stripping circuit is about 2 dm³ and stabilisation takes many hours after any parameters changes in extraction circuit (pH value and temperature changes). Disproportion in nickel(II) concentration (feed sol. v. stripped sol.) limits Ni(II) content in stripped phase to the maximum value of 20 g/dm³ (flow: feed 3.0 dm³/h, acid 0.25 dm³/h – 37.4 g/dm³ of H₂SO₄).

- Catching organic phase residues from the raffinate and stripped solution stream can be solved by syphon tank installation which catches the majority of organic phases in aqueous streams. Also aqueous residues can be collected in special syphon construction, which is avoiding organic phase tank contamination.

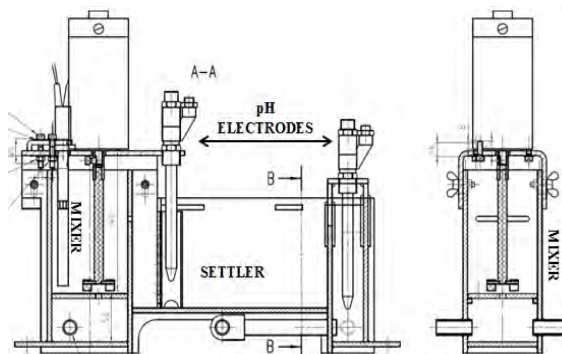


Fig.2. Mixer-settler unit with pH-electrode marked in.

Montan wax extraction using a laboratory belt extractor: development, construction and commissioning

*M. Wollmerstädt¹, V. Herdegen^{*1}, H.-W. Schröder¹, T. Naundorf²,
J.-U. Repke¹*

Summary

Extracted crude montan wax from lignite has various applications in industry and products in form of intermediates or refinements. Nowadays, the extraction of dried lignite particles is executed in a belt extractor in industrial scale. Within the governmental funded research project “ibi”, this extraction process is investigated fundamentally, mainly in respect to differently processed lignite, different organic solvents and different temperatures/ temperature profiles. Therefore, a new belt extractor in lab-scale has to be developed, constructed and set-up based on industrial used belt extractor for minimizing the experimental effort.

Introduction

Crude montan wax from lignite and its derivatives are widely used as intermediates for example in asphalt additives, dyes, polishes or cosmetics. Extractable lignite is mined in Central Germany, where the global market leader ROMONTA is located. The solid/liquid extraction of dried particles is done in industrial scale by a belt extractor. Within the scope of the research project “ibi – Innovative Brown Coal Integration in Central Germany” [1], a new laboratory belt extractor is established: from development, construction, commissioning to experimental set-up. The small scale set-up allows a fast and easy evaluation of changes in lignite processing, solvent, extraction temperature, flow regime etc., but also transferability of results from laboratory scale to industrial scale later-on.

Montan wax extraction and laboratory belt extractor

Evaluation of extraction process

At first, the analytical extraction of lignite samples with differing pre-treatment was executed in an advanced apparatus of Graefe [2]. The extraction yield after complete leaching as well as the kinetics of extraction can be measured hereby at boiling temperature depending on the particular solvent like toluene, alkanes, primary and secondary alcohols and ketones.

The analysis was extended for differently processed lignite in a percolation device as a reference process with a fixed bed. The fluid percolates through the fixed bed and

^{*1} Volker.Herdegen@tun.tu-freiberg.de; Institute of Thermal, Environmental and Natural Products Process Engineering, TU Bergakademie Freiberg, Leipziger Straße 28, Freiberg/ Germany

²ROMONTA Unternehmensgruppe, Seegebiet Mansfelder Land/ Germany

a single-stage extraction at various temperatures and solvent-solid-ratios can be emulated. Influencing factors like the type of solvent or mechanical properties of the solid can be investigated at small scale and the properties of extracted montan wax are analyzed after industrial standards. The inner diameter of the column is 125 mm and the solvent flow can be set up to 5 L/h. Percolation extraction yields and extraction rates were found. Extraction yields could reach for specific operation conditions over 90 % based on the analytical extraction method by Graefe.

The effects of mechanical and chemical strain on the bulk by leaching in the percolation column as reference were included, using methods like grain size distribution or a special developed stress test [3]. But the mechanical stress of the fixed bulk is not comparable with the movement on a conveyor belt, so a laboratory belt extractor has to be developed to investigate the additional mechanical stresses. Besides, the specific influence of process parameters deriving from the different extraction process like temperature profiles, flow regimes and residence time can be identified.

Development and construction

Due to the use of organic solvents in the extractor at elevated temperatures, safety issues were considered during the design phase. Therefore, no electrical heating system was built in for maintaining set-temperature of the solvent and extract tanks and the belt extractor itself. The heat transfer is realized instead by tube bundles at the inside at the collecting trays and at the outside at the casing of the belt extractor. The temperature of the heat transfer fluid is lower than the ignition temperature of used solvents. In addition, the void space in the extractor is first inertised and later on continuously flushed with nitrogen to replace oxygen inside of the extractor.

The three-stage belt extractor has a conveyor belt with effective dimensions of 500 mm length and 150 mm width. The dimensions of the constructed design are based on industrial used extractors. The conveying speed, height of bulk and solvent flow of each stage are adjustable just like the temperatures of the stages and of the extractor itself. Beside a counter-current regime, cross flow and direct-current regime can be established. Figure 1 displays a schematic flow chart of the laboratory belt extractor in cross flow regime:

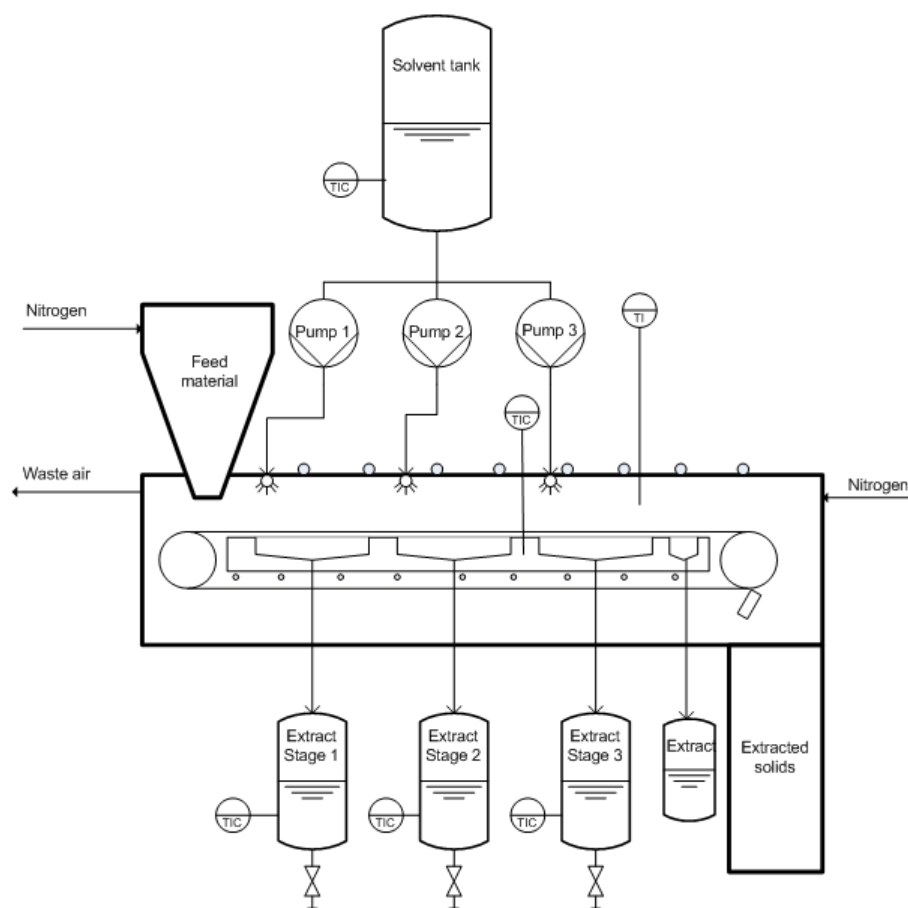


Figure 1. Schematic flow chart of newly designed, laboratory belt extractor in cross flow regime

The comminuted lignite particles or agglomerated lignite built-up the solid bulk on the conveyer belt by free flow. The bulk height can be adjusted by a spacer. The conveyer belt is driven by an electric motor. Flexible-tube pumps transport the hot solvent to the single stages. The extract is collected in trays after the percolation through the bulk for every stage separately and flows into temperature maintained tanks. Samples can be taken from these extract tank to determine the extract concentration by time. A picture of the newly designed belt extractor is shown in Figure 2:



Figure 2. Photo of newly designed, laboratory belt extractor

The downgraded and soaked lignite particles fall or are wiped from the conveyor belt into a bulk container. Thereby, also samples from the solid stream can be obtained for balancing and interpretation purposes. The behavior of lignite bulks under contemporary transport and extraction conditions could be determined afterwards. Now systematic investigations can be conducted under real process conditions in lab-scale to examine the impact of influencing parameters particularly with regard to optimization.

Commissioning and experimental set-up

Commissioning experiments were necessary as start-up for gaining handling experience and for optimization reasons. Therefore, the heat-up behavior of the extractor and calibration data for all three flexible-tube pumps (solvent flow up to 5 L/h) was measured for different solvents at different temperatures. Besides, the polymer material of the flexible tubing of the pumps was tested on its long-term stability because of the corrosiveness of organic solvents, e.g. toluene at temperature up to 100 °C. In a next step, the effectiveness of the three liquid distributors and the flow through the belt into the collecting trays was examined (see Figure 3). Then the interaction of solvent and processed lignite flow (maximal 12.5 kg/h) was investigated. Some adaptations were made along the commissioning experiments at the construction design.



Figure 3. Illustration of the bulk flow at the drop-zone from the opened front side

Now first test experiments were conducted with toluene as solvent at 80 °C in cross flow regime at 3 L/h. An exemplary value pattern is shown in Figure 4 for the normalized wax concentration in the single extract tanks of the three stages.

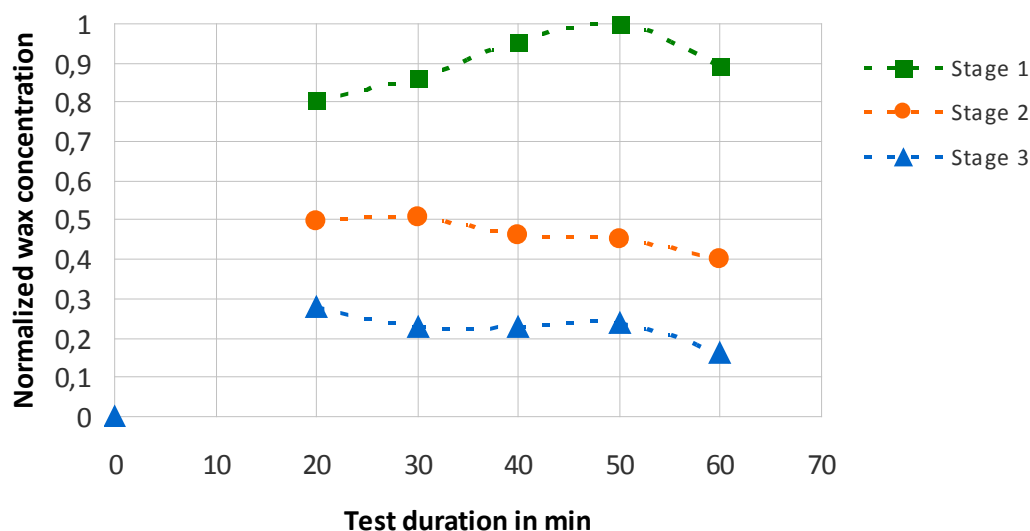


Figure 4. Exemplary value pattern of wax concentration in the single extract stages of the belt extractor

After a time period of round about 30 min an almost steady state in the cross flow extraction process is reached. The wax balance can be calculated from the analytical extraction of the raw material and material probes from the belt extractor in addition to wax concentration/ content in each stage. Also an extensive evaluation on the processed lignite material is executed in comparison to the raw material: bulk and vibrated density, particle distribution and stability in mechanical stress test.

Conclusion

A newly own-designed belt extractor of laboratory scale was built and set-up for extraction investigations on montan wax extraction from comminuted particles or processed lignite. The new developed apparatus is capable of a broad range of organic solvents with feed flows of up to 5 L/h at 100 °C and of solid material flows of maximal 12.5 kg/h. After passing the commissioning phase successfully, systematically extraction experiments can be carried out by varying the influence parameters solvent, temperature, specific solvent flow, bulk height, conveyer speed, different flow regimes, and differently processed lignite raw material. Now an easy handling device with manageable solvent and material consumption is available for investigation at small-scale, but with the possibility of transferring results to industrial extraction process.

Acknowledgements

The research was part of the Growth Core “ibi – Innovative Brown Coal Integration in Central Germany”. The authors are grateful to the Innovation Initiative

“Entrepreneurial Regions” (Federal Ministry of Education and Research, Germany) for the financial support.

References

- [1] Website of research project “ibi – Innovative Brown Coal Integration in Central Germany”, <http://ibi-wachstums-kern.de/tl/index.php>, as per March 2014.
- [2] Dierichs, A., Ludwig, F., Chemie der Kohle [Chemistry of Coal], VEB Deutscher Verlag der Wissenschaften, Berlin (GDR) 1959.
- [3] Lehmann, B., Schröder, H.-W., Wollenberg, R., Repke, J.-U., Effect of miscanthus addition and different grinding processes on the quality of wood pellets. Biomass Bioenergy 2012, 44, 150–159.

Computer Aided Simulation of Liquid-liquid Extraction Columns

*M. W. Hlawitschka^{1,2}, , M. M. Attarakih³, S. S. Al-Zyod³, H.-J. Bart^{*1,2}*

Summary

Liquid-liquid extraction columns have a small footprint, a high number of theoretical stages and allow high throughput. However, the deviation of the flow field from the ideal plug flow makes the simulation and design of these columns a challenging task. In order to help in this tedious design procedure (scale-up experiments) two simulation tools are presented. The first one is the PPBLAB software, which is based on a one-dimensional CFD (Computational Fluid Dynamics) model. Deviations from the ideal plug flow are accounted by the axial dispersion and by population balance modeling, which accounts for the droplet-droplet interactions and forward mixing of the dispersed phase. The second tool is based on a three dimensional modelling of the flow field using 3D CFD simulation, which is able to describe the local flow field without any geometrical dependent correlations more than the drag coefficient correlation. As a case study, a Kühni mini-plant column is simulated using the one-dimensional and the three dimensional tools for comparison. The design procedure of each tool is shown, where the benefits (computational time, local information) of each tool are highlighted.

Keywords: Extraction, Column, CFD, Toolbox

Introduction

Solvent extraction of systems with low distribution coefficients or systems with high demands of purity requires a high number of theoretical stages, which can be provided by solvent extraction columns instead of distillation [1, 2,4, 10]. Therefore, high mass transfer rates can be achieved by additional pulsation or agitation due to a better distribution of the dispersed phase [4, 10]. The complex droplet interactions of the dispersion such as breakage, coalescence, convection and mass transfer are coupled in the same equipment, which makes the scale-up of these columns a challenging task [2, 3, 4, 10]. Due to this complexity and the inability of the lumped correlation based column design to account for these interactions, the design of solvent extraction columns is still based on continuous mini- and pilot plant experiments. This is the case where the investigations in pilot-scale columns (60 to 150 mm diameters) are time-consuming and expensive and require the processing of tons of chemicals. In order to get reliable column modeling and simulation, droplet population balance modelling (PBM) have been used to account for the aforementioned interactions. Based on this approach, two simulation tools were developed, where the first one is based on 1D CFD modelling [9] and the second one is based on a 3D computational fluid dynamics modelling [10].

^{*1} H.-J. Bart, Chair of Separation Science and Technology, TU Kaiserslautern, Kaiserslautern, Germany, bart@mv.uni-kl.de

² Center for Mathematical and Computational Modelling (CM³), TU Kaiserslautern, Kaiserslautern, Germany

³ The University of Jordan, Department of Chemical Engineering, Amman- Jordan

PPBLAB – A 1D Population Balance Model

Instead of the lumped correlation design of solvent extraction columns, spatially one dimensional simulation can predict changes along the column height such as concentration, interfacial tension and droplet size using population balance modelling. This leads to a better prediction of the hold-up profile and hence to a better determination of optimal throughput, pulsation or rotational speed and the required number of transfer units. For this purpose, LLECMOD [1,2], which is a windows-based program based on the bivariate population balance modeling of liquid extraction columns was developed [1,2]. LLECMOD was validated against pilot plant experimental data by many reseraches for different types of agitated extraction columns [2,3,4,5,6]. As a result, the population balance modelling approach was found to be an efficient tool to predict mass transfer efficiency, design and scale up of liquid extraction columns [7,8]. As an advanced step in this direction, Attarakih et al. [9], developed PPBLAB as a new simulator for the simulation and design of liquid extraction columns using the population balance framework. The new software is based on MATLAB GUI and moderen population balance solvers [9], with high efficiency in terms of performance, accuracy and flexibility. The PPBLAB software includes an efficient coupling interface with CAPE-OPEN tools (<http://www.cocosimulator.org>) such as TEA (Thermodynamics for Engineering Applications) as shown in Fig. 1. Currently, PPBLAB has four extraction column modules with validated hydrodynamics and mass transfer correlations. These include agitated columns like RDC and Kühni, as well as pulsed packed and sieve plate columns.

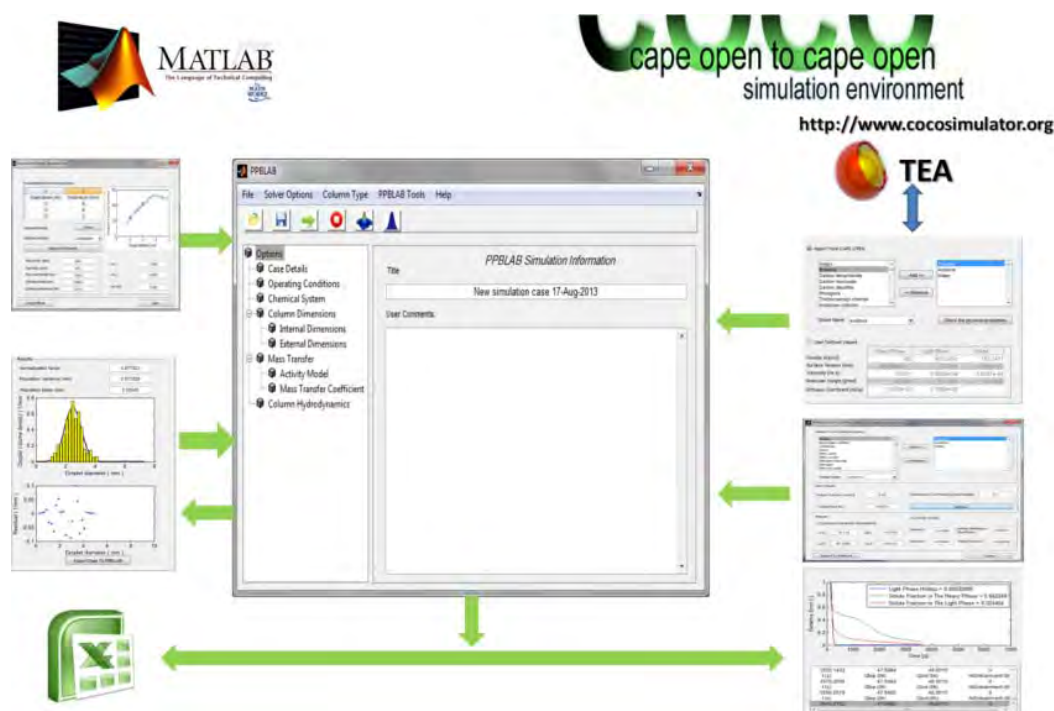


Fig. 1: Sample of PPBLAB interface based on MATLAB environment for simulating pulsed, non-pulsed and agitated solvent extraction columns .

Column Design

The 1D-PBM computer-aided design reduces the required work for scale-up, which is based on lab and mini-plant experiments (see Tab. 1). In addition to the selection of the continuous and the dispersed phases, PPBLAB offers a wide basis of validated correlations for the droplet velocity and swarm effects. The required data for phase equilibrium and chemical and physical properties can be obtained by the PPBLAB internal UNIQUAC solver, where the solvent properties can be estimated from coupling of PPBLAB to TEA [9]. For an adequate description of the hydrodynamics, knowledge about the axial dispersion and the slowing of the droplet rise velocity due to the internals is required. This can be either obtained by existing correlations or by mini-plant experiments. A further experimental knowledge about the droplet size evolution in mini-plant scale columns enables the PPBLAB user to determine the required model parameters for breakage and coalescence. For the first estimation, PPBLAB is also flexible to allow the simulation with constant droplet diameters (by excluding breakage and coalescence). Also, PPBLAB can simulate hydrodynamics or coupled hydrodynamics and mass transfer. This can be used for the initial estimation of droplet interactions parameters without performing mini-plant experiments.

Tab. 1: Work flow for a PPBLAB based column design. The black items are compulsory to perform a simulation, where the grey items as user inputs and are optional for a first estimation.

Lab experiments:	• Solvent selection • Selections of the dispersed phase • Determination of the droplet Phase equilibrium (PPBLAB's internal UNIQUAC prediction) • Chemical and physical properties (TEA coupled in PPBLAB)
Mini-plant experiments:	• Experimental investigation of the hydrodynamics as axial dispersion (required for new column designs) • Experimental investigation of the droplet size • Inverse determination of the required coalescence and breakage parameters • Validation against experimental data
Scale-up:	• Numerical scale-up (requiring information about the axial dispersion) • Optimization of the boundary conditions (pulsation/rotation)
Proof of concept:	• Experimental validation • Investigation of the effect of possible disturbances

Based on the mini-plant experiments, PPBLAB allows a column scale-up and an optimization of the boundary conditions, including the correlation constraints regarding the column diameter and column design (e.g. axial dispersion). Finally, a proof of concept can be done by a reduced number of pilot plant experiments and by numerical investigation of disturbances which can occur in the continuous process (e.g. step change in flow rate, rotational speed). As an example, the simulated

concentration profiles and droplet size distribution in a DN32 Kühni mini-plant extraction column are compared with the experimental data as shown in Fig. 2 .

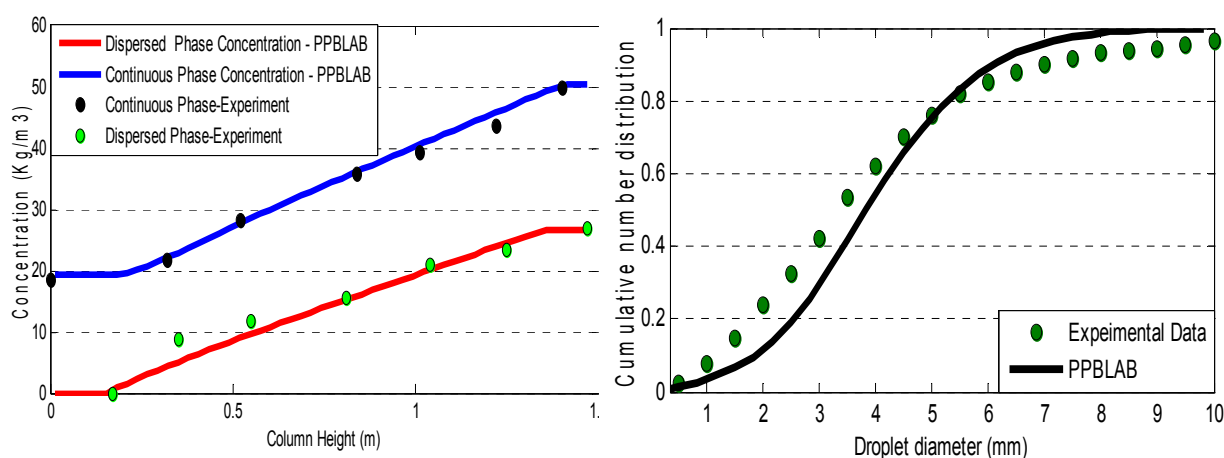


Fig. 2: Comparison between the measured and the PPBLAB simulation of solute concentration profiles and the cumulative number distribution at 200 rpm and a throughput of $14 \text{ m}^3\text{m}^{-2}\text{h}^{-1}$).

3D CFD Simulation

A reduction of the experimental effort, especially in the determination of the axial dispersion coefficient for the continuous and dispersed phase can be obtained by 3D CFD modelling [10]. In recent years, commercial CFD codes were used to investigate the local flow structure in solvent extraction columns. A further improvement of the local hydrodynamics prediction was obtained by coupling CFD with PBM. However, the simulations were constrained by the requirement of high computational resources and the complexity of the pre-processing especially for complex column geometries.

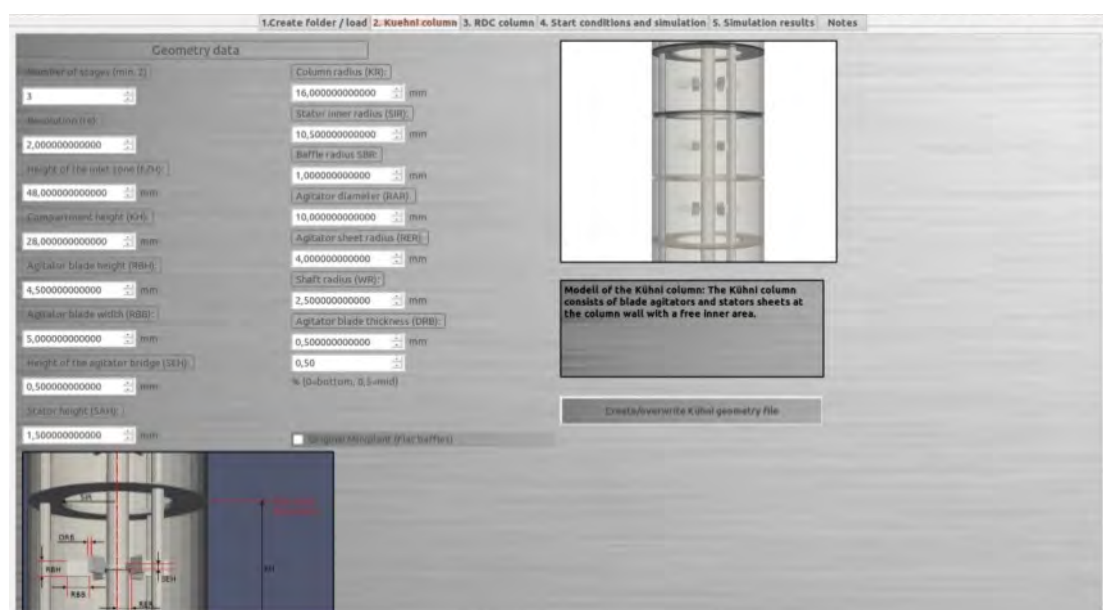


Fig. 3: Graphical user interface for 3D simulation setup.

For this purpose, a simulation toolbox, which is designed for the requirements of agitated solvent extraction columns, was established. The graphical user interface (GUI) based on the cross-platform application framework is shown in Fig. 3. This GUI enables the user to define the column geometry and the boundary conditions (flow rate, droplet size, liquid properties). The CFD solver, which is based on the OpenFOAM® toolbox, can be finally started using the GUI. The used solver “*twoPhaseEulerFoam*” is coupled to a one group population balance model [11] to account for the droplet-droplet interactions. A further mass transfer extension achieves the determination of the local mass transfer inside the column (Fig. 4). Due to the three way coupling of the local hydrodynamics with population balance modelling and mass transfer, the effect of mass transfer on the hydrodynamics and droplet size can be locally investigated (Fig. 5, 6).

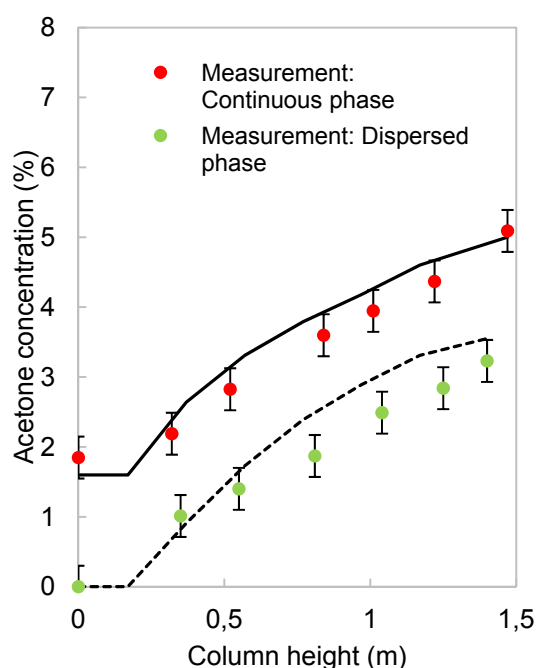


Fig. 4: Simulated concentration profile of acetone in the dispersed and continuous phase along the column height. [10].

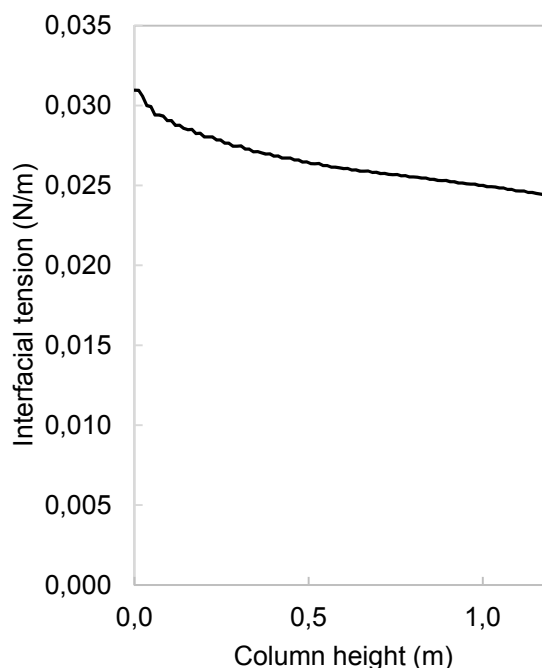
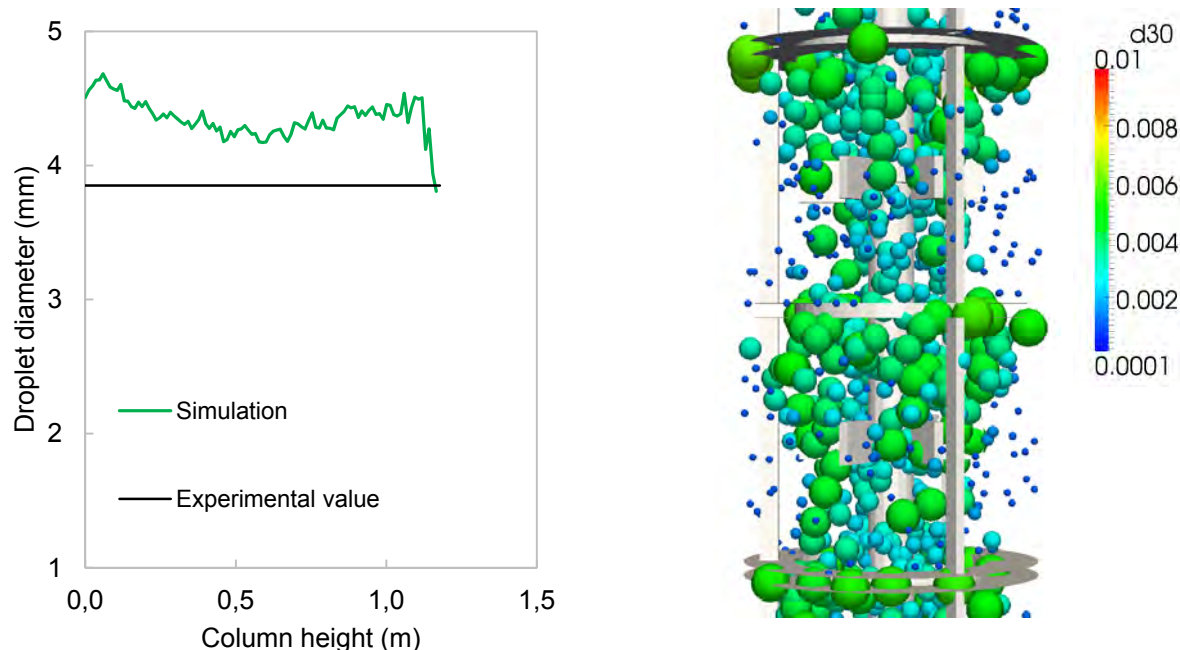


Fig. 5: Simulated interfacial tension along the column height. [10].

Summary and Conclusions

The design of solvent extraction columns is sophisticated due to the complex interactions of the two phase flow and hence still relies on the time consuming and expensive pilot plant experiments. A reduction of these costs can be obtained by numerical modelling, where the application of the complex modelling was mainly limited to academic fields. However, the generation of graphical user interfaces in the presented 1D and 3D tools facilitates the user input (pre-processing) and simulation. Therefore, PPBLAB allows the investigation and design of extraction columns and simulation of different column boundary conditions within minutes. The 3D simulation

tool is free generally from any geometrical constraints. Accordingly, it allows a scale-up of column size and geometry. Investigations of the local hydrodynamics are possible to allow a direct identification of dead zones and possible column optimizations.



1. Fig. 6: Comparison between the measured droplet size at the top of the column and the simulated droplet size along the column height (left) and local droplet size in meter from the CFD simulation tool (right) [10].

References

1. M. M. Attarakih, H.-J. Bart and N. M. Faqir, *Chem. Eng. Process.* 45, 113-123, 2006.
2. M. M. Attarakih, H.-J. Bart, T. Steinmetz, M. Dietzen and N. M. Faqir, *Open Chem. Eng. J.* 2, 10-34, 2008.
3. S. A. Schmidt, M. Simon, M. M. Attarakih, G. Lagar and H.-J. Bart, *Chem. Eng. Sci.* 61, 246-256, 2006.
4. T. Steinmetz, *Fortschr.-Ber. VDI, Reihe 3, Nr. 885*, Düsseldorf: VDI Verlag.
5. M. Jaradat, M. Attarakih and H.-J. Bart, *Chem. Eng. J.* 165 (2), 379-387, 2010.
6. M. Jaradat, M. Attarakih and H.-J. Bart, *Chem. Eng. Res. Des.* 89, 2752-2760, 2011.
7. H.-J. Bart, *Proceedings of ISEC 2008*, 17-28, 2008.
8. T. Steinmetz and H.-J. Bart, *Chem. Eng. Technol.* 32, No. 5, 693-709, 2009.
9. M. Attarakih, S. Al-Zyod, M. Abu-Khader and H.-J. Bart, *Procedia Eng.* 42, 1574-1591, 2012.
10. M. W. Hlawitschka, *Dissertation*, TU Kaiserslautern, Kaiserslautern, Germany, 2013.
11. C. Drumm, M. Attarakih, M. W. Hlawitschka and H.-J. Bart, *Ind. Eng. Chem. Res.* 49, 3442-3451, 2010.

Choose the right material of construction – wetting in extraction columns

Dr.-Ing. Jörg Koch, Dr.-Ing. Juan Ramon Herguijuela

Sulzer Chemtech AG, Gewerbestr. 28, 4123 Allschwil, Switzerland

The most common way to provide the interfacial area for mass transfer in liquid-liquid-extraction is to disperse one liquid phase as droplets into a second continuous liquid phase. The initial dispersion can be generated by a static liquid distributor or by dynamic energy input as pulsation or agitation. In the active section the droplets stay dispersed for the mass transfer to take place. After a certain time the droplets should be collected and coalesce to form again a continuous phase. There are two distinct sections in extraction equipment where the droplet dispersion shows a different behavior. In the active mass transfer section the one liquid phase should remain as stable dispersion with a reasonable droplet size of 1-3 mm while in the coalescing section the droplets should closely approach each other to promote coalescence.

The surface energy of the chosen material of construction has a large impact on the droplet behavior in each of the two sections because it defines the wettability of the solid material by the liquid phases. In the active mass transfer section the droplets must stay in the dispersion surrounded by the continuous phase. Thus the wettability of the materials should be high for the continuous phase and low for the dispersed phase. Otherwise, the droplets will stick to the surface, collect other droplets and reduce the specific surface area of this dispersion and finally the mass transfer efficiency. In addition, the liquid fragments sticking to internals reduce the free cross section and lead to premature flooding in an extraction column.

The desired effect in the coalescing section is exactly the opposite, so the material of construction is allowed to be wetted by the dispersed phase or is even dedicatedly chosen to promote this effect. This is the case if entrainment is a problem and coalescing aids have to be applied.

The presentation will show the effect of the material of construction on the hydrodynamic operation, mass transfer and entrainment in liquid-liquid-extraction column based on the results of pilot trials and industrial experience. It will be shown that the mass transfer efficiency can be enhanced and the entrainment significantly reduced when the material of construction is optimized with respect to the droplet dispersion.

Trivalent actinide and lanthanide separations using tetraalkyldiglycolamides (TC_nDGA) in molecular and ionic liquid diluents

Bruce J. Mincher,¹ Robert V. Fox,¹ Mary E. Mincher,² and Chien M. Wai²

¹Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415, USA

²University of Idaho, Department of Chemistry, Moscow, ID 83499, USA

The use of the diglycolamide, tetrabutyl diglycolamide was investigated for intergroup separations of the lanthanides, focusing especially on those lanthanides (Y, Ce, Eu, Tb, Dy, Er, and Yb) found in lighting phosphors. Tetrabutyl diglycolamide extraction efficiency for the lanthanides varied depending on whether the diluent was the conventional molecular diluent 1-octanol, the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, or a mixture of the two. This was attributed to extraction of either neutral, cationic or anionic lanthanide metal complexes with nitrate ion. Based on the batch contact solvent extraction results measured here, a series of extractions providing product streams containing separated Y, Ce, Eu, Tb/Dy, and Er/Yb are proposed.

Introduction

Separations within the lanthanide series, and between the lanthanides and trivalent actinides are difficult since the elements are nearly universally trivalent and have very similar chemistry. Only the minor changes in trivalent ionic charge density along each series affords chemistry differences that may be exploited in separations. Generally these result in only small separation factors, and column chromatographic techniques have usually been employed to amplify these small separation factors. However, recently the diglycolamides (DGAs) have shown higher separation factors, and separations by solvent extraction may be proposed. Currently, two tetraoctyldiglycolamides (n-octyl, or TODGA and ethylhexyl, or TEHDGA) are being investigated for fuel cycle solvent extraction separations in Europe and the USA, respectively. However, they are being investigated as group extractants rather than for *f*-element intergroup separations. Here, the use of tetrabutyl diglycolamide (TBDGA) as a reagent for lanthanide separations was explored, in both the conventional molecular diluent 1-octanol, and also in the ionic liquid (IL) diluent 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([C₄MIM][Tf₂N]). The lanthanides Ce, Eu, Tb, Dy, Er, Yb, and the pseudo-lanthanide Y were of especial interest, as these metals are found in lighting phosphors. Recycling of such phosphors is desirable to extend the lanthanide supply.

Experimental Methods

Solvent extraction experiments over a range of aqueous-phase acidities using pre-equilibrated 0.007 M TBDGA in 1-octanol or [C₄MIM][Tf₂N] solution were conducted. Room temperature (19±2 °C), equal-volume, one-minute contacts traced with 100 ppb standard solutions of stable lanthanides (10 mM total metals) were performed. The solutions contained the entire complement of stable lanthanides, however, data for only the lighting phosphor lanthanides are shown here. The phases were shaken by hand for 1 min. in 10 mL glass culture tubes and then separated by centrifugation for 2 min. Aliquots of each phase were pipetted into 5 mL disposable beakers, taking care to avoid phase cross-contamination. Then, 1

mL of each phase was pipetted from the disposable beaker, again avoiding cross contamination, into a 20 mL glass scintillation vial. These were analyzed by ICP-MS of only the aqueous phase. Lanthanides in the organic phase were determined by mass balance. The distribution ratios are reported as the mean ratios of concentration in organic: aqueous phases $\pm 1\sigma$, as a relative standard deviation for duplicate determinations.

Results and Discussion

Separations in 1-octanol

As shown in Fig. 1, the extraction of the pertinent lanthanides across a range of HNO_3 concentrations into 0.007 M TBDGA /1-octanol solution allows a grouping of these rare earths into three categories. [1] The light fraction containing Ce had $D_{\text{Ln}} < 1$ at all nitric acid concentrations. The heaviest lanthanides: Tb, Dy, and Yb were highly extractable, with D_{Ln} in the range 10–70 across the same nitric acid concentration range. Finally, Eu, had intermediate behavior, with D_{Eu} in the range 2–4. These results suggest that TBDGA/octanol could be used to separate the lanthanides into these three classes using solvent extraction contacts. This may have practical applications toward lanthanide separations for the recycling of light bulb phosphors. For example, the lanthanide constituents of the common green phosphor contains Ce and Tb. The separation factor $\alpha_{\text{Ce/Tb}}$ for a single solvent extraction contact is ~ 80 in 1 M HNO_3 , based on Fig. 1. Blue phosphors contain Eu and Dy, for which a separation factor $\alpha_{\text{Dy/Eu}} \sim 5$ is obtained from 1 M HNO_3 . Mixed, white light phosphors will contain the most complex mixture, possibly including Y, Ce, Eu, Tb, Dy, Er, and Yb.

Previously it has been reported that the DGA distribution ratios for these lanthanides increase with decreasing ionic radii. [1, 2, 3] This suggests that extraction efficiency is related to the increasing charge density on the metal ion, as the radius decreases along the lanthanide contraction. A discontinuity at Gd is expected, resulting from the stability imparted by the half-filled 4f orbital. These data, and the data shown in Fig.1, are consistent with the extraction of a solvated, neutral metal complex into a molecular diluent.

Separations in $[\text{C}_4\text{MIM}][\text{Tf}_2\text{N}]$

When $[\text{C}_4\text{MIM}][\text{Tf}_2\text{N}]$ was substituted for 1-octanol as the diluent for 0.007 M TBDGA, the extraction behavior of the lanthanides was completely different. This can be seen in Fig. 2, [1] where the highest distribution ratios were found at low nitric acid concentrations. They dropped rapidly with increasing acidity, achieving minimum values for most metals over the range 4–6 M HNO_3 . For most metals this was followed by an increase in distribution ratios at higher acid concentrations. High extraction efficiencies have previously been reported for IL diluents, and this has been considered as evidence that the extracted species are ionic, rather than neutral. [4–6] The data of Fig. 2 suggest that cationic lanthanide nitrates are extracted into the RTIL at low acid concentrations. With an increasing nitrate concentration at higher acidities, the extraction of ionic species is suppressed by the formation of neutral metal complexes, resulting in the low distribution ratios between 4–6 M HNO_3 . Neutral complexes would be less extractable in the ionic liquid than in non-polar 1-octanol. Then, at the highest nitrate concentrations, anionic metal complexes are expected, reflected as increasing distribution ratios at the highest acidity.

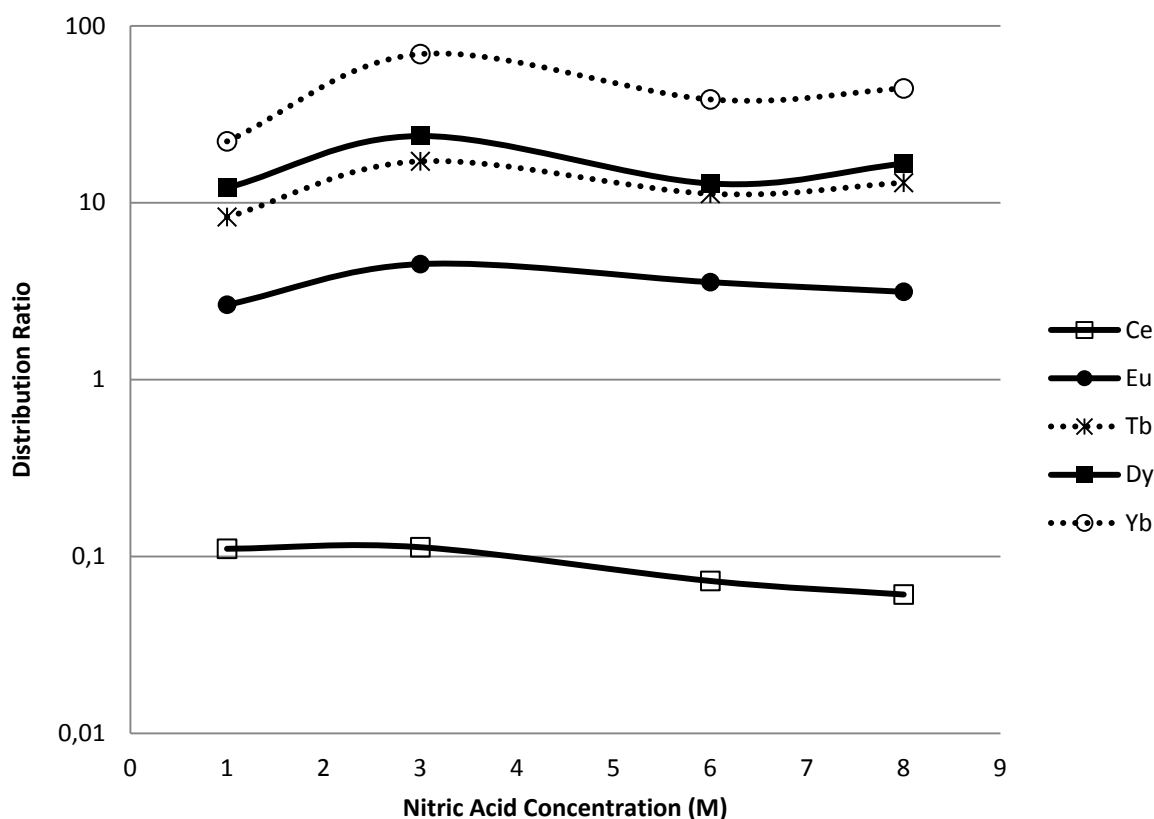


Figure 1. Lanthanide extraction (100 ppb each, 10 mM total metals) from HNO_3 by 0.007 M TBDGA in 1-octanol. The distribution ratios are the mean values of duplicate extractions with an error of $\pm 2.5\%$.

Also noted in Fig. 2 is that the Ce distribution ratios continue to decrease at the highest acid concentrations, rather than increasing with the other lanthanides. This behavior for Ce appears anomalous, however, Mincher et al. [1] reported similar behavior for two other light lanthanides: La and Pr. This suggests that these metals are less likely to form anionic nitrate-complexes. Yttrium, although not strictly a lanthanide, is present in many phosphor mixtures and has lanthanide-like chemistry. It can be seen in Fig. 2 that Y distribution ratios climbed at high acidity, similarly to the heavier lanthanides.

The addition of even small amounts of the IL to the molecular diluent was sufficient to alter the extraction of the lanthanides to favor cationic complex formation. Figure 3 shows the extraction of selected lanthanides using a solvent composed of 0.007 M TBDGA/0.01 M IL in 1-octanol. Very high distribution ratios were achieved at very low acid concentrations, similarly to the neat IL. However, they dropped rapidly with acidity, resulting in low distribution ratios for all metals at all HNO_3 concentrations > 1 M. Thus, anionic complexes are apparently not extracted, perhaps suggesting that transfer of the $[\text{Tf}_2\text{N}]^-$ anion into the aqueous phase is less facile than transfer of the cation. It can also be seen in Fig. 2 that the distribution ratios for the lanthanides at

high acidity never approached the magnitude of those at low acidity for the neat IL diluent, also consistent with less facile anion transfer to the aqueous phase.

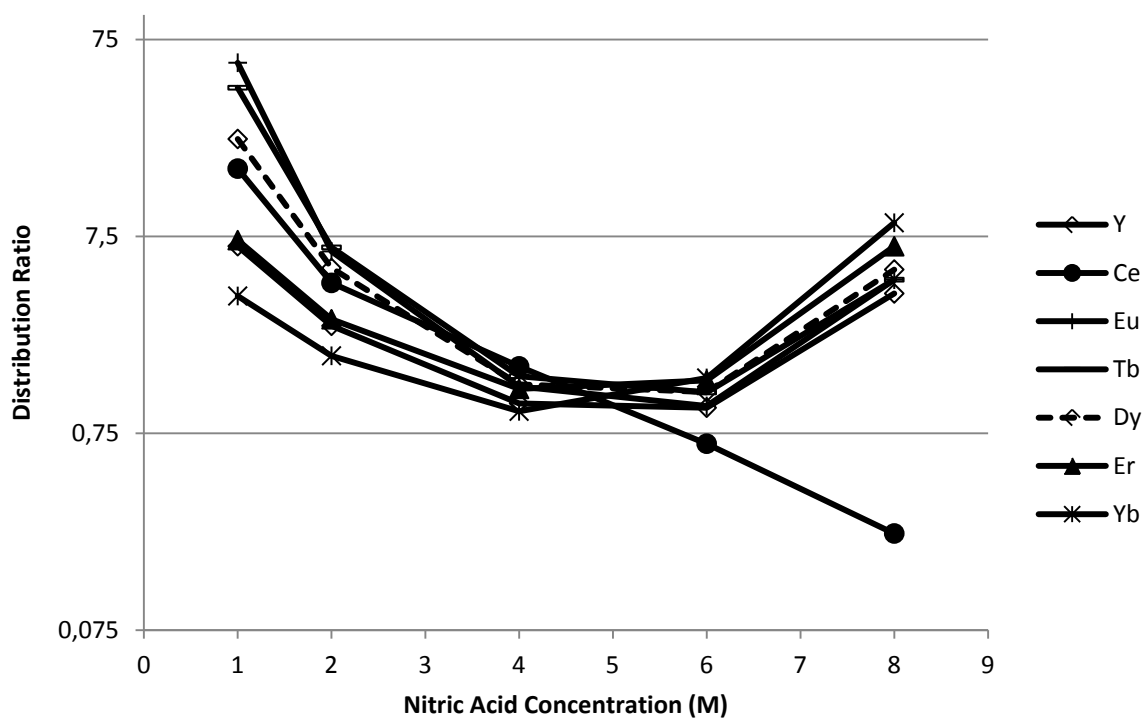


Figure 2. The RTIL extraction of selected lanthanides from acidic solution by 0.007 M TBDGA in $[C_4MIM][Tf_2N]$. The distribution ratios are the mean values of duplicate extractions with an average error of $\pm 2.5\%$.

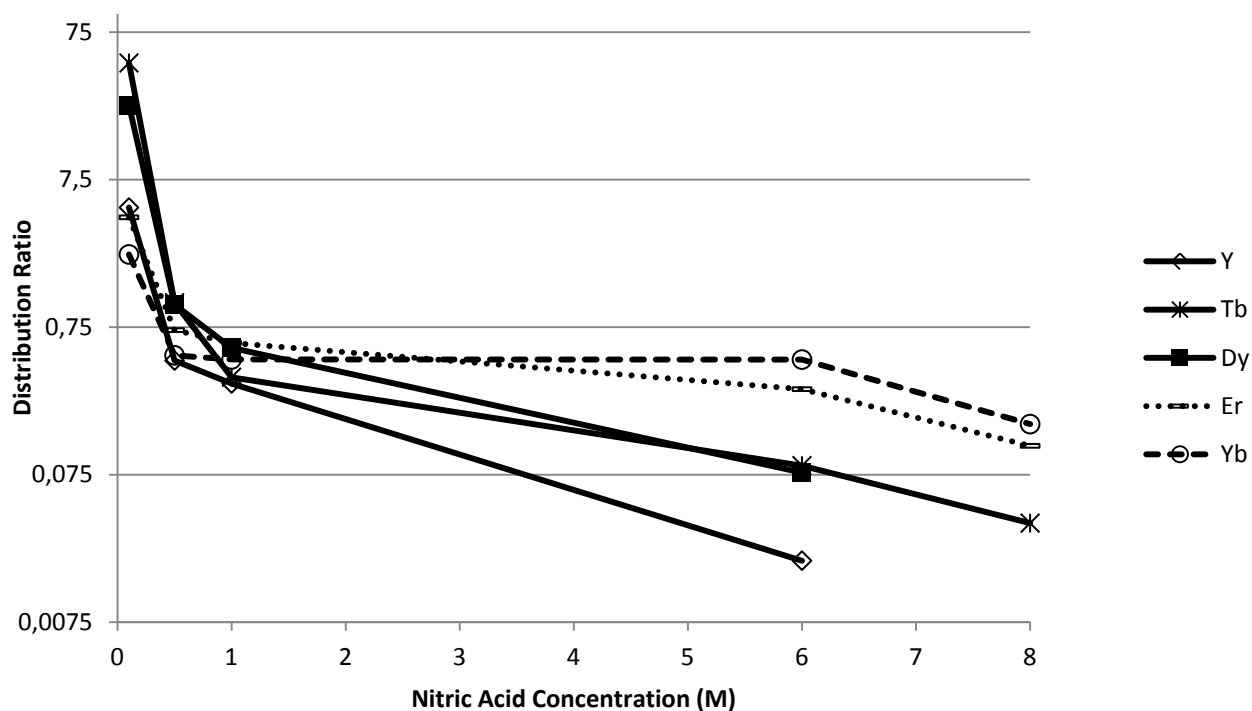


Figure 3. The RTIL extraction of selected lanthanides from acidic solution by 0.007 M TBDGA/0.01 M [C₄MIM][Tf₂N]/1-octanol. The distribution ratios are the mean values of duplicate extractions with an average error of $\pm 2.5\%$.

Given the disparate nature of the solvent extraction profiles for the metals using the same ligand and their diluents shown here, a series of extractions can be proposed to design desired lanthanide separations, all using TBDGA. Mixed phosphors used to generate white light contain a mixture which may include Y, Ce, Eu, Tb, Dy, Er, and Yb. Based on Fig. 1, Ce, or both Ce and Eu would partition to the aqueous phase during an extraction using a low concentration of TBDGA in 1-octanol, while the other metals would be extracted. The organic phase would then contain Y, Tb, Dy, Er, and Yb. These could easily be stripped back to an aqueous phase using 0.1 M HNO₃, in preparation for a subsequent extraction.

Based on Fig. 2 that subsequent extraction could employ a low concentration of TBDGA in 0.01 M IL/1-octanol to partition Dy and Tb from the 0.1 M HNO₃, while Y, Er, and Yb would partition to the aqueous phase. As can next be seen in Fig. 3, Y has good separation factors from Er and Yb, at $\alpha_{Er/Y} \sim 15$ and $\alpha_{Yb/Y} \sim 23$, in 6 M HNO₃, respectively. Thus, Y should be separable from these metals after adjusting the acid concentration of the aqueous phase. The separation of Dy from Tb, and Er from Yb, however, are not possible in this system.

Conclusions and Future Work

The separation of several important lanthanides contained in lighting phosphors by solvent extraction has been proposed, based on preliminary results from batch contacts. In principal, product streams containing separated Y, Ce, Eu, Dy/Tb, and Er/Yb are possible, using TBDGA extraction in sequential contacts using 1-octanol, and 1-octanol modified with [C₄MIM][Tf₂N] as diluents. The differences in the extraction behavior observed when using the IL diluent are attributed to extraction of a cationic, rather than a neutral metal complex.

While such a separation is here proposed, it has not been demonstrated. In future work, it is planned to demonstrate this separation at the bench scale, as well as to investigate the behavior of other DGA derivatives.

Literature Cited

1. Mincher, M.E.; Quach, D.L.; Liao, Y.J.; Mincher, B.J.; Wai, C.M. 2012. The partitioning of americium and the lanthanides using tetrabutyl diglycolamide (TBDGA) in octanol and in ionic liquid solution. *Solvent Extr Ion Exch* **30**: 735–747.
2. Sasaki, Y.; Dugo, Y.; Suzuki, S.; Tachimori, S. 2001. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO₃-dodecane system. *Solvent Extr Ion Exch* **19**: 91–103.
3. Shimojo, K.; Kurahashi, K.; Naganawa, H. 2008. Extraction behavior of lanthanides using a diglycolamide derivative TODGA in ionic liquids. *Dalton Trans* 5083–5088.
4. Dai, S.; Ju, Y.H.; Barnes, C.E. 1999. Solvent extraction of strontium nitrate by crown ether using room temperature ionic liquids. *Dalton Trans* 1201–1202.
5. Jensen, M.P.; Neufeind, J.; Beitz, J.V.; Skanthakumar, S.; Soderholm, L. 2003. Mechanisms of metal ion transfer into room-temperature ionic liquids: The role of anion exchange. *J Am Chem Soc* **125**: 15466–15473.

6. Dietz, M.L.; Dzielawa, J.A. 2001. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for 'greenness' of ionic liquids as diluents in liquid-liquid extraction. *Chem Commun* 2124–2125.

Intramolecular cooperative effect of a macrocyclic receptor bearing β -diketone fragments on the extraction of strontium into an ionic liquid

Hiroyuki Okamura^{*1,2}, Hirochika Naganawa¹, Hisanori Imura², Kojiro Shimojo¹

Summary

The macrocyclic receptor ($H_2\beta DA18C6$) composed of diaza-18-crown-6 and two molecules of 4-acyl-5-pyrazolone was synthesized for the extraction of Sr(II) into ionic liquids (ILs). The extraction performance of $H_2\beta DA18C6$ in 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_n\text{mim}][\text{Tf}_2\text{N}]$) was remarkably enhanced by the intramolecular cooperative effect compared with that in chloroform. From the equilibrium analysis, the neutral complex, $\text{Sr}(\beta DA18C6)$, was extracted into $[C_2\text{mim}][\text{Tf}_2\text{N}]$. The shortening of the average Sr–O distance in the Sr– $\beta DA18C6$ complex in the IL was revealed from the extended X-ray absorption fine structure spectroscopy. This is the cause of the intramolecular cooperative effect in the IL.

Introduction

Ionic liquids (ILs) are composed of an organic cation and either an organic or an inorganic anion, and their solvent properties such as polarity and hydrophobicity are finely tunable by changing the ionic components. Water-immiscible hydrophobic ILs have been widely investigated as novel solvents for the replacement of conventional organic diluents in solvent extraction systems [1]. The IL extraction systems exhibit high extraction performance compared with the conventional organic solvent systems because positively or negatively charged complexes are extracted by ion exchange with the cationic or anionic constituent of the ILs.

Recently, macrocyclic receptors have attracted much attention because the cyclic framework of macrocyclic ligands provides an interesting platform for the complexation of different metal ions. In particular, crown ethers can be functionalized with pendant arms containing chelating moieties, which expects to lead to enhance the extraction performance and the selectivity of the parent crown ethers. In addition, the synergistic extraction using a chelating ligand and a macrocyclic ligand is favorable for the selective and efficient extraction of specific metal ions [2–4]. There has, however, been little progress in the development of novel macrocyclic receptors bearing chelating ligands for use in IL extraction systems.

Strontium-90 is a radioactive fission product and is a matter of serious concern because of its relatively long half-life. Following its uptake into the human body, it is accumulated in the bones, exerting adverse effects on human health. Thus, the removal of ^{90}Sr from contaminated soil and seawater becomes a required task.

In this study, a macrocyclic receptor composed of diaza-18-crown-6 and two molecules of 4-acyl-5-pyrazolone, *N,N'*-bis[(5'-hydroxy-3'-methyl-1'-phenylpyrazol-4'-

^{*1} Division of Chemistry for Nuclear Engineering, Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency; E-mail: okamura.hiroyuki@jaea.go.jp

² Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University

yl)carbonylmethyl]-1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane ($H_2\beta DA18C6$, **Figure 1**), was synthesized for the extraction of Sr(II) into ILs. To examine the extraction performance of $H_2\beta DA18C6$, the extraction behavior of Sr(II) with $H_2\beta DA18C6$ into 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_n\text{mim}][Tf_2N]$; $n = 2, 4$, and 6) and chloroform was compared with that with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), *N,N'*-dibenzyl-4,13-diaza-18-crown-6 (DBzDA18C6), and a mixture of HPMBP and DBzDA18C6 (**Figure 1**). The extraction equilibrium of Sr(II) was determined, and the structures of the Sr(II) complexes were characterized by X-ray spectroscopy [5,6].

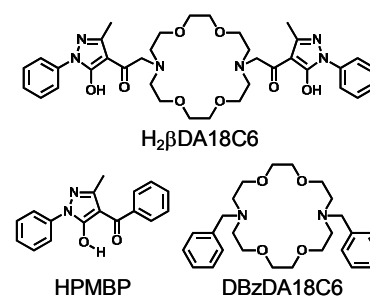


Figure 1. Chemical structures of extractants.

Experimental

Reagents

The synthesis of $H_2\beta DA18C6$ was performed according to published procedures [5]. The ILs $[C_n\text{mim}][Tf_2N]$ were synthesized and purified in the same manner as previously used [7]. Chloroform was washed five times with water prior to use.

Distribution of $H_2\beta DA18C6$

A $[C_2\text{mim}][Tf_2N]$ solution of 1 mM $H_2\beta DA18C6$ was shaken with an equal volume of an aqueous solution containing 0.1 M LiCl and a *N*-(2-hydroxyethyl)-piperazine-*N'*-2-ethanesulfonic acid (HEPES) buffer for 90 min at $25 \pm 1^\circ\text{C}$. After phase separation, the pH value in the aqueous phase was measured. For the aqueous phase, a small amount of concentrated HCl was added to acidify to ca. 1 M HCl. For the IL phase, a small portion of the IL phase was dissolved into 1 M HCl. The concentrations of $H_2\beta DA18C6$ in both solutions were measured from the absorbance at 288 nm. The distribution ratio (D_R) was calculated from the concentrations in the both phases.

Extraction of Sr(II)

Extracting phases were prepared by dissolving each extractant ($H_2\beta DA18C6$, HPMBP and DBzDA18C6, HPMBP, or DBzDA18C6) in $[C_n\text{mim}][Tf_2N]$ and chloroform. An aqueous phase was prepared by dissolving $Sr(NO_3)_2$ (0.01 mM) in an HEPES buffer solution. Equal volumes of the extracting phase and the aqueous phase were shaken at $25 \pm 1^\circ\text{C}$ for 30 min. After phase separation, the pH value in the aqueous phase was measured, and Sr(II) in the extracting phase was back-extracted into 0.01 M HNO_3 . The concentrations of metal ions in both phases were determined by an inductively coupled plasma mass spectrometry or an inductively coupled plasma atomic emission spectrometry. For the competitive extraction, aqueous solutions containing alkaline earth metal ions were prepared with metal concentrations of 0.05 mM each. The percentage extraction (%*E*) and the distribution ratio (*D*) were calculated from the metal concentrations in the both phases.

Results and discussion

Distribution of $H_2\beta DA18C6$

The distribution behavior of $H_2\beta DA18C6$ in the $[C_2mim][Tf_2N]$ /water and chloroform/water systems was examined as a function of pH in the aqueous phase (**Figure 2**). The values of the acid-dissociation constants (K_a) were determined by the non-linear least-squares fitting of the $\log D_R$ -pH plots in the chloroform system, and were obtained as $K_{a1} = 10^{-2.10 \pm 0.12}$, $K_{a2} = 10^{-3.09 \pm 0.10}$, $K_{a3} = 10^{-8.66 \pm 0.12}$, and $K_{a4} = 10^{-9.65 \pm 0.33}$. The calculated values of D_R using those constants were well consistent with the values of experimental data.

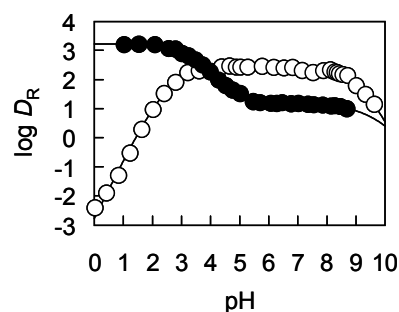


Figure 2. Distribution ratio of $H_2\beta DA18C6$ as a function of pH in the aqueous phase in the $[C_2mim][Tf_2N]$ (●) and chloroform (○) systems [6]. Initial concentration of $H_2\beta DA18C6$ was 1 mM. Ionic strength was 0.1 M (LiCl). The solid lines were obtained by a non-linear least-squares fitting.

In the $[C_2mim][Tf_2N]$ system, the distribution ratio of $H_2\beta DA18C6$ becomes constant in the low pH region of $pH < 2.5$ because the cationic species, $H_4\beta DA18C6^{2+}$ and $H_3\beta DA18C6^+$, are transferred into the IL phase by ion-exchange. In the pH region of 5.5–8.5, the $\log D_R$ value becomes constant again because the neutral species, $H_2\beta DA18C6$, is formed and distributed between the two phases. Furthermore, the $\log D_R$ value decreases with increase in the pH at $pH > 8.5$ because of the acid-dissociation of $H_2\beta DA18C6$ in the aqueous phase. Interestingly, the cationic species are preferable for the transfer into the $[C_2mim][Tf_2N]$ phase.

Extraction behavior of alkaline earth metals

The competitive extraction behavior of alkaline earth metal ions, Mg(II), Ca(II), Sr(II), and Ba(II), with $H_2\beta DA18C6$ in the chloroform and $[C_2mim][Tf_2N]$ systems was investigated, along with that with HPMBP, DBzDA18C6, and the mixture of HPMBP and DBzDA18C6 (**Figure 3**). The concentration of DBzDA18C6 was equal to that of $H_2\beta DA18C6$, but the concentration of HPMBP was 2-fold greater than that of $H_2\beta DA18C6$, to ensure the same number of β -diketone groups. In the chloroform system, Mg(II) was extracted with HPMBP alone because the higher charge density of Mg(II) facilitated an electrostatic interaction with $PMBP^-$, while other ions were hardly extracted with HPMBP alone. In addition, DBzDA18C6 provided poor extraction because of the absence of an appropriate counter anion. The extraction efficiency was remarkably enhanced when HPMBP and DBzDA18C6 were simultaneously used. This improvement in extraction was attributed to the synergistic effect, which was generated by the combination of HPMBP and DBzDA18C6. The extraction of alkaline earth metals was also accomplished with $H_2\beta DA18C6$, although any superiority over the HPMBP–DBzDA18C6 system was not found.

In the $[C_2mim][Tf_2N]$ system, Mg(II) and Ca(II) were extracted with HPMBP alone in contrast to the chloroform system. In addition, the sizes of these ions were

unfavorable for the cavity of DBzDA18C6, which made the extraction of Mg(II) and Ca(II) with DBzDA18C6 impossible. The differences in the extraction behavior between the H₂βDA18C6 system and the HPMBP-DBzDA18C6 system for Mg(II) and Ca(II) were relatively small. The results suggested that superiority of H₂βDA18C6 over the HPMBP-DBzDA18C6 system was not significantly found for Mg(II) and Ca(II). In contrast, very different extraction behavior was observed for Sr(II). DBzDA18C6 was capable of quantitative extraction of Sr(II) into the IL phase, and its

extraction performance was greatly enhanced in the IL system. Similar extraction behavior was observed in the HPMBP-DBzDA18C6 system, implying that HPMBP barely acted as a synergist in the IL system. Surprisingly, H₂βDA18C6 enabled the extraction of Sr(II) from more acidic aqueous solutions compared with the HPMBP-DBzDA18C6 system. The covalent attachment of two β-diketone fragments to diaza-18-crown-6 generated a cooperative interaction within the molecule, which significantly increased the extraction efficiency of Sr(II) in the IL system. This enhancement of the extraction efficiency is ascribed to an “intramolecular cooperative effect”. The intramolecular cooperative effect denotes the phenomenon that combining two different types of extractants leads to an increase in the extraction performance due to their cooperative interactions within the molecule, which is discriminated from general synergistic effect. Furthermore, the extraction behavior of Ba(II) was very similar to that of Sr(II). The magnitude of the intramolecular cooperative effect for Sr(II) and Ba(II) is remarkably high compared with that for Mg(II) and Ca(II). It can be assumed that the cavity of H₂βDA18C6 fits the size of Sr(II) and Ba(II) ions. Therefore, the size-fitting between the metal ion and the cavity of H₂βDA18C6 is an important factor affecting the intramolecular cooperative effect.

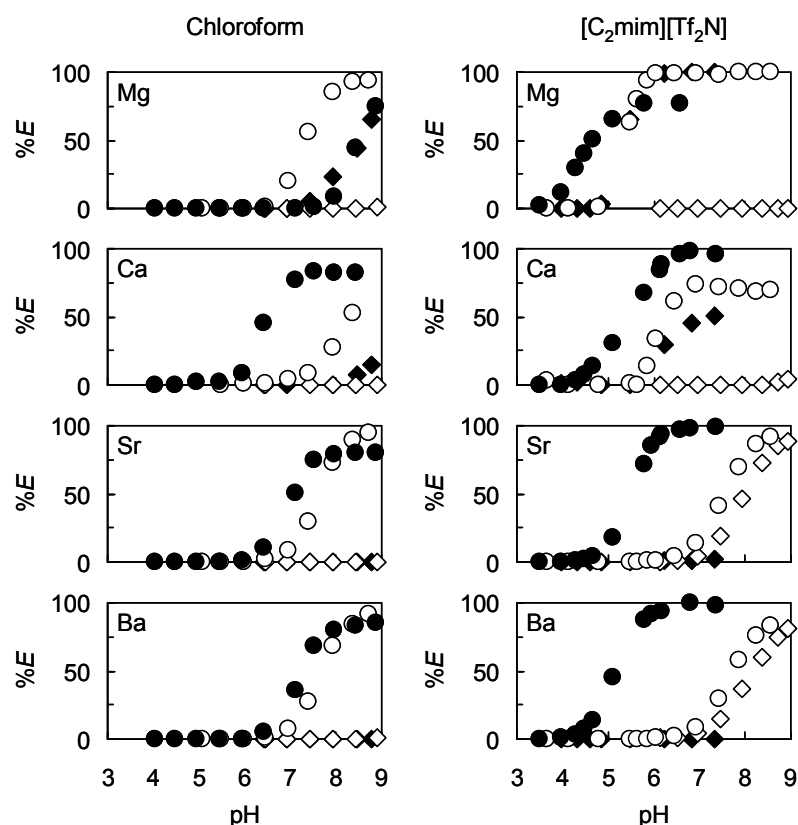


Figure 3. Competitive extraction behavior of Mg(II), Ca(II), Sr(II), and Ba(II) into the chloroform (left) and [C₂mim][Tf₂N] (right) phases as a function of pH in the aqueous phase in the H₂βDA18C6 (●), HPMBP-DBzDA18C6 (○), HPMBP (◆), and DBzDA18C6 (◇) systems. Initial concentrations of H₂βDA18C6, HPMBP, and DBzDA18C6 were 1, 2, and 1 mM, respectively, and initial concentrations of alkaline earth metal ions were 0.05 mM.

Comparison of the extraction of Sr(II)

Figure 4 shows the variation in $\log D$ for Sr(II) obtained with $H_2\beta DA18C6$ in chloroform (a), $[C_2mim][Tf_2N]$ (b), $[C_4mim][Tf_2N]$ (c), and $[C_6mim][Tf_2N]$ (d) as a function of pH in the aqueous phase, along with that obtained with the mixture of HPMBP and DBzDA18C6, and DBzDA18C6 alone. In the chloroform system, as mentioned above, any superiority of $H_2\beta DA18C6$ over the HPMBP–DBzDA18C6 system was not found. The $\log D$ value for Sr(II) was saturated at around 0.5. This result suggests that the distribution constant of the Sr– $\beta DA18C6$ complex is low. In the $[C_nmim][Tf_2N]$ systems, it was confirmed that the extraction of Sr(II) with $H_2\beta DA18C6$ was also enhanced in the $[C_4mim][Tf_2N]$ and $[C_6mim][Tf_2N]$ systems compared with that in the chloroform system. These results indicated that ILs can provide an appropriate environment to enhance the performance of $H_2\beta DA18C6$. The magnitude of the intramolecular cooperative effect was higher in the $[C_2mim][Tf_2N]$ system than in the $[C_4mim][Tf_2N]$ and $[C_6mim][Tf_2N]$ systems.

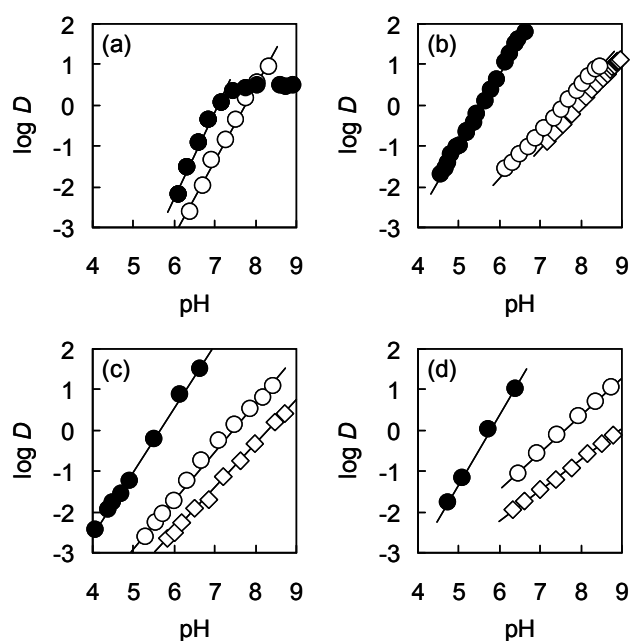


Figure 4. Plots of $\log D$ –pH for the extraction of Sr(II) with $H_2\beta DA18C6$ (●), HPMBP and DBzDA18C6 (○), and DBzDA18C6 alone (◇) in chloroform (a), $[C_2mim][Tf_2N]$ (b), $[C_4mim][Tf_2N]$ (c), and $[C_6mim][Tf_2N]$ (d). Initial concentrations of $H_2\beta DA18C6$, HPMBP, and DBzDA18C6 were 1, 2, and 1 mM, respectively, and initial concentration of Sr(II) was 0.01 mM.

Equilibrium analysis in the $H_2\beta DA18C6$ system

The extraction equilibrium of Sr(II) with $H_2\beta DA18C6$ in the $[C_2mim][Tf_2N]$ and chloroform systems was investigated by the slopes of the $\log D$ – $\log [H_2\beta DA18C6]$ (**Figure 5**) and $\log D$ –pH plots. In the chloroform system, the slopes of the $\log D$ – $\log [H_2\beta DA18C6]$ and $\log D$ –pH plots were 1.00 ± 0.03 and 1.92 ± 0.15 , respectively. Similar slopes were obtained in the $[C_2mim][Tf_2N]$ system, which were 1.03 ± 0.01 and 1.73 ± 0.02 , respectively. These results indicate that Sr(II) is extracted as a neutral complex, Sr($\beta DA18C6$), in both systems. In the $[C_2mim][Tf_2N]$ system, $H_2\beta DA18C6$ provided remarkably high extraction

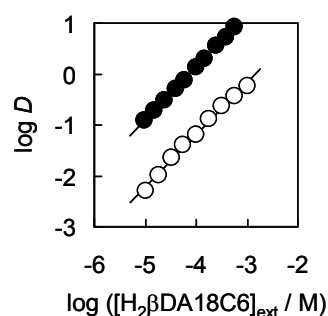


Figure 5. Distribution ratio of Sr(II) as a function of the $H_2\beta DA18C6$ concentration in $[C_2mim][Tf_2N]$ (●) and chloroform (○). Aqueous phase pH was 6.2 ($[C_2mim][Tf_2N]$) or 7.0 (chloroform). Initial concentration of Sr(II) was 0.01 mM.

performance for Sr(II) relative to the chloroform system. This implies a specific solvent effect of IL on the performance of H₂βDA18C6 for the extraction of Sr(II).

Structural comparison of the extracted complexes

The solid-state molecular structure of the extracted complex formed in chloroform was characterized by X-ray diffraction. The molecular formula of the crystallized complex was determined to be Sr(βDA18C6)(DMSO). One solvent molecule was incorporated during the crystallization. Sr(II) was encapsulated in the cavity of the diaza-18-crown-6 ring, and coordinated by four oxygen and two nitrogen atoms. Furthermore, the encapsulated Sr(II) was coordinated by two oxygen atoms from two β-diketone moieties and one oxygen atom from DMSO. The total coordination number was 9. The crystallographic data served as a reference for the structural determination by extended X-ray absorption fine structure (EXAFS) spectroscopy.

The structural arrangements of the Sr-βDA18C6 complexes extracted into chloroform and [C₂mim][Tf₂N] were investigated by EXAFS spectroscopy. The results indicated that coordination arrangement of Sr(II)-βDA18C6 complex extracted into chloroform and [C₂mim][Tf₂N] is highly likely to be identical to that observed in the crystal structure. The geometry of the first coordination shell of the Sr(II) species extracted into chloroform can be assumed to be similar to that in the crystal structure, in that there would be additional water coordination instead of DMSO coordination. The average Sr-O distance in chloroform was 2.55 Å. In contrast, the Sr-βDA18C6 complex in [C₂mim][Tf₂N] displayed a much shorter average Sr-O distance of 2.51 Å. These results clearly indicated that Sr(II) was held by H₂βDA18C6 more rigidly in [C₂mim][Tf₂N] than in chloroform, which would likely be an important factor dominating the magnitude of the intramolecular cooperative effect of H₂βDA18C6 for Sr(II). The observed shortening of Sr-O distance in the [C₂mim][Tf₂N] system is possibly attributed to the solvation of the extracted complex with IL [7].

Conclusions

The efficient extraction of Sr(II) by the intramolecular cooperative effect with diaza-18-crown-6 incorporating β-diketone fragments in IL has been investigated. H₂βDA18C6 in IL provided remarkably high extraction performance for Sr(II) because of the intramolecular cooperative interaction. The present findings suggest that crown ethers incorporating ligand fragments are capable of forming a stable complex in IL.

References

- [1] X. Sun, H. Luo, S. Dai, *Chem. Rev.*, **112**, 2100 (2012).
- [2] N. Hirayama, H. Okamura, K. Kidani, H. Imura, *Anal. Sci.*, **24**, 697 (2008).
- [3] H. Okamura, N. Hirayama, K. Morita, K. Shimojo, H. Naganawa, H. Imura, *Anal. Sci.*, **26**, 607 (2010).
- [4] H. Okamura, H. Takagi, T. Isomura, K. Morita, H. Nagatani, H. Imura, *Anal. Sci.*, **30**, 323 (2014).
- [5] K. Shimojo, H. Okamura, N. Hirayama, S. Umetani, H. Imura, H. Naganawa, *Dalton Trans.*, 4850 (2009).
- [6] H. Okamura, A. Ikeda-Ohno, T. Saito, N. Aoyagi, H. Naganawa, N. Hirayama, S. Umetani, H. Imura, K. Shimojo, *Anal. Chem.*, **84**, 9332 (2012).
- [7] H. Okamura, H. Sakae, K. Kidani, N. Hirayama, N. Aoyagi, T. Saito, K. Shimojo, H. Naganawa, H. Imura, *Polyhedron*, **31**, 748 (2012).

Comprehensive extraction separation study of metal ions using *N,N*-dioctyldiglycolamic acid DODGAA

Kojiro Shimojo^{*1}, Hirochika Naganawa¹

Summary

We report on the feasibility of *N,N*-dioctyldiglycolamic acid (DODGAA) as a novel extractant for selective separation of various metal ions in industrial solvent extraction processes. DODGAA can be synthesized simply and readily in a single step. This extractant enables the quantitative partitioning of all rare-earth metal ions (RE^{3+}) from moderately acidic solutions, while showing selectivity for heavier lanthanides, and provides remarkably high extraction separation performance for RE^{3+} compared with commercial extractants. In fact, the mutual separation abilities of DODGAA for light lanthanides are higher than those of organophosphorus extractants. Furthermore, we found that DODGAA is useful for the separation of RE^{3+} from base metal ions. For other metal ions, DODGAA possesses great potential for the selective recovery of a noble metal ion Pd(II) from Pt(IV) and Rh(III), the removal of toxic metal ions, such as Hg(II) and Pb(II), and the recycling of In(III) from the group-13 elements.

Introduction

The extractant plays a key role in the extraction efficiency and the separation operation for target metal ions. To date, much effort has been devoted to the development of novel extractants, which perform better than commercial conventional extractants. Most approaches, however, involve rather laborious and elaborate synthetic processes requiring a few steps to obtain extractants with high extraction performance and separation ability for target metal ions. These methods are time-consuming and expensive for large-scale applications, and are far from ideal extraction systems for practical use. Therefore, the development of simple, yet superior extractants relative to commercial extractants is a challenging task.

Recently, we developed *N,N*-dioctyldiglycolamic acid (DODGAA, Figure. 1), which is an acidic tridentate ligand with a carbamoyl group and a carboxy group connected by an ether chain.^{1–5} The extractant can be synthesized simply and readily in a single step, which helps to reduce the production cost of the extractant. Furthermore, DODGAA consists only of C, H, O and N atoms, and can be completely incinerated to gaseous products. Thus, the extractant can potentially be used in residual-waste-free extraction processes (CHON principle). DODGAA is somewhat similar in structure to *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA),^{6–10} but it is an ionizable extractant unlike TODGA. This is an advantage compared to neutral extractants because metal transfer can be simply controlled by the pH of the aqueous solution, and the process involves no anionic species.

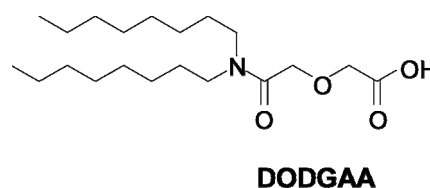


Figure 1. Molecular structure of DODGAA

^{*1} Kojiro Shimojo, Division of Chemistry for Nuclear Engineering, Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan, E-mail: shimojo.kojiro@jaea.go.jp

DODGAA is a novel extractant, and therefore it is important to evaluate its extraction performance and separation ability for various metal ions in an effort to expand its application range.

In this study, we investigated the feasibility of the following extraction applications: (i) the mutual separation of individual rare-earth metal ions (RE^{3+}) from each other; (ii) the separation of RE^{3+} from base metal ions; (iii) the extraction of noble metal ions; (iv) the removal of toxic metal ions; (v) the separation of In(III) from the group-13 elements.

Experimental

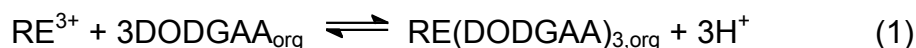
Aqueous phases containing each metal ion were prepared with different pH values. The pH of the aqueous solutions was adjusted by the addition of either HNO_3 or NaOH to a 10 mM 2-morpholinoethanesulfonic acid (MES) buffer. In the extraction tests of metal chlorides (Rh(III) , Pd(II) , and Pt(IV)), the pH was adjusted by the addition of HCl to a 50 mM sodium acetate buffer at a constant ionic strength of 0.1 M NaCl . In extraction tests of RE(III) , the pH was adjusted by dilution with HNO_3 without a buffer. For Hg(II) extraction, the contamination of aqueous solutions by chloride ions from the pH electrode was prevented. For all aqueous phases, stock solutions containing each metal salt were added to the aqueous solutions to give metal ion concentrations of 0.01 mM. An organic phase was prepared by dissolving DODGAA in isooctane containing 5 vol% 1-octanol as a solubilizer. Equal volumes of the organic and aqueous solutions were mixed and shaken mechanically at 25°C for 30 min to attain equilibrium. After separation of the two phases by centrifugation, the metal ions in the organic phase were back-extracted into equal volumes of 1 M HNO_3 . The concentrations of metal ions in the aqueous phase and the receiving phase were determined using inductively coupled plasma mass spectrometry (Hewlett Packard HP 4500 or PerkinElmer NexION 300) to obtain the extractability ($E = [\text{M}^{n+}]_{\text{org}} / [\text{M}^{n+}]_{\text{ini}} \times 100$). The M^{n+} denotes metal ions, and the subscripts org, aq and ini denote the organic phase, the aqueous phase and the initial condition, respectively. The equilibrium pH values of the aqueous phases were also measured.

Results and discussion

Mutual separation of individual rare-earth metal RE

Figure 2 shows the extraction behavior of RE^{3+} with DODGAA as a function of the pH in the aqueous phase. The extractability of RE^{3+} increased with an increase in the pH. Quantitative extraction was achieved in moderately acidic solutions ($\text{pH} \geq 2$ for middle and heavy RE^{3+}), indicating DODGAA provided remarkably high extraction performance for RE^{3+} compared with typical carboxylic-acid-type extractants (e.g., Versatic 10) although the extractant is a CHON-based compound with a carboxy

group. In fact, the extraction performance of DODGAA was comparable to that of organophosphorus extractants (e.g., D2EHPA and PC-88A). Furthermore, it was found that DODGAA exhibits selectivity for the heavier RE³⁺. DODGAA provided remarkably high mutual separation ability for RE³⁺ compared with Versatic 10. In contrast, the separation ability of DODGAA is higher for lighter lanthanides from La³⁺ to Gd³⁺ and is lower for heavier lanthanides from Tb³⁺ to Lu³⁺ and Y³⁺ than that of D2EHPA. In addition, on the basis of the slope analysis (data not shown), it was confirmed that RE³⁺ transfer with DODGAA proceeds through a proton-exchange reaction, and the extraction equilibrium equation is represented as follows:



Separation of rare-earth metals REs from base metal ions

REs are contained in industrial wastes such as fluorescent materials and permanent magnets. Since the industrial wastes contain excess base metals in addition to REs, it is important to separate efficiently REs from base metals in order to recover REs from the industrial wastes. The separation of RE ions from base metal ions (Fe³⁺, Al³⁺, Zn²⁺, and Cu²⁺) using DODGAA was investigated. La³⁺, Eu³⁺, and Lu³⁺ were employed as representative light, middle, and heavy RE ions, respectively. As shown in Figure. 3, DODGAA quantitatively extracted the metal ions with the following selectivity: Lu³⁺ > Eu³⁺ > La³⁺ = Fe³⁺ > Al³⁺ > Cu²⁺ > Zn²⁺. As a result, Lu³⁺ and Eu³⁺ were successfully separated from the base metal ions. In contrast, DODGAA enabled the separation of La³⁺ from Al³⁺, Cu²⁺ and Zn²⁺ but it was difficult to separate La³⁺ from Fe³⁺.

Extraction behavior of noble metal ions Pd(II), Pt(IV), and Rh(III)

In view of the recovery of noble metal ions, extraction behavior of Pd(II), Pt(IV), and Rh(III) using DODGAA was investigated. In Figure 4, quantitative extraction of Pd(II) was achieved in neutral aqueous solutions, but very little Pt(IV) and Rh(III) were extracted. DODGAA is expected to be useful for the separation of Pd(II) from Pt(IV) and Rh(III).

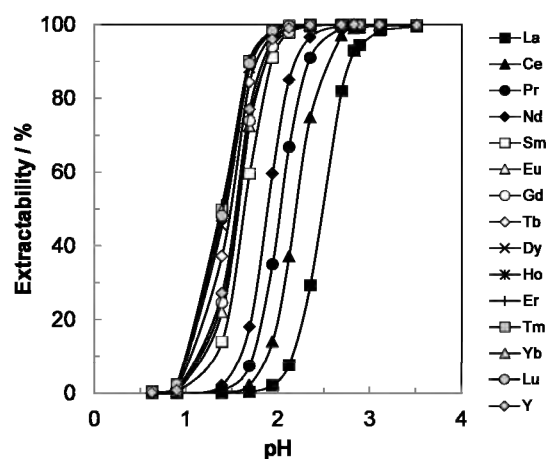


Figure 2. Extraction behavior of rare-earth metal ions using DODGAA as a function of the pH in the aqueous phase. [DODGAA] = 10 mM, [RE³⁺] = 0.01 mM.

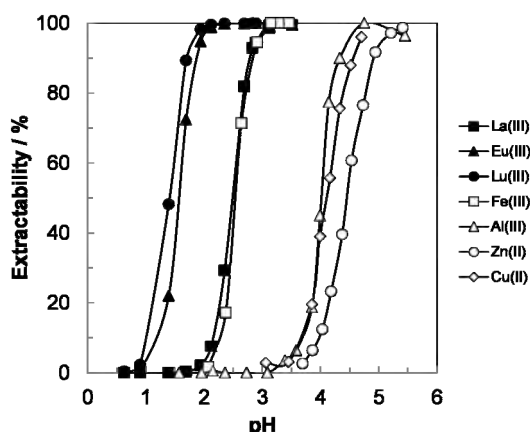


Figure 3. Extraction separation of rare-earth metal ions from base metal ions using DODGAA. [DODGAA] = 10 mM, [metal ion] = 0.01 mM.

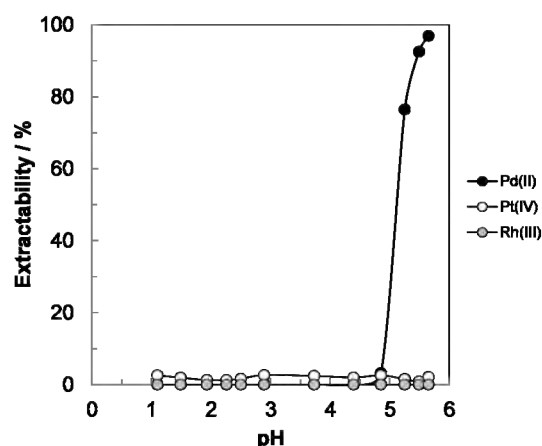


Figure 4. Extraction behavior of noble metal ions Pd(II), Pt(IV), and Rh(III) using DODGAA. [DODGAA] = 10 mM, [metal ion] = 0.01 mM.

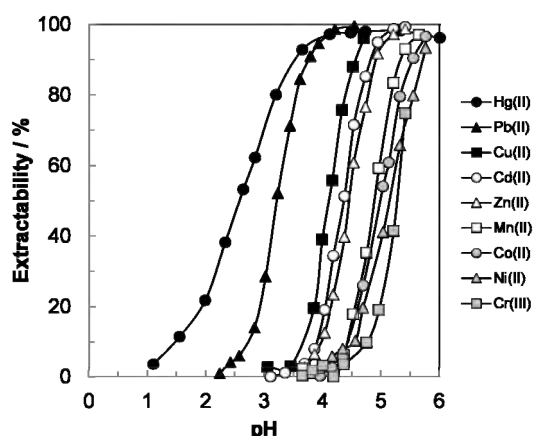


Figure 5. Extraction removal of toxic metal ions Hg(II) and Pb(II) from metal ion mixture using DODGAA. [DODGAA] = 10 mM, [metal ion] = 0.01 mM.

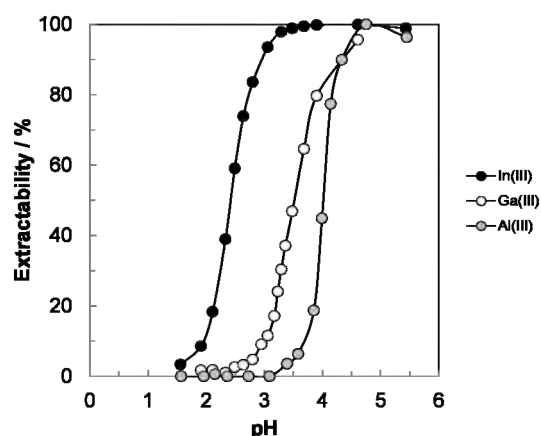


Figure 6. Extraction separation of In(III) from the group-13 elements using DODGAA. [DODGAA] = 10 mM, [metal ion] = 0.01 mM.

Extraction removal of toxic metal ions from metal ion mixture

Mercury and lead are toxic elements that accumulate in the vital organs of humans and animals. Removal of Hg(II) and Pb(II) from industrial effluents and contaminated environmental matrices has become a very important task. Extraction of Hg(II) and Pb(II) from aqueous solutions containing multiple divalent metal ions (Hg(II), Pb(II), Cu(II), Cd(II), Zn(II), Mn(II), Co(II), Ni(II), and Cr(III)) with DODGAA was investigated to assess the selectivity (Figure 5). Quantitative partitioning was observed for all of the metal ions, and DODGAA showed the following selectivity for the metal ions: Hg(II) > Pb(II) >> Cu(II) > Cd(II) > Zn(II) > Mn(II) > Co(II) > Ni(II) > Cr(III). The results indicate that DODGAA enables selective removal of Hg(II) and Pb(II) from various metal ions.

Extraction separation of In(III) from the group-13 elements

The recycling of indium from indium-containing scrap has received much attention in recent years. For indium recovery, extraction separation of In(III) from the group-13 elements with DODGAA was carried out. As shown in Figure 6, DODGAA quantitatively extracted the metal ions from mildly acidic solutions in the following order: In(III) > Ga(III) > Al(III), which indicates that In(III) was efficiently separated from the group-13 elements.

Conclusions

The extraction performance and separation ability of DODGAA for various metal ions were comprehensively investigated. We conclude that DODGAA possesses great potential for the following applications: (i) the mutual separation of individual rare-earth metal ions from each other; (ii) the separation of rare-earth metal ions from base metal ions, such as Fe(III), Al(III), Zn(II), and Cu(II); (iii) the selective recovery of Pd(II) from Pt(IV) and Rh(III); (iv) the removal of toxic metal ions, such as Hg(II) and Pb(II); (v) the separation of In(III) from the group-13 elements. DODGAA has a simple molecular structure but is a promising extractant and is versatile in the extraction separation of metal ions.

Acknowledgements

This research was financially supported by a Research for Promoting Technological Seeds from the Japan Science and Technology Agency (to K. S.). We thank the Center for Instrumental Analysis at Ibaraki University for the elemental analysis, NMR, and MALDI-TOF/MS measurements.

References

1. H. Naganawa, K. Shimojo, H. Mitamura, Y. Sugo, J. Noro, and M. Goto, *Solvent Extr. Res. Dev., Jpn.*, **2007**, *14*, 151.
2. K. Shimojo, H. Naganawa, J. Noro, F. Kubota, and M. Goto, *Anal. Sci.*, **2007**, *23*, 1427.
3. K. Shimojo, A. Nakai, H. Okamura, A. Ohashi, and H. Naganawa, *Anal. Sci.*, **2013**, *29*, 147.
4. K. Shimojo, N. Aoyagi, T. Saito, H. Okamura, F. Kubota, M. Goto, and H. Naganawa, *Anal. Sci.*, **2014**, *30*, 263.
5. K. Shimojo, A. Nakai, H. Okamura, T. Saito, A. Ohashi, and H. Naganawa, *Anal. Sci.*, **2014**, *30*, in press.
6. Y. Sasaki, Y. Sugo, S. Suzuki, and S. Tachimori, *Solvent Extr. Ion Exch.*, **2001**, *19*, 91.
7. S. A. Ansari, P. N. Pathak, V. K. Manchanda, M. Husain, A. K. Prasad, and V. S. Parmar, *Solvent Extr. Ion Exch.*, **2005**, *23*, 463.
8. K. Shimojo, K. Kurahashi, and H. Naganawa, *Dalton Trans.*, **2008**, 5083.

9. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, and V. K. Manchanda, *Chem. Rev.*, **2012**, *112*, 1751.
10. Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, and T. Kimura, *Solvent Extr. Ion Exch.*, **2013**, *31*, 401.

Separation of rhodium from palladium, platinum, and base metals with amide-containing tertiary amine compounds

Hirokazu Narita^{*1}, Kazuko Morisaku¹, Mikiya Tanaka¹, Keishiro Nagao², Takamasa Fuchikami², Takamasa Yoshida², Kazuyuki Kuroda²

A new process for separating palladium, platinum, and rhodium is reported. In this process, rhodium is recovered first, whereas in most of the previously reported processes for separation and purification of platinum group metals, rhodium remains in the raffinate. Two amide-containing tertiary amine compounds, *N*-2-ethylhexyl-bis(*N*-di-2-ethylhexyl-ethylamide)amine (BisAA) and tris(*N*-di-2-ethylhexyl-ethylamide)amine (TrisAA), were used as extractants, and their selectivities for rhodium were compared. When a solution of Rh(III), Pd(II), Pt(IV), Cu(II), Fe(III), and Ni(II) in 2 M HCl was extracted with 0.5 M BisAA or TrisAA in 80 vol% *n*-dodecane–20 vol% 2-ethylhexanol, all the metal ions except Ni(II) were extracted. The Rh(III) could be back-extracted with 10 M HCl more selectively from BisAA than from TrisAA, although the back-extraction efficiency from BisAA was slightly lower than that from TrisAA. In the BisAA system, the base metal ions Cu(II) and Fe(III) were readily scrubbed with distilled water, and Pd(II) and Pt(IV) were back-extracted with 10 M HNO₃.

Introduction

Most automotive catalytic converters used to treat exhaust gas contain platinum group metals (PGMs), particularly Pd, Pt, and Rh; and this use accounts for the largest share of the demand for these metals.^[1] Because the price of PGMs has fluctuated widely in recent years^[2] and because the amount of PGM waste is increasing, the development of methods for improving the recovery of PGMs from the wastes has become important.

In the Inco process,^[3] which is the well-known solvent extraction–based process for PGM separation, Pd and Pt are extracted from HCl solutions with dialkyl sulfide and tri-*n*-butyl phosphate, respectively. However, Rh remains in the raffinate because a practical and effective reagent for extracting Rh from HCl solution has not yet been developed.^[4,5]

In relatively concentrated HCl (>1 M), Rh(III) exists as $[\text{RhCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}$ ($n = 5$ and 6).^[4,6] These Rh(III) aquo-chloro complexes are kinetically inert,^[7] which makes replacement of Cl/H₂O in the inner coordination sphere of Rh(III) by extractants difficult. In addition, the efficiency of ion-pair extraction of Rh(III) with protonated extractants is also insufficient.

Recently, we found that tertiary amine compounds with *N,N*-dialkylamide groups efficiently extract Rh(III) from HCl solutions.^[8,9] Specifically, *N*-*n*-hexyl-bis(*N*-methyl-*N*-*n*-octyl-ethylamide)amine and tris(*N*-methyl-*N*-*n*-octyl-ethylamide)amine extract more than 80% and 90% of Rh(III), respectively, from ~2 M HCl, and the Rh(III) extracted into the organic solutions can readily be back-extracted into 10 M HCl.

^{*1} Corresponding Author, Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST). E-mail: hirokazu-narita@aist.go.jp

² Chemicrea Inc.

Further studies of the solubility of the extractants in organic diluents for practical use and studies of the formation of a third phase or a precipitate during extraction revealed that *N*-2-ethylhexyl-bis(*N*-di-2-ethylhexyl-ethylamide)amine (BisAA) and tris(*N*-di-2-ethylhexyl-ethylamide)amine (TrisAA) (Fig. 1) display good extraction properties.^[10]

In this study, we investigated the separation of Rh(III), Pd(II), and Pt(IV) from base metals Fe(III), Cu(II), and Ni(II) in a 2 M HCl solution using BisAA and TrisAA diluted with 80 vol% *n*-dodecane–20 vol% 2-ethylhexanol, and we focused on the selective recovery of Rh(III) prior to recovery of Pd(II) and Pt(IV). We also compared the Rh(III) selectivities of BisAA and TrisAA.

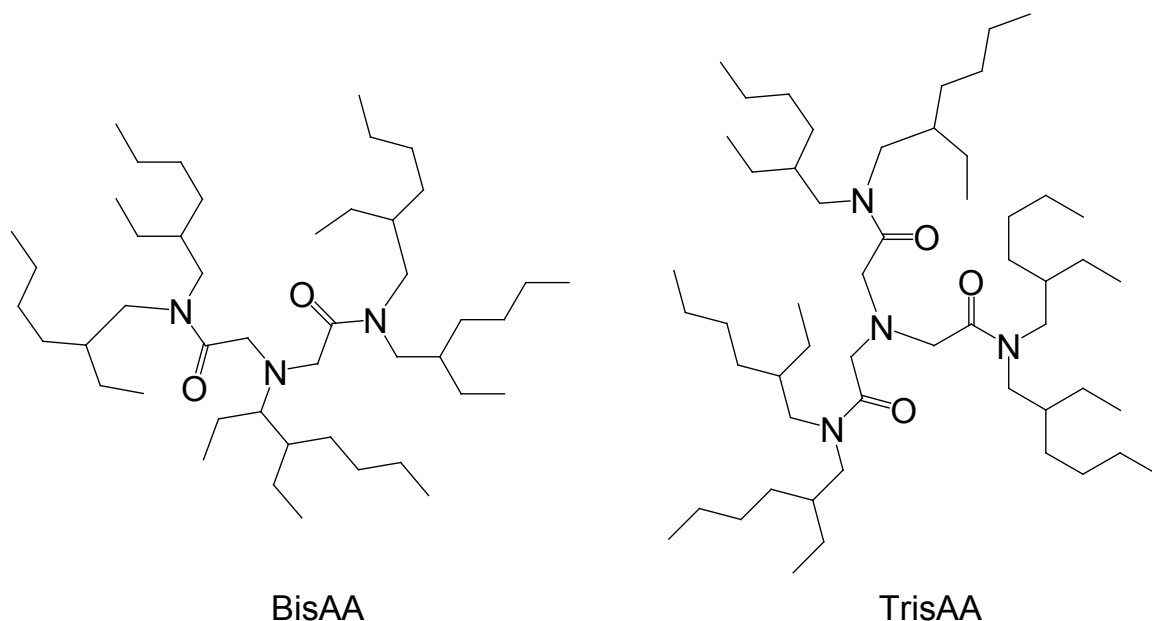


Fig.1 Structures of BisAA and TrisAA

Experimental

Reagents

Stock solutions of metal ions were prepared by dissolving PdCl₂, H₂PtCl₄, and RhCl₃·3H₂O (Soekawa Chemical Co.) and CuCl₂·2H₂O, FeCl₃·6H₂O, and NiCl₂·6H₂O (Wako Pure Chemical Industries) in HCl solutions at the concentrations specified in the next section. All the other chemicals used in this study were of reagent grade. BisAA and TrisAA were synthesized by means of our previous papers.^[8,9]

Extraction experiments

All extraction experiments were carried out at 23 ± 2 °C. The concentrations of metal ions in aqueous phases were measured by ICP-AES (Horiba ULTIMA2). The forward extraction percentage (*E*%) of metal ions is defined as [(concentration of metal ion in organic phase after forward extraction)/(initial concentration of metal ion in aqueous

phase)] $\times 100$, and the back extraction percentage is defined as [(concentration of metal ion in aqueous phase after back-extraction)/(concentration of metal ion in organic phase after forward extraction)] $\times 100$. The volume ratio of the organic phase to the aqueous phase was 1 for all extraction operations.

An organic solution containing BisAA or TrisAA diluted with 80 vol% *n*-dodecane–20 vol% 2-ethylhexanol was pre-equilibrated with an equal volume of metal-free 2 M HCl. A portion of the pre-equilibrated organic phase and an equal volume of 2 M HCl containing 2 g/L of each metal ion were vertically shaken for 120 min in a 10-mL glass tube at an amplitude of 100 mm and a frequency of 200 spm, and then the mixture was centrifuged. After extraction, a portion of the organic phase was transferred to another glass tube, and an equal volume of an aqueous solution (distilled water, 10 M HCl, 10 M HNO₃, 0.1 M thiourea in 0.1 M HCl, or 1 M NaOH) was added. The mixture was shaken and then centrifuged as described for the forward extraction.

Results and Discussion

Extraction efficiency of metal ions from 2 M HCl

Figure 2 shows *E*% of the metal ions from 2 M HCl with 0.5 M BisAA and TrisAA in 80 vol% *n*-dodecane–20 vol% 2-ethylhexanol. In both systems, Pd(II) and Pt(IV) were quantitatively extracted. The *E*% of Rh(III) with TrisAA (~75%) was slightly higher than that with BisAA (~70%). As for the base metal ions, the *E*% of Cu(II) with TrisAA was ~10% larger than that for extraction with BisAA; Ni(II) was barely extracted by either extractant, and both reagents extracted ~90% of the Fe(III).

The amino group of both BisAA and TrisAA are readily protonated; therefore, the relatively high *E*% values were due to formation of an ion pair with the metal complex anions, except in the case of Ni(II). Ni(II) is not present as complex anions even in highly concentrated HCl solutions.^[12] Extraction of Rh(III) may have been affected by other factors, such as outer-sphere coordination^[12] (e.g., interaction between the amide groups and the outer-sphere of the Rh chloro complex), as suggested by the fact that the *E*% values obtained here were much higher than those obtained with tri-*n*-octylamine.^[9,10]

Because all the metal ions except Ni(II) were present in the organic phase after the extraction from HCl solution, scrubbing and back extraction were used to selectively retrieve Rh(III) prior to Pd(II) and Pt(IV), as described in the next section.

Scrubbing with distilled water

The base metal ions in the metal-containing organic solutions were removed by scrubbing with distilled water. In both extractant systems, all the PGM ions remained in the organic solution after scrubbing. In the BisAA system, 80–90% of the Fe(III) and Cu(II) were transferred into the aqueous phase. In contrast, in the TrisAA system, less than half of the Fe(III) and Cu(II) were scrubbed.

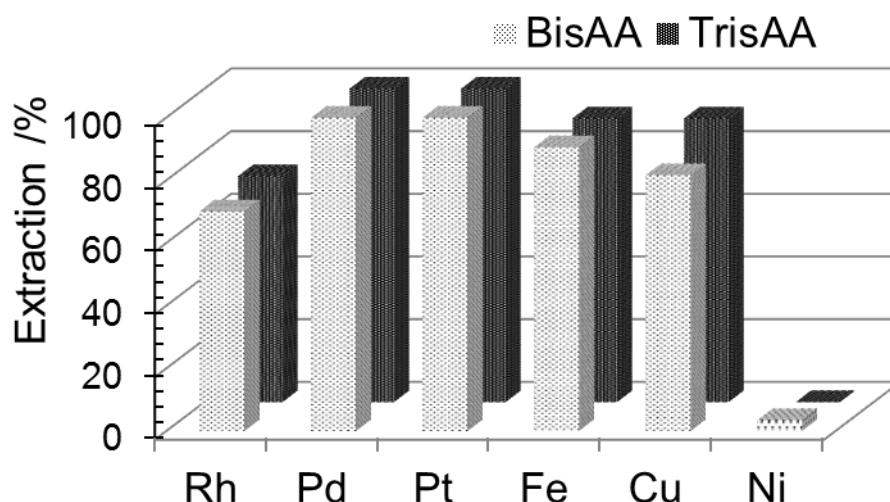


Fig.2 E% of metal ions: (organic phase) 0.5 M BisAA or TrisAA in 80 vol% *n*-dodecane—20 vol% 2-ethylhexanol; (aqueous phase) 2 M HCl at the equilibrium; (metal concentration) 2 g/L each.

Selective back extraction of Rh(III) with 10 M HCl

In both the BisAA system and the TrisAA system, most of the Rh(III) (~70%) was back-extracted with 10 M HCl. None of the Pd(II), Pt(IV), Fe(III), or Cu(II) were back-extracted from BisAA. This means that with the BisAA system, Rh(III) could be selectively recovered even before the scrubbing of the base metal ions. In contrast, a small amount of Cu(II) was back-extracted from TrisAA, in spite of the poor efficiency of Cu(II) scrubbing with distilled water. Hence, the selectivity for Rh(III) in the TrisAA system was inferior to that in the BisAA system.

Back extraction of Pd(II) and Pt(IV)

All the Pd(II) and Pt(IV) extracted with BisAA or TrisAA remained in the organic solution after the scrubbing with distilled water and shaking with 10 M HCl. These metals were simultaneously back-extracted into 10 M HNO₃ (the BE% values of Pd(II) and Pt(IV) were both ~70% for BisAA and ~50% for TrisAA). Most of the Rh(III), Fe(III), and Cu(II) were also back-extracted into the 10 M HNO₃ solution. Pd(II) and Pt(IV) could be selectively back-extracted from the BisAA organic solution after removal of Fe(III), Cu(II), and Rh(III); Pd(II) was selectively back-extracted with 0.1 M thiourea–0.1 M HCl solution and then Pt(IV) was back-extracted with 1 M NaOH.

Conclusions

We investigated the separation of PGMs Rh(III), Pd(II), and Pt(IV) from base metals Fe(III), Cu(II), and Ni(II) in a 2 M HCl solution by means of extraction with BisAA or TrisAA. The following results were observed: all the metal ions except Ni(II) were extracted; Cu(II) and Fe(III) were scrubbed with distilled water; Rh(III) was selectively back-extracted with 10 M HCl; and Pd(II) and Pt(IV) were back-extracted with 10 M HNO₃. For each metal ion, the selectivity of the BisAA system was superior to that of

the TrisAA system. To improve the recovery ratio of the PGM ions, we are currently studying multistage extractions.

Acknowledgement

We thank Ms. Kaeko Takada for technical assistance. This work was financially supported by JSPS KAKENHI Grant Number 23360407.

References

1. Cowley, A. *Platinum 2013 Interim Review*; Johnson Matthey: Hertfordshire, England, 2013.
2. Platinum Today, Johnson Matthey. <http://www.platinum.matthey.com/> (accessed Mar 2014).
3. Barnes, J. E.; Edwards, J. D. Solvent extraction at Inco's Acton precious metal refinery. *Chem. Ind.* **1982**, 6, 151.
4. Benguerel, E.; Demopoulos, G. P.; Harris, G. B. Speciation and separation of rhodium(III) from chloride solutions: a critical review. *Hydrometallurgy* **1996**, 40, 135-152.
5. Cox, M. Solvent extraction in hydrometallurgy. In *Principles and Practices of Solvent Extraction*; Rydberg, J., Cox, M., Musikas, C., Choppin, G. R., Eds.; Marcel Dekker, Inc.: New York, 2004, pp. 455-505.
6. Narita, H.; Tanaka, M.; Shiwaku, H.; Okamoto, Y.; Ikeda-Ohno, A.; Yaita, T. Inner-sphere Structure of Rhodium Complexes with Tin(II) Chloride in Concentrated Hydrochloric Acid Solution. *Bull. Chem. Soc., Jpn.* **2013**, 86, 203-209.
7. Edward, R. I.; te Riele, W. A. M. Commercial processes for precious metals. In *Handbook of Solvent Extraction*; Lo, T. C., Baird, M. H. I., Hanson C., Eds.; John Wiley & Sons: New York, 1983; pp. 725-732.
8. Narita, H.; Morisaku, K.; Tanaka M. The first effective extractant for trivalent rhodium in hydrochloric acid solution. *Chem. Commun.* **2008**, 5921-5923.
9. Narita, H.; Tanaka M.; Morisaku, K. Separation reagent of platinum group metal, method for separating and recovering platinum group metal, and amide-containing tertiary amine compound. US Patent 8,609,898, December 17, 2013.
10. Narita, H.; Morisaku, K.; Tanaka M. Extraction of Rhodium with amide-containing tertiary amine compounds —Effect of *N*-substituents on extraction properties—. In *Proceedings of Hydrometallurgy 2014*, in press.
11. Lee, S. L.; Nam, S.-H. Chemical equilibria of nickel chloride in HCl solution at 25°C. *Bull. Korean Chem. Soc.* **2009**, 30, 2203-2207.
12. Bell, K. J.; Westra, A. N.; Warr, R. J.; Chartres, J.; Ellis, R.; Tong, C. C.; Blake, A. J.; Tasker, P. A.; Schröder M. Outer-sphere coordination chemistry: Selective

extraction and transport of the $[\text{PtCl}_6]^{2-}$ anion. *Angew. Chem. Int. Ed.*, **2008**, *47*, 1745-1748.

Modelling the outer-sphere bonding and solvation of chloridometalate extraction

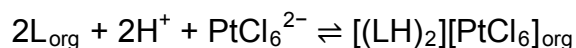
*Kirstian J. MacRuary¹, Innis Carson¹, Richard A. Grant²,
Ross J. Gordon², Jason B. Love¹, Carole A. Morrison^{*1},
Peter A. Tasker^{*1}, A. Matthew Wilson¹*

Summary

Density function theory calculations on a series of aminoamide and etheramide molecules (L) have been used to predict the relative ease of protonation and binding energies to PtCl_6^{2-} and Cl^- of the resulting cationic receptors (LH^+). The calculations predict that the aminoamide extractants $\text{R}_2\text{NCH}_2\text{CH}_2\text{CONHR}$ will be stronger extractants of PtCl_6^{2-} from acidic chloride solutions than the ether analogues $\text{ROCH}_2\text{CH}_2\text{CONHR}$. Solvent extraction experiments show that aminoamide and etheramide reagents are selective for the recovery of PtCl_6^{2-} over Cl^- from 6M HCl.

Introduction

Platinum Group Metals (PGMs) are generally recovered from highly acidic chloride solutions in which the platinum is present as the kinetically inert chloridometalate, PtCl_6^{2-} .^{1,2} Consequently, on the timescale of a conventional solvent extraction process, it is not practicable to use reagents which displace chloride ions to form inner-sphere, organic-soluble Pt-complexes. As such, formation of an outer-sphere complex (ion-pair) to generate a charge-neutral species provides an alternative strategy for Pt-extraction,^{3,4} for example in the pH-dependent equilibrium:



Extraction is favoured by a high proton activity in the feed and can be reversed by raising the pH to deprotonate and recycle the reagent. Tripodal aminoamides of type (Figure 1) have been shown to operate by this mechanism.⁵ The presence of amide substituents which form hydrogen bonds in the outer sphere of the chloridometalate is thought to be responsible for the greater strength of Pt extraction and selectivity over that shown by simple trialkylamine extractants such as the Alamines®.

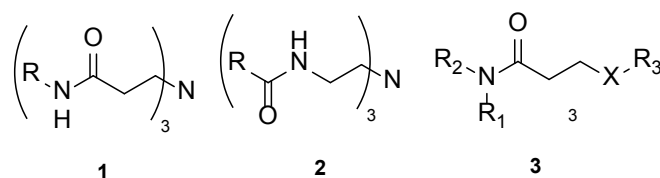


Figure 1: Tripodal aminoamides **1** and **2** which have been used previously as PtCl_6^{2-} extractants³ and the simpler difunctional aminoamides and etheramides **3** discussed in this paper.

This paper uses a combination of computational and experimental methods to investigate the mode of action of extractants of this type and, in particular, the origins of their selectivity for PtCl_6^{2-} over Cl^- .

^{*1} EaStCHEM School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

² Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK

Results and discussion

Four aminoamides and two etheramides were designed (Table 1), with the aminoamide L1 and the etheramide L5 used in solvent extraction experiments. Computational work was undertaken with shorter chain, *n*-butyl analogues, L3, L4 and L6 and with the more conformationally rigid L1, which also afforded crystals of $[(L1H)_2PtCl_6]$ suitable for X-ray structure determination.

L	X	R ₁	R ₂	R ₃
1	N-C ₆ H ₅	C ₆ H ₅	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂
2	N-CH ₃	H	2-ethylhexyl	C ₆ H ₅
3	N-CH ₃	H	<i>n</i> -C ₄ H ₉	C ₆ H ₅
4	N-CH ₃	CH ₃	<i>n</i> -C ₄ H ₉	C ₆ H ₅
5	O	H	2-ethylhexyl	C ₆ H ₅
6	O	H	<i>n</i> -C ₄ H ₉	C ₆ H ₅

Table 1: Reagents discussed in this paper

Calculation of the energy of formation of charge-neutral chloridometalate assemblies, $[(LH)_2PtCl_6]$, or chloride salts, $[(LH)Cl]$, can be broken down into protonation reactions (Eq 1) and complex forming reactions (Eqs 2 and 3).



The dependence of the calculated energies of formation (ΔU_o) of the chloridoplatinate outersphere complexes, $[(LH)_2PtCl_6]$ (Table 2, column 4) on the structures of the reagents L1, L3, L4 and L6 was analysed by considering variations in protonation energies (ΔU_p) to give LH^+ (column 2) and in the binding energies (ΔU_b) of these cations to $PtCl_6^{2-}$ (column 3). In order to make valid comparisons, it is essential that the lowest energy forms of the various entities shown in equations 1-3 are used in the calculations of energies of reactions.

L	ΔU protonation (ΔU_p) (kJ mol ⁻¹)	ΔU binding $\Delta (U_b PtCl_6^{2-})$ (kJ mol ⁻¹)	ΔU overall ($\Delta U_o PtCl_6^{2-}$) (kJ mol ⁻¹)	Relative ΔU_o (kJ mol ⁻¹)
1	-690.36	-773.33	-1463.70	35.31
3	-600.06	-887.51	-1487.57	11.44
4	-653.03	-845.98	-1499.01	0.0
6	-451.11	-953.41	-1404.52	94.49

Table 2: Energy changes involved in formation of $[(LH)_2PtCl_6]$

Some interesting issues arise when identifying the most stable gas-phase structures and considering if similar structures are likely to be the most stable forms in the low-polarity solvents used in solvent extraction experiments. In the first instance, the unprotonated extractants that contain secondary amide groups associate to form dimers; for example, L3 forms the dimer $(L3)_2$ with an energy of dimerization of -60.8

kJ mol^{-1} . In contrast, the tertiary amide extractants L1 and L4 have no amido N-H to form intermolecular H-bonds and show no propensity for dimerization. Protonation of the reagents can give rise to a number of different structures, the relative stabilities of which are dependent on which functional group is protonated and on the propensity to form intramolecular H-bonds. Due to the higher basicity of the amines, the aminoamides (L1, L3 and L4) all have more favourable protonation energies than the etheramide (L6). They also all form the six-membered proton-chelate structure (Table 3, bottom row) similar to that seen previously⁶.

	Protonated structure of amino amide ligand			
Relative ΔU protonation energy (kJ mol^{-1})	L1H ⁺	50.75	117.86	0.0
	L3H ⁺	48.65	117.34	0.0
	L4H ⁺	59.32	112.32	0.0

Table 3: Relative energies of formation of tautomers of the protonated aminoamides L1, L3 and L4

The lowest energy form of the protonated etheramide (L6) has the proton attached to the carbonyl oxygen atom, suggesting that this is more basic than the ether group. However, the tautomers containing a “chelated” proton are significantly more stable, and the preferred site for proton attachment may reflect this.

The most stable forms of the “ion pairs”, LH^+Cl^- , obtained involve a close contact between an amino N-H group and the chloride ion, which is consistent with the latter being a “hard” anion and the N-H unit being a strong hydrogen-bond donor.

L	ΔU protonation (ΔU_p) (kJ mol^{-1})	ΔU binding ($\Delta U_b\text{Cl}^-$) (kJ mol^{-1})	ΔU overall ($\Delta U_o\text{Cl}^-$) (kJ mol^{-1})	ΔU anion exchange (ΔU_{ae}) (kJ mol^{-1})
1	-690.36	-835.08	-1525.46	61.76
3	-600.06	-851.75	-1451.80	-32.77
4	-653.03	-756.01	-1409.03	-89.98
6	-451.11	-908.42	-1359.53	-44.99

Table 4: Energy changes involved in formation of $[2(\text{LH})\text{Cl}]$

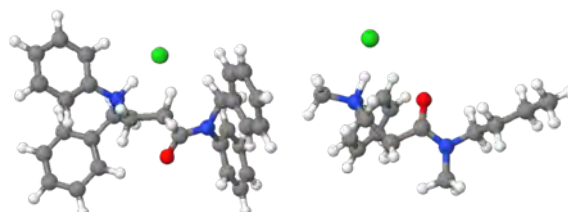


Figure 2: Energy minimized structures of the ion pairs, $\text{LH}\cdot\text{Cl}$, formed by L1 (left) and L4 (right)

For the aminoamides L3 is the most strongly bound to chloride (Table 4, column 3) and uses the amino N-H bond to address the chloride ion, creating a near linear N-H...Cl contact (Figure 2).

Very different modes of interaction are observed for the “softer” hexachloridoplatinate(IV) anions. Conventional strong N-H or O-H hydrogen bond donors

combine with polarized C-H groups to present “multidentate” binding sites for this larger anion. This arrangement is seen in the lowest energy structure of $[(L1H)_2PtCl_6]$ (Figure 3, top left).

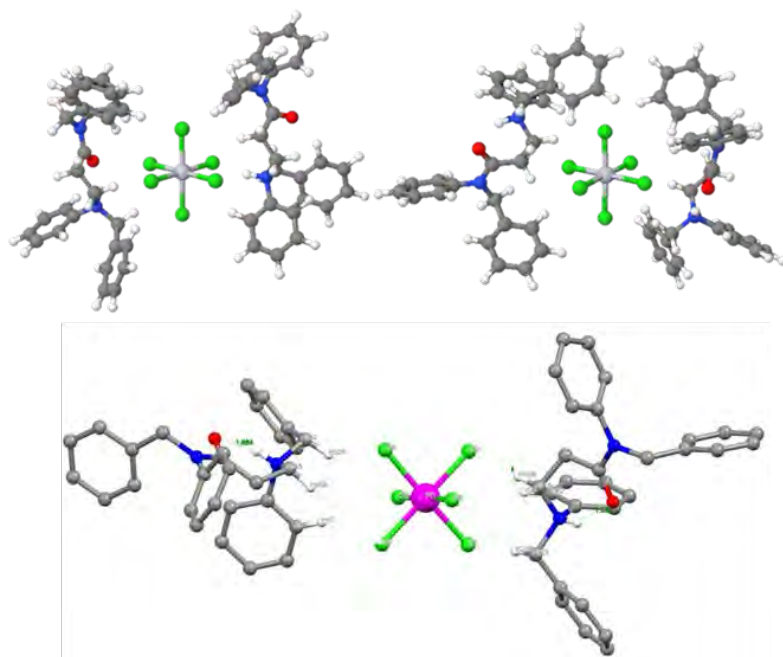


Figure 3: The lowest energy minimized structure for $[(L1H)_2PtCl_6]$ (left) compared with that 23 kJmol^{-1} higher in energy (right) which most resembles the X-ray crystal structure (bottom).

However, this lowest energy structure contrasts with that determined experimentally by X-ray crystallography (Figure 3, bottom) which exhibits a receptor in which a six-membered *pseudo*-chelate is formed by H-bonding to the amide carbonyl group. This feature allows the ligand to align three C-H groups to form hydrogen-bonding interactions with $PtCl_6^{2-}$. The receptor structure is associated with the higher energy form of $[(L1H)_2PtCl_6]$ (Figure 3, top right). There is concern that the minimum energy form of $[(L1H)_2PtCl_6]$ has not yet been identified, leading to $L1H^+$ showing a significantly less favourable calculated binding energy to the chloridometalate (Table 2) and falling out of line of its predicted selectivity over chloride binding (Table 4); work is in currently progress to evaluate this.

Under the highly acidic conditions used for PGM recovery from chloride streams (6M HCl is used in this work) it is assumed that most of the extractant will be in the protonated form, and consequently Pt-loading is dependent on an anion-exchange equilibrium (Equation 4) which results in formation of $[(LH)_2PtCl_6]$. The energies of the related gas-phase anion-exchange reactions (column 5, Table 4) were calculated by subtracting the differences in the energies for the reaction in equation 3 from the energies for the reaction in equation 2.



(4)

We would expect the selectivity values for PtCl_6^{2-} over Cl^- (ΔU_{ae} , Table 4) to be a major factor in predicting the efficiency of Pt loading from 6M HCl solutions in which the chloride ion is present in large excess. The calculated selectivities ΔU_{ae} in Table 4 predict an order of strength $\text{L4} > \text{L6} \geq \text{L3} \gg \text{L1}$. However, the overall formation energies (ΔU_o , Table 2) of the extracted $[(\text{LH})_2\text{PtCl}_6]$ assemblies will also be an influence and these vary in the order $\text{L4} > \text{L3} > \text{L1} > \text{L6}$. While the selectivity factor suggests that the ether-substituted secondary amide L6 will be a slightly stronger Pt-extractant than the amine-substituted secondary amide L3, the order of overall formation energies (ΔU_o , Table 2) indicates that L3 would be much stronger.

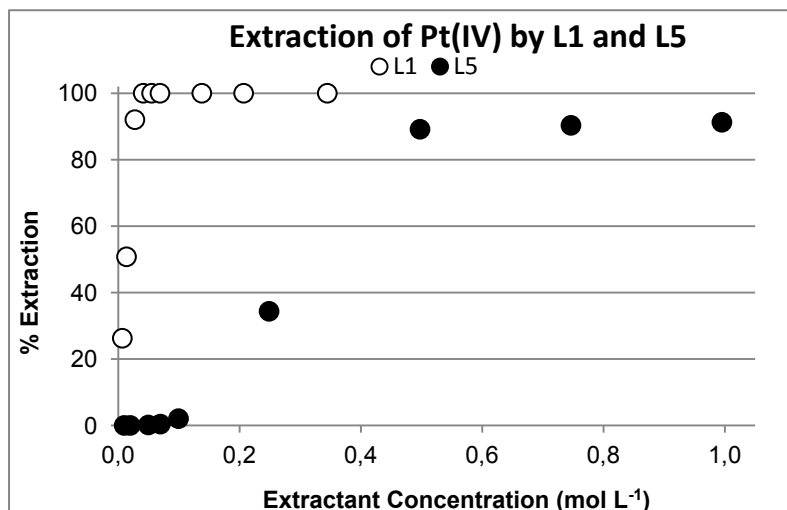


Figure 4: Pt recovery from a solution of H_2PtCl_6 in 6M HCl by solutions of L1 and L5 in toluene as a function of reagent concentration. The % extraction of Pt using L1 is derived from that remaining in aqueous solution after filtration of $[(\text{L1H})_2(\text{PtCl}_6)]$.

The breakdown of the calculated energies for reactions involving L3 and L6 suggests that L1 and L2 should be a much stronger extractants than L5. The similarities of their structures lead to Pt-receptor assemblies with similar anion receptor sites which are templated by formation of the proton-chelated unit. This leads to binding energies of the two LH^+ ligands that are more favourable for the etheramide than the aminoamide (-953 vs -857 kJ mol^{-1}) because the polarities of N-H and C-H are larger in the former (the ether unit is less basic). However, the much larger basicity of the amine unit ensures that the protonation step is more favourable for L3 than L6 (-600 vs 451 kJ mol^{-1}), leading to potentially stronger extraction by the aminoamides.

As predicted by the calculations, solvent extraction experiments using L1 and L5 as receptors show efficient recovery of PtCl_6^{2-} and selectivity over Cl^- from 6 M HCl (Figure 4). However, due to the lack of lipophilic groups on L1, quantitative precipitation of $[(\text{L1H})_2(\text{PtCl}_6)]$ is observed and so a comparison of the strength of aminoamides and etheramides for the extraction of Pt cannot be drawn. Experiments using the more lipophilic aminoamide L2 are ongoing, with the expectation that this will be a stronger extractant than the etheramide L5.

Conclusions

We have shown that gas-phase calculations of energies of formation of host-guest assemblies can be used to predict their relative energies in solvent extraction experiments. As the dependence of the relative energies of formation of $\text{LH}\cdot\text{Cl}$ or $[(\text{LH})_2\text{PtCl}_6]$ on variation of the structure of the reagent involves the same reaction in the aqueous phase, differences in hydration energies of species can be ignored. In the low-polarity solvent used in solvent extraction experiments, the solvation energies of reactants and products in the water-immiscible phase show only a small dependence on the variation of structures of the extractants. A fortunate property of the reagents used in this and related studies is that formation of the proton-chelated structures reduces the tendency for the proton transfer from the aqueous phase to be accompanied by incorporation of water in the assembly found in toluene.

Computational Methods

All calculations were executed using the Gaussian '09 program⁷. Density functional calculations were used with the B3LYP exchange/correlation functional. For all atoms apart from transition metals the 6-31G(d) basis set was applied and the LANL2DZ pseudo potential/basis set for all transition metals. Assembly formation energies and protonation energies are calculated using the difference internal energy values of the sum of the products and the sum of individual reactants.

Experimental procedure

All synthetic and solvent extraction experiments followed procedures similar to those described previously and are detailed in the supplementary electronic material.

Acknowledgements

We thank the EPSRC and Johnson Matthey for funding of the PhD studentships for KJM and AMW.

References

- ¹ J. Reedijk, *Platinum Met. Rev.* (2008), **52**, 2
- ² F. L. Bernardis, R. A. Grant, D. C. Sherrington, *React. Funct. Polym.* (2005) **65**, 205
- ³ A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant, J. B. Love, *Chem. Soc. Rev* (2014) **43**, 123
- ⁴ J. R. Turkington, P. J. Bailey, J. B. Love, A. M. Wilson, P. A. Tasker, *Chem. Comm.* (2013) **49**, 1891
- ⁵ R. J. Ellis, J. Chartres, D. K. Henderson, R. Cabot, P. R. Richardson, F. J. White, M. Schröder, J. R. Turkington, P. A. Tasker, K. C. Sole, *Chem. Eur. J.* (2012) **18**, 7715
- ⁶ J. R. Turkington, V. Cocalia, K. Kendall, C. A. Morrison, P. Richardson, T. Sassi, P. A. Tasker, P. J. Bailey, K. C. Sole, *Inorg. Chem.* (2012) **51**, 12805
- ⁷ M. J. Frisch *et al*, Gaussian Inc., Wallingford CT, 2009

Synergistic extraction of divalent metal ions with *p*-tert-octylphenoxyacetic acid and N-donors

Tatsuya Oshima, Keisuke Kaneizumi, Yoshinari Baba

Department of Applied Chemistry, University of Miyazaki, Miyazaki, Japan

Summary

Alkylated phenoxyacetic acids are attractive for the extraction of metal ions under lower pH condition than aliphatic alkylated carboxylic acid extractants, due to greater acid dissociation constants. Separation factor of metal ions would further increase by certain combination of extractants on the basis of synergistic effect. In the present study, synergistic extraction of divalent metal ions Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with *p*-tert-octylphenoxyacetic acid (ROCH₂COOH) and nitrogen-containing ligands was studied. Pyridine (Py) and *o*-phenanthroline (Phen) were added as synergists. ROCH₂COOH extracts the divalent metal ions under weakly acidic condition through proton exchange reaction, however, the selectivity among the divalent metal ions was small. Addition of Py increased the extraction of Cu(II), Zn(II), and Ni(II), and separation factor for metal ions was also improved. Phen and ROCH₂COOH showed significant synergistic effect for the extraction of metal ions. However, selectivity for metal ions using the mixture of Phen and ROCH₂COOH was small. Synergistic extraction using the mixture of ROCH₂COOH and Py was more effective for the separation of the divalent metal ions.

Introduction

Synergistic effect is defined as cooperation of two extractant molecules to increase the extractability compared with a single extractant. In case of a combination between an acidic extractant and an electron donor for the extraction of metal cation, the acidic extractant complexes with the metal ion and neutralizes charges. While, the electron donor promotes dehydration of the metal ion by replacing a water molecule and occupying a coordination site. [1] To date, a number of synergistic extraction systems has been developed to improve extractability and/or selectivity. [2,3]

Alkylated carboxylic acid extractants are representative acidic extractants for metal cations, as well as organophosphates. Several carboxylic acid extractants such as Versatic 10, naphthenic, 2-bromodecanoic and 3,5-diisopropylsalicylic acids have been developed for the extraction of various metal ions. [4] A commercial tertiary carboxylic acid Versatic 10 has been used for a number of solvent extraction systems. Various synergistic extraction systems using Versatic 10 and other extractants have also been studied. For instance, addition of 4-(5-nonyl)pyridine shows synergistic effect for the extraction of Ni(II) with Versatic 10, thereby improving separation between Ni(II) and Ca(II). [5] Otherwise, an extraction system using LIX 63 and Versatic 10 was effective for the separation of Co(II) and Zn(II) from Mn(II), Mg(II), and Ca(II). [6] On the other hand, the alkylated phenoxyacetic acids are more effective for the extraction of metal ions under lower pH conditions compared with

aliphatic alkylated carboxylic acid extractants, due to greater acid dissociation constants. Extraction of metal ions using sec-nonylphenoxy acetic acid (CA100) was studied. A phenoxyacetic acid extractant 2-(4-nonylphenoxy) acetic acid and its analog 2-[(4-octylphenyl)amino] acetic acid have also been prepared for the separation of In(III), Ga(III), and Zn(II). [7] Jia and coworkers reported synergistic extraction of rare earths using CA100 and o-phenanthroline (Phen). [8] The mixtures of CA100 and Phen showed higher selectivities for the separation of lanthanoids and yttrium compared with single CA100 system. Synergistic extraction of In(III) from chloride medium using mixture of CA100 and trialkyl amine was also studied. [9] Thus the combination between alkylated phenoxyacetic acid and N-donors would be developed for the synergistic extraction system.

In the present study, synergistic extraction of divalent metal ions such as Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with *p*-tert-octylphenoxyacetic acid [*p*-(1,1,3,3-tetramethylbutyl) phenoxyacetic acid] (abbreviated as ROCH₂COOH) and nitrogen-containing ligands was studied. Extraction profiles of metal ions with single ROCH₂COOH system and mixture of ROCH₂COOH and N-donors were compared.

Experimental

Reagents

Analytical grade manganese (II), cobalt(II), nickel(II), copper(II), and zinc(II) chlorides (Wako Pure Chemical Ind. Ltd.) were used for the metal ion solutions. Analytical grade Py (Wako Pure Chemical Industries Ltd.) and Phen (Tokyo Kasei Co.) for the extraction tests were purchased and employed without further purification. Versatic 10, which is a synthetic tertiary carboxylic acid consisting of a mixture of highly branched isomers of C₁₀ monocarboxylic acids, was kindly supplied from Shell Chemicals and used as received. The synthesis scheme for ROCH₂COOH is shown in Figure 1. ROCH₂COOH was prepared by introduction of ethyl acetate to *p*-tert-octylphenol followed by alkaline hydrolysis, according to the literatures [7,10]. All other reagents were of reagent grade and were used as received.

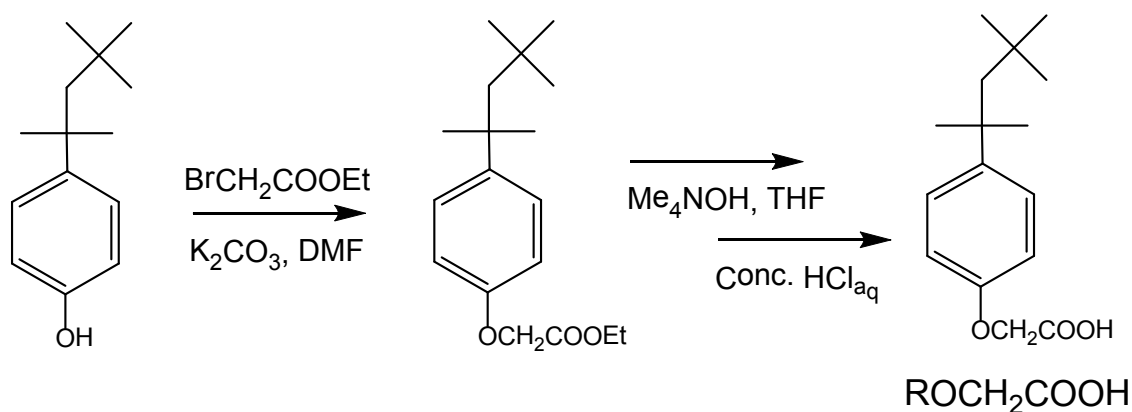


Figure 1 Synthesis scheme for ROCH₂COOH.

Extraction of metal ions using ROCH_2COOH in the absence and presence of *N*-donors

Liquid-liquid extraction tests were conducted by a batchwise method as follows: An aqueous solution was prepared by dissolving 0.10 mM of metal ions Mn(II) , Co(II) , Ni(II) , Cu(II) , or Zn(II) . The pH in the aqueous solution was adjusted using 100 mM HEPES buffer and small amount of HCl or NaOH. An organic solution was prepared by dissolving 12 mM of ROCH_2COOH into chloroform. For synergistic extraction tests, 12 mM of Py or Phn was also added into the organic phase. Equal volumes (5.0 cm^3) of the aqueous and organic solutions were mixed in a stoppered Erlenmeyer flask and shaken (120 rpm) in a thermostated water bath at 30°C . After 24 hours, as the extraction attained an equilibrium state, each phase was separated and the equilibrium pH was measured. The initial and equilibrium concentrations of metal ions in the aqueous phases were determined using a polarized zeeman atomic absorption spectrometer (HITACHI Z-2310). The metal ion concentration in the organic phase was calculated from the mass balance. Extraction percentage of metal ions were calculated according to Equation (1).

$$\text{Extraction}[\%] = \frac{[\text{M}]_{\text{org,eq}}}{[\text{M}]_{\text{aq,ini}}} \times 100 \quad (1)$$

where $[\text{M}]_{\text{aq,ini}}$ represents the initial concentration of metal ions in the aqueous phase. $[\text{M}]_{\text{org,eq}}$ is the total concentration of metal ions in the organic phase after equilibrium, which was calculated from the decrease of metal ions in the aqueous phase after equilibrium.

Results and discussion

Figure 2 shows extraction profiles of Cu(II) using Versatic 10 and ROCH_2COOH as a function of pH. As the extraction metal ions using the acidic extractants proceeds by proton-exchange reaction, the extraction increased with increasing the pH value.

Cu(II) was quantitatively extracted with Versatic 10 at pH around 7. In contrast, Cu(II) was extracted with ROCH_2COOH under lower pH conditions and quantitatively extracted at pH around 6. As ROCH_2COOH have a phenyl group close to the carboxyl groups, the acid dissociation constants must be higher than that of Versatic 10. [7] Therefore, Cu(II) was extracted with ROCH_2COOH by proton-exchange reaction under lower pH condition.

Figure 3 shows extraction profiles of Mn(II) , Co(II) , Ni(II) , Cu(II) , and Zn(II) using ROCH_2COOH as a function of pH. The divalent metal ions were extracted under

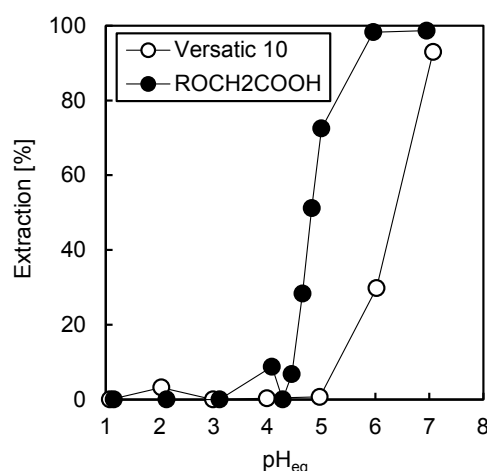


Figure 2 Extraction profiles of Cu(II) using Versatic 10 and ROCH_2COOH : $[\text{Extractant}] = 12 \text{ mM}$; $[\text{Cu(II)}]_{\text{ini}} = 0.1 \text{ mM}$.

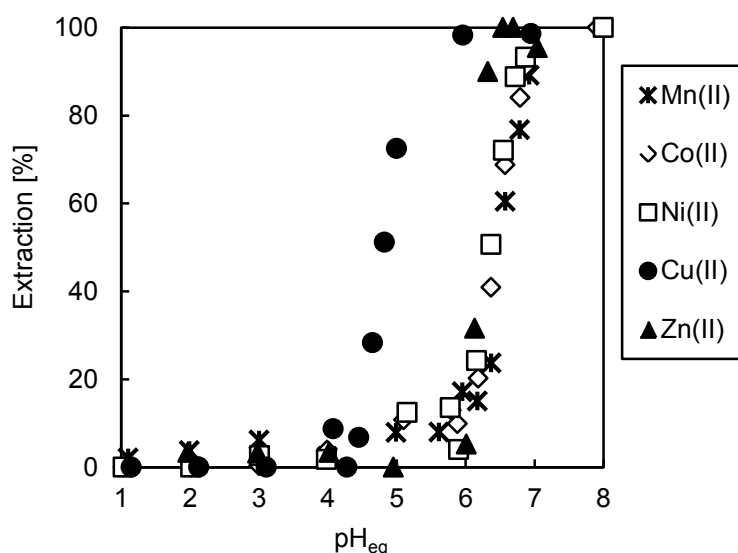


Figure 3 Extraction profiles of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) using ROCH_2COOH as a function of pH: $[\text{ROCH}_2\text{COOH}] = 12 \text{ mM}$; $[\text{metal ion}]_{\text{ini}} = 0.1 \text{ mM}$.

weakly acidic condition. The orders of extraction for metal ions with ROCH_2COOH was $\text{Cu(II)} \gg \text{Zn(II)} > \text{Ni(II)} \approx \text{Co(II)} \approx \text{Mn(II)}$. The order roughly agrees with that of Irving-Williams series. As the extraction profiles for Zn(II), Ni(II), Co(II), and Mn(II) are close to each other, separation of these divalent metals is difficult.

Figure 4 shows extraction profiles of metal ions using ROCH_2COOH in the presence of Py. As shown in Figs. 3 and 4, addition of Py caused enhanced extraction of metal ions under lower pH condition. The pH values for the extraction of Cu(II), Zn(II), and Ni(II) decreased compared with those under synergist free condition. In contrast, the addition of Py was less influential for the extraction of Co(II) and Mn(II). As the results, separation factors among Zn(II), Ni(II), Co(II), and Mn(II) were improved by adding Py.

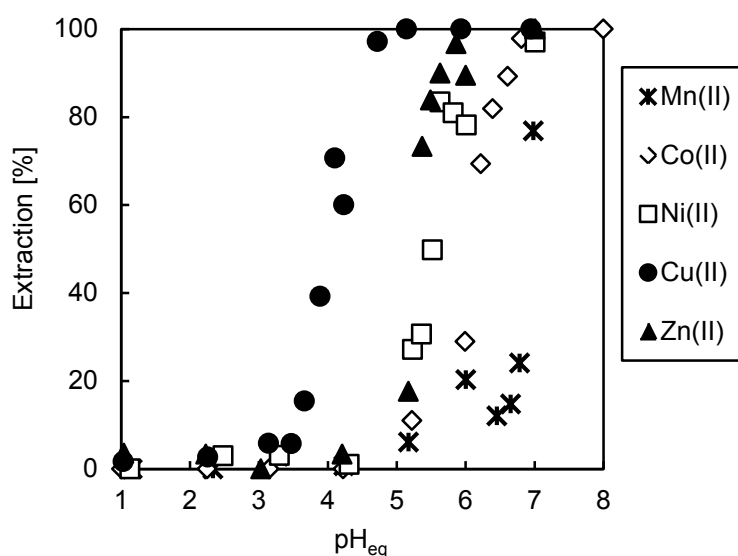


Figure 4 Extraction profiles of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) using ROCH_2COOH and Py as a function of pH: $[\text{ROCH}_2\text{COOH}] = 12 \text{ mM}$; $[\text{Py}] = 12 \text{ mM}$; $[\text{metal ion}]_{\text{ini}} = 0.1 \text{ mM}$.

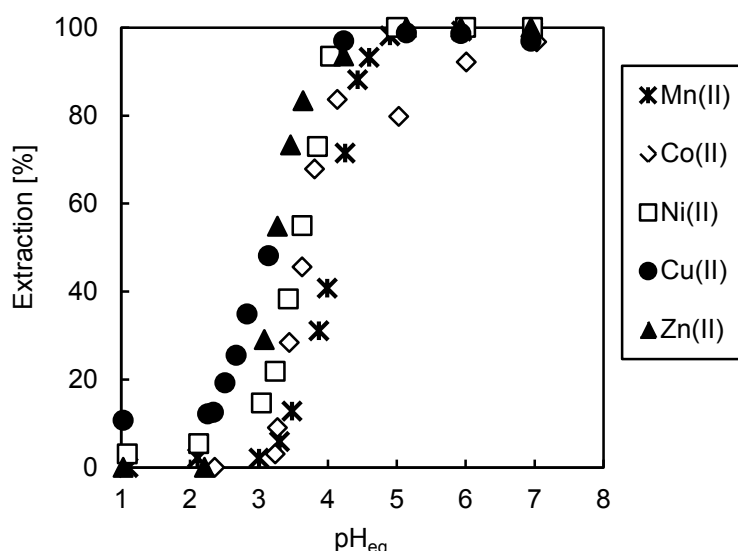


Figure 5 Extraction profiles of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) using ROCH_2COOH and Py as a function of pH: $[\text{ROCH}_2\text{COOH}] = 12 \text{ mM}$; $[\text{Phen}] = 12 \text{ mM}$; $[\text{metal ion}]_{\text{ini}} = 0.1 \text{ mM}$.

Figure 5 shows extraction profiles of metal ions using ROCH_2COOH in the presence of Phen. The extraction of metal ions was drastically improved by adding Phen. All of the divalent metal ions were extracted under lower pH condition compared with synergist free condition. Cu(II), Zn(II), and Ni(II) were quantitatively extracted at pH less than 5 using the mixture of ROCH_2COOH and Phen.

The pH value for 50% extraction of the metal ions (pH_{50}) was determined in order to compare the extractability of the extraction systems with only ROCH_2COOH (N_0 : synergist free) and the mixture of ROCH_2COOH and N-donors. As the extraction precedes proton-exchange reaction, lower pH_{50} value means higher extractability. Table 1 summarizes the pH_{50} values for the extraction of metal ions, as well as the difference of pH_{50} values between synergist free system (N_0) and synergistic extraction system (ΔpH_{50}). Most of the pH_{50} values decreased in the presence of Py and Phen due to the synergistic effect. Addition of a chelating ligand Phen was more effective for the extraction of divalent metal ions under acidic condition. However, the separation factor using the mixture of ROCH_2COOH and Phen was small because the extraction of all metal ions is improved. Addition of Py was less influential for the extraction under acidic condition compared with Phen. However, the selectivity among metal ions was higher.

Table 1 pH_{50} and ΔpH_{50} values for the extraction of metal ions using ROCH_2COOH and N-donors.

Extractant: (ROCH_2COOH)=12 mM)		metal ions				
		Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
N_0 : Synergist free	pH_{50}	6.47	6.41	6.37	4.83	6.18
	ΔpH_{50} (N_0 -Py)	-0.40	0.28	0.90	0.82	1.04
Py 12 mM	pH_{50}	6.87	6.13	5.47	4.01	5.14
	ΔpH_{50} (N_0 -Phen)	2.74	2.94	2.80	1.79	2.93
Phen 12 mM	pH_{50}	3.73	3.47	3.57	3.04	3.25
	ΔpH_{50} (N_0 -Phen)	2.74	2.94	2.80	1.79	2.93

Conclusions

Synergistic extraction of divalent metal ions with an alkylated phenoxyacetic acid ROCH_2COOH and N-donors was studied. In the presence of N-donors Py and Phen, metal ions were extracted under lower pH conditions compared with single ROCH_2COOH system. The system using the mixture of ROCH_2COOH and Phen was more effective for the extraction of all of metal ions under weakly acidic condition. On the other hand, the mixture of ROCH_2COOH and Py was more effective for the separation of the divalent metal ions. Thus the extractability or separation factor for divalent metal ions using alkylated phenoxyacetic acid can be improved by the synergistic effect using N-donors.

References

- Andrade, F. & Elizalde, M. P. (2005) Synergistic Extraction of Ni(II) by Mixtures of LIX 860 and Bis(2-Ethylhexyl) Phosphoric Acid. *Solvent Extraction and Ion Exchange*, 23, pp. 85–99. [1]
- Lumetta, G. J. Gelis, A. V. & Vandegrift, G. F. (2010) Review: Solvent Systems Combining Neutral and Acidic Extractants for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extraction and Ion Exchange*, 28, pp. 287–312. [2]
- Cheng, C. Y. Barnard, K. R. Zhang, W. & Robinson, D. J. (2011) Synergistic Solvent Extraction of Nickel and Cobalt: A Review of Recent Developments. *Solvent Extraction and Ion Exchange*, 29, pp. 719–754. [3]
- Preston, J. S. (1985) Solvent Extraction of Metals by Carboxylic Acids. *Hydrometallurgy*, 14, pp. 171–188. [4].
- Preston, J. S. & Du Preez, A. C. (2000) Separation of Nickel and Calcium by Solvent Extraction Using Mixtures of Carboxylic Acids and Alkylpyridines. *Hydrometallurgy*, 58, pp. 239–250. [5]
- Cheng, C. Y. Zhang, W. & Pranolo Y. (2010) Separation of Cobalt and Zinc from Manganese, Magnesium, and Calcium Using a Synergistic Solvent Extraction System Consisting of Versatic 10 and LIX 63. *Solvent Extraction and Ion Exchange*, 28, pp. 608–624. [6]
- Kai, C. Oshima, T. & Baba Y. (2010) Synthesis of New Extractants Containing a Carboxylic Acid Group and Their Extraction Equilibria with Indium(III), Gallium(III) and Zinc(II). *Solvent Extraction Research and Development, Japan*, 17, pp. 175–185. [7]
- Fan, S., Zhao, X. Song, N. Shi, Y. Jia, Q., & Liao, W. (2010) Studies on the Synergistic Extraction of Rare Earths from Nitrate Medium with Mixtures of Sec-nonylphenoxy Acetic Acid and 1,10-Phenanthroline. *Separation and Purification Technology*, 71, pp. 241–245. [8]
- Fan, S., Jia, Q., Song, N., Su, R., & Liao, W. (2010) Synergistic Extraction Study of Indium from Chloride Medium by Mixtures of Sec-nonylphenoxy Acetic Acid and Trialkyl Amine. *Separation and Purification Technology*, 75, pp. 76–80. [9]
- Ohto, K. Yano, M. Inoue, K. Yamamoto, T. Goto, M. Nakashio, F. Shinkai, S. & Nagasaki, T. (1995) Solvent Extraction of Trivalent Rare Earth Metal Ions with Carboxylate Derivatives of Calixarenes. *Analytical Sciences*, 11, pp. 893–902. [10]

IN-SITU DROPLETS MONITORING IN A LAB-SCALE PULSED COLUMN (poster)

A. Amokrane¹, S. Maaß², H. Roussel¹, F. Lamadie¹, S. Charton¹

¹CEA, DEN, DTEC, SGCS, F-30207, Bagnols-sur-Cèze, France; tel. +33 4 66796186,

²SOPAT GmbH, D-10587, Berlin, Germany, tel. +49 30 314-21134

Liquid-liquid extraction in an industrial apparatus is a complex process involving chemistry, interface dynamics, mass transfer and fluid mechanics. Among these phenomena, transport processes, which are size-dependent, deserve a particular attention.

While large diameter pulsed columns are widely in use in the nuclear fuel treatment industry, allowing concentration profiles and emulsion properties to be controlled by sampling, size-reduction is highly encouraged in the scope of R&D studies. In this aim, small diameter (i.e. 15 mm) columns, operated at flow-rates from 1 to 2 L/h are used.

Because of the small column's holdup, droplets characterization from sampling would be hazardous and external or in-situ techniques must be preferred. Among them, recent experiments showed that direct and in-situ analysis of the drop size distribution can be achieved using a two-dimensional reflectance technique [1]. The probe is 6 mm in diameter and contains the camera and optical lenses. It was introduced in the column through an existing sample port and located tangentially along the column wall, while the light source was positioned externally.

Although the optical field was reduced (packing elements, etc.) nice quality raw images were recorded, allowing efficient automated image analysis [2] and therefrom the derivation of the drop size distribution, concentration, etc. (see Fig. 1).

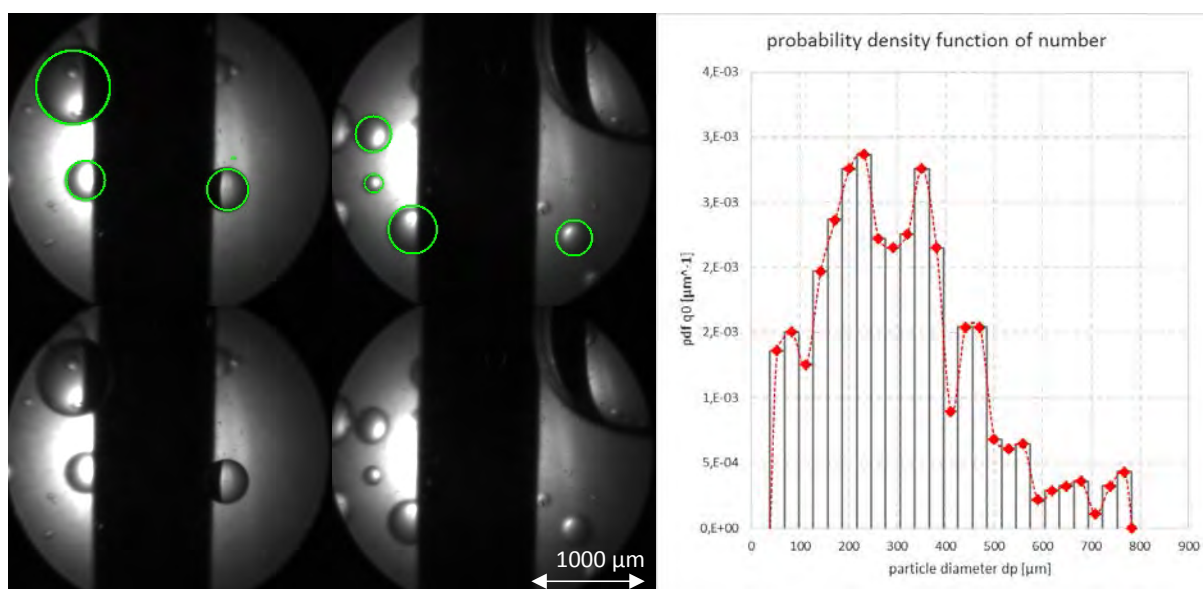


Fig. 1 – raw images and processed images with drop detection results (left), resulting drop size distribution (right)

On-line emulsion monitoring is helpful for models improvement, as well as for control purpose.

[1] Maaß, S., Wollny, S., Voigt, A., Kraume, M., Exp. Fluids (2011) 50:259-269.

[2] Maaß, S., Rojahn, J., Hänsch, R., Kraume, M., Comp. Chem. Eng. (2012) 45:27-37.

Liquid-Liquid Extraction of Scandium with O,O-Bis(2-Ethylhexyl) Hydrogen Thiophosphate

*Kaoru Fujinaga¹, Yasushi Nakajima², Syunichi Oshima¹, Yujiro Watanabe¹,
Shigekazu Tsurubou³, Junji Noro⁴, Yu Komatsu¹*

¹ College of Bioscience and Chemistry, Kanazawa Institute of Technology, Japan

² Daiichi Kigenso Kagaku Kogyo Co., Ltd.

³ Department of Chemistry, School of Dentistry, Asahi University, Japan

⁴ Nissan Arc. Ltd., Japan

Summary

The previous paper reported for the first time that oxidized di(2-ethylhexyl)dithiophosphate (Phoslex DT-8[®], I in Figure 1) could extract Sc(III) selectively and that Sc(III) was successfully stripped with 3M HCl from the loaded organic phase with excellent recovery percentage (R%). In this study, the extractability of O,O-bis(2-ethylhexyl) hydrogen thiophosphate, which is the active species for Sc(III) extraction formed in Phoslex DT-8 by air-oxidation, was examined with Sc(III), ZrO(II), Ti(IV) and Y(III).

INTRODUCTION

Recently, global demand for scandium (Sc) has greatly increased, since an excellent electrode material containing Sc was developed for solid oxide fuel cells. Sc is mainly obtained as a by-product by recovery from waste water in the refining of the other metals, because no ores containing Sc exist on Earth [1,2]. In the Zr mining, the waste solution containing Sc(III) and ZrO(II) is constantly produced but the recovery of Sc(III) from this waste solution has never attempted yet since it is difficult to separate Sc(III) from ZrO(II) due their similarity in chemical properties. In this study, we report for the first time a recovery method for Sc from waste solution by the liquid-liquid extraction separation. Many studies report the extraction of Sc(III) and the selectivity from other metals with a variety of chelate extractants[3-8]. Sc(III) is a hard acid and is therefore easily extracted from aqueous solution with conventional hard base extractants such as alkyl phosphorous compounds. However, most of these extractants combine with Sc(III) so strongly that it becomes bound to the organic phase and can't be effectively stripped by acid. We previously reported that oxidized di(2-ethylhexyl)dithiophosphate (Phoslex DT-8[®], I in Figure 1) by long term preservation could extract Sc(III) selectively and successfully separate Sc(III) from ZrO(II) [9]. It was confirmed that the active species produced by air exposure of Phoslex DT-8[®] was O,O-bis(2-ethylhexyl) hydrogen thiophosphate (Abbreviate as BOHTP, II in Figure 1) by utilizing ³¹P NMR-spectroscopy and mass spectrometry [10]. Pure BOHTP was synthesized separately and was examined with the extraction ability and selectivity for Sc(III) in this study.

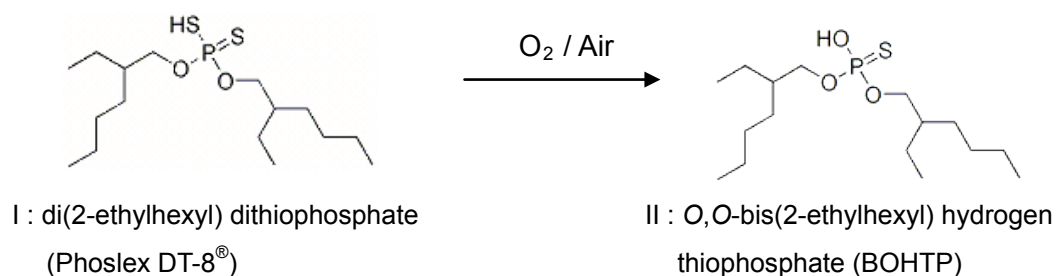


Figure 1. Conversion of Phoslex DT-8[®] to BOHTP by air oxidation.

METHODOLOGY

Reagents

BOHTP was synthesized by Daihachi Chemical Industry Co., Ltd. using the same method as previously reported [10] and was used without further purification. All other reagents were of analytical reagent grade and were used as received.

Extraction procedure

In this study, n-hexane was used as the diluent for BOHTP. Metal extraction was carried out by the usual batch method at 25°C ± 1 °C in the same manner as the previous study [9].

RESULTS AND DISCUSSION

Extraction separation of Sc(III) from ZrO(II)

BOHTP/n-hexane solution extracted Sc(III) with a percent extraction (E%) of 99±1.5% but not ZrO(II) (E%=0.17±0.33%), in the pH range of 2.08-4.57. Figure 2-A clearly shows that not only the separation between Sc(III) and ZrO(II) could be achieved successfully but also the Sc(III) could be readily back-extracted using 3 M HCl (R%=90±3.3%). Here, stripping percent (R%) of Sc(III) from the loaded phase was obtained by the following equation,

$$R\% = \frac{[M]_{aq} + [M]_o}{[M]_{init}} \times 100 \dots (1)$$

where [M]_o is the metal ion concentration in the organic phase, [M]_{aq} that in the aqueous phase and [M]_{init} is the initial concentration of metal ion. Since Sc(III) is a strong hard acid, it binds strongly to many hard base extractants such as Cyanex 272 and PC88A. Consequently it is very difficultly stripped Sc(III) from the organic phase with acids in many conventional extraction systems [3]. Cyanex 302 is the conventional dialkylmonothio-phosphinic acid and has the same O,S-ligand as to BOHTP, so that its extraction behavior for Sc(III) and ZrO(II) was examined to evaluate the extraction performance of BOHTP. As shown in Figure 2-B, the extractability of Cyanex 302 for Sc(III) and ZrO(II) looked almost similar to that of BOHTP, but Cyanex 302 gave comparatively low R% for Sc(III), 41±11% in the pH range of 1.19-4.94, compared to BOHP. In order to clarify the difference in R% value between two extractants, the extraction of Sc(III) with these two extractants were examined in the HCl concentration of 0.5-6.0 M (Figure 3).

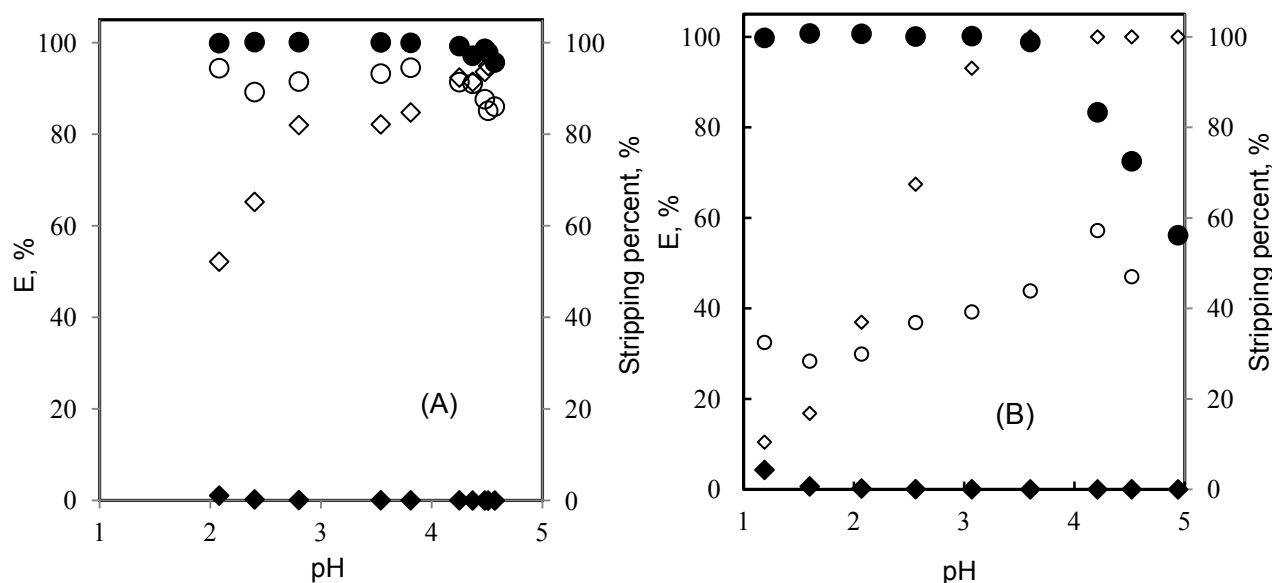


Figure 2. Effect of pH on the extraction of Sc(III) and ZrO(II).

(A): $[\text{BOHTP}]_{(O)} = 0.1 \text{ M}$ in n-hexane, (B): $[\text{Cyanex 302}]_{(O)} = 0.1 \text{ M}$ in n-hexane.

$[\text{Sc(III)}] = [\text{ZrO(II)}] = 1 \text{ mM}$, $[\text{tripotassium citrate}]_{(aq)} = 0.01 \text{ M}$. $\bullet, \circ$: Sc(III), $\blacklozenge, \diamond$: ZrO(II). Closed symbols are E% and open symbols are R%.

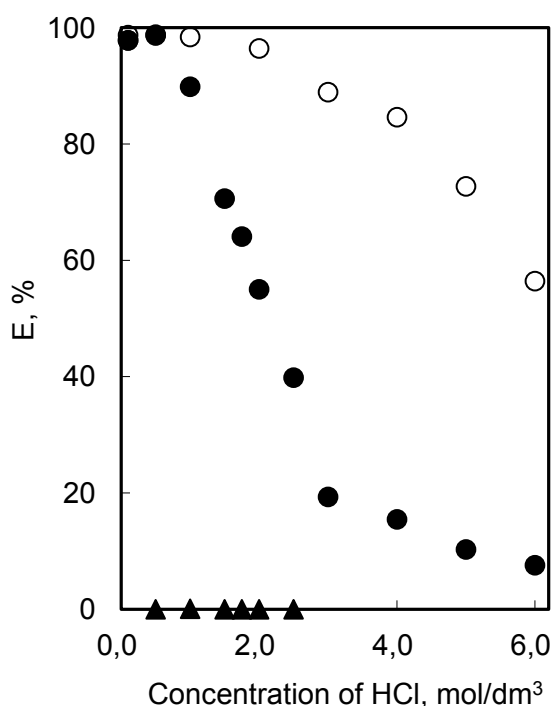


Figure 3. Effect of H^+ ion concentration on the extraction of Sc(III) and Y(III).

$[\text{BOHTP}]_{(O)} = [\text{Cyanex 302}]_{(O)} = 0.1 \text{ M}$ in n-hexane, $[\text{Sc(III)}] = [\text{Y(III)}] = 1 \text{ mM}$,

$\bullet, \circ$: Sc(III), $\blacktriangle$: Y(III). Closed symbols are BOHTP and open symbols are Cyanex 302..

The E% of Sc(III) obtained with BOHTP was 19% at 3 M HCl and 7% at 6 M HCl, while those with Cyanex 302 were 89% at 3 M HCl and 56% at 6 M HCl respectively. That is, weaker affinity of BOHTP for Sc(III) than that of Cyanex 302 brings about the better stripping of Sc(III) when extracted by BOHTP.

Incidentally, the plots of Sc(III) obtained with BOHTP in Figure 3 produce a straight line of $y = 2.89X + 0.71$ by converting into the relationship of $\log D$ vs. $-\log[\text{HCl}]$, suggesting that Sc(III) was extracted in the form of a 1:3 complex with BOHTP.

Elimination of influence of Ti(IV) and Y(III) on the Sc(III) extraction

Ti(IV) and Y(III) are major constituents in Zr waste water and therefore their extraction behavior was examined

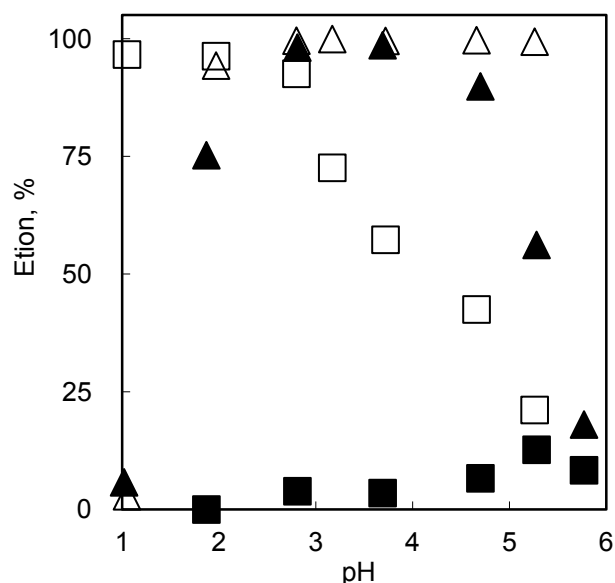


Figure 4. Effect of pH on the extraction of Ti(IV) and Y(III).

[Ti(IV)]=[Y(III)]=1 mM, [BOHTP]_(O)=0.1 M in n-hexane.

□, ■: Ti(IV), △, ▲ : Y(III). Closed symbols are obtained with [tripotassium citrate]_(aq)=0.1 M and open symbols are that with [tripotassium citrate]_(aq)=0.01M.

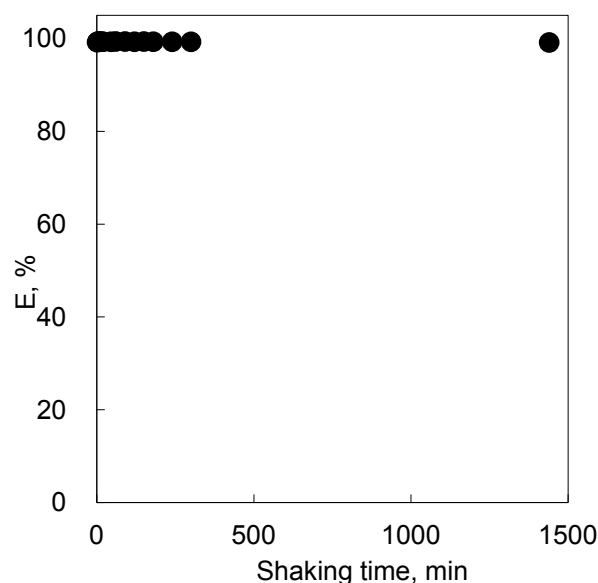


Figure 5. Effect of shaking time on the extraction of Sc(III).

[Sc(III)]=1 mM, [BOHTP]_(O)=0.1 M, [tripotassium citrate]_(aq)=0.1 M, pH: 4.09±0.02.

in order to separate Sc(III) from these species. As for Ti(IV), when 0.01 M tripotassium citrate was used as a masking reagent, Ti(IV) was easily extracted (Figure 4). By increasing the concentration of tripotassium citrate to 0.1 M, the E% of Ti(IV) was sufficiently depressed to $5.8 \pm 4.4\%$ in the pH range of 1.87-5.77 and the separation of Sc(III) from Ti(IV) was successfully achieved by a single batch extraction.

While, Y(III) was extracted with high E% value of $98.9 \pm 1.9\%$ in the pH range of 1.97-5.26 when the concentration of tripotassium citrate was 0.01 M. This extraction could not be masked effectively by increasing the concentration of tripotassium citrate to 0.1 M. In the oxidized Phoslex DT-8 extraction system, Y(III) was hardly extracted (E% was less than 17% in the pH range of 1.00-4.63) under the same conditions [9] and two results are disagree. The discrepancy may be ascribed to the difference in the purity of O,O-bis(2-ethylhexyl) hydrogen thiophosphate in oxidized Phoslex DT-8 and reagent BOHTP. In the oxidized Phoslex DT-8, O,O-bis(2-ethylhexyl) hydrogen thiophosphate was formed by 450 hours air oxidation of di(2-ethylhexyl)dithiophosphate (Figure 1) and the concentration of O,O-bis(2-ethylhexyl) hydrogen thiophosphate in 0.1 M oxidized Phoslex DT-8 n-hexane solution was estimated to be 0.016 M by ^{31}P -NMR [10]. That is, it is difficult to separate Sc(III) from Y(III) by a single batch extraction in this system, however, E% of Y(III) rapidly decreased to at lower than pH 1.87 irrespective of the concentration of

tripotassium citrate and then the extraction of Y(III) was carried out in the HCl concentration range of 0.50-2.5 M (Figure 3). As can be seen in Figure 3, E% of Y(III) was 0 in the entire range of HCl concentration, so that it can be expected that interference of Y(III) on the recovery of Sc could be avoided successfully by rinsing the loaded organic phase with dilute acid before back-extraction of Sc(III) ion with 3 M HCl.

Effect of shaking time

The effect of shaking time on the Sc(III) extraction was examined (Figure 5). In the oxidized Phoslex DT-8 extraction system, it took 5 min at pH 1.5 and 30 min at pH 3.0 to attain 95% extraction [9], respectively, however BOHTP could extract Sc(III) perfectly within a minute at pH 4.09. This difference may be attributed to the difference of the concentration of O,O-bis(2-ethylhexyl) hydrogen thiophosphate in between oxidized Phoslex DT-8 and reagent BOHTP extraction systems.

CONCLUSION

The extraction behavior of BOHTP for Sc(III) and ZrO(II) was almost similar to that of oxidized Phoslex DT-8[®] reported previously. It was confirmed that BOHTP is the active species having a selective extractability for Sc(III). By using pure BOHTP, the Sc(III) extraction proceeded rapidly and equilibrium was accomplished within 1 minute at pH 4.09. Therefore, the BOHTP extraction system is applicable to the multistep extraction methods such as the countercurrent extractor.

References

- [1] N. Iyatomi and M. Nanjo, Intelligent metallurgy of rare metals, Scandium, Bulletin of the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, 45, 66-76 (1989).
- [2] W. Wang, Y. Pranolo and C.Y. Cheng, Metallurgical processes for scandium recovery from various resources: A review, Hydrometallurgy, 48, 301–312 (2011).
- [3] W. Wang and C.Y. Cheng, Separation and purification of scandium by solvent extraction and related technologies: a review, Journal of Chemical Technology and Biotechnology, 86, 1237–1246 (2011).
- [4] D. Li and C. Wang, Solvent extraction of scandium(III) by Cyanex 923 and Cyanex 925. Hydrometallurgy, 48, 301–312 (1998).
- [5] R. K. Singh and P. M. Dhadke, Extraction and separation studies of scandium(III) from perchlorate media by D2EHPA and PC-88A, Bulletin of the Chemists and Technologists of Macedonia, 22, 1–11 (2003).
- [6] C. Wang, Solvent extraction of Sc(III), Zr(IV), Th(IV), Fe(III), and Lu(III) with thiosubstituted organophosphinic acid extractants, Solvent Extr. Ion Exch., 13, 503-522 (1995).

- [7] M. Karve and B. Vaide, Selective separation of scandium(III) and yttrium(III) from other rare earth elements using Cyanex302 as an extractant, *Sep. Sci. Technol.*, 43, 1111-1123 (2008).
- [8] D. Wu, C. Nju, D. Li and Y. Bai, Solvent extraction of scandium(III), yttrium(III), lanthanum(III) and gadolinium(III) using Cyanex 302 in heptane from hydrochloric acid solutions, *J. Alloys Compd*, 374, 442-446 (2004).
- [9] K. Fujinaga, M. Yoshimori, Y. Nakajima, S. Oshima, Y. Watanabe, G. W. Stevens and Y. Komatsu, Separation of Sc(III) from ZrO(II) by solvent extraction using oxidized Phoslex DT-8, *Hydrometallurgy*, 133, 33-36 (2013).
- [10] D. Abe, S. Kado, K. Tamura, H. Seki, K. Fujinaga and H. Masu Identification of the Active Species for Scandium Extraction by Phoslex DT-8, *Solvent Extr. Res. Dev., Jpn.*, 21, 65-70 (2014).

Corresponding author: College of Bioscience and Chemistry, Kanazawa Institute of Technology, Japan, 3-1 Yatsukaho, Hakusan, Ishikawa, 924-0838 Japan. Phone: +81-76-274-8267. FAX: +81-76-274-9251. Email: fujinaga@neptune.kanazawa-it.ac.jp

Ammonium and phosphonium ionic liquids as extractants for metal ions from aqueous solutions

*Irene García-Díaz¹, Francisco Jose Alguacil¹, Felix A. López¹,
Magdalena Regel-Rosocka^{*2}, Maciej Wiśniewski²*

Summary

The behavior of several ionic liquids (ILs) in the extraction of Cr(III) from alkaline aqueous solution, Cr(VI), Zn(II) and Co(II) from HCl solutions was studied. Ammonium ILs were generated using the reaction of the primary amines Primene JMT (PJMT) and Primene 81R (P81R) and the tertiary amine Hostarex A324 (HA324), as cationic precursors, with HCl, HNO₃ and H₂SO₄ solutions, thus, using these mineral acids as anionic precursors for the respective ILs. Phosphonium ILs (Cyphos IL 101, Cyphos IL 104) and a mixture of Cyphos IL 101 with Cyanex 272 were used as extractants for Zn(II) and Co(II).

The cationic and anionic moieties of the ILs affect the metal extractability, and though some of these ILs showed excellent extraction properties for the above metals with quantitative yields (i.e. Zn(II) with phosphonium ILs), others are considered unsuccessful for this task, with yields less than 50% (i.e. Cr(III), Zn(II), Co(II) with primary amine based ILs).

Introduction

Several technologies can be used to remove/separate and/or concentrate such toxic and valuable metals as chromium, cobalt, nickel, copper, zinc, cadmium, mercury, lead or gold from liquid effluents. In these techniques are included precipitation, ion exchange, solvent extraction, electrochemical removal, etc. [1, 2]. Solvent or liquid-liquid extraction is widely used in the recovery and separation of metals from aqueous solutions [3-5], even at industrial scale (i.e. copper).

Ionic liquids (ILs) exhibit unique and attractive properties that made of these compounds an alternative to the classical organic solvents. The main advantage of ILs is their negligible vapor pressure, which results in lower emissions and, consequently, in a reduced exposure, their good chemical and thermal stabilities, being therefore considered as environmental benign solvents as compared to classical VOCs.

Recently the ionic liquids have attracted considerable attention for metal extraction from aqueous solutions. Application of ILs can be divided into some specific systems where ILs replace typical solvents, ILs are used as new extractants, ILs form pure extracting phase or they can be additives to traditional systems [6].

The present research aims in studies on the behavior of several ILs as extractants in the extraction of Cr(VI), Zn(II) and Co(II) from acid aqueous solutions and Cr(III) from alkaline aqueous solutions.

¹ Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

^{*2} e-mail: magdalena.regel-rosocka@put.poznan.pl, Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

Experimental

Reagents

The ionic liquids were generated using as the cationic precursor three commercial amines, Primene JMT (PJMT) and Primene 81R (P81R) (primary aliphatic amines with carbon chains C₁₆₋₂₂ and C₁₂₋₁₄, respectively) and Hostarex A324 (HA324) (tertiary aliphatic amine, C₈ with isopropyl group), whereas the counter anions were provided by the mineral acids HCl, H₂SO₄ and HNO₃. Exxsol D100 (aliphatic) and Solvesso 120 (aromatic) diluents were received from Exxon Chem. Iberia.

Phosphonium ILs (trihexyltetradecylphosphonium chloride, Cyphos IL 101 and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate, Cyphos IL 104) and well known acidic extractant Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) were supplied by Cytec Industries Inc., USA, and were used as extractants for Zn(II) and Co(II) from chloride solutions. Toluene (POCh, Poland) was applied as a diluent for the phosphonium IL organic phase preparation.

Methods

Extraction was carried out in a typical way: equimolar aqueous feeds, containing metal ions in aqueous media were mechanically shaken with IL phase (volume ratio w/o = 1) for 15-30 minutes at 20°C in glass separatory funnels and then allowed to stand for phase separation.

Samples of the equilibrated aqueous phases were taken and analyzed for metal concentration by standard AAS (Perkin Elmer 1100B or Hitachi Z-8200 spectrometer). The efficiency of the extraction process was evaluated by the extraction percentage (%E), which was calculated using the following equation:

$$\%E = \frac{[M]_{0,aq} - [M]_{t,aq}}{[M]_{0,aq}} \cdot 100 \quad (1)$$

where [M]_{0,aq} and [M]_{t,aq} are the metal concentrations in the initial aqueous and equilibrated aqueous solutions, respectively.

Results and discussion

Generation of the ammonium ionic liquids

A basic nitrogen atom of each amine studied reacts with the inorganic acids (1 or 2 M HCl, HNO₃ and H₂SO₄) to yield the ionic liquids in the form of quaternary ammonium salts. As a result of these series of experiments the following ionic liquids were obtained: PJMTH⁺Cl⁻, PJMTH⁺NO₃⁻, PJMTH⁺HSO₄⁻, P81RH⁺Cl⁻, P81RH⁺NO₃⁻, HA324H⁺Cl⁻, HA324H⁺NO₃⁻, (HA324H⁺)₂SO₄²⁻.

Generation of the primary amines based ILs involves the following equilibrium:





In the case of the ionic liquids generated in the reaction between the tertiary amine and the minerals acids, other equilibria must be considered:



In all the equations, X^- represents Cl^- and NO_3^- anions, org and aq state for the respective equilibrated organic and aqueous phases.

Solvent extraction experiments

The amine organic phase was prepared by dissolving the appropriate concentration of the amine (10% v/v or their molar equivalent) in a mixture of 5% v/v n-decanol (modifier) and Exxsol D100 (diluent). The phosphonium ILs were dissolved in toluene to obtain 0.2 or 0.4 M solutions of the organic phases. Additionally, mixtures of Cyphos IL 101 with Cyanex 272 were also used as extractants for metal ions. Cyanex 272 was mixed with Cyphos IL 101, assuming formation of a new IL in the organic phase containing phosphonium cation coming from IL 101 and bis(2,4,4-trimethylpentyl)phosphinate anion originating from Cyanex 272. Extraction with such mixtures was compared to Cyphos IL 104 organic phase.

The percentage of metal extraction (%E) by the ammonium ILs generated in this work and phosphonium ILs is given in Tables 1 and 2.

Table 1. Percentage extraction of Cr(III), Cr(VI), Zn(II) and Co(II) with ammonium ILs generated in this work (initial concentrations of: Cr(III) 0.1 g/dm³ in 0.1 M NaOH; Cr(VI) 0.1 g/dm³ in 0.1 M HCl; Zn(II) 0.1 g/dm³ in 2 M HCl; 0.1 g/dm³ in 6 M HCl).

Ionic liquid	%E _{Cr(III)}	%E _{Cr(VI)}	%E _{Zn(II)}	%E _{Co(II)}
PJMT ⁺ H ⁺ Cl ⁻ (0.24 M)	52.7	87.8	6.9	1.7
PJMT ⁺ H ⁺ NO ₃ ⁻ (0.24 M)	59.4	68.2	4.5	1.1
PJMT ⁺ H ⁺ HSO ₄ ⁻ (0.24 M)	82.1	91.3	19.3	2.8
P81RH ⁺ H ⁺ Cl ⁻ (0.36 M)	18.3	84.9	19.4	23.7
P81RH ⁺ H ⁺ NO ₃ ⁻ (0.36 M)	15.0	84.2	29.6	0.9
HA324H ⁺ H ⁺ Cl ⁻ (0.24 M)	Quantitative	95.6	99.4	57.3
HA324H ⁺ H ⁺ NO ₃ ⁻ (0.24 M)	0	81.2	86.2	19.1
((HA324H ⁺) ₂ SO ₄ ²⁻) (0.12 M)	5.7	86.6	91.3	82.5

Cr(III) extraction from alkaline solutions, Table 1, is the best with the IL generated by the tertiary amine and hydrochloric acid (HA324H⁺Cl⁻), whereas extraction efficiency is the worst when the same tertiary amine and sulphuric acid are the precursors of the IL ((HA324H⁺)₂SO₄²⁻). When using the primary amines as precursors of the ILs, better extraction results are always obtained when Primene JMT is compared with

Primene 81R, and with respect to the anionic moiety of the IL, following the approximate sequence $\text{HSO}_4^- > \text{NO}_3^- = \text{Cl}^-$ for Primene JMT and $\text{Cl}^- = \text{NO}_3^-$ for Primene 81R.

Good extraction yields of Cr(VI) (higher than 80%, Table 1) are obtained for all the ionic liquids investigated but $\text{PJMTH}^+\text{NO}_3^-$. Generally, all these ILs generated from the primary and tertiary amines and aqueous solutions of HCl, HNO_3 and H_2SO_4 are acceptable extractants for chromium(VI) from a diluted hydrochloric acid medium.

Table 2. Percentage extraction of Zn(II) and Co(II) with phosphonium ILs and mixtures of Cyphos IL 101 and Cyanex 272 (extractant) (initial concentration of metal ions: 5 g/dm^3 in 0.58 M HCl).

Ionic liquid/extractant	%E _{Zn(II)}	%E _{Co(II)}
IL 101 (0.2 M)	Quantitative	83.0
IL 104 (0.2 M)	Quantitative	70.0
Cyanex 272 (0.2 M)	Quantitative	14.4
IL 101/Cyanex 272 (0.2/0.05 M)	Quantitative	70.3
IL 101/Cyanex 272 (0.2/0.1 M)	Quantitative	70.7
IL 101/Cyanex 272 (0.2/0.2 M)	Quantitative	76.9
IL 101/Cyanex 272 (0.2/0.3 M)	Quantitative	68.8

The ionic liquids generated from the tertiary amine are the best extractants for Zn(II) from medium acidic HCl aqueous solution. They do not show great variations in percentage extraction of Zn(II) when the three anionic moieties of the ammonium ILs are compared (Table 1). When the ILs generated from the primary amines Primene JMT and Primene 81R and the various aqueous acid solutions are used, the extraction yields do not exceed 30%, thus, precluding use of these organic compounds as extractants for zinc from moderate HCl medium.

Both phosphonium ILs (IL 101 and 104) and mixtures of IL 101 with Cyanex 272 quantitatively extract Zn(II), and their effectiveness can be compared to the tertiary amine based ILs shown in Table 1. At the HCl concentration studied, even Cyanex 272 extracts almost 100% Zn(II).

Finally, cobalt(II) is effectively extracted only by $(\text{HA324H}^+)_2\text{SO}_4^{2-}$ IL (yield exceeding 80%), and only moderately extracted (57% extraction) by $\text{HA324H}^+\text{Cl}^-$. The extraction yield with other ammonium ILs is in the range from 1 to 24%. Thus, indicating the lack of usefulness of these ILs as extractants for Co(II) from highly acidic medium, or in other words, non-extractability of CoCl_4^{2-} complex by primary amine based ionic liquids. Phosphonium ILs extract Co(II) less effectively compared with Zn(II) (Table 2). The presence of Cyanex 272 in the organic mixtures of IL 101 and Cyanex 272 does not affect Co(II) extraction, so it cannot be unambiguously indicated that a new IL, corresponding to IL 104, is formed. Both phosphonium ILs show good extraction efficiency, i.e. near 70-80% of Co(II) is transported to the organic phase. Moreover,

extraction yield with the mixtures of IL 101 and Cyanex 272 is near 70%, whereas 0.2 M Cyanex 272 extracts only 14% Co(II) from HCl solution.

Conclusions

The various ammonium and phosphonium ionic liquids are being tested as potential extractants for Cr(III), Cr(VI), Zn(II) and Co(II) present in different aqueous environments. With few exceptions, the ILs generated from the tertiary amine are the best extractants of the metal ions studied from their respective aqueous solutions. However, the ILs generated from the reaction of the primary amines and the mineral acids showed remarkable efficiency in the extraction of Cr(VI) from diluted HCl medium. High efficiency of Co(II) and Zn(II) extraction with phosphonium ILs can be compared with the tertiary amine based ILs. IL 101 is such strong extractant of both Zn(II) and Co(II) that an effect of Cyanex 272 addition to the organic phase cannot be unambiguously observed.

These preliminary results suggest that the tertiary amine based ILs and phosphonium ILs extract various metal complexes according to an anionic exchange reaction between the metal complex and the respective anionic moiety of the ionic liquid.

Acknowledgments

Authors thank CSIC (Spain) for support. Dr. Irene García Díaz expresses her gratitude to the Spanish National Research Council (CSIC) for her contract through the JAE Program (JAEDoc-09-00893) co-financed by the European Social Fund.

The research of the Polish group was supported with 32/441/14 DS-PB grant.

References

1. M.A. Barakat, *Arab. J. Chem.*, 4 (2011) 361-377.
2. M. Regel-Rosocka, *J. Hazard. Mater.*, 177 (1-3) (2010) 57-69.
3. L. Li, H. Zhong, Z. Cao, L. Yuan, *Sep. Sci. Eng.*, 19 (2011) 926-930.
4. A.A. Leopold, M.T. Coll, A. Fortuny, N.S. Rathore, A.M. Sastre, *J. Hazard. Mater.*, 182 (2010) 165-175.
5. A.P. De Los Rios, F.J. Hernández-Fernández, F.J. Alguacil, L.J. Lozano, A. Ginestá, I. García-Díaz, S. Sánchez-Segado, F.A. López, C. Godínez, *Sep. Purif. Technol.*, 97 (2012) 150-157.
6. I. Billard, Ionic liquids: new hopes for efficient lanthanide/actinide extraction and separation? In J.-C.G. Bünzli and V. K. Pecharsky, (Eds). *Handbook on the physics and chemistry of rare earths*. Elsevier (2013) pp. 213-273.

Molybdenum(VI) extraction from sulfate media by quaternary 3-pyridinium ketoxime

*Katarzyna Ochromowicz¹, Katarzyna Wejman¹,
Aleksandra Wojciechowska², Karolina Wieszczycka²*

Summary

A novel quaternary salt 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide (3PC10-PrBr) was investigated as an extractant of molybdenum(VI) ions from sulfate media. Its extraction ability was compared to 1-(3-pyridyl)undecan-1-one oxime.

The influence of an equilibrium pH and contact time on the extraction efficiency, as well as the type of stripping agent on stripping efficiency was examined. It was shown that the extraction of Mo(VI) was satisfactory for both studied compounds and at a pH 2.5 reached 87% and 96% for quaternary salt and ketoxime, respectively. The obtained results indicated clearly that distribution ratio depended linearly on the initial acid concentration in the aqueous phase, although this effect was stronger for 3PC10-PrBr. The extraction with both extractants was fast and after 5 minutes reached 93%, further contact did not improve the extraction yield significantly. Sodium and ammonium sulfate salts solutions turned out to be best stripping agents, when organic contained loaded 3PC10-PrBr. In case of second extractant, stripping was not satisfactory and only 48% of Mo(VI) could be removed with NaOH solution.

Introduction

Molybdenum is an important refractory metal, which finds significant usage as an alloying agent and in numerous chemical applications, including catalysts, lubricants, and pigments [1]. Its recovery becomes economically attractive even from low-grade materials, thanks to the use of solvent extraction.

The behavior of molybdenum in a solvent extraction process is strongly affected by the type of predominant species present in the aqueous phase. Molybdenum chemistry is rather complicated. This metal exhibits several oxidation states in an aqueous solution. The stable valency of molybdenum, important for solvent extraction is +6. However, it tends to hydrolyse and to form polyheteroacids, thus the number of species present in solution is large. It is well known that polymolybdate anions predominate in the region of pH greater than 3 and that molybdenum forms cationic species only at a pH below 2. That different acid–base behavior of Mo suggests that three kinds of liquid extractants (cationic, anionic and solvating) can be used for the separation of molybdenum ions.

¹ Division of Chemical Metallurgy, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 23, 50 370 Wrocław, Poland, katarzyna.ochromowicz@pwr.wroc.pl

² Institute of Chemical Technology and Engineering, Poznań University of Technology, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland

A vast majority of research works is related to molybdenum extraction with the use of commercial extractants, mainly Aliquat 336, Alamine 304, Alamine 336, DEHPA, Cyanex, TBP and LIX series reagents [2-6].

The presented work focuses on extraction performance of hydrophobic quaternary pyridinium ketoxime 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide (3PC10-PrBr) and 1-(3-pyridyl)undecan-1-one oxime (3PC10), which were used for the first time as extractants of Mo(VI) from sulfate solutions.

Over the last few years the hydrophobic pyridylketoximes have been proposed as ligands for Cu(II), Zn(II), Fe(III), Ni(II) and Cd(II) ions removal using a liquid-liquid extraction technique from chloride, ammonia, sulfate and chloride/sulfate aqueous media [7-11]. However, the extraction ability of the ligand towards molybdenum(VI) ions has not yet been studied.

In the present paper the influence of equilibrium pH, acid concentration, phase ratio and contact time on Mo(VI) extraction efficiency were examined. The possibilities of the reextraction was also tested and compared between four stripping agents.

Experimental

The synthesis of 1-(3-pyridyl)undecan-1-one oxime and its quaternary bromide salt (3PC10-PrBr) is described elsewhere [7]. The organic phase was prepared as 0.1M solution of ligand (ketoxime or its quaternary salt) in toluene with 10% (v/v) addition of decan-1-ol.

The sulfate feed solutions were prepared by dissolving sodium molybdate dihydrate in the de-ionized water. The initial concentration of Mo(VI) in the aqueous phase was 0.01M. The ionic strength of an aqueous phase was adjusted with H₂SO₄ and/or Na₂SO₄ (or Na₂SO₄ and NaOH) solutions and was equal to 0.1M. The acidity of feed solution was regulated to the desired value by means of sulfuric acid solutions (0.01-0.1M). 0.3M solutions of Na₂SO₄, NaOH, (NH₄)₂SO₄ and NH₃·H₂O were used as the stripping agents. The organic and aqueous phases were shaken at room temperature (~22°C) using a bio-mix BWR04. Molybdenum(VI) concentration in the aqueous phase was analysed with AAS using Varian SpectrAA 20 Plus.

Results and discussion

The effect of equilibrium pH, acid concentration and phase ratio A/O

The aqueous and organic phase ratio (A/O=1) were shaken for 30 minutes. The obtained results showed that the extraction of Mo(VI) highly depended on the acidity of the aqueous phase and the applied extractant, yielding 87% and 96% at equilibrium pH ~2.5, respectively for oxime (3PC10) and its quaternary salt (3PC10-PrBr). Further decrease of solution acidity resulted in reduced the extraction efficiency for both ligands reaching below 15% at pH values above 7 (Fig.1).

Additionally, the effect of the initial sulfuric acid concentration in the aqueous phase on distribution coefficient (D) was examined. The obtained results (Fig. 2) showed significant differences in the behaviour of both extractants and confirmed superiority of quaternary bromide salt over the ketoxime. In case of 3PC10 – PrBr no physical

problems were noticed, and phase separation times were rather short (<1min.), whereas, for 3PC10 white precipitate occurred at the interface over the pH 5.

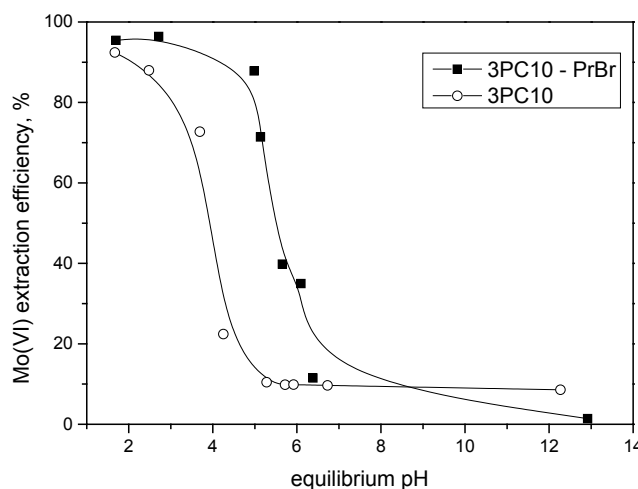


Fig. 1. Influence of pH on extraction of Mo(VI) ($[Mo_6^{6+}] = 0.01\text{ M}$, $[ligand] = 0.1\text{ M}$, $I=0.3\text{ M}$)

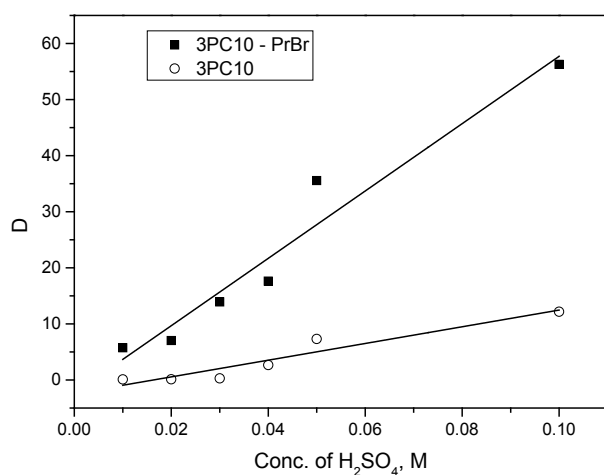


Fig. 2. Influence of sulfuric acid concentration in aqueous phase on extraction of Mo(VI) ($[Mo_6^{6+}] = 0.01\text{ M}$, $[ligand] = 0.1\text{ M}$, $I=0.3\text{ M}$)

A completely opposite behavior was observed for both reagents when the phase ratios were raised to A/O=2 and 3. A stable emulsion was formed while using 3PC10-PrBr and it was not possible to separate phases. In case of the ketoxime, an emulsion separated quickly and the analysis of molybdenum(VI) concentration showed that yield of extraction was relatively high (Table 1).

Table 1. The effect of A/O phase ratio on extraction efficiency of Mo(VI) ($[Mo_6^{6+}] = 0.01\text{ M}$, $[ligand] = 0.1\text{ M}$, $I=0.3\text{ M}$, eq. pH=2.5, time 30 min.)

A/O phase ratio	Extraction efficiency, %	
	3PC10	3PC10-PrBr
2	88.8	*
3	88.7	*

* emulsion

The effect of contact time

In order to study the effect of the contact time on the extraction percentage, the process was performed in the time range of 1 to 30 minutes at equilibrium pH of 2.5. The obtained results showed that the majority of molybdenum(VI) ions (93%) was removed after 5 minutes for both tested reagents. Longer contact slightly increased the yield of the extraction, reaching 96% after 30 min. (Fig. 3).

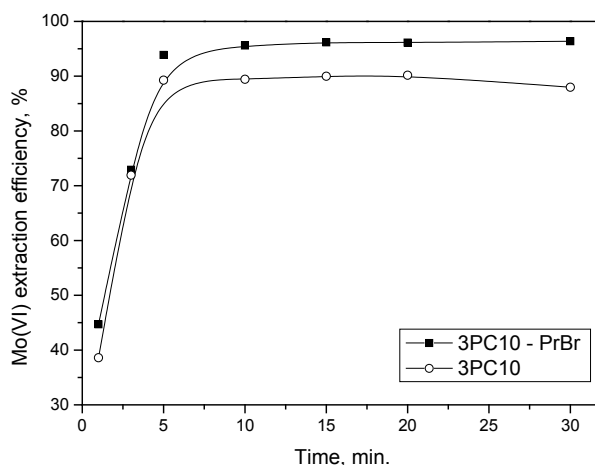


Fig. 3. Influence of contact time on extraction of Mo(VI) ($[Mo^{6+}] = 0.01\text{ M}$, $[ligand] = 0.1\text{ M}$, $I=0.3M$)

The effect of stripping agent

The stripping test was conducted using the fresh loaded organic phase containing 0.01 M of Mo(VI) ions. Before the stripping test the loaded organic solution was filtered through Whatman 1ps phase separating paper to remove any entrained aqueous from loading. Four strip agents were tested: Na_2SO_4 , $NaOH$, $(NH_4)_2SO_4$ and $NH_3 \cdot H_2O$. Stripping contacts lasted for 10 min with vigorous mixing at A/O phase ratio of 1.

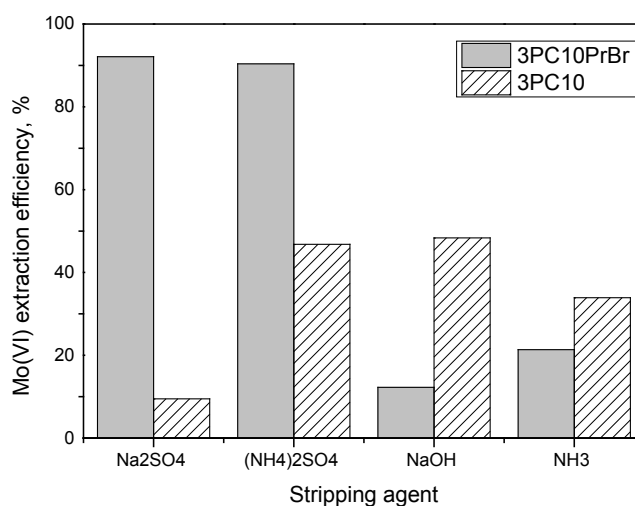


Fig. 4. The dependence of stippant type on extraction of Mo(VI) ($[Mo^{6+}] = 0.01\text{ M}$, $[ligand] = 0.1\text{ M}$, $I=0.3M$)

Fig. 4 shows that the two sulfate salts are very effective stripping agents of molybdenum from the loaded 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide. Over 90% of Mo(VI) was stripped in one contact and phases separation was rapid. The remaining strip agents were not that efficient and less than 20% of

Mo(VI) was back extracted to aqueous phase. Furthermore, the mixing of the organic phase with sodium hydroxide or ammonia solutions caused the change of the organic phase color to brown, which may suggest a stripping agents interaction with the pyridinium ketoxime.

In case of the organic phase containing loaded 1-(3-pyridyl)undecan-1-one oxime the formed complexes were too strong to decompose using the tested strip agents. The best results of the stripping were observed for the ammonia sulfate and sodium hydroxide solutions, but the efficiency of the one stage process was no higher than 48%.

Conclusions

The synthesized quaternary pyridinium ketoxime is the effective extractant and can be proposed to remove molybdenum(VI) from sulfate solutions. However, the high organic phase loadings are not possible regarding the stable emulsion forming during the extraction at raised phase ratios ($A/O = 2$ and 3). Further work is required to find a proper modifier and its concentration in the organic phase, to prevent third phase formation. Extraction with the two tested reagents was relatively fast and after 5 minutes over 90% of Mo(VI) was removed from the aqueous feed solution. Only loaded organic phase containing quaternary salt of pyridinium ketoxime could be effectively stripped with sodium and ammonium sulfate solutions.

Future work should be implemented to examine the possibility of reducing the amount of precipitation (and emulsion formation) taking place in both - the extraction and stripping steps.

References

- [1] Li Zeng, Chu Yong Cheng, 2009, A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurization catalysts. Part II: Separation and purification, Hydrometallurgy, 98, 10-20
- [2] An J.W., Lee Y.H., Kim S.J., Tran T., Lee S.O., Kim M.J., 2009a, Production of high purity molybdenum compounds from a Cu–Mo acid-washed liquor using solvent extraction. Part 1: laboratory studies, Miner. Eng., 22, 1020–1025.
- [3] An J.W., Jung B.H., Lee Y.H., Tran T., Kim S.J., Kim M.J., 2009b, Production of high-purity molybdenum compounds from a Cu–Mo acid-washed liquor using solvent extraction. Part 2: Pilot and plant operations, Minerals Engineering, 22, 1026–1031.
- [4] Wu J., Wei Ch., Li X., Wang S., Wang M., Li C., 2012. Selective extraction of Mo using Cyanex-272 and tributyl phosphate from low grade Ni–Mo ore leach liquor, Separation and Purification Technology 99, pp. 120–126.
- [5] Sastre A.M., Cahner S., Alguacil F.J., 2000. Extraction of molybdenum (VI) from sulfate solutions by LIX 622, Journal of Chemical Technology and Biotechnology 75, pp. 54–58.

- [6] Mons M.A., Diez F.V., Coca J., 1999. Solvent extraction of molybdenum and tungsten by Alamine 336 and DEHPA in a rotating disc contactor, *Separation & Purification Technology* 17, pp. 173–179.
- [7] Wieszczycka K., Wojciechowska A., Krupa M., Kordala-Markiewicz R., 2013, Quaternary Pyridinium Ketoximes as Zinc Extractants from Chloride Solutions, *Journal of Chemical and Engineering Data*, [dx.doi.org/10.1021/je400646z](https://doi.org/10.1021/je400646z)
- [8] Wieszczycka K., Krupa M., Olszanowski A., 2012. Extraction of copper(II) ions from sulphate and chloride solutions using hydrophobic pyridyl ketoximes, *Sep. Sci. Technol.* 47, pp. 1278-1284.
- [9] Parus A., Wieszczycka K., Olszanowski A., 2011. Solvent extraction of iron(III) from chloride solutions in the presence of copper(II) and zinc(II) using hydrophobic pyridyl ketoximes, *Sep. Sci. Technol.* 46, pp. 87-93.
- [10] Parus A., Wieszczycka K., Olszanowski A., 2010. Solvent extraction of cadmium(II) from chloride solutions by pyridyl ketoximes, *Hydrometallurgy* 105, pp. 284-289.
- [11] Wieszczycka K., Krupa M., Wojciechowska A., Olszanowski A., 2013. Recovery of nickel(II) ions from sulphate/chloride solutions using hydrophobic pyridylketoximes. *Solvent Extr. Ion Exch.*, DOI: 10.1080/07366299.2013.850334.

Transport of zinc(II) ions from chloride solutions with phosphonium ionic liquids as metal ion carriers by liquid-liquid extraction and polymer inclusion membranes

*Magdalena Regel-Rosocka^{*1}, Ruben Casas Jaraices¹, Monika Baczyńska¹, Maciej Wiśniewski¹*

Summary

This work aims in studies on application of three phosphonium ionic liquids, i.e. trihexyltetradecylphosphonium chloride (Cyphos IL 101), trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104), tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167), for zinc ions removal from chloride solutions with liquid-liquid extraction or polymer inclusion membranes. These phosphonium salts extract zinc(II) quickly and almost completely, thus, they are effective and prospective extractants. The composition of the PIMs is the most important factor influencing zinc(II) transport across the membrane. Successful application of the phosphonium ILs (Cyphos IL 101, IL 104, IL 167) for zinc(II) transport in two different separation systems is presented.

Introduction

Phosphonium ionic liquids are frequently used for separation of metal ions both in extraction and adsorption systems. Application of ILs can be divided into some specific systems where ILs replace typical solvents, ILs are used as new extractants, ILs form pure extracting phase or they can be additives to traditional systems [1]. The reason for such an interest with ILs comes from almost unlimited possibilities of design of new ILs for very specific applications, insignificant volatility, high thermal stability and ionic conductivity, as well as, broad electrochemical window [2, 3].

Recently, looking for environmentally friendly separation techniques, a number of researchers propose polymer inclusion membranes (PIMs) for efficient separation of metal ions and small organic compounds from diluted or not big amounts of effluents as an alternative to liquid-liquid extraction (SX). PIMs consist of polymer matrix (mostly cellulose triacetate (CTA) or poly(vinyl)chloride (PVC)), a plasticizer (e.g. 2-nitrophenyloctyl ether) and a carrier (e.g. acidic, basic extractants). Up to now, PIMs are reported to be applied for separation processes including transport of: precious metals, lanthanides, alkali metals, heavy metals such as lead(II), zinc(II) or cadmium(II) [1-6].

This work aims in studies on application of three phosphonium ionic liquids, for the first time tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167), for removal of zinc ions from chloride solutions with liquid-liquid extraction and polymer inclusion membranes.

^{*1} e-mail: magdalena.regel-rosocka@put.poznan.pl, Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

Experimental

Reagents

Three phosphonium ionic liquids, i.e. Cyphos IL 101, Cyphos IL 104 and Cyphos IL 167 supplied by Cytec Industries Inc. (USA) were used as extractants or carriers in SX or PIM separations, respectively. Other organic reagents i.e. cellulose triacetate (CTA), poly(vinyl) chloride (PVC), o-nitrophenyloctyl ether (ONPOE), tetrahydrofuran (THF) and dichloromethane (DCM) were of analytical grade and used without further purification. Toluene was applied as a diluent for the organic phase preparation to overcome the high viscosity of ILs. The structures of the ILs applied are presented in Table 1.

Table 1. Structures of the extractants used.

<i>Cyphos IL 101,</i> <i>Trihexyltetradecylphosphonium</i> <i>chloride</i>	<i>Cyphos IL 104,</i> <i>Trihexyltetradecylphosphonium</i> <i>bis(2,4,4-trimethylpentyl)</i> <i>phosphinate</i>	<i>Cyphos IL 167,</i> <i>Tributyl(tetradecyl)phosphonium</i> <i>chloride</i>

Model aqueous feeds contained 0.1-80 g/dm³ of Zn(II), 0.58 M HCl, 5 M Cl⁻ (chloride content was adjusted with NaCl). 1 M H₂SO₄ was used as a stripping or receiving phase. Inorganic chemicals were of analytical grade and were purchased from POCh (Gliwice, Poland).

Methods

Extraction was carried out in a typical way: equimolar aqueous feeds, containing metal ions in 0.58 M HCl were mechanically shaken with IL phase (volume ratio w/o = 1) for 30 minutes at 20°C in glass separatory funnels and then allowed to stand for phase separation. Loaded organic phase was stripped with various stripping solutions at a volume ratio of o/w = 1.

Polymer inclusion membranes were prepared from three basic substrates: polymeric matrix (CTA or PVC), carrier (phosphonium ILs), plasticizer (ONPOE). A portion of three-substrate solution in suitable solvent (DCM or THF, respectively for CTA or PVC) was poured into a 7.0 cm diameter Petri dish. The organic solvents were allowed to evaporate overnight and the resultant membrane was separated from glass plate by immersion in cold water. Membranes were fixed in the membrane module-sandwich type-presented in our previous paper [3].

The samples were taken periodically for determination of Zn(II) concentration by atomic absorption spectroscopy at 213 nm in acetylene-air flame.

Results and discussion

Solvent extraction experiments

As it was reported in the previous papers [3], the kinetics of Zn(II) extraction with the studied phosphonium ionic liquids was fast. Different results for Zn(II) extraction with Cyphos IL 101 were presented elsewhere, however, here Cyphos IL 167 is reported for the first time as an extractant of zinc ions. The efficiency of Zn(II) extraction is expressed as percentage extraction, and is shown in Fig. 1 as E_{Zn} dependence on molar ratio of IL/ Zn_i .

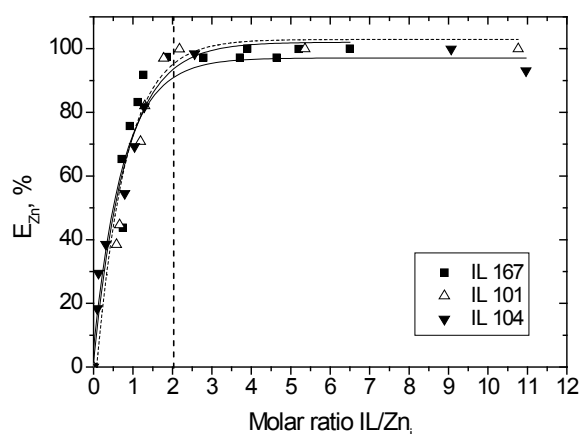
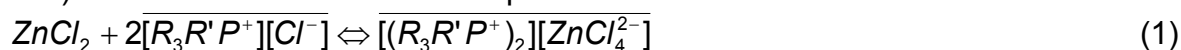


Fig. 1. Effect of IL/ Zn in feed ratio on zinc(II) extraction to the IL phase (feed: 0.1–68 g/dm³ Zn(II), 0.58 M HCl, 5 M Cl⁻; organic: Cyphos IL 101, 104 or 167 in toluene).

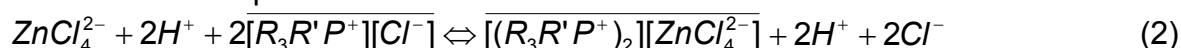
Zn(II) percentage extraction decreases with increasing Zn(II) content in the feed due to decrease of molar ratio between phosphonium IL and Zn(II) content (Fig. 1). At 68 g/dm³ (1 M) Zn(II) percentage extraction with Cyphos IL 104 reaches less than 20% whereas at 5 g/dm³ (0.076 M) E_{Zn} is higher than 80%. At molar ratio Cyphos IL/ Zn (II) less than 2 a distinct decrease in Zn(II) extraction with all ILs studied is observed. Above the ratio of 2 zinc(II) extraction amounts to 100%. Additionally, there are no significant differences in extraction efficiency with the phosphonium ILs, though various structure of their anions, even for Cyphos IL 104.

Depending on the distribution of Zn(II) chlorocomplexes extraction with phosphonium chlorides (Cyphos IL 101 and 167) may be considered in terms of:

- a) addition of neutral chlorocomplex to IL molecule



- b) anion exchange of two chlorides for a negatively charged zinc tetrachlorocomplex



During extraction chlorocomplexes of zinc(II) form ionic pairs with the phosphonium cations. Therefore, Cyphos IL 104 can also extract Zn(II) according to the eq. 2, but chloride anion is replaced with bis(2,4,4-trimethylpentyl)phosphinate [Bis⁻], and could also participate in Zn(II) transport, in the form of $[Zn^{2+}][Bis^-]$. However, almost 100%

extraction at the molar ratio of IL 104/ Zn_i equal 2 suggest that $[Bis^-]$ anion does not extract $Zn(II)$ additionally.

Positive results of $Zn(II)$ extraction with the studied phosphonium ILs enhanced the authors to apply the ILs as metal ion carriers in polymer inclusion membranes (PIM).

Polymer inclusion membrane experiments

Figure 2 illustrates the influence of polymer matrix on percentage extraction and recovery factor of $Zn(II)$. The concentration of $Zn(II)$ transported across CTA membranes decreases in the feed phase faster and finally reaches lower values compared to PVC membranes (Fig. 2). Generally, transport across PVC membranes is fast only in the beginning of the process. Hence, the initial decrease of $Zn(II)$ concentration in the feed can be attributed to adsorption of metal ions on the surface of the membrane or formation of strong complexes with the carrier that are not efficiently transported across the PVC PIMs.

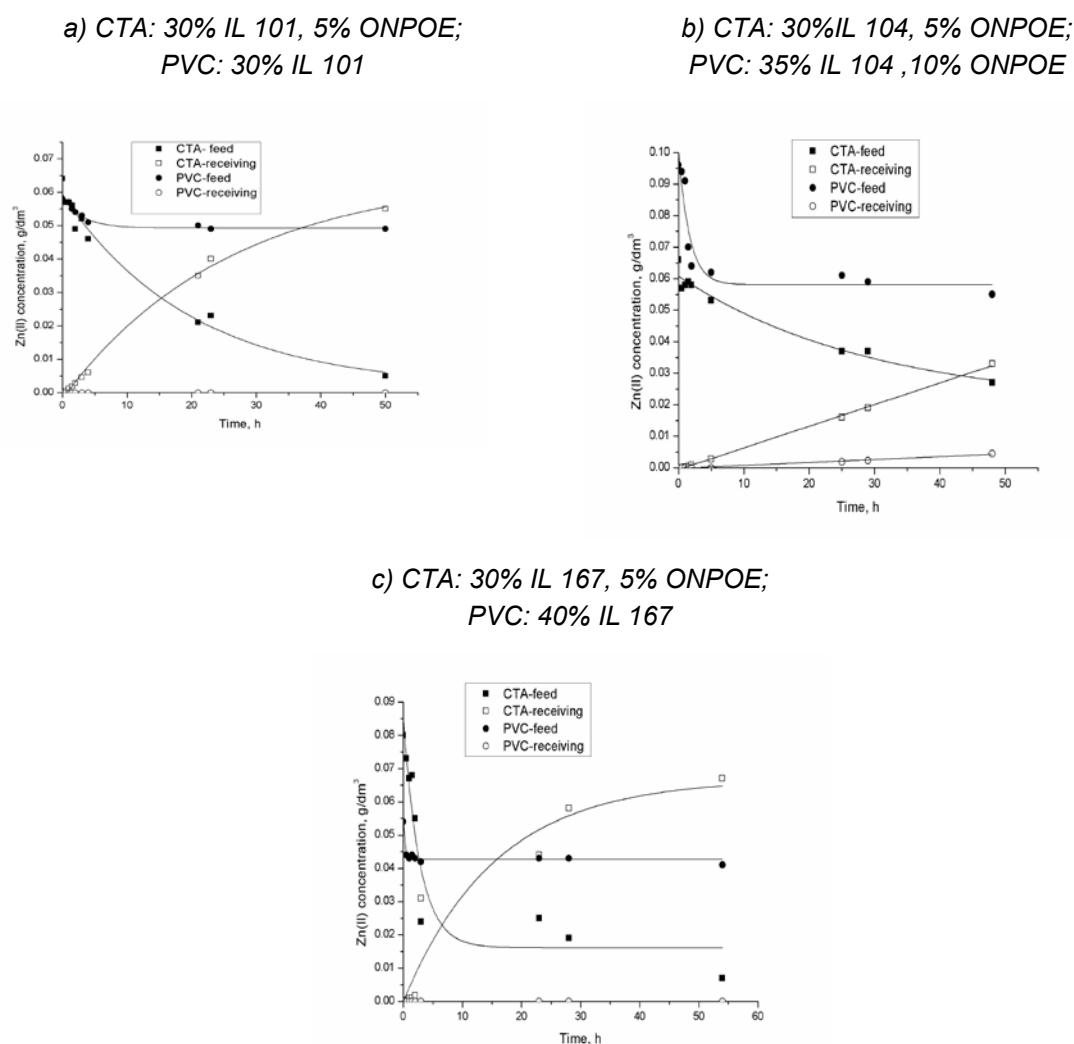


Fig. 2. Concentration profiles of $Zn(II)$ in the feed and receiving phases vs. time of PIM process.

Transport abilities of PIMs can be characterized by extraction efficiency and recovery factor of metal ions (here after 48 hours of a process) defined by eqs 3 and 4.

$$E = \frac{c_0 - c}{c_0} \cdot 100\% \quad (3)$$

$$RF = \frac{c_s}{c_0} \cdot 100\% \quad (4)$$

where c_0 , c and c_s are Zn(II) concentrations in the feed, aqueous after selected time and stripping solution after selected time, respectively.

Higher values of recovery factors and extraction efficiency are obtained for Zn(II) transport through CTA-based membranes than PVC-based ones (Fig. 3). CTA membranes containing Cyphos IL 101, IL 104 or IL 167 transport over 90% of Zn(II) from the feed to the receiving phase, while in case of PVC membranes RF values are less than 5% (Fig. 3). It should be noticed that the mass transfer across CTA membranes is rather slow due to small membrane area. Thus, significant increase in Zn(II) concentration in the receiving phase is reported after 20-30 hours of separation process.

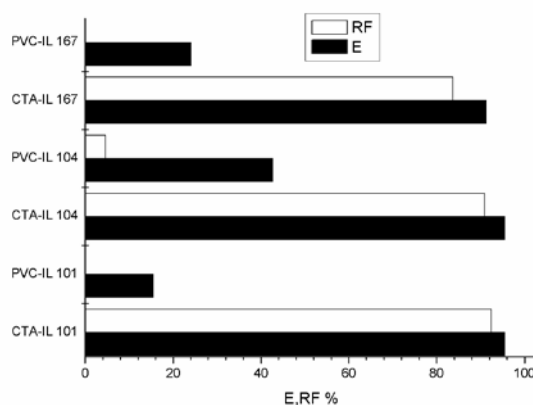


Fig. 3. Effect of polymer matrix on E and RF through membranes containing: 40% IL 101, 55% CTA, 5% ONPOE; 40% IL 104, 55% CTA, 5% ONPOE; 30% IL167, 65%CTA, 5%ONPOE; 30% IL 101, 70% PVC; 35% IL 104, 55% PVC, 10% ONPOE and 40% IL 167, 60% PVC.

Conclusions

The obtained results show that phosphonium ILs studied, especially Cyphos IL 167 - used for the first time as metal ion carrier - efficiently extract Zn(II) both in liquid-liquid extraction and polymer inclusion membranes. Despite the tendency of ILs to form strong ion pairs with metal ions, sulfuric acid effectively receives Zn(II) from CTA membranes containing Cyphos IL 101, 104 or 167. The polymer matrix seems to play a crucial role for the efficiency of metal ion transport, and CTA membranes with phosphonium ILs as metal ion carriers have not only good mechanical but also transport properties in the systems studied.

Acknowledgments

This research was supported by the 32/441/14 DS-PB grant.

References

1. I. Billard, Ionic liquids: new hopes for efficient lanthanide/actinide extraction and separation? In J.-C.G. Bünzli and V. K. Pecharsky, (Eds). Handbook on the physics and chemistry of rare earths. Elsevier, 2013, pp. 213-273.
2. D. Kogelnig, A. Regelsberger, A. Stojanovic, F. Jirsa, R. Krachler, B.K. Keppler, *Monatsh. Chem.*, 142 (2011) 769-772.
3. M. Regel-Rosocka, Ł. Nowak, M. Wiśniewski, *Sep. Purif. Technol.*, 97 (2012) 158-163.
4. M. Baczyńska, M. Regel-Rosocka, *Przem. Chem.*, 92/9 (2013) 1574-1576.
5. L.D. Nghiem, P. Mornene, I.D. Potter, J.M. Perera, R.W. Catrall, S.D. Kolev, *J. Membr. Sci.*, 281 (2006) 7-41.
6. M. Inês, G.S. Almeida, R.W. Catrall, S.D. Kolev, *J. Membr. Sci.*, 415-416 (2012) 9-23.

Solvent Impregnated Resin: Cyanex272 immobilised Amberlite XAD-2 Column for Gd(III) Enrichment

Manjusha Karve^{*1}, Kinny Pandey²

Summary

Gd(III) is a rare earth element (REE) which has varied applications. It is used in nuclear reactors, as an alloying element, in colour TV tubes and in magnetic resonance imaging as a contrast agent. Considering its uses Gd(III) separation and enrichment was studied in HNO₃ media using a solvent impregnated resin (SIR) prepared from Amberlite XAD-2 immobilized with Cyanex272. The SIR was prepared by mixing the solid support with the liquid extractant in methanol in 1:1 ratio. The stirring was done for 4 hours till the solvent almost evaporated. The SIR (100 mg) was packed in a column to study systematically various resin parameters influencing Gd(III) sorption and desorption. These included the amount of Cyanex272, HNO₃ concentration, nature and concentration of eluting agents, and aqueous and eluent flow rate. A 10.0 ml solution containing 30 µg Gd(III) was studied from 1×10^{-4} M to 1.0 M HNO₃. The amount of Gd(III) recovered was detected spectrophotometrically using Arsenazo(III) at 652 nm. Gd(III) was quantitatively (99.8±0.2) % sorbed using 1×10^{-3} M HNO₃. The flow rate of the aqueous solution was varied and using flow rates 0.2, 0.4, 0.6 ml/min the amount of Gd(III) sorbed was 99.8 ± 0.2%, 90.4 ± 1.2%, 85.4 ± 0.8% respectively. Hence we chose 0.2 mL min⁻¹ flow rate. The eluents HCl, HNO₃, H₂SO₄ and HClO₄ were investigated for Gd(III) and it was completely recovered (99.5±0.4)% with 10.0 mL of 0.5 M H₂SO₄ at a flow rate of 0.1 mL min⁻¹. Under the optimised conditions behaviors of other rare earth elements, Th(IV) and U(VI) indicated their quantitative recovery. The analytical performance of the method was checked. The LOD and LOQ for Gd(III) was 0.88 µg L⁻¹ and 2.93 µg L⁻¹ respectively. An enrichment factor of >10 with a relative standard deviation of ≤ 1.5 % was achieved. The SIR had reusability for 42 cycles.

¹Manjusha Karve, Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai 400 098, India

²Kinny Pandey Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai 400 098, India

Introduction

Gadolinium is a naturally occurring, silvery white element with a metallic shine. In nature it is never found as a free element, but is contained in such rare minerals as monazite and bastnasite. Interestingly, the mineral gadolinite after which the element gadolinium was named contains only trace amounts of gadolinium. Due to its scarcity and industrial importance, gadolinium is often enriched through ion exchange and solvent extraction techniques [1].

The resins based on impregnated sorbents was first contrived by Warwasky et al. [2] and much work has been done so far to understand the sorption process and equilibrium involved [3]. Gd(III) sorption was studied using Cs₂H₂PMo₁₁Vo₄₀ impregnated on mesoporous silica SBA-15 [4] and Kaolinite KGa-16 [5]. While, extraction behavior of Gd(III) studied in phosphoric acid media using Tulsion CH-93 and CH-90 [6]. Silica functionalized with 1-hydroxy-2-pyridinone was evaluated for Gd(III) removal from dialysate and blood [7]. Styrene divinyl benzene and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester was synthesized [8,9] and the addition of polyvinyl alcohol during the suspension polymerization enabled Gd(III) separation from Tb(III) [8]. Gd(III) was separated from HNO₃ media with SIR based on Aliquat336S and Amberlite XAD-4 resin [10].

In present work a SIR using Cyanex272 impregnated on Amberlite XAD-2 resin was packed in a column to optimize the conditions for sorption and desorption of Gd(III).

Materials & Method

Cyanex272 obtained from Cytec Canada as a gift sample was used without purification. Amberlite XAD-2 resin (20-60 mesh size, $330 \text{ m}^2\text{g}^{-1}$ average surface area, pore diameter of $90\text{\AA}$.) obtained from Supelco, Sigma Aldrich Co. was pretreated prior to use [11]. A stock solution of Gd(III) 1.0 mg mL^{-1} was prepared by dissolving appropriate amount of gadolinium nitrate (Central Drug House Pvt. Ltd., India) in slightly acidified double distilled water and standardized volumetrically [12]. A working solution containing $30 \text{ }\mu\text{g mL}^{-1}$ of Gd(III) were prepared by appropriate dilution. A standardized stock solution of 1.0 mg/mL of REEs, Th(IV) and U(VI) were prepared by dissolving appropriate quantity of their respective salts in slightly acidified double distilled water. For spectrophotometric determination 0.1% (w/v) aqueous solution of Arsenazo(III) (S.D.Fine chemicals, India) was prepared.

A digital balance Mettler Toledo, Model-AB204, Switzerland was used for weighing. Double distilled water was obtained from quartz double distiller (make Lab-Sil, India). A digital pH meter model Elico LI-127, India coupled with a combined glass electrode was used for pH measurements. Shimadzu UV-visible spectrophotometer model UV-2450, Japan was used for spectrophotometric determinations.

Result and Discussion

Preparation & Characterization of SIR

Amberlite XAD-2 resin was pretreated with 2.0 M HNO_3 and 2.0 M NaOH followed by washings with double distilled water and acetone to remove manufacturing impurities if any [11].

Preparation of solvent impregnated resin (SIR) was done by shaking a known amount of Cyanex272 and Amberlite XAD-2 resin in 10 mL of methanol until the solvent almost evaporated and then kept overnight at ambient temperature.

FT-IR analysis of the solvent impregnated resin prepared by impregnation of Cyanex272 on the surface of Amberlite XAD-2 resin, indicated only physical interaction [13].

General Procedure

The SIR was uniformly packed in a glass column (150 mm length and 10 mm internal diameter) with a glass wool support. The column was preconditioned with 10 bed volumes of $1 \times 10^{-3} \text{ M HNO}_3$. A sample solution containing $30 \text{ }\mu\text{g Gd(III)}$ in 10 mL of $1 \times 10^{-3} \text{ M HNO}_3$ was sorbed on a column packed with the impregnated resin at a flow rate of 0.2 mL min^{-1} .

The sorbed Gd(III) was recovered with 10 mL of $0.5 \text{ M H}_2\text{SO}_4$ at a flow rate of 0.1 mL min^{-1} . Gd(III) was determined spectrophotometrically using 0.1% Arsenazo(III) at 652 nm [14].

Optimisation of Gd(III) sorption and elution conditions

Effect of aqueous acidity

Gd(III) sorption was studied as a function of HNO_3 concentration on the column packed with the impregnated resin.. The sorption of Gd(III) was maximum ($99.8 \pm 0.2\%$) when the aqueous phase acidity was $1 \times 10^{-3} \text{ M HNO}_3$ (Fig.1). Its sorption continuously decreased beyond $1 \times 10^{-2} \text{ M HNO}_3$ indicating that a cation exchange behavior was operative for its sorption [15]. Consequently, $1 \times 10^{-3} \text{ M HNO}_3$ was used as aqueous phase acidity throughout the studies.

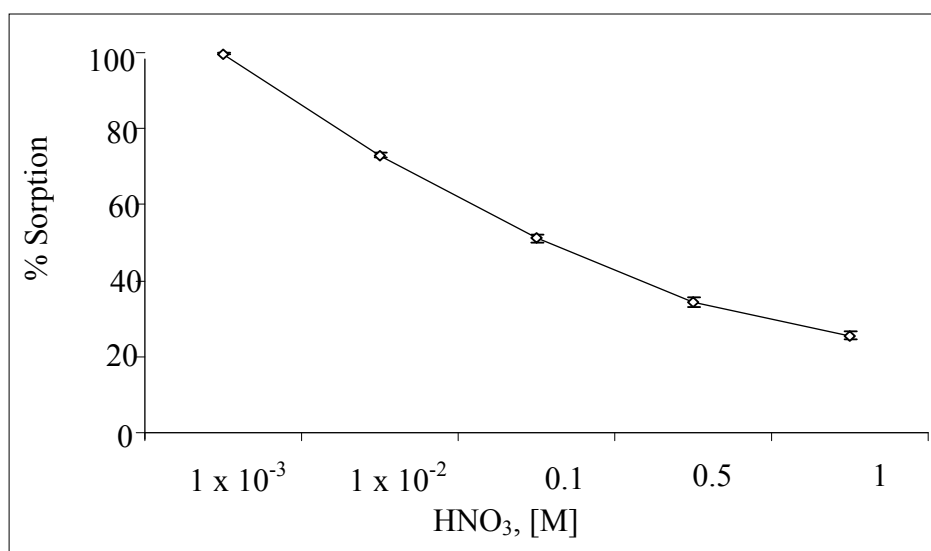


Fig.1: Influence of aqueous phase acidity on sorption of Gd(III) ($n = 3$)

Effect of aqueous flow rates on sorption of Gd(III)

The influence of the aqueous phase flow rate on the sorption of Gd(III) was studied and is presented in Fig.2. A 30 μg Gd(III) in 10.0mL of $1.0 \times 10^{-3}\text{M}$ HNO₃ was passed through the column at 0.1 – 1.0 ml min^{-1} flow rates. The sorption of Gd(III) was $99.8 \pm 0.2\%$ using a sample flow rate of 0.2 ml min^{-1} . The sorption of Gd(III) decreased to $51.0 \pm 0.6\%$ with the sample flow rates greater than 0.2 ml min^{-1} due to its insufficient contact with the modified sorbent. Hence, a flow rate of 0.2 mL min^{-1} was considered as the optimum for all further studies.

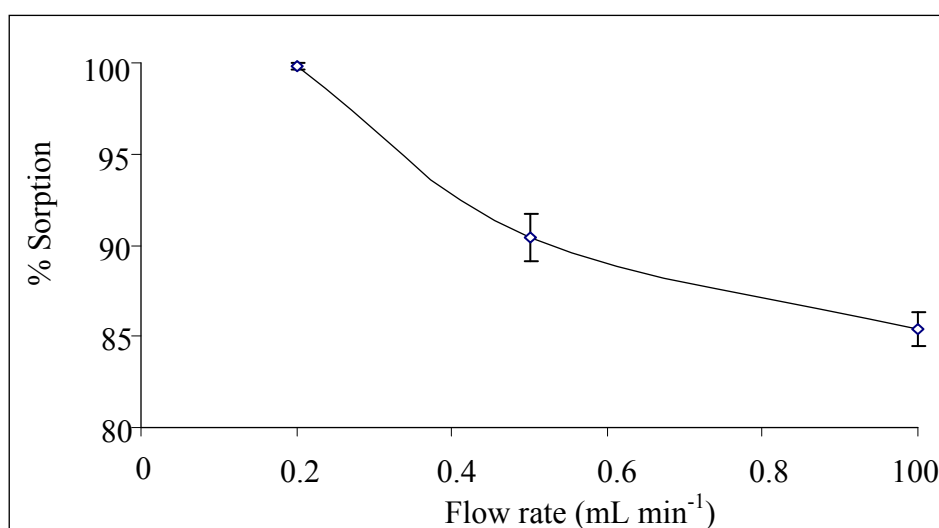


Fig.2: Effect of aqueous phase flow rate on the sorption of Gd(III) ($n = 3$)

Desorption Studies of Gd(III)

Recovery of metal ion is one of the most important steps in solid phase extraction for preconcentration of the metal. Gd(III) elution was studied using different eluents such as HCl, HNO₃, H₂SO₄, and HClO₄ (Table.1). Higher concentrations of HNO₃ and H₂SO₄ were not studied as preliminary experiments indicated leaching of Cyanex272 from the impregnated resin. Using 10mL of 0.5 M H₂SO₄ at 0.1 mL min^{-1} resulted in quantitative ($98.7 \pm 0.9\%$) recovery of Gd(III). It was observed that irrespective of volume, its recovery decreased at a flow rate higher than 0.1 mL min^{-1} .

Eluents Conc.[M]	HCl	HNO ₃	H ₂ SO ₄	HClO ₄
	Recovery of Gd(III) (%) ± a			
1.0×10^{-1}	74.2 ± 1.2	85.1 ± 1.3	86.2 ± 0.7	56.0 ± 1.4
5.0×10^{-1}	58.4 ± 1.4	91.6 ± 0.1	98.7 ± 0.9	71.5 ± 1.0
1.0	69.3 ± 1.0	94.3 ± 0.9	96.4 ± 1.4	80.0 ± 0.8
2.0	75.4 ± 1.1	-	-	-
3.0	86.4 ± 0.9	-	-	-
4.0	97.6 ± 1.4	-	-	-

Table1: Influence of eluents on Gd(III) recovery

Sorption of rare earth elements, Th(IV) and U(VI) using SIR

The effect of different concentrations of HNO₃ ranging from 1×10^{-3} M to 1.0 M at a constant amount (30 µg) of each REE viz., La(III), Ce(IV), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), Th(IV), and U(VI) in 10 mL of aqueous phase was studied on column packed with 100 mg of impregnated resin at a flow rate of 0.2 mL min^{-1} is presented in Fig.3. Elution of each REE were done by 0.5 M H₂SO₄. The amount of the element sorbed were determined in the respective phase spectrophotometrically with 0.1 % (w/v) Arsenazo(III). It was observed that the sorption of rare earth elements continuously decreased beyond 1×10^{-3} M HNO₃. This decrease in its sorption with increase in aqueous phase acidity is a consequence of cation exchange mechanism exhibited by Cyanex272 [14]. It was observed that the sorption of REEs and Th(IV) and U(VI) followed the similar sorption pattern was observed for Gd(III) sorption indicating their co-extraction and recovery under Gd(III) condition.

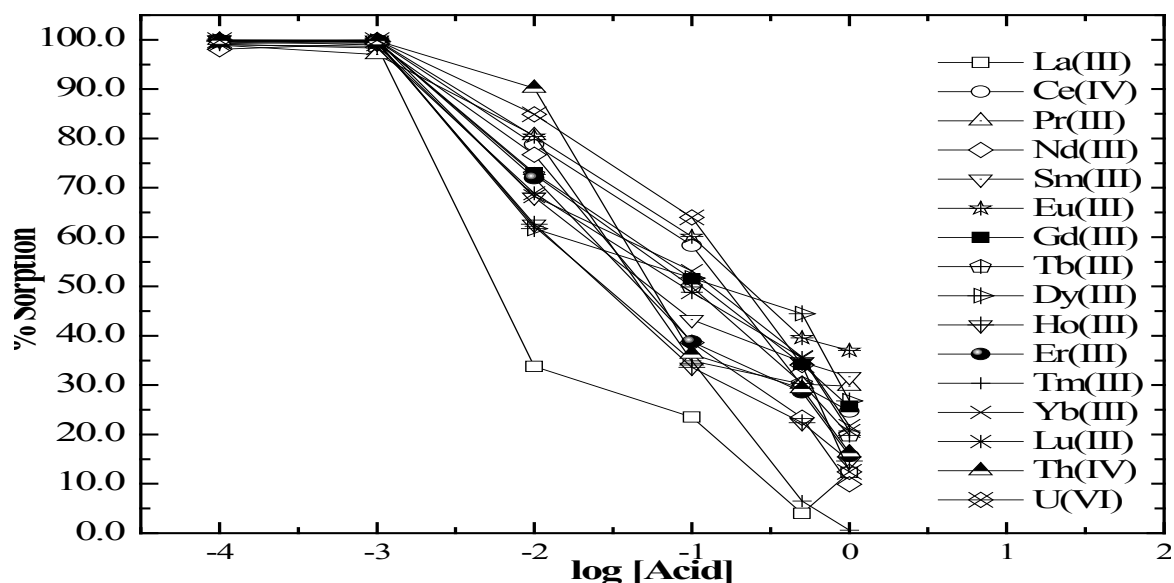


Fig.3: Sorption of REEs, U(VI) and Th(IV) on SIR in acidic solution

Breakthrough volume

The breakthrough volume is one of the most important parameter in column studies, which helps in process development, as it decides the preconcentration of analyte from large volumes of sample. A 30 μg of Gd(III) was preconcentrated from the aqueous volume in the range of 10–100 mL using the general procedure(Fig.4). It could be seen that Gd(III) was quantitatively sorbed on Cyanex272 impregnated Amberlite XAD-2 resin even from 100.0 mL of the aqueous phase. The elution was carried out with 10.0 mL of 0.5 M H_2SO_4 . Hence, the preconcentration factor is >10 for Gd(III).

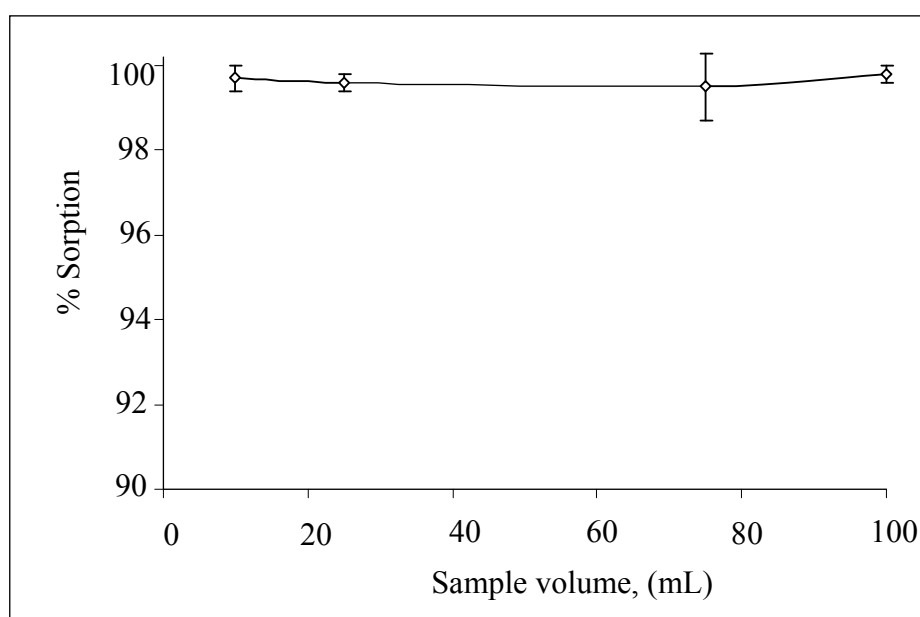


Fig. 4. Breakthrough volume for the sorption of Gd(III) ($n=3$)

Column Reusability

Gd(III) was passed through the column packed with SIR as per the general procedure and its sorption desorption studied for repeated cycles. Quantitative sorption of Gd(III) was observed upto the 42nd cycle indicating a very high reusability of the column.

Analytical performance

The limit of detection (LOD) and limit of quantification (LOQ) of the proposed method for the determination of Gd(III) were studied under the optimum experimental conditions. The LOD was calculated using the relation $3\sigma m^{-1}$ was 0.88 $\mu\text{g L}^{-1}$ and LOQ was calculated using the relation $10\sigma m^{-1}$ to be 2.93 $\mu\text{g L}^{-1}$, where, σ is the standard deviation of the blank measurements(25 replicates), m is the slope of the linear calibration graph [16].

It was found that the method was highly reproducible with relative standard deviation (R. S. D.) of $\leq 1.5\%$.

Conclusions

Impregnation of Cyanex272 on Amberlite XAD-2 resin is relatively simple. Sorption of Gd(III) on SIR was systematically studied by using a column mode. Gd(III), along with other REEs, U(VI) and Th(IV) were completely sorbed from 1×10^{-3} M HNO_3 due to the cation exchange behaviour of Cyanex272 towards them. The present procedure had good sensitivity for Gd(III) with LOD of 0.88 $\mu\text{g L}^{-1}$ and LOQ of 2.94 $\mu\text{g L}^{-1}$ for Gd(III). The reusability of the column packed with SIR was for 42

sorption - desorption cycles with % R. S. D. ≤ 1.5 . The SIR exhibits potential for separation and preconcentration of REEs as a unified block from various complex matrices.

References

1. P. Maestro and D. Huguenin.: J. Alloys Compd., 225, 520 (1995).
2. Warshawsky, A.: Extraction with solvent impregnated resins. In: Marinsky JA, Marcus Y (eds) Ion exchange and solvent extraction, vol 8. Marcel Dekker, New York (1984).
3. Kabay, N., Cortina, J.L., Trochimczuk, A., Streat, M.: React. Funct. Polym. 70, 484 (2010).
4. Aghayana, H., Khanchib, A.R., Mahjouba, A.R.: Appl. Surf. Sci. 274, 7 (2013).
5. Kautenburger R., Beck, H. P.: J. Environ. Monit. 12, 1295 (2010).
6. Radhika, S., Nagaraju, V., Kumar, B. N., Kantam, M. L., Reddy, B. R.: J. Rare Earths, 30, 1270 (2012).
7. Yantasee, W., Fryxell, G. E., Porter, G. A., Pattamakomsan, K., Sukwarotwat, V., Chouyyok, W., Koonsiripai boon, V., Xu, J. Raymond, K. N.: Nanomedicine: Nanotech. Bio. Med. 6 1 (2010).
8. Joon-Seok, K., Choon H., Jung-Ho, W., Joon-Soo, K.: Talanta 68, 963 (2006).
9. Park J.-S., Han C., Lee I.-Y, Kim S.-D, Kim J.-S, Wee J.-H.: Sep. Purif. Technol. 43, 111 (2005).
10. El-Sofany, E. A.: J. Hazard. Mater. 153, 948 (2008).
11. Matsunaga, H., Ismail, A. A., Wakui, Y., Yokoyama, T.: React. Funct. Polym. 49, 189 (2001).
12. Welcher, F.J.: The Analytical Uses of Ethylenediamine Tetra Acetic Acid, D. Van Nostrand Co. Inc.: New Jersey, (1978).
13. Karve M, Pandey K.: J Radioanal Nucl Chem 285, 627 (2010).
14. Snell, F.D.: Photometric and Fluorometric Methods of Analysis of Metals; John Wiley and Sons: New York, (1978).
15. Dogmane, S.D., Singh, R.K., Bajpai, D.D., Mathur, J.N.: J Radioanal. Nucl. Chem. 253, 477 (2002).
16. Skoog, D. A., Holler, F. J., Nieman, T.A.; Principles of Instrumental Analysis, 5th ed., Harcourt Brace and Company, Florida, 1998.

3-Pyridylketoxime as Zn(II) extractant from chloride solutions in pseudo-emulsion based hollow fibre strip dispersion (PEHFSD)

*Karolina Wieszczycka¹, Magdalena Regel-Rosocka^{*1}, Katarzyna Staszak¹, Teresa A. Reis², M. Rosinda C. Ismael², M. Lurdes F. Gameiro², Jorge M.R. Carvalho²*

Summary

Zn(II) removal from chloride solutions is an important problem in case of spent pickling solutions that are generated in hot-dip galvanizing processes. In this work operational parameters for PEHFSD with 1-(3-pyridyl)undecan-1-one oxime as the extractant of Zn(II) are presented.

Introduction

Zn(II) removal from chloride solutions is an important problem in case of spent pickling solutions that are generated in hot-dip galvanizing processes. 1-(3-pyridyl)undecan-1-one oxime is proposed as a novel extractant for metal ions in liquid-liquid extraction. Its performance in pseudo-emulsion based hollow fiber strip dispersion (PEHFSD), a new technology that attracts scientific interest as it joins advantages of extraction and membrane processes, is examined. During this separation extraction and stripping occur simultaneously in a single hollow fiber contactor without membrane stability issues. In PEHFSD, a pseudo emulsion of organic and stripping phase runs through the shell side while the aqueous feed phase flows in the lumen side. The solute is transported from the feed to the membrane and then to the stripping phase simultaneously. As soon as the process stops, the strip phase and organic phase get separated. Pseudo-emulsion based hollow fiber strip dispersion is proposed for the recovery of i.e. Cu(II) [1], Au(I) [2], Co(II) [3], Cr(III) [4] ions from aqueous solutions.

The aim of this work was to study possibility to use novel extractant, i.e. oxime of 1-(3-pyridyl)undecan-1-one for recovery of Zn(II) from chloride medium using PEHFSD technique. The modeling of mass transfer was performed and the overall mass transfer coefficient of permeation was related to the overall mass transfer coefficient of single extraction to analyze the contribution of each resistance to mass transfer.

Experimental

Reagents

Oxime of 1-(3-pyridyl)undecan-1-one was synthesized in a two-stage reaction. In the first stage 1-(3-pyridyl)undecan-1-one was synthesized by treating 3-pyridylcarbonitrile with decylmagnesium bromide. In the second stage, the

^{*1} e-mail: magdalena.regel-rosocka@put.poznan.pl, Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

² Department of Chemical Engineering, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

synthesized ketone was treated with hydroxylamine hydrochloride in the presence of sodium carbonate (at pH = 7). After hot filtration and cooling, yellow crystals were obtained. Recrystallization from ethanol and next from petroleum ether yielded pure (99.8%) yellow crystals melting at 124.3-125.7°C.

The yield of the oxime was 59% (LC-MS/MS, $[MH]^+$ - 263.4).

NMR (1H , ^{13}C) and MS(ESI) spectra proved the structure of the synthesized oxime:

1H NMR ($CDCl_3$) δ in ppm: 8.6 (d); 7.93 (t); 7.32 (d); 8.8 (s); 2.7 (t); 1.54 (q); 1.31-1.24 (m); 0.86 (t); 9.9 (s).

^{13}C NMR ($CDCl_3$) δ in ppm: 147.2; 132.2; 133.7; 149.3; 122.9; 157.0; 32.8; 31.6; 29.8; 29.6; 29.3; 29.1; 26.2; 25.6; 22.5; 14.0.

ESI-MS/MS m/z (% rel. intensity): 263.4 (100); 245.4 (5); 120.2 (22); 105.2 (43); 93.2 (34); 79.2 (39).

Toluene (Sigma-Aldrich, Germany) and decan-1-ol (Merck, Germany) were used as components of the organic phase. Sodium chloride, hydrochloric acid (38%) and chloride salts of Zn(II) (Sigma-Aldrich, Germany) were used as components of the aqueous phase. All the chemicals were of high purity analytical grade.

The aqueous solutions were analysed for metals concentration by AAS using a Perkin Elmer-AAnalyst 200.

Methods

The experimental setup used for carrying out PEHFSD experiments is shown in Figure 1. In this schematic diagram HF represents the microporous fiber module, which was a Liqui-Cel® Extra-Flow 2.5 in.×8 in. membrane contactor from Celgard (USA). Further module details are given in Table 1.

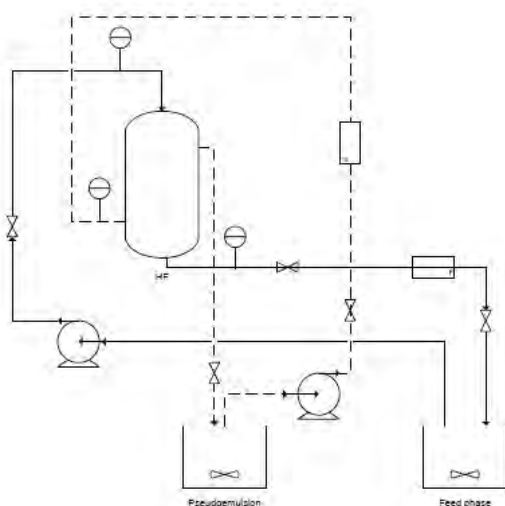


Figure 1. PEHFSD experimental setup.

Table 1. Characteristics of hollow fiber membrane module.

Type of module	G501 (contactor)
Module length (cm)	28
Module diameter (cm)	7.7
Case inner diameter (cm)	5.55
Centre tube diameter (cm)	2.22
Number of fibers	~10,800
Fiber	X50 – polypropylene
Effective fiber length (cm)	15.6
Inner diameter of the fibers (μm)	214
Outer diameter of the fibers (μm)	300
Pore size (μm)	0.03
Porosity (%)	40
Tortuosity	2.6
Inner interfacial area (m^2)	1.13
Area per unit volume (cm^2/cm^3)	28

The volume of pseudo-emulsion phase used in the experiment was 800 mL (400 mL of organic phase (0.1 M oxime in toluene with 10% v/v decan-1-ol) + 400 mL of stripping solution), whereas 2000 mL of feed solution contained 0.16 g/L Zn (II), 20 g/L HCl and 58 g/L NaCl.

Results and discussion

The data for the extraction experiments provide very regular and smooth solute concentration profiles in both processes considered (Figure 2).

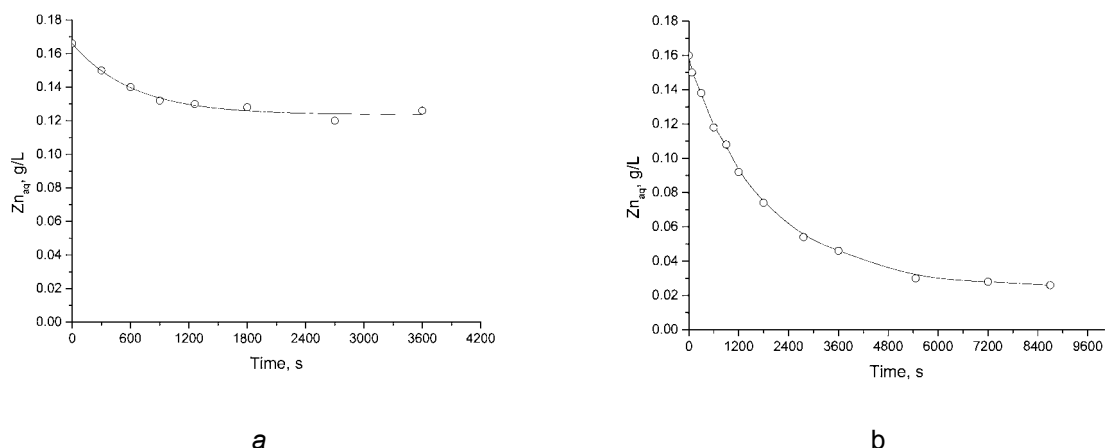


Figure 2. Zinc concentration profiles in the aqueous phases in process of: a) the single extraction b) PEHFSD.

The transfer of zinc ions from the aqueous phase to the organic phase can be described in terms of the overall mass transfer coefficient, K_{aq} [5]:

$$J = K_{aq} \cdot A_m \cdot (c_a - c_{a,eq})$$

where J is the solute flux, A_m the membrane area, c_a the concentration of zinc ions in the aqueous solution at time t and $c_{a,eq}$ is the concentration of zinc ions in the aqueous phase in equilibrium with the organic phase at this same time.

In the presented processes the overall mass transfer coefficient of extraction are equal to $4.4 \cdot 10^{-7}$ and $3.2 \cdot 10^{-7}$ m/s in single extraction and PEHFSD processes, respectively.

Moreover, resistances of mass transfer for single extraction were compared and presented in Table 2.

Table 2. Effect of diffusion on the mass transfer resistance and the overall mass transfer resistance values.

Diffusion of zinc ions in the feed phase:	< 5%
Diffusion through the pores:	> 60%
Diffusion of zinc complex in the organic phase:	> 20%
Overall mass transfer resistance of extraction, s/m	$2.3 \cdot 10^6$
Overall mass transfer resistance of permeation, s/m	$3.1 \cdot 10^6$
Resistance due to stripping, s/m	$8.4 \cdot 10^5$
% resistance due to stripping	27%

Conclusions

The PEHFSD technique was found to be a feasible process for the simultaneous separation and recovery of zinc from chloride medium using novel extractant - oxime of 1-(3-pyridyl)undecan-1-one as the carrier. For the system investigated, the transport of metal can be described by a time independent overall mass transfer coefficient. This overall mass transfer coefficient of permeation was compared with the overall mass transfer coefficient determined for single extraction.

Acknowledgments

This research was supported with 32-374/14 DS-PB and 32/441/14 DS-PB grants. PEHFSD studies were realized in the frame of Polish-Portuguese scientific and technological co-operation for the years 2013-2014 „Selective extractants for the removal of minor metallic elements from chloride spent pickling baths”.

References

1. S. Agarwal, M.T.A. Reis, M.R.C. Ismael, M.J.N. Correia, J.M.R. Carvalho, *Sep. Purif. Technol.*, 102 (2013) 103–110.
2. J.V. Sonawane, A.K. Pabby, A.M. Sastre, *AIChE J.*, 54 (2) (2008) 453–463.
3. F.J. Alguacil, I. Garcia-Díaz, F. Lopez, A.M. Sastre, *Sep. Purif. Technol.*, 80 (2011) 467–472.
4. F.J. Alguacil, M. Alonso, F.A. Lopez, A. Lopez-Delgado, *Sep. Purif. Technol.*, 66 (2009) 586–590.
5. M.J. González-Muñoz, S. Luque, J.R. Álvarez, J. Coca, *J. Membr. Sci.*, 213 (2003) 181–193.

Encapsulation of PC-88A in microcapsules of cross-linked gel of poly(vinyl alcohol)/ alginic acid and its extraction property of Co(II)

*K. Shiomori^{*1}, S. Komatsu¹, N. I. Inda¹, S. Kiyoyama²,
T. Takei³, M. Yoshida³*

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), which is an effective extractant of Co(II), was microencapsulated by two step crosslinking of sodium alginate by Ca^{2+} ion and polyvinylalcohol by glutaraldehyde. Globular microcapsules containing PC88-A droplets with the diameter around 4 mm were successfully prepared and had a relatively high strength. The microcapsules had smooth surface with large pores and many droplets of PC-88A in their inner side. The percentage content of PC-88A in the microcapsules was 18 % for wet state of the microcapsule. The extraction of Co(II) using the microcapsules containing PC-88A sharply increased at pH values greater than 5. Zn(II) extracted in the microcapsules was successfully back-extracted at pH values less than 4. No destruction of the microcapsules was observed during the repeated use of several times.

Introduction

The process of solvent extraction has been used for separation and recovery of various substances such as metal ions, organic acids, antibiotics, amino acids and proteins [1]. Solvent extraction sometimes has some problems in that the phase separation of organic and aqueous phases is difficult in some cases and extractants and/or organic solvents are lost by being dissolved in the aqueous phase. To solve these problems, the immobilization of the extractant [2, 3] and microencapsulation [4, 5] of the extractant have been investigated. Microencapsulation of extractants for metal ions, organic acids, amino acids and various compounds is one of effective methods to overcome some disadvantages on the liquid-liquid extraction process. The wall material of microcapsules is important to determine the characteristic of microcapsules. Calcium alginate is often used for a wall material of microcapsules due to easy preparation, especially for the microencapsulation of enzymes and microorganisms. However, the microcapsules prepared from calcium alginate have not so high durability. Therefore, mixed gels with calcium alginate and other polymers, chitosan, polyvinyl alcohol and so on, have been used to enhance strength and durability of microcapsules.

In this study, microencapsulation of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in a microcapsules with hydrophilic wall were investigated using two step crosslinking of sodium alginate by Ca^{2+} ion and polyvinyl alcohol by glutaraldehyde. The morphologies of the microcapsules prepared and during the preparation were investigated. The extraction properties of Co(II) in ammonium sulfate solution using the microcapsules were also investigated under various conditions.

^{*1} Corresponding Author, Dept. Applied Chem., Univ. Miyazaki, Gakuenkibanadai-nishi 1-1, 889-2192, Miyazaki, Japan,

² Dept. Chem. Sci. Eng., Miyakonojo National College of Technology

³ Dept. Chem. Eng., Kagoshima Univ.

Experimental

Reagents

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A, Daihachi Chemicalindustry Co., Ltd.) was used as the extractant. Sodium alginate and polyvinyl alcohol as a wall material, calcium chloride, glutaraldehyde, ammonium sulfate, cobalt (II) sulfate heptahydrate were purchased from Wako Pure Chemicals Co.

Preparation of microcapsules containing PC-88A

The preparation scheme of the microcapsules containing PC-88A is shown Fig.1. An aqueous solution containing poly vinyl alcohol (PVA) and sodium alginate (Na-Alg) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) as an organic phase were mixed to form O/W emulsion at 5,000 rpm for 5 min. at room temperature. In some cases, the O/W emulsion was treated by ultrasonic irradiation to reduce the droplet diameter. The O/W emulsion was extruded from a glass needle to a calcium chloride aqueous solution to form microcapsules and immersed for 30 min with gentle stirring for crosslinking of Na-Alg by Ca^{2+} ion. The microcapsules were then transferred to hydrochloric acid aqueous solution dissolving glutaraldehyde, and immersed for 2 h with gentle stirring for crosslinking of PVA by glutaraldehyde. The microcapsules prepared were washed with distilled water and stored in water until use.

The morphologies of the microcapsules were observed by scanning electron microscopy (Hitachi S-4100M and TM-1000, SEM) and a digital microscope (KEYENCE VH-8000). The internal structure of the microcapsules was examined by cross-sectioning of the microcapsules. The diameter of the microcapsules was measured from the digital microscope images.

The amount of PC-88A entrapped in the microcapsules was determined by the titration of ethanol solution eluted PC-88A from the microcapsules with $0.01 \text{ mol} \cdot \text{dm}^{-3}$ KOH/MeOH-BuOH using bromocresol green as the indicator.

Extraction of Co(II) with the microcapsules

The extraction of Co(II) from aqueous solution with the microcapsules containing PC-88A was carried out in a batch wise by contacting 1.0 g of the microcapsules and

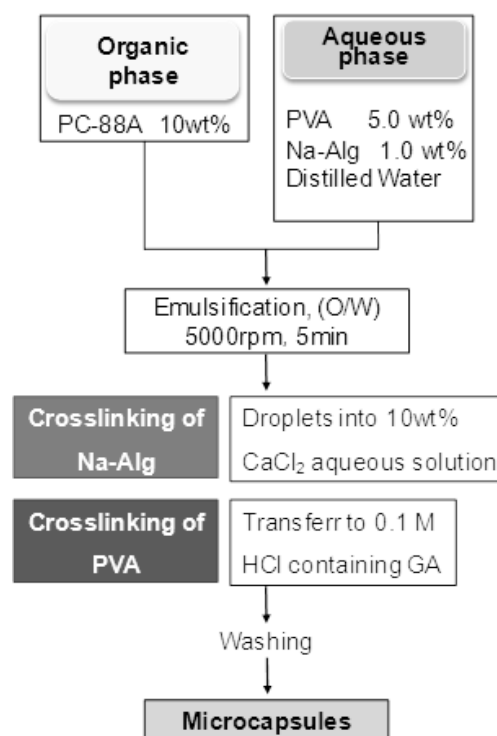


Fig. 1 The preparation scheme of the microcapsules containing PC-88A.

15 dm³ of the aqueous solution containing Co(II) at given time on several hours. After extraction, the microcapsules were filtrated from the raffinate. The Co(II) concentration in the raffinate and feed solutions were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of Co(II) adsorbed on to the microcapsules was calculated from the mass balance between the initial and the equilibrium metal concentrations in the aqueous solutions.

Results and discussion

Preparation of microcapsules containing PC-88A

The microscope photographs of O/W emulsion and the microcapsules are shown in Fig. 2. The diameters of O/W emulsion and the surface of the microcapsules measured from the photographs are shown in Table. 1. PC-88A was dispersed well in the aqueous solution of the polymers with the diameter around 2 μ m. Spherical and oval microcapsules containing PC88-A droplets with the diameter around 4mm were successfully prepared. The inside of the microcapsule was observed darkly by a lot of small droplets of PC-88A. The microcapsules shrank by the crosslinking of PVA with glutaraldehyde. The percentage content of PC-88A in the microcapsules was 18 %. The SEM images of the surface and the inside of the microcapsules are shown in Fig. 3. The microcapsules had dimpling pores on their

Table 1 The diameters of O/W emulsion and microcapsules.

	O/W emulsion [μ m]
	microcapsules [mm]
O/W emulsion	2.01 $\pm$ 0.19
before crosslinking of PVA	4.27 $\pm$ 0.19
after crosslinking of PVA	4.00 $\pm$ 0.19

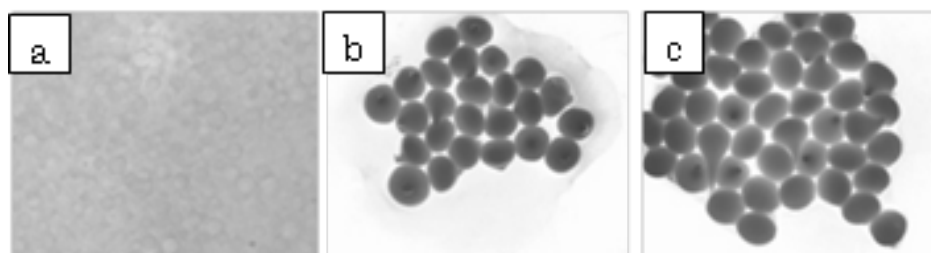


Fig. 2 The digital microscope images of O/W emulsion (a) and the microcapsules before crosslinking of PVA (b), and after crosslinking of PVA (c).

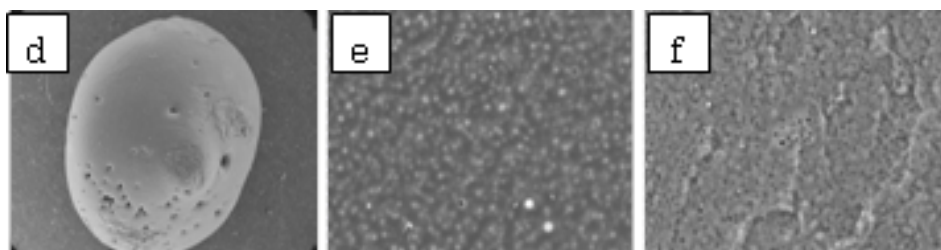


Fig. 3 The SEM images of the microcapsules. (d) : surface $\times$ 50; (e) : surface $\times$ 1000; (f) : cross-section $\times$ 1000

surface. These pores would be traces of the droplets of PC-88A which were released from the surface in the first crosslinking of alginate. A lot of small pimples, which were frequently observed as bright spots by SEM, were observed on the surface and inside of the microcapsules. These would be caused by the existence of the droplets of PC-88A in the gel wall.

Extraction properties of Co(II) using the microcapsules containing PC-88A

The effect of the pH in the aqueous phase on the forward and back extraction of Co(II) is shown in Fig. 4. The extraction of Co(II) increased sharply above pH 5. This result was almost the same pH dependence as reported for the solvent extraction system using PC-88A [6]. Therefore, PC-88A encapsulated into the microcapsules shows the same extraction properties as in the solvent extraction system. The back extraction of the Co(II) extracted into the microcapsules was successfully carried out by using a sulfuric acid solution at a pH value lower than 4.

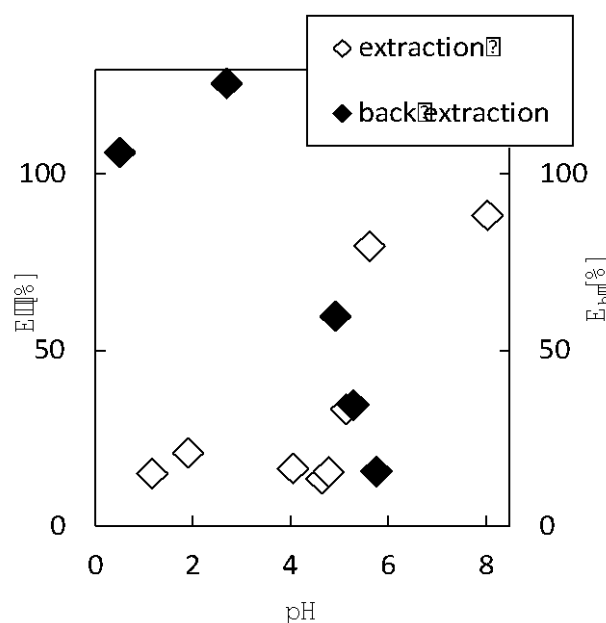


Fig. 4 Effect of the aqueous pH on the extraction of Co(II) by the microcapsules. $E_{PC-88A}=18$ wt%, $M_{MC}=0.20$ g, $C_{Co,aq,ini} = 200$ mg·dm⁻³, aqueous solution = 15×10^{-3} dm³

The extraction of Co(II) was carried out using the microcapsules prepared with and without ultrasonic treatment of O/W emulsion as shown in Fig. 5. The amount of Co(II) extracted to the microcapsules gradually increased with time and reached equilibrium values. The extraction properties of Co(II) using the microcapsules prepared with and without the ultrasonic treatment were almost same. The droplets of PC-88A became small and their surface area increased by the ultrasonic treatment, however the effect of ultrasonic treatment was not observed on the extraction rate. This suggests that the diffusion of Co(II) in the wall of the microcapsules is the rate determining step of the extraction of Co(II) with the microcapsules prepared in this study.

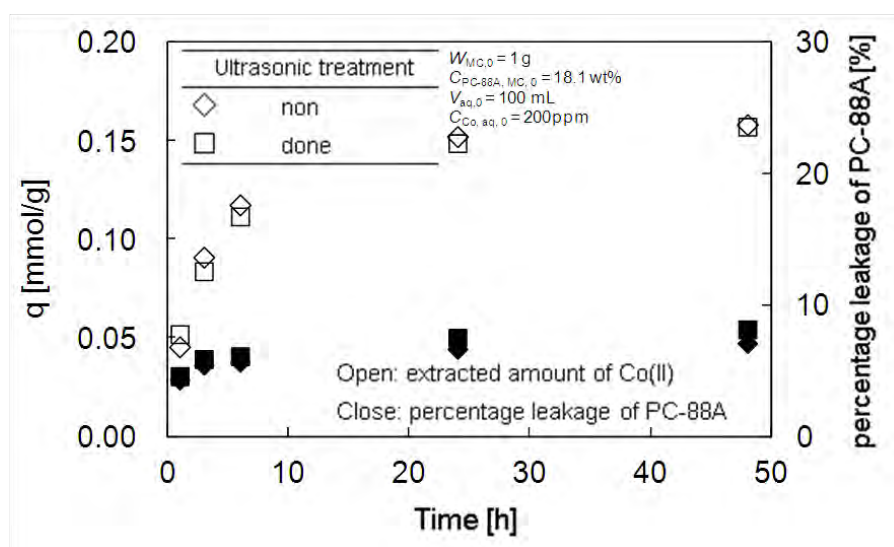


Fig. 5 Effect of time on the extraction of Co(II) by the microcapsules prepared with and without ultrasonic treatment of O/W emulsion. $E_{PC-88A}=18$ wt%, $M_{MC}=1.0$ g, $C_{Co, aq, ini} = 200 \text{ mg} \cdot \text{dm}^{-3}$, aqueous solution $=100 \times 10^{-3} \text{ dm}^3$

Conclusion

Microcapsules containing PC-88A were successfully prepared by crosslinking of Na-Alg by Ca^{2+} ion and crosslinking of PVA by glutaraldehyde. The diameter of the microcapsules was around 4 mm and the percentage content of PC-88A in the microcapsules was 18 %. The extraction of Co (II) increased sharply above pH 5. The back extraction of Co (II) extracted into the microcapsules was successfully carried out by using the sulfuric acid solution at pH lower than 4. The diffusion of Co(II) in the wall of the microcapsules was suggested to be the rate determining step of the extraction of Co(II) with the microcapsules.

References

- 1) Kanto Branch of The Society of Chemical Engineers, Japan, The Society of Separation Process Engineers, Japan, "Chushutu Gijyutu Shuran", 1995, Kagaku Kogyosha, Inc., Japan.
- 2) N. Kabay, O. Solak, M. Arda, U. Topal, M. Yuksel, A. Trochimczuk, M. Streat, *React. Func. Polym.*, **64**, 75 (2005).
- 3) T. Kitabayashi, T. Sana, S. Kiyoyama, M. Yoshida, K. Shiomori, *Solvent. Extr. Res. Dev. Jpn*, **20**, 137, (2013)
- 4) S. Kiyoyama, K. Shiomori, M. Yoshida, *Ars Separatoria Acta*, **7**, 45 (2009).
- 5) K. Shiomori, K. Fujikubo, Y. Kawano, Y. Hatate, Y. Kitamura, H. Yoshizawa, *Sep. Sci. Tech.*, **39**, 1645 (2004).
- 6) N.V. Thakur, *Hydrometal.*, **48**, 125 (1998)

Development of a highly selective solvent extraction system for the separation of Pd(II) from a solution of a leached automotive catalyst

*Juliane Traeger^{*1}, Hans-Jürgen Holdt^{*2}*

Summary

A chelating dithioether ligand for Pd(II), which is aimed to be used in industrial practice, has been designed. Based on this new extractant, which is outstanding in terms of its selectivity and extraction rate, a solvent extraction system has been customised for the recovery of Pd(II) from hydrochloric, oxidising leach solutions gained from automotive catalysts. The organic phase of the extraction system can be used several times without any decline of selectivity and efficiency. Additionally it was found that a small amount of the mono-oxidised extractant may act as a phase transfer catalyst.

Introduction

Palladium is not only classified as one of the critical raw materials for the European Union, but also as one of the 'green minor metals', which are the basis for cleaner technology innovation.[1,2] The recovery of this rare and valuable metal from secondary sources is important from an economic as well as an environmental perspective. Automotive catalysts represent the most important demand segment for this PGM and, at the end of their life, they also play a major role as a secondary source.[3,4] Rising scrappage rates and constantly high price levels make the development of new customised extraction systems for palladium rewarding.

Process streams containing PGM are usually strongly hydrochloric and oxidising, so that the metals form chlorido-complexes. Under these conditions palladium occurs in the divalent oxidation state and is mainly present as the square-planar anion $[\text{PdCl}_4]^{2-}$. [5] In contrast to most other PGM chlorido-complexes, that are commonly found in such streams, this species is relatively labile, which is why palladium can be extracted by a ligand exchange mechanism.[6] Usually this type of mechanism is able to provide a higher selectivity than ion exchange-based processes, though often this is also accompanied by slower extraction kinetics.

Typical leach liquors from spent automotive catalysts contain also platinum and rhodium, rare earth and base metals as well as alkaline earths, which makes high demands on the selectivity of the palladium extractant. Aside of that, main criteria for a practical application of an extractant are: a high loading capacity (even at high HCl concentrations of the feed solution), fast extraction kinetics, a good stability towards oxidation, a low solubility in the aqueous phase, an easy stripping of the loaded Pd(II)

1

^{*}University of Potsdam, Institute of Chemistry, Department of Inorganic Chemistry, Karl-Liebknecht Straße 24-25, 14476 Potsdam, Germany; Tel.: +49 331 9775750; fax: +49 331 9775055. E-mail address: traegerj@uni-potsdam.de.

2

University of Potsdam, Institute of Chemistry, Department of Inorganic Chemistry, Karl-Liebknecht Straße 24-25, 14476 Potsdam, Germany; Tel.: +49 331 9775180 fax: +49 331 9775055. E-mail address: holdt@uni-potsdam.de

and a cost-efficient synthesis. Additionally there must be an appropriate diluent with not only good solubility characteristics for the extractant and the palladium complex that is formed, but also a high flash and boiling point, a low solubility in the aqueous phase and a density which aids phase separation.[7a]

Up to now, the solvent extraction (SX) of palladium in industry is mainly done with hydroxyoximes or long-chain thioethers.[8,9] However, the disadvantage of these ligands is, that they suffer from quite slow extraction rates. Although the slow kinetics can be accelerated with the help of phase-transfer catalysts, this in expense of the selectivity.[6,7b]

Therefore it was our aim to design a new, highly selective extractant for palladium, that does not only fulfill all the criteria mentioned above, but especially enables shorter equilibrium times than the industrially used ligands. Beyond that, an extraction system including an appropriate diluent and stripping agent had to be found, whose organic phase has the potential to be used over and over again.

Results and discussion

Design of the Extractant

It is well known that dithioethers based on *cis*-1,2-dithioethene are rigid, chelating ligands that perfectly meet geometric requirements for a square-planar complexation of Pd(II) and hence the formation of [PdCl₂(L)].[10] In order to be able to cope with oxidising process streams, the resistance of such ligands to oxidation can be improved by implementation of electron-withdrawing substituents. Figure 1 shows the unsaturated 1,2-dithioethers **1–12** that we have synthesised with varying electron-withdrawing backbones and end-groups differing in polarity and rigidity. These include a set of six acyclic dithioether ligands that has been recently developed by us, namely **1, 2, 4, 5, 7, 8**. [11] Furthermore we synthesised the acyclic ligands **3, 6, 9** [10,12,13] and the crowns ethers **10, 12** [14,15], which has been known before, but with the exception of **12** never had been tested for SX. The crown ether **11** is new and its synthesis is analogous to **10**. We investigated these ligands systematically in matters of their extraction performance in a model system, their solubility in water and also in matters of their oxidation potential and complex stability constant (see Table 1) to evaluate their suitability as solvent extractant. Experimental details are analogous to those described in reference [11].

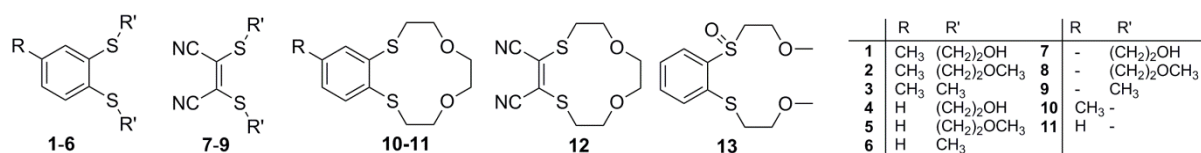


Figure 1. Structures of the dithioether ligands **1–12** tested for SX of Pd(II) and structure of the thioether-sulfoxide **13**.

The oxidation potential E_{P}^{Ox} of the dithioether ligands is mainly determined by their backbone. While E_{P}^{Ox} of the reference compound (*Z*)-1,2-bis(methylthio)ethane is only 0.93 V, the values of our ligands are much higher and increase in the following

order: 4-methylbenzene < backbone benzene backbone < double bound with cyano groups. This is caused by an increasing reduction of electron density on the sulfur atoms. However, the trend for the stability of the palladium complex $[PdX_2(L)]$ points just in the opposite direction. Since a potential Pd(II) extractant has to feature both, a high resistance to oxidation and a high complex stability, dithiobenzene-based ligands (**4–6**, **11**) emerge as an acceptable compromise relating to these two criteria. The $\log K_{[PdX_2(L)]}$ values are also considerably influenced by the polarity of the end-groups. Ligands with polar 2-hydroxyethyl groups form more stable complexes than those containing less polar 2-methoxyethyl groups. A comparison between the complex stability constants of **8** and **12** shows that rigid crown ethers form more stable complexes than their open-chain equivalents, which is due to a smaller loss of entropy.

Table 1. Selected properties of the ligands 1-12: the oxidation potential E_P^{Ox} in MeCN, the complex stability constants $\log K_{[PdX_2(L)]}$ as determined by UV/Vis titration in water ($X = Cl^-, H_2O$), the concentration of the ligand in an acidic aqueous phase $c(L)_{aq}$ after mixing organic and aqueous phase ($c_0(L)_{CHCl_3} = 10^{-2}$ M, $c(HCl)_{aq} = 1.5 \times 10^{-2}$ M, $t = 90$ min, $A/O = 1$), the time t_{eq} it takes to establish the extraction equilibrium and the extraction yield at this time E_{eq} at low HCl concentration ($c_0(L)_{CHCl_3} = 10^{-2}$ M, $c_0(Pd)_{aq} = 10^{-4}$ M, $c(HCl)_{aq} = 1.5 \times 10^{-2}$ M, $A/O = 1$), selected extraction yields E_{eq} in equilibrium state at higher HCl concentrations ($c_0(L)_{CHCl_3} = 10^{-2}$ M, $c_0(Pd)_{aq} = 10^{-4}$ M, $A/O = 1$).

L	E_P^{Ox} [V]	$\log K_{[PdX_2(L)]}$	$c(L)_{aq}$ [M]	t_{eq} [min]	E_{eq} [%]	$c(HCl)_{aq}$ [M]	E_{eq} [%]
1	1.21	7.98	2×10^{-4}	1440	0		
2	1.22	6.01	$< 1 \times 10^{-6}$	60	98.9	6	98.8
3				90	98.7	6	96.4
4	1.29	7.99	7×10^{-4}	1440	0		
5	1.29	5.97	2×10^{-6}	60	98.5	6	98.8
6				60	97.7	6	87.6
7	1.79	-*	7×10^{-3}	-*	-*		
8	1.84	4.74	5×10^{-6}	90	57.9	0.3	0
9				90	4.9		
10				10	98.5	6	92.5
11				10	97.4	6	91.6
12		6.2**		15	97.3	1.5	2.2

* The value could not be determined as an insoluble precipitate was formed.

** The value is taken from reference [15] and was determined in MeOH.

The trends described above reflect partially in the extraction experiments. In equilibrium the extraction yields E_{eq} of maleonitrile dithioether ligands are generally lower than those of the comparable dithioether ligands with aromatic moiety. The only exception is the crown ether **12** at a low HCl concentration of the aqueous phase, albeit at higher HCl concentrations, meaning an excess of Cl^- and a competition for binding places at Pd(II), its extraction yield also decreases drastically. In contrast, the dithiotoluene- and dithiobenzene-based ligands exhibit high extraction yields even at

a concentration of 6 M HCl. Although the complex stability constant of $[\text{PdX}_2(\mathbf{1})]$ and $[\text{PdX}_2(\mathbf{4})]$ have been very high, the extraction yield obtained with these ligands was 0%. This can be explained by an enhanced solubility in water caused by the polar 2-hydroxyethyl groups. A mixing experiment showed that the concentration of **1** and **4** in the aqueous phase was more than 100 times higher than that of **2** and **5**, respectively. Looking at the time t_{eq} it takes for the individual ligands to establish the extraction equilibrium, demonstrates that a certain polarity, which in turn enhances the interfacial activity, is advantageous. The t_{eq} value of **2**, whose end groups are 2-methoxyethyl, is 60 minutes, whereas that of **3**, which has methyl groups instead, is 90 minutes. The fastest kinetics could be observed by using the crown ethers, which is again attributable to their rigidity. However, besides **1**, **4** and **7** all of the dithioether ligands we investigated in this study exhibit substantially shorter equilibrium times than the industrial used extractants dihexyl sulfide and Aloxime[®]840, for which t_{eq} values of 240 and 300 minutes, respectively, have been found.

Taking all the criteria discussed above into account, the acyclic ligand **5** and the analogue crown ether **11** are potentially suitable Pd(II) extractants. Since the synthesis of **5** is easier and gives higher yields and furthermore because its extraction yield at 6 M HCl is higher, this ligand was chosen for further testing.

Extraction system

The next step was to create an extraction system considering requirements of industrial practice. Therefore the aqueous phase and the diluent have been modified and furthermore an effective stripping agent has been found. The chloroform, which was used as diluent for the SX tests described above, has been replaced by 1,2-dichlorobenzene, which offers a high boiling point (180.5 °C) and a very low solubility in water (0.0156 wt.% at 25 °C) [17]. Due to the polarity of the Pd(II) chelate complex formed, a relatively polar diluent is needed.

Using 1,2-dichlorobenzene we observed somewhat lower extraction yields than with chloroform, but the extraction equilibrium also establishes faster. In the next step the oxidising leach liquor of an automotive catalyst, whose preparation is described in reference [16], was chosen as the aqueous phase. Table 2 demonstrates the balance of the extraction yield, which was determined for several stages by taking into account the matrix of that leach liquor as well as its palladium content.

Table 2. Balance of the extraction yield determined for several stages with the help of a McCabe-Thiele plot ($c_0(\text{Pd})_{\text{aq}} = 4.5 \times 10^{-6} - 4.7 \times 10^{-3} \text{ M}$ in 1:2 diluted, abreacted aqua regia; $c(\mathbf{5})_{\text{C}_6\text{H}_4\text{Cl}_2} = 10^{-2} \text{ M}$).

Stage	[%]
1	92.5
2	99.4
3	99.96
4	99.997
5	99.9998

The extractant **5** forms a stable coordination complex with Pd(II), hence a strongly nucleophilic stripping agent was needed to back-extract the palladium into the aqueous phase. Of the 13 reagents tested [16] the

best results, meaning the highest stripping yields ($98.9 \pm 0.2\%$) and fastest kinetics, have been obtained by using 0.5 M thiourea (tu) in 0.1 M hydrochloric acid.

Finally the performance of the new SX system was evaluated by repeatedly extracting Pd(II) out of the leach liquor, back-extracting it with the help of the stripping agent and using the organic phase again for the next cycle. Figure 2 shows that the organic phase possesses an outstanding selectivity for Pd(II). Even after the 5th cycle the separation factor towards all other metals contained in the aqueous phase was higher than 7000 and the extraction yield was also constantly high ($= 93.0 \pm 0.3\%$).

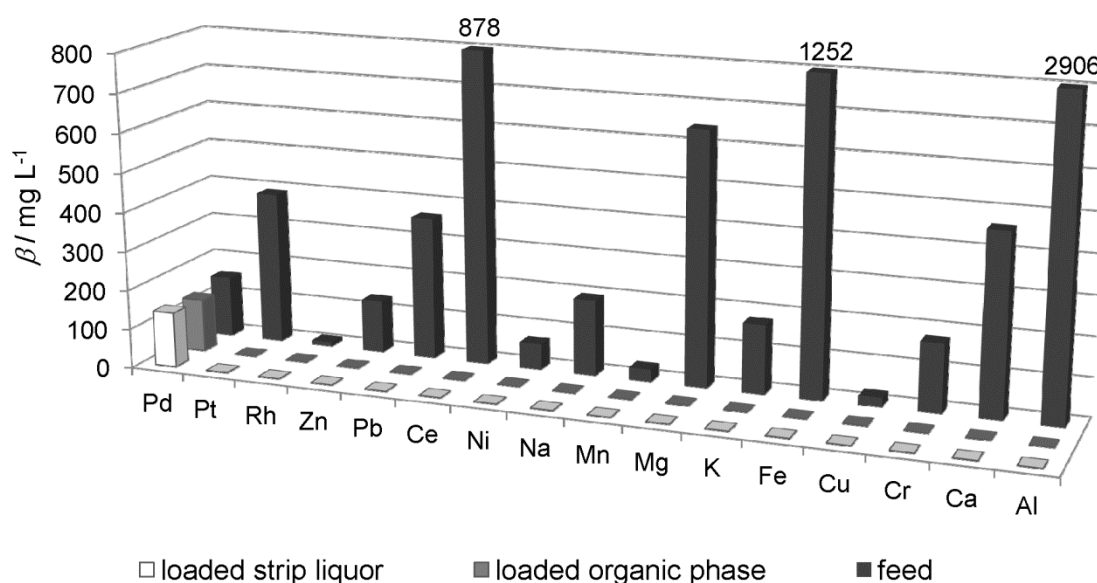


Figure 2. Composition of the leach liquor (automotive catalyst dissolved in aqua regia and diluted 1:2, oxidation potential 1.09 vs. SHE), the loaded organic phase ($c(\mathbf{5})_{\text{C}_6\text{H}_4\text{Cl}_2} = 10^{-2} \text{ M}$) and the loaded strip liquor ($c(\text{tu}) = 0.5 \text{ M}$, $c(\text{HCl}) = 0.1 \text{ M}$) after the 5th extraction/stripping cycle ($A/O = 1$).

Furthermore it was found that during the extraction a small amount of the thioether-sulfoxide **13**, which could only be detected via HPLC, can form. This compound is the first oxidation product of extractant **5** and can also form an inner-sphere chelate complex with Pd(II) via its two sulfur atoms.[18] However, at higher HCl concentrations **13** can be protonated. In the protonated form it acts as a kind of phase transfer catalyst and accelerates the extraction. The mechanism is believed to be similar to that reported by Preston and duPreez for dialxylsulfoxides.[19]

Conclusion

Out of a series of twelve dithioether ligands we selected 1,2-bis(2-methoxyethyl)-benzene as a promising new candidate for the solvent extraction of Pd(II). For that, properties like the stability towards oxidation, the stability of the $[\text{PdCl}_2(\text{L})]$ complex formed, the extraction yield and kinetics, as well as expenses for synthesis have been considered. With that ligand the extraction proceeds faster than with industrial

used extractants. Due to the geometric and electronic preorganisation of its chelating unit, this ligand is highly selective for Pd(II). In order to be able to use this extractant in practice, we created a SX system with an appropriate diluent and stripping agent. Although we found out that during extraction a small amount of the ligand is being oxidised and forms a thioether-sulfoxide, this is not impairing the extraction performance of the organic phase. Even after several extraction/stripping cycles the separation factor towards all other metals found in the leach liquor of an automotive catalyst is extremely high.

References

1. European Commission, *Critical raw materials for the EU*, 2010.
2. UNEP, *Critical Metals for Future Sustainable Technologies and their Recycling Potential*, 2009.
3. J. Butler, *Platinum 2013 Interim Review*, Johnson Matthey PLC.
4. C. Hagelüken, *Metall*, 61, 24–39.
5. F. Bernardis, R. A. Grant, D. C. Sherrington, *React. Funct. Polym.*, 65, 205–217.
6. M. J. Cleare, R. A. Grant, P. Charlesworth, *Extr. Metall. 81 Pap. Symp.*, 5, 34–41.
7. K. C. Sole, In: M. Aguilar, J. L. Cortina, (Eds.), *Solvent Extraction and Liquid Membranes*, Taylor & Francis Group, Boca Raton, 2008, a) 145–146, b) 171–176.
8. S. F. Woollam, R. A. Grant, *Proceedings of ISEC 2008*, 281–286.
9. F. K. Crundwell, M. S. Moats, V. Ramachandran, T. G. Robinson, W. G. Davenport, W.G., *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*, Elsevier, Oxford, 2011, 498–533.
10. F. R. Hartley, S. G. Murray, W. Levason, H. E. Soutter, C. A. McAuliffe, *Inorg. Chim. Acta*, 35, 265–277.
11. J. Traeger, T. Klamroth, A. Kelling, S. Lubahn, E. Cleve, W. Mickler, M. Heydenreich, H. Müller, H.-J. Holdt, *Eur. J. Inorg. Chem.*, 2012, 2341–2351.
12. E.W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik, B. L. Williams, *Polyhedron*, 1, 289–298.
13. R. Heber, *J. Prakt. Chem.*, 318, 19–25.
14. H.-J. Holdt, H. Müller, A. Kelling, H.-J. Drexler, T. Müller, T. Schwarze, U. Schilde, I. Starke, *Z. Anorg. Allg. Chem.*, 623, 114–122.
15. H.-J. Holdt, *Pure Appl. Chem.*, 65, 477–482.
16. J. Traeger, J. König, A. Städtke, H.-J. Holdt, *Hydrometallurgy*, 127-128, 30-38.
17. Y. Marcus, In: J. Rydberg, C. Musikas, G. R. Choppin (Eds.), *Principles and Practices of Solvent Extraction* (Eds.), Marcel Dekker, New York, 1992, 22–32.
18. J. Traeger, A. Kelling, U. Schilde, Prof. H.-J. Holdt, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, C68, m238–m241.
19. J. S. Preston, A. C. du Preez, *Solvent Extr. Ion Exch.*, 20, 359–374.

THERMORESPONSIVE GELS INCLUDING THIOCROWN ETHER UNIT FOR EXTRACTION OF CLASS *b* METAL IONS

Kenji Chayama¹

Professor, Department of Chemistry, Faculty of Science and Engineering, Konan University, Japan

Takumi Hirooka

Department of Chemistry, Faculty of Science and Engineering, Konan University, Japan

and

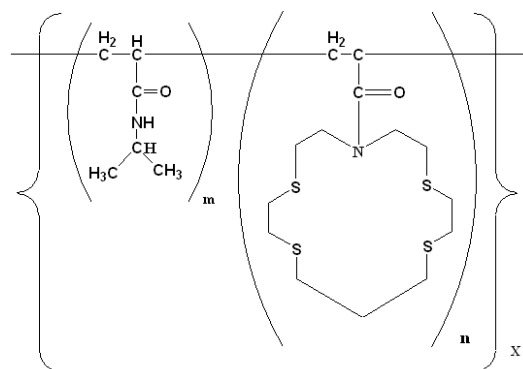
Satoshi Iwatsuki

Associate Professor, Department of Chemistry, Faculty of Science and Engineering, Konan University, Japan

ABSTRACT

Polymer extraction of class *b* metal ions using the copolymers of poly(N-isopropylacrylamide) and monoazatetrathiocrown ether derivatives were examined. One of the reagent containing cyclic monoazatetrathioether unit, 1-aza-4,7,11,14-tetrathiacyclohexadecane (ATCH) were synthesized by the cyclization reaction between bis(2-chloroethyl)amine hydrochloride and 1,4,8,11-tetrathiaundecane (TTU) in alkaline solution. The monomer unit 1-acryloyl-1-aza-4,7,11,14-tetrathiacyclohexadecane were synthesized. Reagents

synthesized were isolated by NMR spectra. The polymerization reaction was performed with N,N-dimethylformamide as a solvent and $\alpha\alpha'$ -azobisisobutyronitrile as the initiator. The molar ratio of the monomers N-isopropylacrylamide and 1-acryloyl-ATCH were varied in a range between 20:1 and 150:1 in feed. The resulting products were precipitated in double distilled water and washed for two or three days then evaporated. The polymer synthesized (ATCH-NIPAAm) were dissolved in an aliquot volume of water. The sulfur atom concentration of the solution was determined by ICP-AES. The extraction behaviour of metal ions were clarified with those of with the copolymer incorporating monoaza-tetrathioether units. When the temperature of the solution containing the copolymer increases, the phase transfer occurred and lipophilic species might be absorbed into the polymer phase and separated from the aqueous phase. As the polymer contains the monoaza-tetrathiocrown ether unit, a metal ion which is familiar with thioether group may be coordinated with the thioether groups in the polymer chain. Then, the metal ion might be transferred into the polymer phase with an appropriate anion to compensate the charge.



¹ Corresponding author. Department of Chemistry, Faculty of Science and Engineering, Konan University, Okamoto 8-9-1, Higashinada, Kobe, 658-8501 Japan, Phone: +81-78-435-2500. Email: chayama@konan-u.ac.jp.

Recovery of Gallium and Indium from Synthetic Leach Solution of Zinc Refinery Residue using Novel Synergistic Solvent Extraction

Sankum Nusen^{1,2}, Torranin Chairuangsr¹, Zhaowu Zhu², Chu Yong Cheng^{2*}

Summary

A synergistic solvent extraction (SSX) system consisting of LIX 63 and Versatic 10 has been developed to recover In and Ga from a synthetic sulphate leach solution of zinc refinery residues. The SSX system was able to selectively extract In and Ga over other metals. About 20-30% Ni, Co and Ge were co-extracted while only very small amounts Zn, Cd, Sb and almost no Mn, Mg and Ca were co-extracted from the synthetic leach solution. Ferric iron was reduced with iron powder and copper removed using LIX 984 before Ga and In extraction to avoid their co-extraction. Ga and In were stripped readily using 0.05 M H₂SO₄. The SSX system consisting of 0.12 M LIX 63 and 0.12 M Versatic 10 in ShellSol D70 was selected for the extraction of In and Ga from synthetic feed solutions containing 1 g/L In and Ga, respectively. At pH 3.0, 86% In and 92% Ga were extracted in a single contact. The synergistic effect on In extraction was significant while no or weak synergistic effect on Ga extraction. The novel SSX system has a great potential for the recovery of In and Ga from leach solutions of zinc refinery residues.

Introduction

Indium and gallium are valuable but scattered elements and one significant source is the zinc refinery residue (Mihaylov and Distin, 1992; Paiva, 2001). After leaching with sulphuric acid in most cases, solvent extraction (SX) is widely studied and used for their separation and purification.

Acidic organophosphorus extractants including M2EHPA (mono(2-ethylhexyl)phosphoric acid), D2EHPA (di(2-ethylhexyl)phosphoric acid), PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) were widely tested for the recovery of In with Fe(III) reduced to Fe(II) and Cu(II) and As(III) cemented with iron powder before SX (Levin et al., 1967; Tomii and Tsuchida, 1981; Aavila et al., 1992; Sato and Sato, 1992; Fortes et al., 2003). High In extraction is obtained with these extractants, but high stripping efficiency can only be achieved with high concentration HCl or HClO₄ solutions (Virolainen et al., 2011; Yang et al., 2013). This is a significant disadvantage of using the above reagents.

Judd and Harbuck (1990) studied the extraction of Ga from leach solutions of zinc plant residues using OPAP (octylphenyl acid phosphate) and isodecanol in kerosene. Overall Ga recovery with this system reached 94%. However, the reagent is not commercially available. Katsura and Abe (1975) reported that after Fe(III) reduction, over 93% Ga and 94% In were co-extracted with 20% Versatic 10 at pH 3.5 and only 0.26% Cu, no Zn, 2.5% Fe(II) and 1.1% Al(III) were co-extracted. Ga and In were stripped with low acidity strip solutions. The separation of Ga and In by acidifying the loaded strip liquor to >2.5 M H⁺ and using two SX circuits is un-economical.

In a process developed by Zhou et al. (1989), D2EHPA was used for the separation of In and iron from the solution and then H106 (a mixture of neo-tridecyl and neo-pentadecyl hydroxamic acid) was used for co-extraction of Ga and Ge. Over 90% In, 94% Ga and 93% Ge were recovered. In this process, further separation of In and Fe(III) is required and H106 is not commercially available.

The aim of the current study is to identify the more efficient and effective SX and SSX systems in terms of extraction and stripping for the recovery of In and Ga from sulphuric acid leach solutions of zinc residues using commercially available reagents.

*Corresponding author email: chu.cheng@csiro.au

¹Department of Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

²CSIRO Minerals Down Under National Research Flagship, Australia

Experimental

To select suitable SX and SSX systems, metal extraction pH isotherm tests were conducted using a synthetic leach solution (Table 1). The solution was prepared by dissolving the required amounts of analytical grade metal sulphates in de-ionised water. Extractants LIX 63 and Versatic 10 and all diluents were used as received, with purities as advised on the relevant MSDS.

All shaking-out tests were carried out in a reactor immersed in a temperature controlled water bath. The pH of the aqueous solution was measured during mixing using a pH electrode and a pH meter. Where necessary, solution pH was adjusted by the addition of 10-100 g/L NaOH or 100 g/L H₂SO₄ solutions.

The aqueous and organic phases of the samples were separated using 1PS separation filter. The organic samples were stripped using 100 g/L H₂SO₄ or 80 g/L NaOH. The loaded strip liquors and aqueous samples from each test point were taken for chemical analysis using ICP-AES.

Table 1. Composition of the synthetic leach solution of typical cementation residue

Elements	Cd	Zn	Co	In/Ga/Ge/Ni/Al/Fe/Cu/Sb/Mn/Mg/Ca
Concentration (g/L)	71.9	17.0	0.90	0.05-0.06

Results and discussion

Selection of an organic system

Scoping tests were conducted with organic systems consisting of M2EHPA, D2EHPA, Ionquest 801, Cyanex 272, Versatic 10, LIX 63 and all combinations thereof to select an effective system for the extraction of Ga and In together in terms of extraction and stripping. The SSX system consisting of LIX 63 and Versatic 10 performed best. With the SSX system containing 0.25 M LIX 63 and 0.20 M Versatic 10 in ShellSol D70, 92% In, 98% Ga and Cu and 94% Fe(III) were extracted at pH 3.5, A/O ratio of 1 and 40 °C (Figure 1). About 20-30% Ni, Co and Ge were also co-extracted while only very small amounts of Zn, Cd, Sb and almost no Mn, Mg and Ca were co-extracted at this pH. Due to very low concentration of Ni, Co and Ge, small amounts of these co-extracted metals would be crowded out or scrubbed in a counter-current operation. The phase separation was fast and no third phase or precipitate was observed in the pH range of 0.2-3.5.

Most importantly, it was found that In, Ga, Cu and Fe(III) were completely stripped from the loaded organic solution with H₂SO₄ solution at pH 1.0 (Figure 2). This also indicates that Fe(III) and Cu must be removed before solvent extraction to prevent their co-extraction. In the current study, over 99.5% Fe(III) was reduced to Fe(II) with iron powder at 70 °C and the re-oxidation of Fe(II) to Fe(III) was prevented by bubbling N₂ gas during extraction. The Cu was eliminated before In and Ga extraction using the organic system consisting of 0.05 M LIX 984N in ShellSol D70 at 40 °C. Over 98% Cu was extracted at pH 2.0 while only 8-11% Ga, In and Fe(III) were co-extracted. After Fe(III) reduction and Cu removal, 97% In and 99% Ga were extracted while only 15% Fe(II) and 12% Ge was co-extracted at pH 3.5 with the organic system consisting of 0.25 LIX 63 and 0.20 Versatic 10 in ShellSol D70 at 40 °C (Figure 3). Almost 100% In and 91% Ga were stripped using 0.05 M H₂SO₄ solution (Figure 4). This is a very significant finding for the separation and recovery of In and Ga from synthetic sulphate solution due to their high extraction at pH 3.5 and very easy stripping using 0.05 M H₂SO₄ solution.

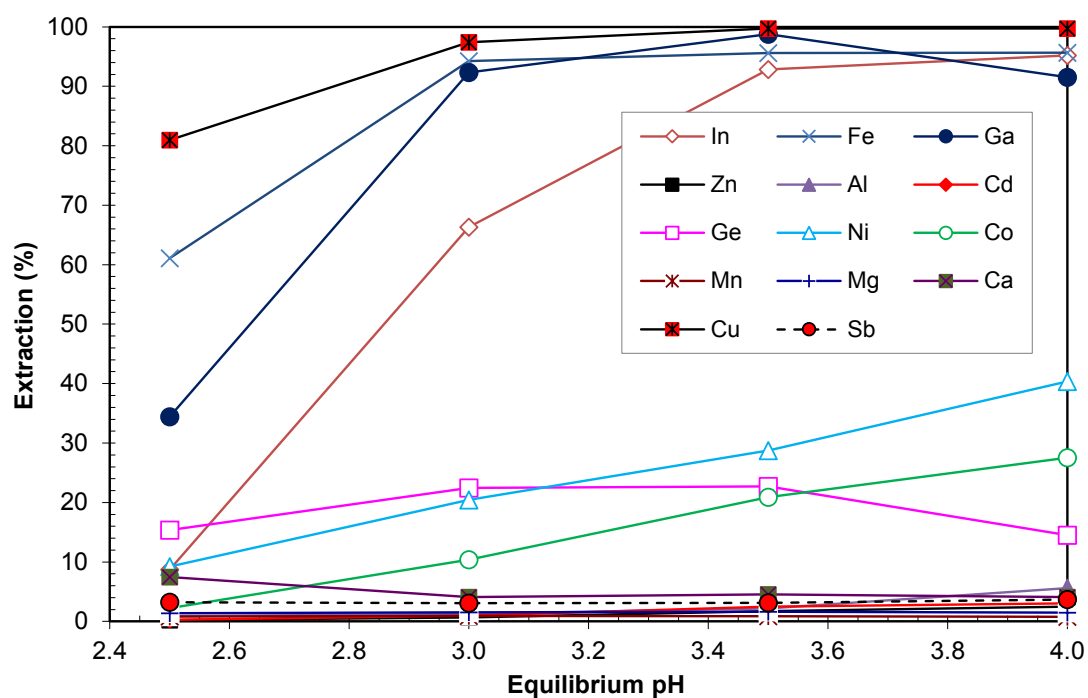


Figure 1. Metal extraction pH isotherms with 0.25 M LIX 63 and 0.20 M Versatic 10.

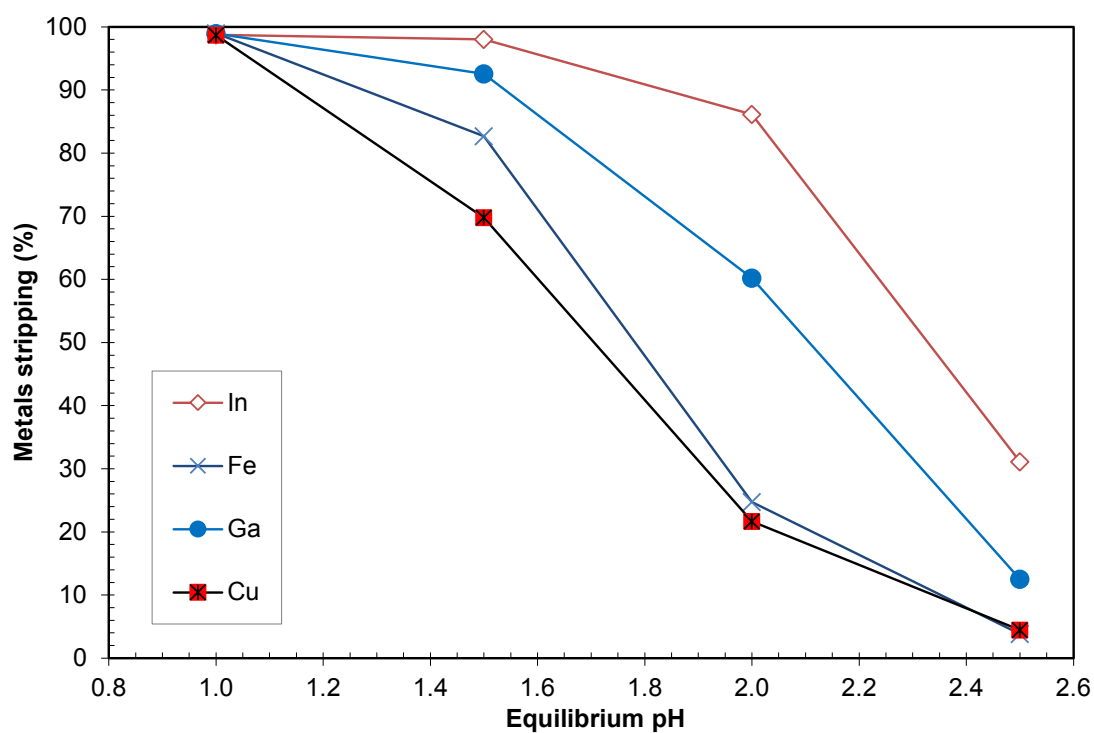


Figure 2. Metal stripping pH isotherms with loaded 0.25 M LIX 63 and 0.20 M Versatic 10.

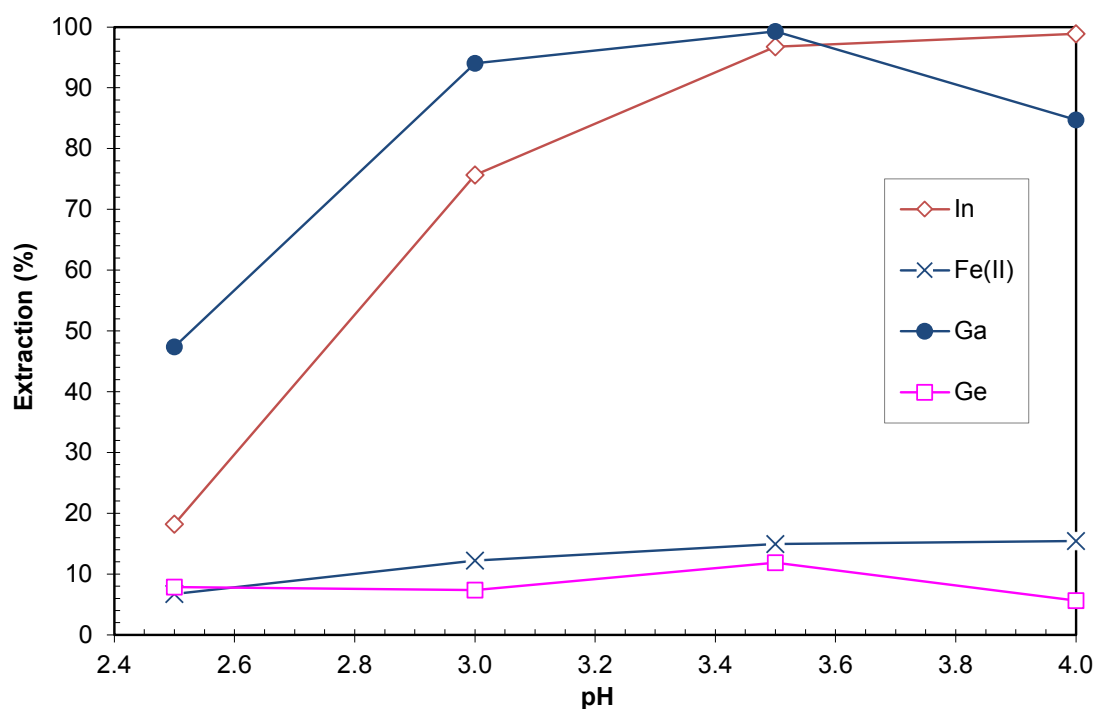


Figure 3. Metal extraction pH isotherms with the 0.25 M LIX 63/0.20 M Versatic 10 organic solution system.

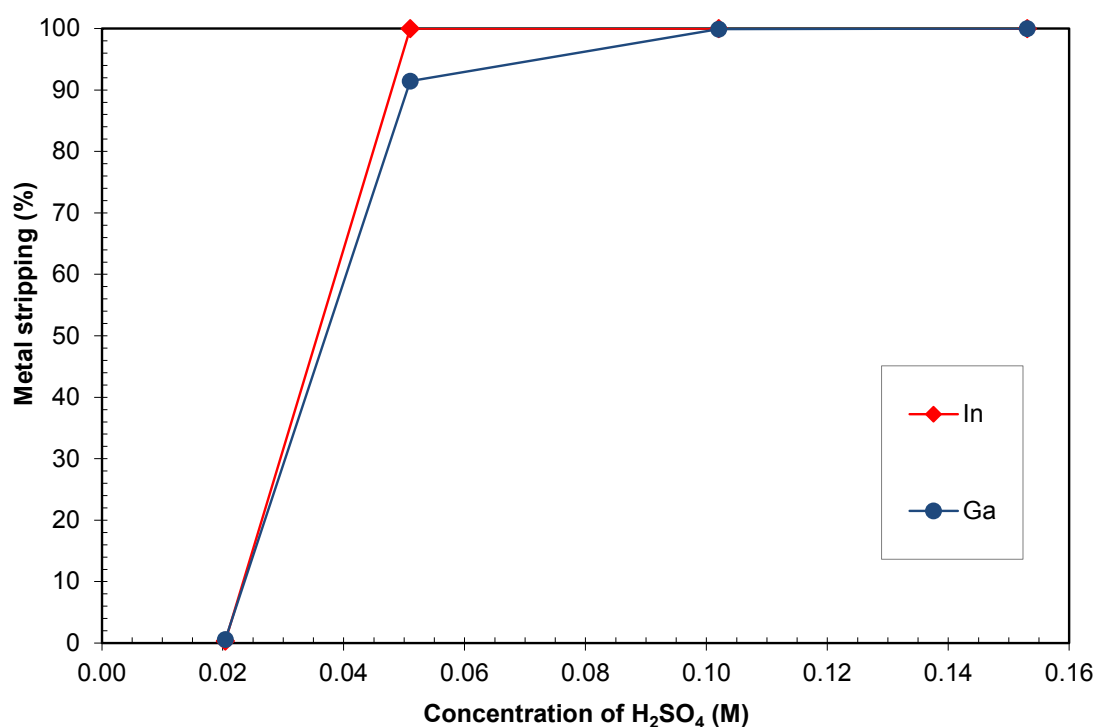


Figure 4. Metal stripping acidity isotherms with the 0.25 M LIX 63 and 0.20 M Versatic 10 system.

Effect of organic system composition

The synergistic effect on the extraction of indium and gallium was determined with two synthetic solutions containing 1 g/L In(III) and 1 g/L Ga(III), separately, and the organic solutions with different fractions of LIX 63 and Versatic 10 in ShellSol D70 for a total concentration of 0.24 M of the extractants at an O/A ratio of 1, pH 3.0 and 40

°C. It was found that over 86% In and 92% Ga were extracted with 50% or 0.12 M LIX 63 and 50% or 0.12 M Versatic 10 (Figure 5). The extraction of indium and gallium with the LIX 63 alone system was 5% and 74%, respectively, and the Versatic 10 alone system 25% and 30%, respectively, suggesting very strong synergistic effect on indium extraction, but weak or no synergistic effect on gallium extraction with the mixed LIX63/Versatic 10 system. The optimum pH for In and Ga extraction was found to be 3.0 with the selected organic composition.

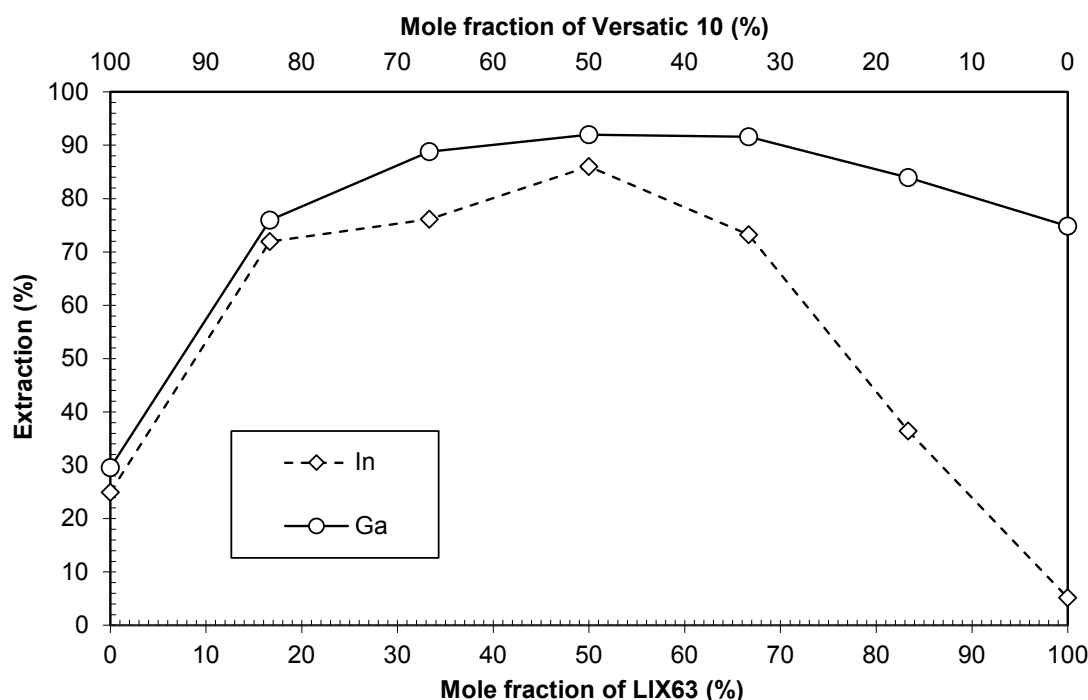


Figure 5. Extraction of indium and gallium with different fractions of Versatic 10 and LIX 63 system.

Conclusions

A mixed extractant system consisting of LIX63 and Versatic 10 was selected and developed to separate and recover In and Ga from synthetic sulphuric acid leach solution of zinc refinery residues. After Fe(III) reduction and Cu removal, 97% In and 99% Ga were extracted while only 15% Fe(II) and 12% Ge was co-extracted at pH 3.5 with the organic system consisting of 0.25 M LIX 63 and 0.20 M Versatic 10 in ShellSol D70 at an A/O ratio of 1 and 40 °C. The small amounts of co-extracted Fe(II), Ge, Ni and Co would be crowded out or scrubbed in counter-current operation. Almost 100% In and 91% Ga were stripped with 0.05 M H₂SO₄ solution.

For synthetic feed solutions containing 1.0 g/L In and Ga, respectively, the selected organic solution composition was 0.12 M LIX 63 and 0.12 M Versatic 10 in ShellSol D70. With the selected organic system, the optimum extraction pH for both In and Ga was 3.0. It was found that the synergistic effect on indium extraction was very significant, but that on gallium extraction was weak or nil with the mixed LIX63/Versatic 10 system. The novel SSX system has a great potential for the recovery of In and, especially Ga from leach solutions of zinc refinery residues.

Acknowledgement

The authors would like to thank Mr Yoko Pranolo and Mr Nicholas Kelly for technical assistance and Dr Keith Barnard for reviewing the manuscript and providing valuable

comments. The support of the CSIRO Minerals Down Under National Research Flagship is gratefully acknowledged. One of authors (S. Nusen) thanks the funding from Thailand Research Fund and Padaeng Industry Public Company Limited through the Royal Golden Jubilee PhD Program (RGJ. -Industry, Grant No. PHD/0111/2552) and also from the Graduate School of Chiang Mai University, Thailand.

References

- Aavila, R. M., Cote, G., Bauer, D., 1992. Recovery of In (III) from Mixed Hydrochloric Acid - Sulphuric Acid Media by Solvent Extraction with Cyanex 301®. *Solv. Extr. Ion Exch.* **10**, 811–827.
- Fortes, M.C.B., Martins, A.H., Benedetto, J.S., 2003. In Recovery from Acidic Aqueous Solutions by Solvent Extraction with D2EHPA: A Statistical Approach to the Experimental Design. *Braz. J. Chem. Eng.* **20**, 121–128.
- Judd, J.C., Harbuck, D.D., 1990. Ga Solvent Extraction from Sulfuric Acid Solutions Using OPAP. *Sep. Sci. Technol.* **25**, 1641–1653.
- Katsura, T., Abe, H., 1975. Solvent Extraction of In and/or Ga. *US Patent 3920450 A*.
- Levin, I.S., Shatalova, A.A., Azarenko, T.G., Vorsina, I.A., Burtovaya-Balakireva, N.A., Rodina, T.F., 1967. Concentration and Separation of In, Ga, Thallium, Antimony and Bismuth by Extraction with Alkylphosphoric acids. *Talanta* **14**, 801–808.
- Mihaylov, I., Distin, P.A., 1992. Gallium Solvent Extraction in Hydrometallurgy: An Overview. *Hydrometallurgy* **28**, 13–27.
- Paiva, A.P., 2001. Recovery of In from Aqueous Solutions by Solvent Extraction. *Sep. Sci. Technol.* **36**, 1395–1419.
- Sato, T., Sato, K., 1992. Liquid-liquid Extraction of In (III) from Aqueous Acid Solutions by Acid Organophosphorus Compounds. *Hydrometallurgy* **30**, 367–383.
- Tomii, K., Tsuchida, H., 1981. Solvent Extraction Recovery Process for In. *US Patent 4292284 A*.
- Violainen, S., Ibana, D., Paatero, E., 2011. Recovery of In from In Tin Oxide by Solvent Extraction. *Hydrometallurgy* **107**, 56–61.
- Yang, J., Retegan, T., Ekberg, C., 2013. In Recovery from Discarded LCD Panel Glass by Solvent Extraction. *Hydrometallurgy* **137**, 68–77.
- Zhou, T., Zhong, X., Zheng, L., 1989. Recovering in, Ge and Ga from Zinc Residues. *JOM* **41**, 36–40.

Selective Enrichment of Palladium in HNO₃ solution by Micro-sized Silica Particles Grafted with Macrocyclic Ligands

Gang Ye, Institute of Nuclear and New Energy and Technology, Beijing, PR China

Yuxiao Leng, Faculty of Chemical Science and Engineering, China University of Petroleum, Beijing, PR China

Palladium recovery in HNO₃-containing radioactive liquid waste is of great value due to its considerable amount and benign radioactivity level. In this study, a amino-bearing calixcrown receptor was synthesized for the selective extraction of Pd(II) in HNO₃ media. High distribution ratio was obtained. Then, the calixcrown receptor was grafted to micro-sized silica particles to result in a new solid phase extraction (SPE) material (Fig. 1), which shown favorable adsorption capacity and fast kinetics towards Pd(II) in HNO₃ solutions. Parameters influencing the adsorption ability such as contact time, acidity and initial metal concentration were comprehensively investigated. Kinetic equations and adsorption isotherm models were employed to fit the experimental data for inspecting the adsorption mechanism. On this basis, a conceptual chromatographic process for enrichment of palladium in simulated high-level liquid waste (HLW) was proposed.

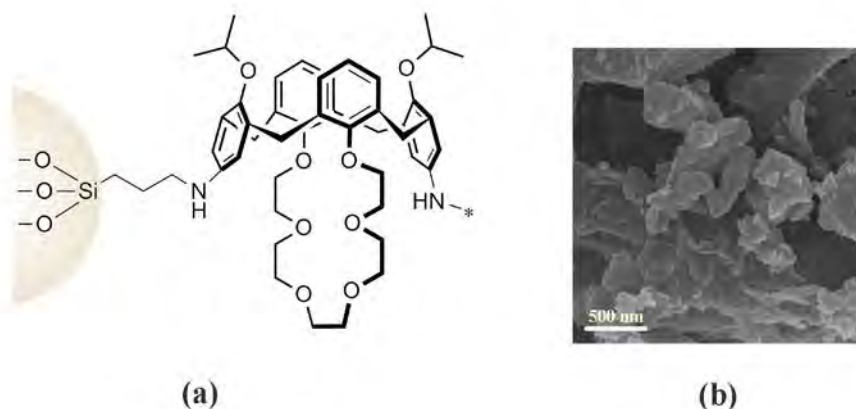


Fig. 1 Illustration of chemical structure of the macrocyclic ligand-grafted silica (a) and the micro-morphology under SEM (b)

Molecular simulations of solvent extraction of lanthanides and actinides with diglycolamide and pyridine amide

*K. Yoshizuka^{*1}, M. Hirata², T. Kimura³*

Summary

We have studied the molecular simulation of lanthanide and actinide complexes with diglycolamide and pyridine amide extractants. At first, molecular mechanics calculations of lanthanide and actinide complexes were conducted. New force field for molecular mechanics for calculating lanthanide and actinide complexes with diglycolamide and pyridine amide was developed by using both the molecular orbital calculations of extractants and metal complexes. Using the above force field, molecular simulations of lanthanide and actinide complexes adjacent to the interface between organic and aqueous phases were conducted to obtain the quantitative structure-property relationship of extraction and separation behavior of lanthanides and actinides with diglycolamide and pyridine amide extractants.

Introduction

The development and improvement of extractant should be necessary for establishing the fundamental separation technologies for the reduction of nuclear waste and environmental loading by nuclear cycles. As the fundamental research on the theoretical approach to the development of novel extractant, we have studied molecular simulations of lanthanide and actinide complexes with several amide-type extractants.

Computing of the structures and properties of chemical compounds is gaining increasing importance as computational techniques become increasingly accurate, and as high-performance computing and molecular graphics become available at relatively low cost. Computational chemistry is now widely recognized as a powerful tool for the design of new molecules with specified properties, and for interpreting their stabilities, reactivities and other physical properties [1, 2]. Molecular mechanics (MM) calculations are among the simplest and fastest techniques, and are therefore extremely useful when considering very large molecules or a large number of structures. Molecular dynamics (MD) simulations using empirical potential functions and parameters are being widely applied to elucidate the dynamic behavior and the thermodynamic properties of molecules in dense phases, such as aqueous and organic solutions.

We have been developing the force field parameters of MOMEK for lanthanide and actinide complexes [3]. In this paper, we describe a novel molecular modeling of lanthanide and actinide complexes with diglycolamide and pyridine amide combined with both the computational chemistry and quantitative structure-property relationship (QSPR) for estimating the extractability of these derivatives. Figure 1 shows the

^{*1} K. Yoshizuka, The University of Kitakyushu, yoshizuka@kitakyu-u.ac.jp

² M. Hirata, Japan Atomic Energy Agency

³ T. Kimura, Japan Atomic Energy Agency

chemical structures of amide derivatives. These extractants, tetraoctyl diglycolamide (TODGA), tetraoctyl pyridine amide (Oct-PDA) have been investigated in Japan Atomic Energy Agency for the actinide and lanthanide extraction from nitric acid into *n*-dodecane [4, 5].

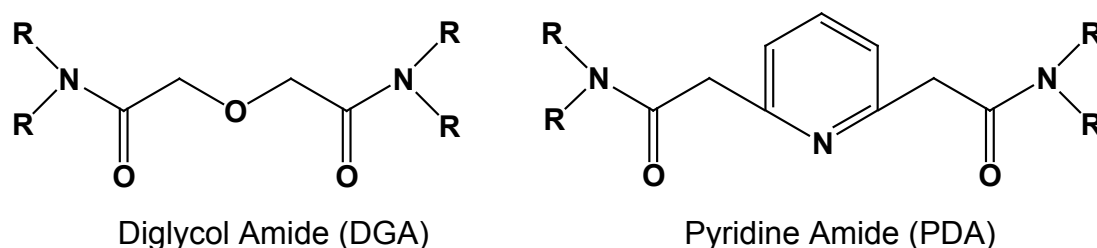


Figure 1 Amide derivatives extractants used in this study; DGA with *R* = octyl: tetraoctyl diglycolamide (TODGA), PDA with *R* = octyl: tetraoctyl pyridine amide (Oct-PDA).

Calculations

MM calculations

The MM calculations were performed with the strain minimization program, "MOMEC97" [6, 7]. Within the molecular mechanics frame work, the structure of a molecule is modified in order to minimize its total strain energy (E_{total}) consisting of bond length deformation (E_b), valence angle deformation (E_θ), torsion angle deformation (E_ϕ) and non-bonded interaction (E_{nb}), as expressed by Eq.(1).

$$E_{\text{total}} = \sum E_b + \sum E_\theta + \sum E_\phi + \sum E_{\text{nb}} \quad (1)$$

where

$$E_b = \frac{1}{2} k_b (r - r_0)^2, \quad E_\theta = \frac{1}{2} k_\theta (\theta - \theta_0)^2,$$

$$E_\phi = \frac{1}{2} k_\phi (1 - \cos(m\phi - \phi_0))^2, \quad E_{\text{nb}} = \frac{q_i q_j}{\epsilon r} + A r_{ij}^{-12} + B r_{ij}^{-6},$$

where k_b , k_θ and k_ϕ are the potential constants, and r_0 , θ_0 and ϕ_0 are the ideal values of bond length, bond angle and torsion angle, respectively. q , ϵ , A and B are the partial charge on atom, dielectric constant and the constants of Lenard-Jones potential function for expressing *van der Waals* interaction, respectively.

A harmonic M-L stretching potential is also used for the metal-donor interaction. The angular geometry around the metal center is modeled by interligand nonbonded interactions, and torsional potentials, as well as nonbonded interactions involving the metal center is neglected [3, 8, 9]. Terms for out-of-plane deformation and hydrogen bonding were excluded in the present study. The MOMEC force field parameters for Tc/Re-DMSA derivatives were implemented from the literature data [3, 10].

Input coordinates were obtained from X-ray crystal structure data in the Cambridge Crystallographic Data Centre (CCDC) [11-14]. The constant values of force field parameters were adjusted until an optimal agreement between calculated and observed structures was obtained throughout the entire range of available structures.

MD Simulations

The MD simulations were performed the MD program, “Material Explorer 4.0” [15]. The potential parameters for MD calculations were transferred from those of MM described above. The structure, position and orientation of 900 molecules of water and 72 molecules of *n*-dodecane were optimized in ca. 3.0×3.0×6.0 nm quadratic prism boundary cell at 298 K, to realize the practical density of the binary system ($\rho = 0.874 \text{ g/cm}^3$). Each bulk phase was optimized for 10 ps at 298 K under NPT ensemble in advance. The periodic boundary conditions were applied to all three directions. One molecule of metal complex was set either into *n*-dodecane, *n*-dodecane/water boundary phase or into water phase, respectively. All the metal complexes for MD calculations are the types of M(III)-3DGA or M(III)-3PDA complexes elucidated in the previous papers [4, 5]. Calculation was performed by each 0.1 fs for 10 ps under the NTV ensemble at 298 K.

Results and Discussion

MM calculations

Figure 2 shows the lowest energy structure of Am(III) complex with tetraoctyl diglycolamide (TODGA) calculated by MOMECC. In the previous papers [4,5], Am(II) was elucidated to be extracted by 3 molecules of TODGA in *n*-dodecane. This complex structure is used as initial structures of metal complexes for MD simulation in *n*-dodecane/water binary system described later.

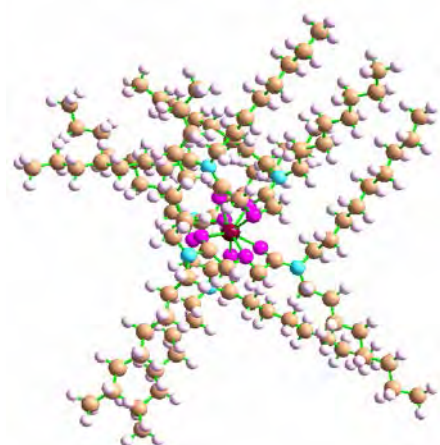
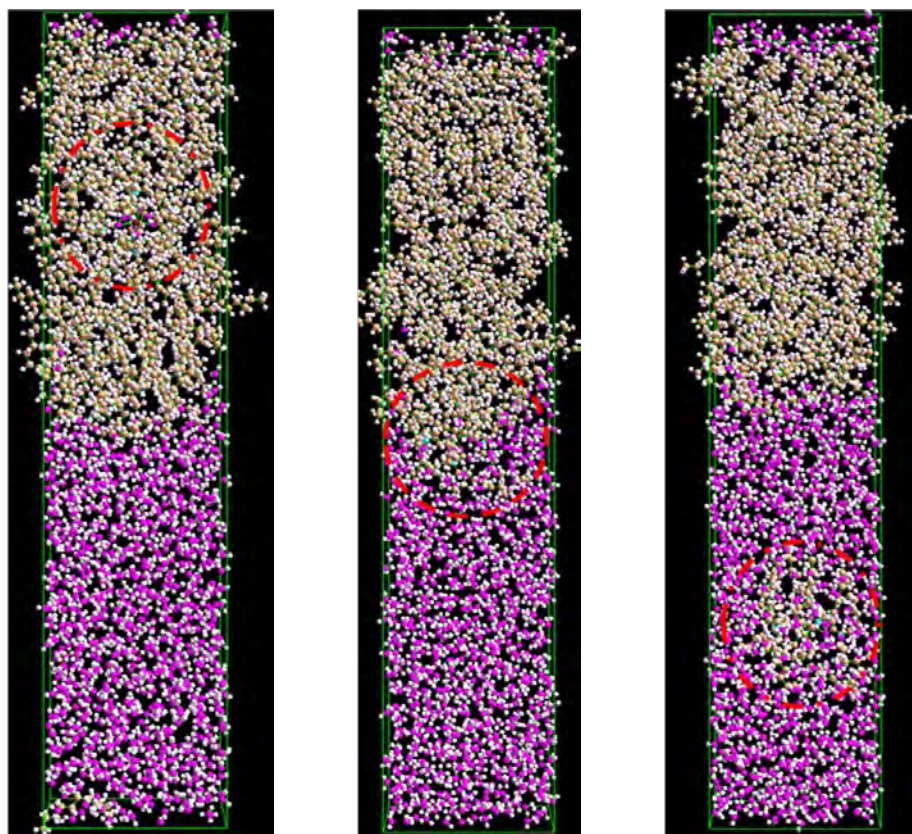


Figure 2 Molecular structure of Am(III) complex with TODGA calculated with MOMECC; red: Am(III), brown: carbon, pink: oxygen, white: hydrogen, blue: nitrogen.

MD simulations

Figure 3 shows the MD snapshots of Am(III) complex with TODGA in *n*-dodecane/water binary system after 10 ps. Am(III) complex is stabilized by interaction (solvation) of TODGA moieties with surrounding lipophilic *n*-dodecane molecules.



Insert into *n*-dodecane phase Insert into binary interface Insert into water phase

Figure 3 MD snapshots of Am(III)-3TODGA in 1-octanol-water and *n*-dodecane-water binary systems; upper phase: *n*-dodecane, lower phase: water, circle indicates the position of Am(III)-3TODGA complex.

QSPR for estimating the extractability of lanthanides and actinides with DGA and PDA derivatives

MD simulations were applied for the estimating of the stabilization energies of the metal complexes with DGA and PDA, for estimating the extractability of metal complexes. Firstly, an MD simulation of *n*-dodecane/water binary system with a metal complex was performed to obtain feasible configurations of the solute and solvent molecules either *n*-dodecane or water at the equilibrium state, to obtain the overall internal energy, U_{all} . This internal energy contains all bonding and non-bonding interactions in the binary system. Secondly, after removing the metal complex from the *n*-dodecane/water binary system was calculated, to obtain the internal energy of all solvent molecules in the system, U_{sol} . Finally, the internal energy of the removed metal complex *in vacuo*, U_{com} , was calculated [16].

$$\Delta U = U_{\text{all}} - U_{\text{sol}} - U_{\text{com}} \quad (2)$$

where U_i ($i = \text{all, sol, com}$) are the relevant internal energies of all molecules in the binary system, solvent molecules in the system and metal complex alone, respectively.

The solute-solvent interaction energy, ΔU , can be calculated under two cases of insertion area of metal complex into *n*-dodecane phase, $\Delta U_{n\text{-dodecane}}$, and that into water phase, ΔU_{water} , in *n*-dodecane/water binary system. From the difference in these interaction energies, $\Delta\Delta U$, the QSPR equation for estimating the distribution coefficient determined experimentally, D , can be obtained:

$$\Delta\Delta U = \Delta U_{n\text{-dodecane}} - \Delta U_{\text{water}} = \alpha \log D \quad (3)$$

where α is the apparent QSPR constant of above relationship, and subscript “*n*-dodecane” and “water” indicate the internal energy difference of metal complex existing either in *n*-dodecane phase or water phase in the boundary cell. When $\Delta\Delta U$ is negatively larger, solute molecule is more stable in *n*-dodecane (larger $\log D$ value), and *vice versa*.

Figure 4 shows the relationship between $\Delta\Delta U$ and $\log D$ for lanthanide and actinide complexes with TODGA. The $\log D$ values were experimentally obtained by the solvent extraction of actinides and lanthanides with TODGA in *n*-dodecane [4, 5].

The plot of $\Delta\Delta U$ vs. $\log D$ lies on a straight line with slope = -19.7 (= α) and intercept = -119.26 with sufficient correlation factor ($r^2 = 0.93$). The $\log D$ values experimentally determined [4, 5] corroborate the difference in these interaction energies, $\Delta\Delta U$, calculated with MD simulations of metal complexes in *n*-dodecane/water binary interface.

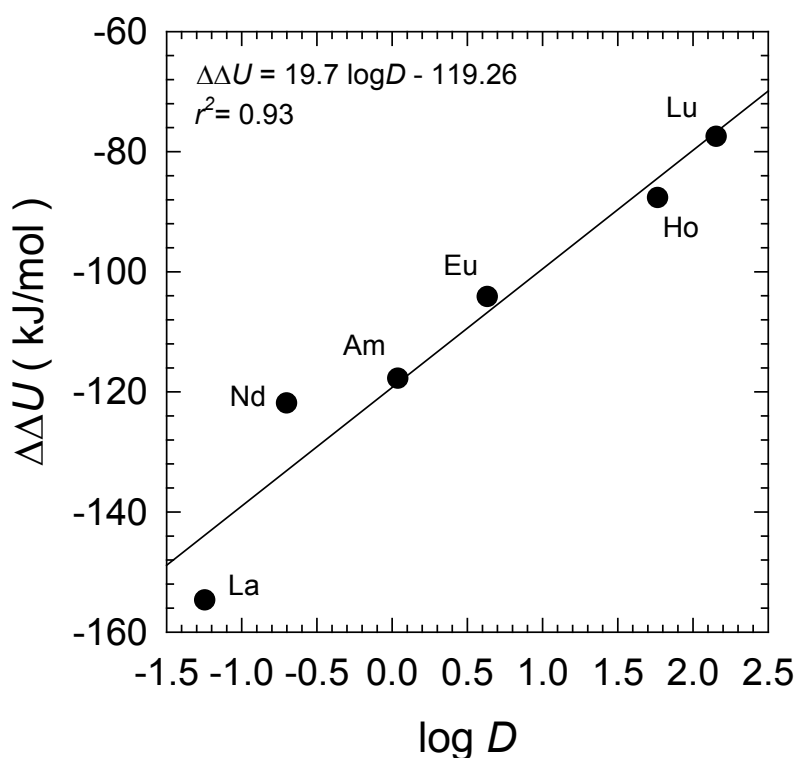


Figure 4 QSPR between $\Delta\Delta U$ and $\log D$ of lanthanide and actinide complexes with TODGA [4, 5].

Conclusion

We propose a novel molecular modelling of lanthanide and actinide complexes with diglycolamide and pyridine amide combined with the molecular mechanics and the molecular dynamics for estimating $\log D$ values. The force field parameters of MM program (MOMEC) for the metal complexes developed in this study were transferred from MOMEC to MD program (Materials Explorer). The MD simulations were performed to obtain the dynamic behavior and thermodynamic property of metal complexes in *n*-dodecane/water binary system. The quantitative structure property relationship (QSPR) between the internal energy differences of metal complex in *n*-dodecane/water binary system and the $\log D$ value were evaluated. QSPR equation for estimating $\log D$ values of metal complexes can be linearly expressed as $\Delta\Delta U = -19.7 \log D - 119.26$. The model can be applied for the prediction of $\log D$ values of metal complexes with DGA and PDA derivatives.

Acknowledgements

Present study includes the results of “Development of separation technology of transuranium elements and fission products by using new extractants and adsorbents” entrusted to JAES by the Ministry of Education, Science, Sports and Culture of Japan (MEXT).

References

- 1) P. Sarmah, R. C. Deka, *J. Computer- Aided Molecular Design*, **23**, 343–354 (2009).
- 2) A. R. Leach, “Molecular Modeling, Principles and Applications”, Longman (1999).
- 3) P. Comba, K. Gloe, K. Inoue, T. Krüger, H. Stephan, K. Yoshizuka, *Inorg. Chem.*, **37**, 3310-3315 (1998).
- 4) Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, *Solv. Extra. Ion Exch.*, **19(1)**, 91-103 (2001).
- 5) H. Suzuki, Y. Sasaki, Y. Sugo, A. Apichaibukol, T. Kimura, *Radiochimica Acta*, **92(8)**, 463-466 (2004).
- 6) J. Singh, A. K. Powell, S. E. M. Clarke, P. J. Blower, *Chem. Commun.*, 1115-1117 (1991).
- 7) P. Comba, T. W. Hambley, “Molecular Modeling of Inorganic Compounds”, VCH, Weinheim (1995).
- 8) R. Mannhold, G.I. Poda, C. Ostermann, I.V. Tetko, *J. Pharma. Sci.*, **98**, 861-893 (2009).
- 9) P. Leibnitz, G. Reck, H.-J. Pietzsch, H. Spies, *Report FZR-311*, Forschungs-zentrum Rossendorf, 46-47 (2001).
- 10) K. Yoshizuka, K. Inoue, P. Comba, *Kagaku Kogaku Ronbunshu*, **26**, 517 (2000).
- 11) K. Yoshizuka, *Anal. Sci.*, **20**, 761-765 (2004).
- 12) S. Seifert, R. Syhre, H. Spies, B. Johannsen, *Appl. Radiat. Isot.*, **48**, 1051-1057 (1997).
- 13) S. Seifert, R. Syhre, H. Spies, B. Johannsen, *Nucl. Med. Commun.*, **24**, 1175-1181 (2003).

- 14) P. Comba, T. W. Hambley, N. Okon, "MOMEC97, a molecular mechanics package for transition metal complexes", University of Heidelberg, Germany (1997).
- 15) Fujitsu Co. Ltd., "Material Explorer 4.0" (2006).
- 16) H. Watarai, Y. One, *Solv. Extra. Ion Exch.*, **19**, 155-166 (2001).

Stability Studies of Considered Grouped Actinide Extraction (GANEX) Solvent System

*Ana Núñez¹, Hitos Galán^{*1}, Joaquín Cobos¹*

The Grouped Actinide EXtraction (GANEX) process is being developed for actinide recycling within future nuclear fuel cycles. Different approaches have been proposed and the formulation TODGA + DMDOHEMA in kerosene has been shown to effectively co-extract TRU (including Pu) and lanthanide ions.

The behaviour of the extraction system along the process is one of the most important issues in defining the process development. Selected systems for the partitioning of minor actinides by hydrometallurgical processes will be in contact with highly radioactive aqueous solutions containing high nitric acid concentrations. So far, TODGA and DMDOHEMA stability have been studied in detail separately, however there is no information about the GANEX solvent system resistance to chemical and radiolytic degradation and its behaviour along the extraction process. Thus, solutions of GANEX selected solvent have been irradiated with gamma radiation and a systematic and complete characterization of the degraded samples has been carried out.

Introduction

Partitioning and Transmutation (P&T) concepts are studied worldwide to reduce the long-term radiotoxicity of the nuclear waste, and the main objective is to achieve, an efficient recovery and multi-recycle of the long-lived radiotoxic elements. Due to the high radiotoxicity of the minor actinides (MA: Am, Np, Cm) they are of special interest and it is necessary to develop suitable partitioning processes. [1] A new concept under investigation within Europe [2,3] is the Grouped Actinide EXtraction process (GANEX) [4,5] which is simpler and shows a higher proliferation resistance since all of the actinides are recovered together. [6,7] Where, once the bulk part of the uranium already has been removed, [6,8,9] a solvent composed of TODGA (*N,N,N',N'*-tetraoctyl diglycolamide) and DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2'-(hexyloxy)ethyl)-malonamide) in kerosene has been shown to effectively co-extract TRU (including Pu) and lanthanide ions. [9] Then, they can be stripped from the loaded solvent using selective hydrophilic complexing agents. [10]

To evaluate the applicability of solvents for process development, it is necessary to demonstrate not only their good extraction properties, but also their degradation resistance, since the organic phase is in contact with highly radioactive solutions and high nitric acid concentrations. The degradation leads to undesirable effects such as decrease of selectivity, third phase formation, poor phase separation, etc. Therefore, it minimizes the regeneration of the used solvent, increasing the volume of the secondary wastes and thus the process cost. Most often, the new species generated have extracting properties that markedly differ from those of the original ligands.

¹ Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid (Spain).

^{*} hitos.galan@ciemat.es

Despite the stability of TODGA [11] and DMDOHEMA [12] has been widely studied, separately, the behaviour of whole selected solvents has not been studied yet. Thus, in this paper is described a characterisation of TODGA, DMDOHEMA and GANEX formulation (0.2 M TODGA + 0.5 M DMDOHEMA) after gamma irradiation, using external ^{60}Co sources, to explore how the radiation affects on the behaviour of the system. Analytical methods based on HPLC-DAD/MS have been used to identify and quantify the composition of solvents along the irradiation process

Experimental

Chemicals, solutions and isotopes

N,N,N',N'-tetraoctyl diglycolamide (TODGA) was synthesised at CIEMAT in multi-gram scale, modifying an existing literature procedure under air and without drying solvent and glassware. [13] *N,N*-dimethyl-*N,N*-dioctyl-hexylethoxymalonamide (DMDOHEMA) was purchased from PANCHIM (now PHARMASYNTHÈSE, France). Odourless kerosene (OK), purity 98%, from Alfa Aesar and octanol, PRS purity, from Merck. All reagents were used from commercially available sources without further purification. The diluents were OK, used in Sellafield Ltd (Cumbria, UK) reprocessing plant, and octanol. Nitric acid solutions were prepared by diluting concentrated nitric acid (65%) with ultrapure water (18 M Ω /cm). The radiotracers ^{241}Am and ^{152}Eu were supplied by Isotope Products Laboratories, California (USA).

Sample preparation and procedures

Three different types of samples were prepared to be irradiated: 1/ 0.2 M TODGA, 2/ 0.5 M DMDOHEMA and 3/ 0.2 M TODGA+ 0.5 M DMDOHEMA. The corresponding amount of each one was diluted in (100)% OK and (95:5)% OK/octanol and pre-equilibrated with 5 M HNO_3 twice by 5 min of contact time.

The irradiation was performed at CIEMAT Náyade facility, which is a pool 1.2 m² by 4.5 m deep. It consists of 60 sources of ^{60}Co distributed in six lots with total activity of 1.1×10^{14} Bq. The irradiation container used provides homogeneous irradiation flux.

TODGA, DMDOHEMA and GANEX (TODGA+DMDOHEMA) samples were irradiated up to 100 and 1000 kGy at 1.8 kGy/h dose rate. Reference samples for aging control were kept in the laboratory during the irradiation process. The Am(III) and Eu(III) extraction was performed after the last step of irradiation.

The behaviour of trivalent actinides and lanthanides were simulated by ^{241}Am and ^{152}Eu , respectively. The extraction experiments were performed by contacting for 15 min 500 μL of the corresponding organic phase and the aqueous phase (^{241}Am and ^{152}Eu (1.5 kBq/mL each) in 5 M HNO_3). Both phases were separated by centrifugation at 5000 rpm and 300 μL of each phase was conditioned into a 2 mL plastic eppendorf vials for energy gamma spectrometry measurements, using the γ -lines at 59.5 keV, and 121.8 keV for ^{241}Am and ^{152}Eu determination, respectively. The distribution ratios ($D_{\text{M(III)}}$) were calculated as $[\text{M(III)}]_{\text{org}}/[\text{M(III)}]_{\text{aq}}$.

The chemical composition of the irradiated samples was characterised by HPLC-DAD/MS. HPLC-DAD measurements were performed by using a C-18 column (150 mm, 5 μ m), using a gradient of CH₃CN/H₂O as mobile phase, at 205 nm. Calibration curves, 0.001-0.2 M and 0.005-0.5 M, were performed for TODGA and DMDOHEMA, respectively. All measurements were repeated twice. HPLC-MS measurements were performed by using an HPLC-MS Agilent 1100 (Quadrupole detector 6120A) with a Protonsil C-8 column (50 mm, 5 μ m) at 40 °C using a gradient of mobile phase [(A: 0.1 % in CH₃CN), (B:0.1 % HCOOH in H₂O)] in the APCI⁺ ionization mode (SCAN). Samples were analysed without pre-evaporation and diluted 200 times in a (90:10)% MeOH/octanol mixture.

Results and Discussion

The selected GANEX systems composition is 0.2 M TODGA + 0.5 M DMDOHEMA in OK (odorless kerosene). Our previous TODGA stability studies indicated that a small proportion of octanol favors nitric acid extraction, which has a protective effect on ligand stability. Therefore, two kind of systems were planned to be irradiated up to 100 kGy and 1000 kGy, at 1.8 kGy/h using ⁶⁰Co sources: a) 0.2 M TODGA + 0.5 M DMDOHEMA in (100)% OK, pre-equilibrated with 5 M HNO₃ and b) 0.2 M TODGA + 0.5 M DMDOHEMA in (95:5)% OK/octanol, pre-equilibrated with 5 M HNO₃. To compare the stability of TODGA and DMDOHEMA systems with GANEX solvent, both extractant were also studied separately under the same experimental conditions. Reference samples of all irradiated samples were kept in the laboratory for aging control. After irradiation the samples become slightly yellow and only those which were in presence of octanol showed the formation of insoluble drops in the bottom of the vial. The extraction properties of the irradiated GANEX samples were evaluated by determining Am(III) and Eu(III) distribution ratios ($D_{M(III)}$). The $D_{M(III)}$ values obtained for the co-extraction of Am(III)/Eu(III) (Fig 1) with aging control samples were quite similar than those obtained with fresh samples. The effect of radiation was not drastic and the $D_{M(III)}$ values decreased slightly. No third phase formation was observed despite insoluble drops appeared in samples irradiated up to 1000 kGy. The result obtained for the Am(III)/Eu(III) extraction with samples irradiated in (100)% OK and (95:5)% OK/octanol are also compared in Fig 1, where it can be seen a less reduction of the $D_{M(III)}$ values in (100)% OK along the irradiation. This effect could be attributed to the formation of different proportion of degradation compounds, to a less degradation of the extractants or a higher extraction as it is expected for systems in OK.

The HPLC-DAD chromatograms obtained for degraded samples in (100)% OK are shown in Fig 2. In general the same degradation was observed for TODGA and DMDOHEMA separately than in the GANEX solvent. As expected, the HPLC chromatograms of irradiated GANEX solvent show a much more complex mixture of compounds. It is remarkable that TODGA seems to be less affected in the GANEX mixture than when it is alone. This fact, could explain the high $D_{M(III)}$ values observed

for Am(III)/Eu(III) after the irradiation in Fig 1. Results obtained for samples in (95:5)% OK/octanol were quite similar, however a high number of degradation compounds was found. On the other hand, hydrolytic degradation does not be a relevant problem, even in those samples which had been irradiated in presence of octanol.

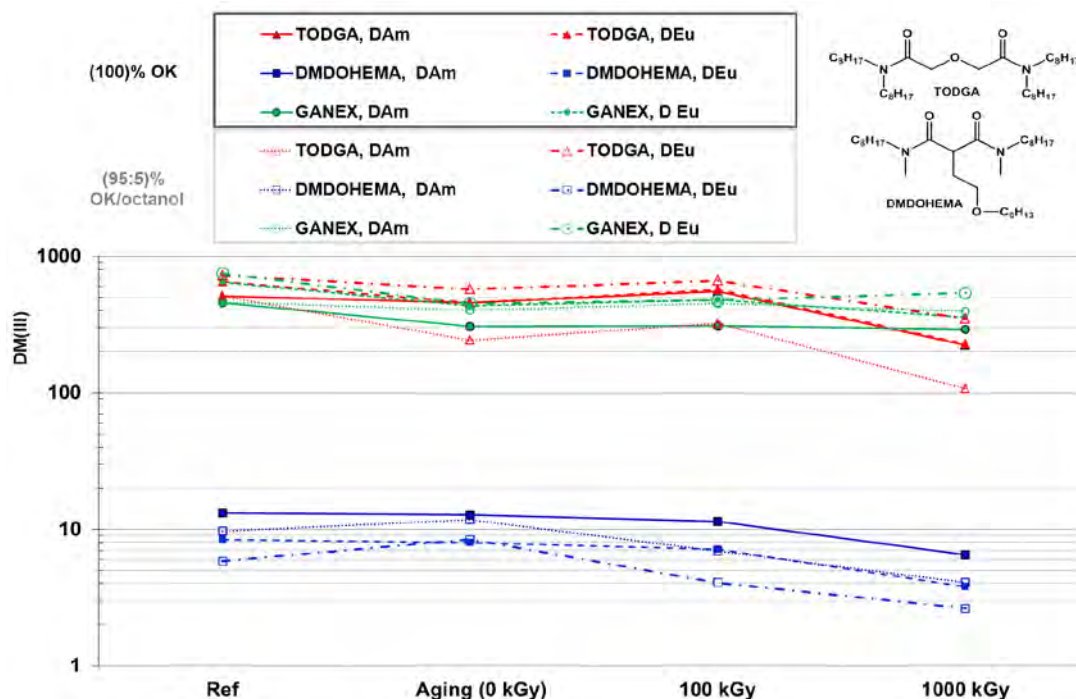


Fig 1. Am(III)/Eu(III) distribution ratios by reference, aging and irradiated TODGA, DMDOHEMA and GANEX samples (TODGA-DMDOHEMA). Organic: 0.2 M of TODGA or 0.5 M of DMDOHEMA or both (GANEX) in (100)% OK or (95:5)% OK/octanol. Aqueous: $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ in 5 M HNO_3 .

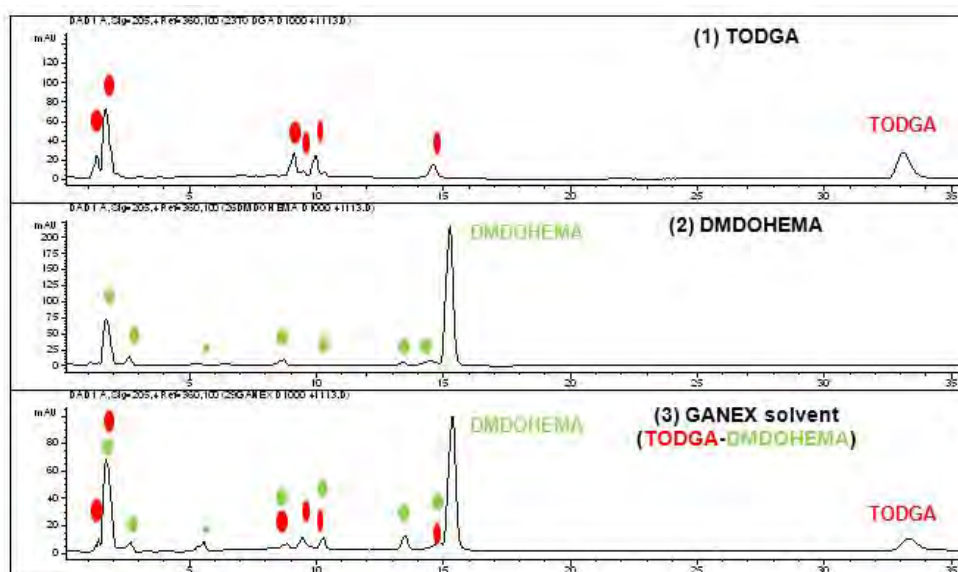


Fig 2. HPLC-DAD chromatograms of irradiated samples up to 1000 kGy, in (100)% OK: (1) TODGA, (2) DMDOHEMA and (3) GANEX solvent (TODGA-DMDOHEMA).

In Fig 3 it is shown the quantitative study of TODGA and DMDOHEMA for samples irradiated in both solvent formulations. After 1000 kGy, it can be seen that in

presence of octanol there is a higher resistance of both ligands and GANEX solvent, according to $D_{M(III)}$ values (Fig 1). Therefore, higher $D_{M(III)}$ values could be attributed to less degradation of the extractants. In absence of octanol, it is also remarkable that DMDOHEMA and TODGA concentrations are lower in the GANEX mixture than when they are alone.

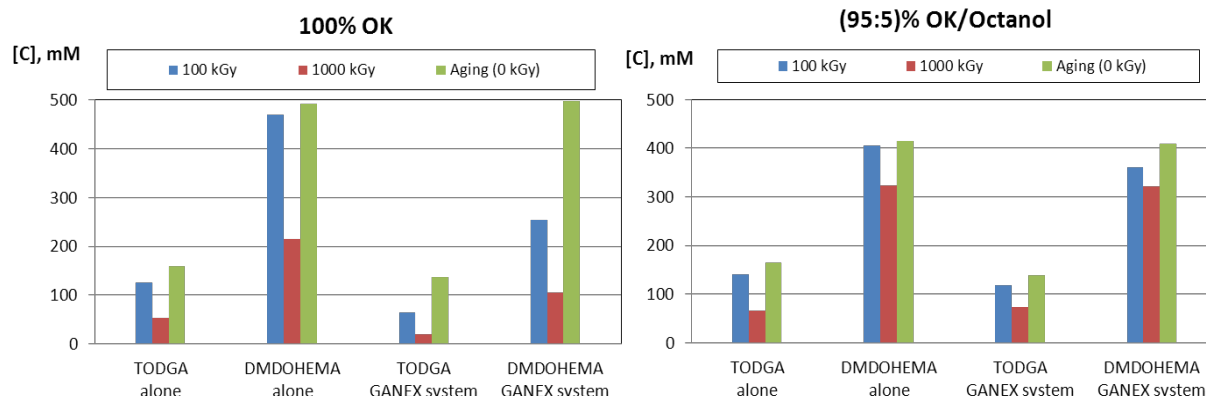


Fig 3. Quantitative study by HPLC-DAD of the final concentration of TODGA, DMDOHEMA in irradiated samples in (100)% OK or (95:5)% OK/Octanol: 1) TODGA solvent, 2) DMDOHEMA solvent and 3) GANEX system.

The HPLC-MS (APCI⁺) qualitative analysis of irradiated GANEX systems have been also performed to identify DMDOHEMA degradation fragments or any other unknown TODGA degradation compound. The radiolytic degradation of DMDOHEMA was explored in the past, where eight degradation compounds were found. [12] The chromatograms of irradiated GANEX systems show the presence of at least five peaks (Fig 4).

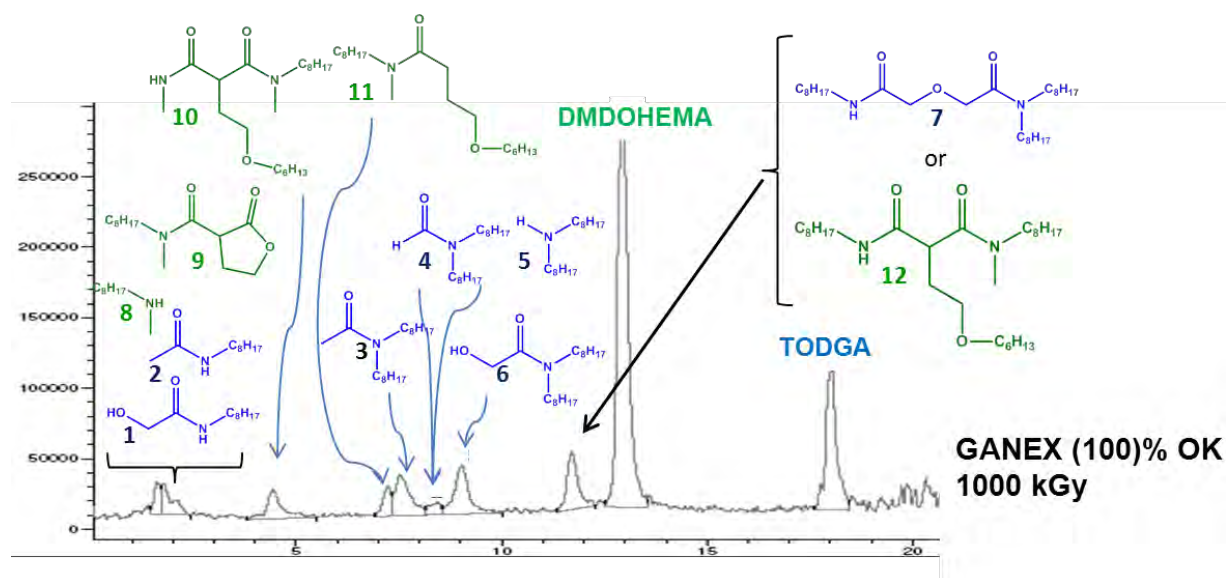


Fig 4. HPLC-MS (APCI⁺) chromatogram of GANEX system irradiated up to 1000 kGy in (100)% OK pre-equilibrated with 5 M HNO₃.

So far, the presence of seven degradation compounds for TODGA (1-7) and five for DMDOHEMA (8-12) have been assigned by mass spectrum analysis, however it was not possible to confirm the DMDOHEMA degradation compounds previously

described due to they are still not available in pure form. The main degradation compounds in samples irradiated up to 1000 kGy seem to be fragments **3**, **6** and **7** or **12**². At least two of TODGA degradation compounds, **6** and **7**, could affect the behavior of system during the stripping step since they extract Am(III) and Eu(III) themselves, [14] and three of DMDOHEMA degradation compounds (**8**, **10** and **11**) had been described as partially responsible of the decrease in extraction properties. [12] So far, it was not possible to confirm the DMDOHEMA degradation compounds previously described due to they are still not available in pure form.

Conclusions

GANEX system has shown a high resistance to the hydrolytic and radiolytic degradation. After irradiation, for selected GANEX solvent neither important alterations or third phase formation were observed. The octanol presence seems to be a positive effect in the extractant stability. Despite TODGA and DMDOHEMA degradation compounds present in the final mixture, that complicate the system, the extraction assessed for Am and Eu is in a good agreement with the properties requested. The presence of seven degradation compounds for TODGA and five degradation compounds for DMDOHEMA were identified by HPLC-MS. In order to avoid possible mal-operation situation during the counter-current extraction process, some of the indentified degradation compounds must be taken into account. Therefore, an expanded study about the stripping and loading capacity behaviour is being carried out for the degraded GANEX system and for each degradation fragments separately as well.

Acknowledgements

This work has been developed under the framework of the European Project SACSESS project, 7th Framework Programme (n° 323282). Authors would like to thank Laureano Anta for his valuable technical work.

References

- 1 Serrano-Purroy, D. *et al. Radiochim. Acta* **2005** 93, pp. 357.
- 2 Bourg, S. ACSEPT Homepage. <http://www.acsept.org/>
- 3 Bourg, S. *et al. Proceedings of GLOBAL 2009*, Paris, France; pp 937.
- 4 Marie, C.; *et al. Solvent Extr. Ion Exch.* **2011**, 29 2, pp. 292.
- 5 Nash, K. L. *et al. Nuclear Energy and the Environment*, Vol. 1046, Wai, C. M.;Mincher, B. J., American Chemical Society: Washington, DC, **2010**; pp. 19.
- 6 Miguiditchian, M. *et al. Proceedings of GLOBAL 2007*, Boise, Idaho, September 10-14, 2007. pp. 550.
- 7 Miguiditchian, M. *et al. Proceedings of GLOBAL 2009*, Paris, September 6-11, 2009; Paper 9378.
- 8 Aneheim, E. *et al. Nuclear Energy and the Environment*, Vol. 1046, Wai, C. M.; Mincher, B. J., American Chemical Society: Washington DC, **2010**; pp. 119.
- 9 Brown, J. *et al. Solvent Extr. Ion Exch.* **2012**, 30 2, pp. 127.
- 10 Geist, A.; *et al. Solvent Extr. Ion Exch.* **2012**, 305, pp. 433.
- 11 Galán H., *et al. Procedia Chemistry*, **2012**, pp. 195.
- 12 Berthon, L *et al. Separation Science and Technology* **2001**, 365&6, pp. 709.
- 13 Horwitz, E. P *et al. Solvent Extr. Ion Exch.* **2005**, 23. pp. 319.
- 14 Galán H. *et al. Eur. J. Org. Chem.* **2011**; pp. 3959.

² Peak corresponding to **7**, identified as the loss of an octyl group of TODGA, it can also be **12**, the loss of the methyl group of DMDOHEMA.

Plutonium loading of GANEX solvents with phenyl trifluoromethyl sulfone and cyclohexanone as diluents

*Jenny Halleröd^{*1}, Christian Ekberg², Mark Foreman² Elin Löfström Engdahl² and Emma Aneheim²*

Currently, the primary research focus at Chalmers University of Technology within the field of partition and transmutation is in developing a Grouped ActiNide Extraction (GANEX) separation process. The basic concept of partition and transmutation is to separate the transuranic elements from the fission products in used nuclear fuel and then transmute them using a fast neutron spectrum. The principle of the GANEX process uses two cycles; the first to remove the uranium bulk is removed from the fuel dissolution liquor and the second (where GANEX extraction actually occurs) to extract the transuranic elements and remaining uranium together as a group thereby avoiding pure plutonium streams. The GANEX process previously developed at Chalmers combines the two extractants 6,6'-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) and tri-butyl phosphate (TBP) in cyclohexanone. However, cyclohexanone has a low flash point (44°C compared to kerosene (37-65°C), for example) and it is somewhat soluble in the acidic aqueous phase. An attempt has therefore been made to replace cyclohexanone with phenyl trifluoromethyl sulfone (FS 13). FS 13 was developed for use in the UNiversal EXtraction (UNEX, extracts elements through ion-exchange) process as an alternative to highly polar nitrobenzene. FS 13 was considered as an alternative to cyclohexanone in the GANEX process, due to its stability for irradiation and acid, and its higher flash point (122 °C). This study investigated the possibility of extracting plutonium into a GANEX solvent containing 70 % FS 13, 30 % TBP and 10 mM CyMe₄-BTBP. It was shown that the system based on FS 13 resists plutonium loading, no metal precipitation was observed up to 40 g L⁻¹. However, the separation of plutonium from americium increased at higher plutonium concentrations due to competitive extraction between the metals.

INTRODUCTION

Separation and transmutation research in the field of long-lived nuclear waste has been conducted in several European Union framework programmes since the early 1990s. At first, actinides and lanthanides were co-extracted from used nuclear fuel (DIAMEX process) and the main research focus was to find suitable extraction agents for the next step, the difficult separation between trivalent lanthanides and trivalent actinides (SANEX process) (Hill, 2007). Since then several extraction agents have been developed, synthesised, and tested for this purpose. The agents found to be suitable candidates for separation purposes, were tested and evaluated in a hot test (Magnusson, 2009). Subsequently, focus shifted to the Grouped ActiNide EXtraction (GANEX) separation processes whereby several suggested processes were developed (Adnet, 2005, ACSEPT final report). Today, GANEX research continues with focus on development of safe processes for safe operation (SACSESS, 2013).

^{*1} Corresponding Author, Nuclear Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology. Email: hallerod@chalmers.se.

² Author, Nuclear Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology.

Grouped actinide extraction (GANEX)

The GANEX separation system is based on the principle that the actinides should be extracted together as a group from the lanthanides and fission/corrosion/activation products. The GANEX process operates under highly acidic conditions after the uranium bulk is removed from the spent nuclear fuel. The actinides are then stripped for transmutation purposes, as illustrated in Figure 1.

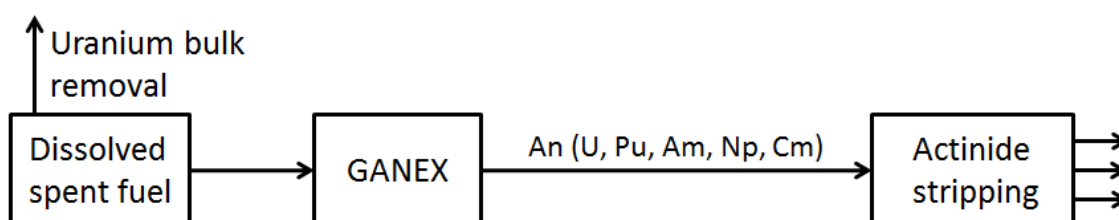


Figure 1. Schematic illustration of the GANEX process.

The Chalmers GANEX process is based on the principle of combining two well-known extractants and enabling taking advantage of their specific properties. The ligands selected for this process are 6,6'-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) and tri-butyl phosphate (TBP in Figure 2, combined into a single diluent.

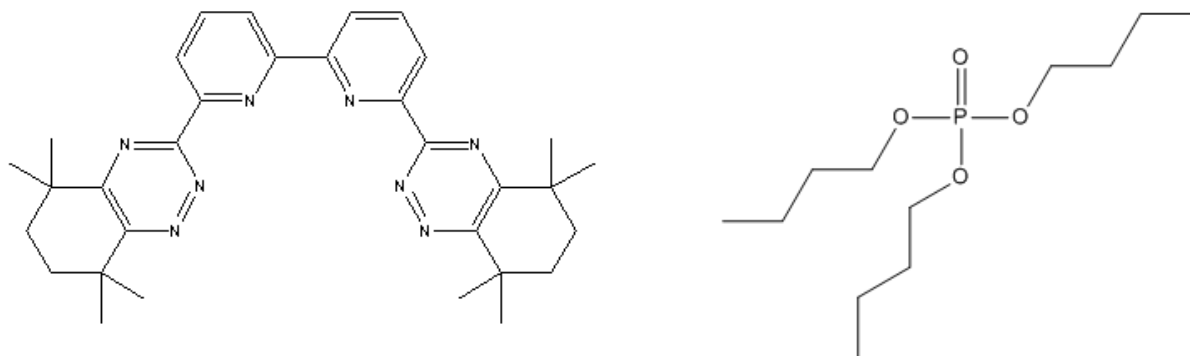


Figure 2. Molecular structure: left: 6,6'-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) and right: tri-Butyl phosphate (TBP).

The previous GANEX process developed at Chalmers University of Technology in the ACSEPT project used cyclohexanone as diluent. However, cyclohexanone has a low flashpoint (44°C) and is somewhat soluble in the acidic aqueous phase (Riddick, 1970). Due to these issues Phenyl trifluoromethyl sulfone (FS 13) was investigated as an alternative diluent to cyclohexanone.

Phenyl trifluoromethyl sulfone

FS 13 was initially developed for the universal extraction (UNEX) process (Rzhekhina, 2007). FS 13 is a polar diluent with good chemical stability and low viscosity (Sinha, 2011).

Since FS 13 has been used in the UNEX process it may be a suitable diluent in the GANEX process rather than cyclohexanone. Molecular structures of FS 13 and cyclohexanone are illustrated in Figure 3.

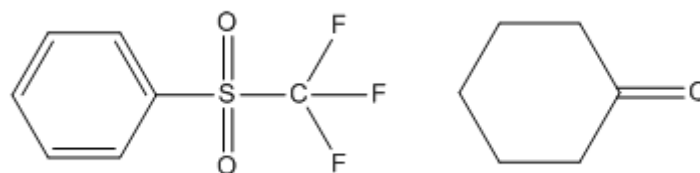


Figure 3. Molecular structure: left: phenyl trifluoromethyl sulfone (FS 13) and right: cyclohexanone.

Plutonium extraction

One issue when utilizing CyMe₄-BTBP as extracting agent is that it extracts plutonium. This can be a problem in the GANEX process, since extracting high concentrations of plutonium will hinder co-extraction of americium, eliminating the primary function of grouped actinide extraction. Therefore, finding a diluent that extracts the plutonium using the TBP ligand instead of CyMe₄-BTBP is of interest. Extracting plutonium using TBP instead of CyMe₄-BTBP reduces the risk of plutonium precipitation and plutonium loading, since the TBP concentration in the solvent is considerably higher than the CyMe₄-BTBP concentration.

Plutonium loading of the two BTBP/TBP based GANEX solvents developed at Chalmers was performed. The objective was to investigate the tolerance for possible high plutonium concentrations (in this study Pu concentration up to 40 gL⁻¹ Pu was investigated) in reprocessing of future transmutation fuels. Plutonium precipitation has been observed in other extraction systems under high concentrations and in a real life process. This raised the risk of criticality (Brown, 2010).

METHODOLOGY

A plutonium stock solution consisting of HNO₃ (14.4 M) and plutonium (0.75 M) was used. The stock solution was diluted to three different aqueous phases with HNO₃ (SigmaAldrich, ≥69%) concentration of 4 M (diluted in MilliQ-water >18MΩ) and plutonium concentration of 40 gL⁻¹, 10 gL⁻¹, and 1 gL⁻¹ respectively. Photographic images of the samples are presented in Figure 4.



Figure 4. Photo of the three aqueous phases, from left: 40 gL⁻¹ Pu, 10 gL⁻¹ Pu and 1 gL⁻¹ Pu.

Two GANEX solvents were prepared, one containing 70% FS 13 (CarboSynth), 30% TBP (SigmaAldrich, 97%) and 10 mM CyMe₄-BTBP (synthesised in-house according to (Foreman, 2006)), and the other containing 70% cyclohexanone (SigmaAldrich, 99%), 30% TBP and 10 mM CyMe₄-BTBP. The samples containing 1 gL⁻¹ Pu and 10 gL⁻¹ Pu were made in triplicate. For FS 13, samples were prepared with all three aqueous phases and cyclohexanone samples were prepared with the aqueous phases containing 10 gL⁻¹ and 1 gL⁻¹. Each sample contained 200 μ L aqueous phase and 200 μ L solvent. Samples before contacting are presented in Figure 5 (left).

All samples were vigorously mixed by hand-shaking for ten minutes and samples with FS 13 as diluent were centrifuged for approximately one minute, and the samples with cyclohexanone as diluent were separated by gravitation. Samples after shaking are presented in Figure 5 (right).

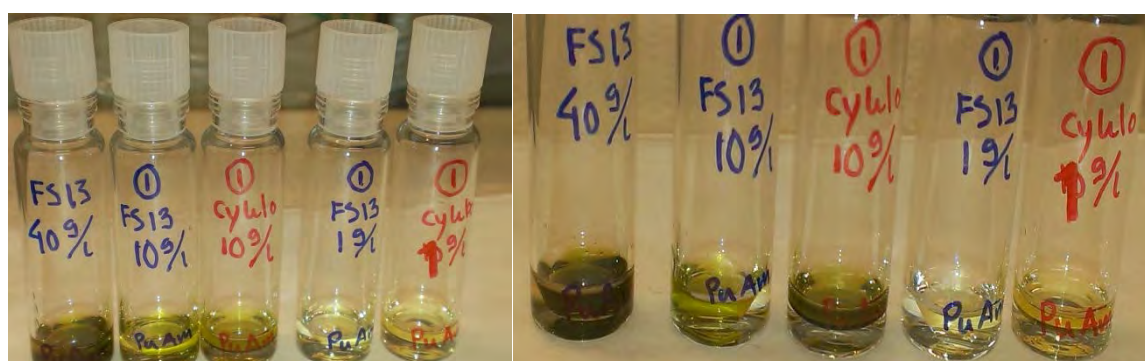


Figure 5. Left: Samples before shaking. Right: Samples after shaking. Samples from the left: FS 13 with 40 gL⁻¹ Pu, FS 13 with 10 gL⁻¹ Pu, cyclohexanone with 10 gL⁻¹ Pu, FS 13 with 1 gL⁻¹ Pu, and cyclohexanone with 1 gL⁻¹ Pu.

Fifty (50) μ L of each sample and phase was removed for gamma spectrometry (HPGe, Ortec, Gamma Analyst GEM 23195) and alpha spectrometry (Ortec, alpha duo, Octète TM PC) and 10 μ L of each aqueous phase was removed for inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000 DRC).

RESULT AND DISCUSSION

In Figure 5 (right), decolourization of the aqueous phase can be noted in the cyclohexanone samples and in the FS 13 10 gL⁻¹, and 40 gL⁻¹ Pu samples. This clearly indicates plutonium extraction. Based on mass-balance calculation, it was shown that no metals precipitated.

Noting distribution ratios in the different samples (Figure 6) it is obvious that the Am extraction is decreased with an increase in Pu concentration. Also, the Pu extraction decreases but not as much as the Am extraction. Table 1 shows the separation factor of Pu from Am. It appears that the separation increases with the amounts of Pu in both solvents. This indicates that the Pu extraction is stronger than the Am extraction so Pu loading suppresses Am. This issue needs to be addressed in the development

of a GANEX process, to ensure that the grouped actinide extraction does not turn into a pure Pu extraction.

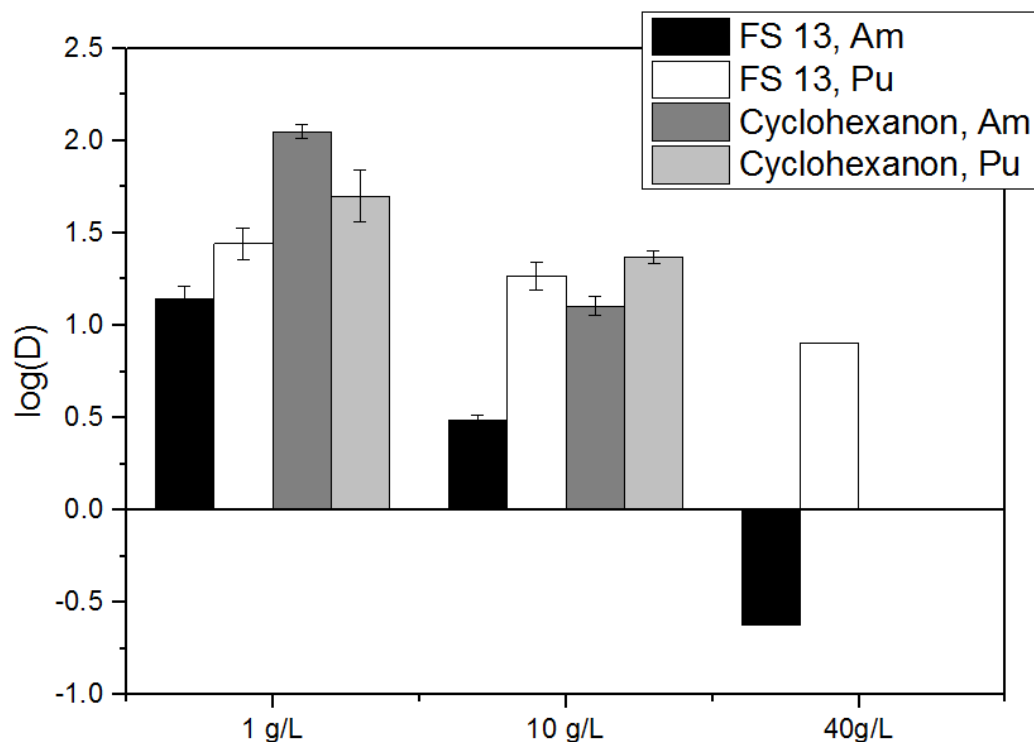


Figure 6. Logarithmic distribution of Pu and Am in the different solvents, uncertainties are standard deviations.

Table 1. Separation factors of plutonium from americium in the five different samples.

Solution	SF Pu/Am
FS 13 1 gL ⁻¹	1.6906
FS 13 10 gL ⁻¹	3.8452
FS 13 40 gL ⁻¹	25.3053
Cyclohexanon 1 gL ⁻¹	0.4592
Cyclohexanon 10 gL ⁻¹	2.2158

CONCLUSION

It was found that distribution ratios of both Am and Pu are decreased at higher Pu concentrations in both diluents. In FS 13 the Pu extraction and the Am extraction are competitive and are both extracted by the CyMe4-BTBP at high Pu concentrations. At low Pu concentration the Pu metal is extracted only by the TBP. In the cyclohexanon based solvent the Pu is extracted by the CyMe4-BTBP also at trace amounts of the metal.

ACKNOWLEDGEMENTS

The Swedish nuclear fuel and waste management company (SKB) and the European Union seventh Framework Project SACSESS (no. 323282) are both acknowledged for funding this work.

REFERENCES

ACSEPT (2012), 'ACTINIDE RECYCLING BY SEPARATION AND TRANSMUTATION: FINAL PROJECT REPORT Part I: Publishable Summary & Part II: Use & Dissemination of Foreground'.

Adnet, J.-M., Miguiritchian, M., Hill, C., Heres, X., Lecomte, M., Masson, M., Brossard, P. and Baron, P. (2005), Development of new hydrometallurgical processes for actinide recovery: GANEX concept, in 'Proceedings of GLOBAL'.

Brown, J., McLachlan, F., Sarsfield, M., Taylor, R., Modolo, G. and Wilden, A. (2012), 'Plutonium loading of prospective grouped actinide extraction (GANEX) solvent systems based on diglycolamide extractants', *Solvent Extraction and Ion Exchange* 30(2), 127-141.

Foreman, M., Hudson, M., Drew, M., Hill, C. and Madic, C. (2006), 'Complexes formed between the quadridentate, heterocyclic molecules 6,6'-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III)', *Dalton Transactions* (13), 1645-1653.

Hill, C., Arnaud-Neu, F., Espartero, A.G., Desreux, J.F., Modolo, G., Bourg, S., Malmbeck, R., Caravaca, C., Harrison, M., De Angelis, G., Uhler, J., Ouvrier, N. and Madic, C. (2007), 'EUROPART Final Activity Report, Contract Number: F16W-CT-2003-508 854.

Magnusson, D., Christiansen, B., Foreman, M., Geist, A., Glatz, J.-P., Malmbeck, R., Modolo, G., Serrano-Purroy, D. and Sorel, C. (2009), 'Demonstration of a SANEX Process in Centrifugal Contactors using the CyMe4-BTBP Molecule on a Genuine Fuel Solution', *Solvent extraction and ion exchange* 27(2), 97-106.

Riddick, J. A. and Bunger, W. B. (1970), *Techniques of Organic Solvents*, Vol. 2, 3 edn, Wiley-Interscience, New York.

Rzhekhina, E., Karkozov, V., Alyapyshev, M. Y., Babain, V., Smirnov, I., Todd, T., Law, J. and Herbst, R. (2007), 'Reprocessing of spent solvent of the UNEX process', *Radiochemistry* 49(5), 493-498.

SACSESS (2013), 'SACSESS: Safety of ACTinide Separation proceSSes', <http://www.sacsess.eu/>. 12 March 2014.

Sinha, P. K., Kumar, S., Kamachi Mudali, U. and Natarajan, R. (2011), 'Thermal stability of UNEX/HCCD-PEG diluent FS-13', *Journal of Radioanalytical and Nuclear Chemistry* 289(3), 899-901.

PAREX code, a powerful tool for La Hague reprocessing plant operators

*J. BISSON^{*1}, B. DINH², C. HUEL³*

The PAREX code developed by the CEA is able to simulate the PUREX process in steady or transient state. From an operator point of view, this numerical code for simulation of liquid-liquid extraction operations is an outstanding tool for process flow sheet optimization, troubleshooting and safety analysis calculations. Additional tools are also derived from it for training purpose or for plant exploitation aid. This paper provides an overview of those applications and shows some examples. Most of the paper is dedicated to safety and criticality studies as safety is one of AREVA's first priorities.

I - Introduction

Liquid-liquid extraction operations conducted in the PUREX process at La Hague reprocessing plant must meet strict requirements. A high degree of performance is indeed desired with respect to finished product purity and the recovery yield of these products. Other requirements must be guaranteed such as safety and operational longevity.

To allow the optimization of the process and face with the exhaustive approach required in the analysis of criticality risk, a major effort has been made by the CEA and AREVA at an early date to model the PUREX operations. A digital code named PAREX has thus been developed.

The methodology adopted to develop the code was to experimentally study the basic phenomena like the distribution data for the relevant species, their mass transfer kinetic, and the redox reaction kinetics when a change of oxidation state is needed to perform a separation. Contactor hydrodynamics were also studied in order to take their special features into account in the final simulation code. The elementary models, addressing each of the phenomena mentioned above were then implemented in the PAREX code.

Prior to any application purpose, PAREX code was qualified by confronting models predictions to experimental data (laboratory scale or industrial scale). Confrontation of experimental data with PAREX show that main extraction operations of the PUREX process are effectively calculated by the PAREX code either in steady or in transient state. [1-4]

This digital code for the simulation of a liquid-liquid extraction operation is an outstanding tool as a plant operator point of view. At La Hague reprocessing plant, PAREX code is indeed widely used for different purposes like support to safety

1 ^{*}AREVA NC, La Hague Plant, Technical Department, 50444 Beaumont-Hague, France, julia.bisson@areva.com

2 CEA, Nuclear Energy Division, Radiochemistry and Process Department, F- 30207, Bagnols-sur-Cèze, France, binh.dinh@cea.fr

3 AREVA NC, La Hague Plant, Technical Department, 50444 Beaumont-Hague, France, claude.huel@areva.com

demonstration, process flow sheet evolution (new fuels), procedures improvement (transitory, flush out), troubleshooting or operators training.

Some of those applications will be illustrated in this paper. Most of it will be dedicated to safety and criticality studies as safety is one of AREVA's first priorities. Methodology and results of safety analysis, and process adjustment to new fuels reprocessing derived from those studies will be presented.

II – Safety analysis

II-1 Criticality risk in extraction operations

Some isotopes of plutonium are fissile and can lead to an uncontrolled fission chain reaction named criticality. Fission reactions lead to energy release, gamma radiation and neutrons production. Criticality events can occur when fissile material such as plutonium is accumulated above the critical mass which depends on its chemical environment, its chemical form and the container geometry.

In liquid-liquid extraction cycles at La Hague Plant, various control modes of criticality are used to maintain fissile materials in subcritical conditions:

- Concentration controlling : criticality event can not occur below the maximum admissible plutonium concentration,
- Geometry controlling: some equipments (such as pulsed columns, centrifugal extractors, subcritical tanks...) are designed to allow any plutonium concentration.

In normal operations, facilities and flowsheet are designed to avoid any criticality events. To prevent excessive accumulation in non subcritical equipments process parameters are controlled (flow rates, feed composition, reagent concentration, temperatures...). Most sensitive parameters are controlled by two different and independent devices.

II-2 Safety analysis methodology

Safety demonstrations of extraction cycles in disturbed modes are realized with PAREX code. For these analyses, the approach includes two steps.

The first step, named the sensitivity analysis, is aimed to determine for each operating parameters (feed, flowrates, feed composition, solvent flowrate...) the maximum admissible misadjustment level with respect of plutonium accumulation and leakage in non subcritical equipments (conventional tanks or mixer-settlers). Parameters sensitivity is determined by modifying each process parameters stepwise and calculates for each step the new equilibrium with PAREX code. When plutonium concentration is unacceptable in the equipment (or in a raffinate flow), safety margin is reached.

The second step, named the disturbance study, consists of a transient analysis of the process in case of malfunction in order to appreciate its dynamic response and check

the reliability of indicators which must react quite earlier before the criticality event appearance. Precocity of detection gives operators reaction time to apply suitable procedures (process shutdown or corrective action). Dynamic response of the process to a disturbance is evaluated by applying a large change on one process parameter (higher than its margin). Time evolution of plutonium concentration and of process state indicators is then calculated (transient calculation). State indicator is relevant if disturbance is early detected before plutonium concentration exceeds the safety limit.

Safety analyses of extraction cycles with PAREX code are realized for any new spent fuel treatment or for any flowsheet change in order to check the relevance of current procedures or process configurations. If any deficiencies are revealed by these analyses, procedures or configurations are then adjusted.

II-3 Example of safety analysis results on the first extraction cycle

Uranium and plutonium separation from fission products is realized in the extraction and scrubbing section (**Fig. 1**).[5-6] Four operations are realized in this section:

- AX: extraction of U and Pu by TBP 30%,
- AS: scrubbing with nitric acid of small quantities of FP (mainly Zr) previously extracted in AX,
- ASS: scrubbing of Tc with nitric acid
- AXX: complementary extraction by TBP 30% of U and Pu scrubbed in ASS.

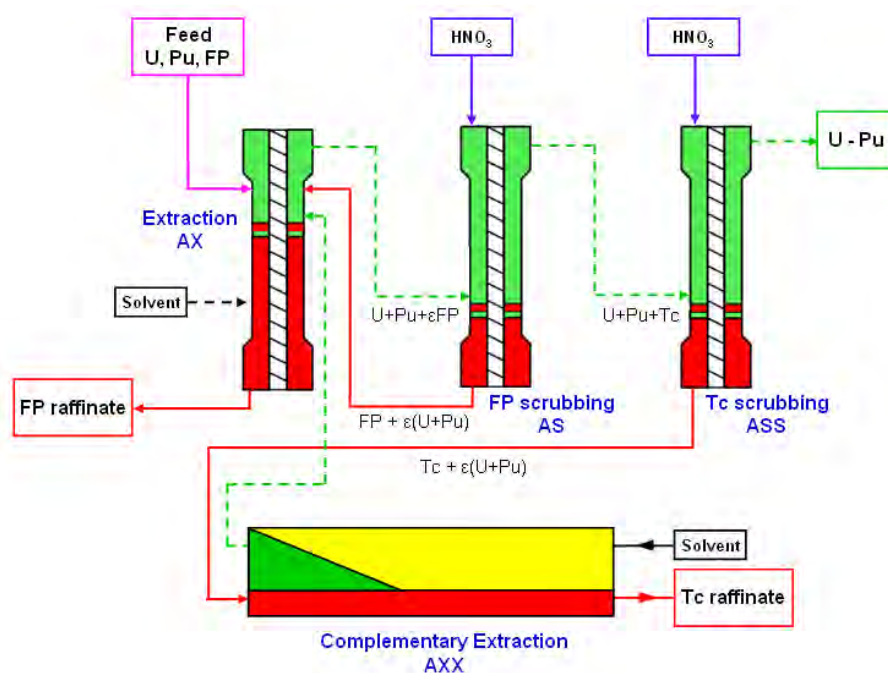


Fig. 1 : Extraction and scrubbing section of first extraction cycle – PUREX process

Annular pulsed columns have been chosen for AX, AS and ASS operations, because their central shaft filled with neutron poison ensures a safe geometry towards criticality for any plutonium concentration. Complementary extraction AXX and

raffinate vessels, which don't contain much Pu in normal operations, are respectively designed to receive maximum 10g/L and 6g/L of plutonium. Excessive accumulation of plutonium in AXX or plutonium leakage in raffinate vessels must thus be prevented.

Sensitivity analysis

Sensitivity analyses of the extraction-scrubbing section show that most sensitive parameters are solvent flowrates and TBP concentration in the organic phase. This feature can be explained by the way of conducting the extraction operation: to avoid fission product extraction and to reach a high degree of fission product decontamination, AX is operated with a high solvent phase level of uranium loading, very close to saturation level (120 gU/l). A small decrease of solvent related parameters leads to a plutonium leakage in FP raffinate at equilibrium state. Solvent loading level must thus be monitored. The most reliable indicator of solvent loading is the density of the aqueous phase coming back to the extraction column from the AS operation, as its value largely increased for a solvent misadjustment lower than for Pu leakage appearance (*Fig. 2*).

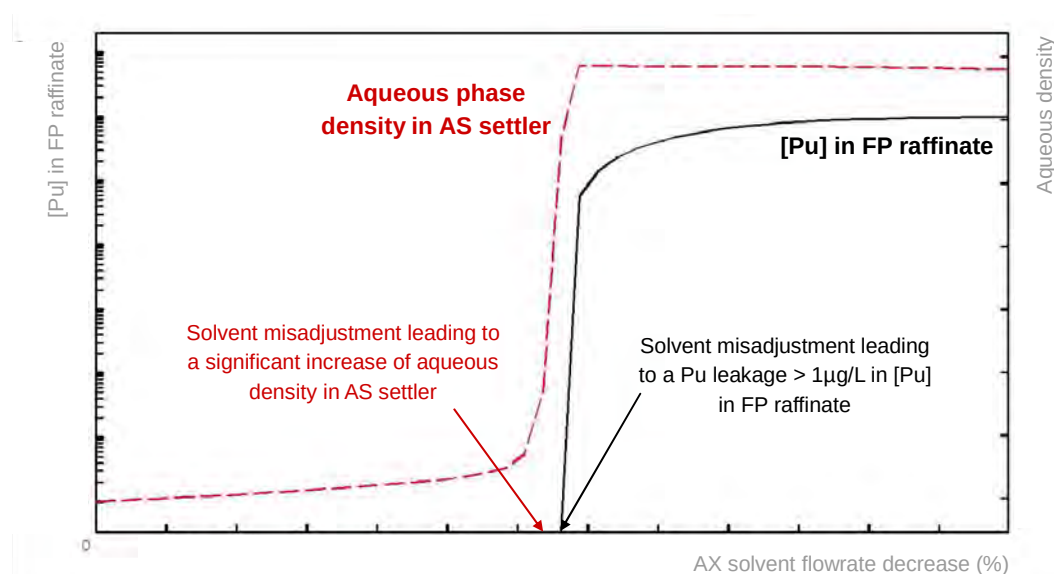


Fig. 2 : AX solvent flowrate margin evaluation

Parameters linked to scrubbing operations (acidity and flowrates) are less sensitive and allow a higher level of misadjustment than solvent related parameters.

Disturbance analysis

Disturbance analysis of the extraction-scrubbing section show that a 20% decrease of the solvent flowrate leads to a plutonium leakage in FP raffinate after few hours. Aqueous phase density in AS settler is a relevant indicator as it exceeds its maximum operating value several hours before plutonium leakage appearance (*Fig. 3*). This precocity of detection gives operators several hours to apply suitable procedures to avoid Pu leakage in FP raffinates. It is interesting to note that even if operators don't detect this disturbance, the maximum plutonium concentration value won't exceed 3

gPu/l. This value is unacceptable from a process point of view but is quite far below the safety limit towards criticality of 6 gPu/L in FP raffinate vessel.

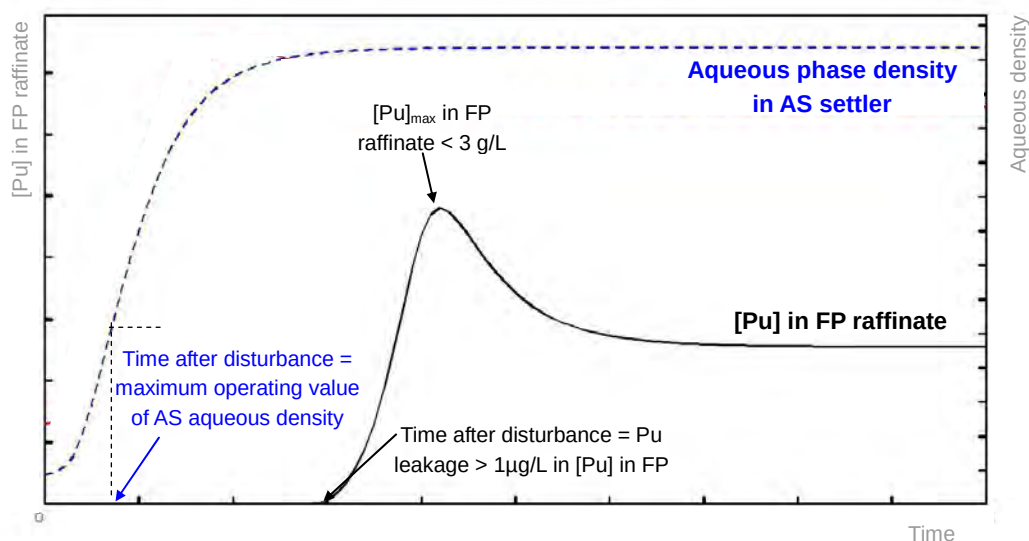


Fig. 3 : Dynamic response to a 20% decrease of the AX solvent flowrate

II-4 Disturbance equivalences

Recently, we have been interested in looking at the process response in the extraction-scrubbing section to simultaneous disturbances in the range of process parameters average variation. The aim was to determine disturbance combination behavior in this section.

Steady-state analysis

Phenomenology of the extraction-scrubbing section is driven by the extraction factor E, product from the organic to aqueous flowrate ratio and the distribution coefficient of selected species:

$$E = O/A \times K_d$$

In this section, plutonium (and uranium) extraction factor must be maximized in order to extract plutonium (and uranium) in the organic phase.

The main consequences due to the decrease of the plutonium extraction coefficient are an increase of the plutonium accumulation in AX column and then a plutonium leakage in FP raffinate. Those phenomena can come from:

- A direct solvent deficit through the decrease of AX or AXX solvent flowrates (O/A decrease) or the decrease of TBP concentration (K_d decrease). Those parameters are sensitive due to the high uranium loading in solvent phase.
- An indirect solvent deficit through the increase of plutonium flow returning to the column either by the AS aqueous phase or by the AXX solvent phase. This feature arises when scrubbing flowrates are increased (O/A decrease) or when acidity of scrubbing is reduced (K_d decrease). Those parameters are less sensitive.

Fig. 4 illustrates the sensitivity of each extraction-scrubbing section process parameters. To obtain a similar plutonium leakage in FP raffinate, a lower misadjustment is needed for parameters directly related to solvent (AX solvent flowrate or TBP concentration) than for scrubbing parameters (AS acid flowrate or ASS acidity).

Fig. 4 also highlights that equivalence relations can be established between extraction-scrubbing section process parameters disturbances, regarding Pu leakage in FP raffinate. For example, a 3.3% decrease of the AX solvent flowrate is equivalent to a 26% increase of the AS acid flowrate or to a 14% decrease of AXX solvent flowrate as it leads to the same plutonium leakage in FP raffinate.

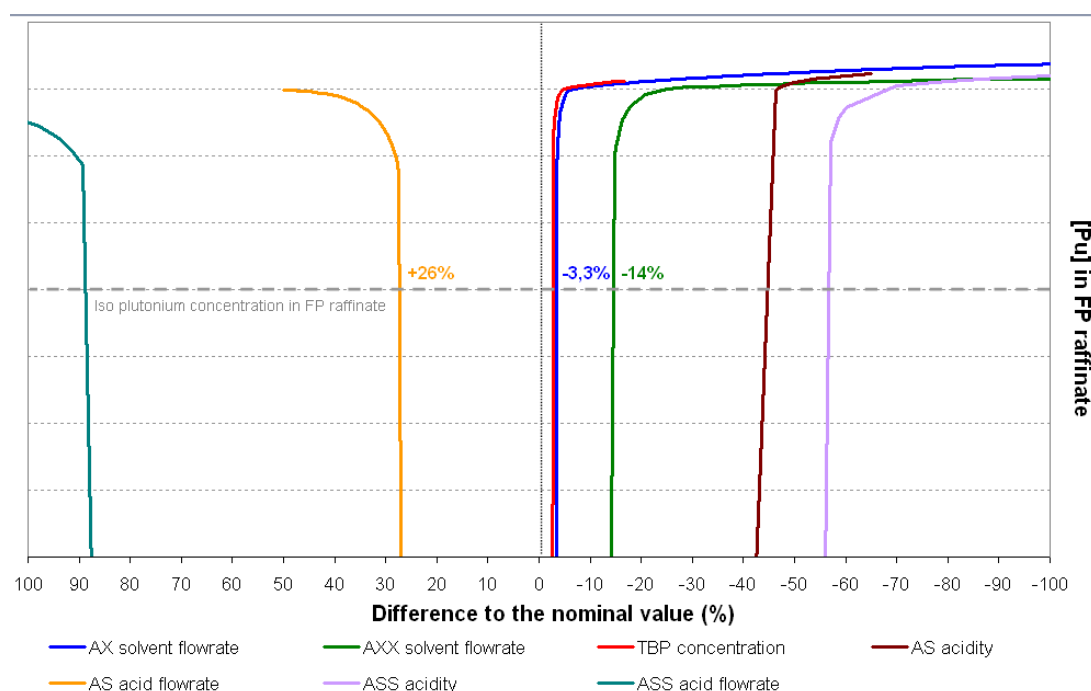


Fig. 4 : Pu leakage in FP raffinate for extraction-scrubbing parameters

Dynamic analysis

From the previous established equivalences regarding the plutonium leakage in FP raffinate, we expect to observe a similar dynamic response for a combination of equivalent disturbances. The dynamic response to a 20% decrease of the AX solvent flowrate has thus been compared to the dynamic response to (**Fig. 5**):

- a 42% decrease of AXX solvent flowrate + a 80% increase AS acid flowrate
- a 4% decrease of TBP concentration + a 5% decrease of the AX solvent flowrate + a 40% decrease of AS acid flowrate + a 66% decrease of the AS acidity

As expected, dynamic response of the process is similar for the several calculated cases towards the plutonium leakage in FP raffinate, validating our equivalence rules.

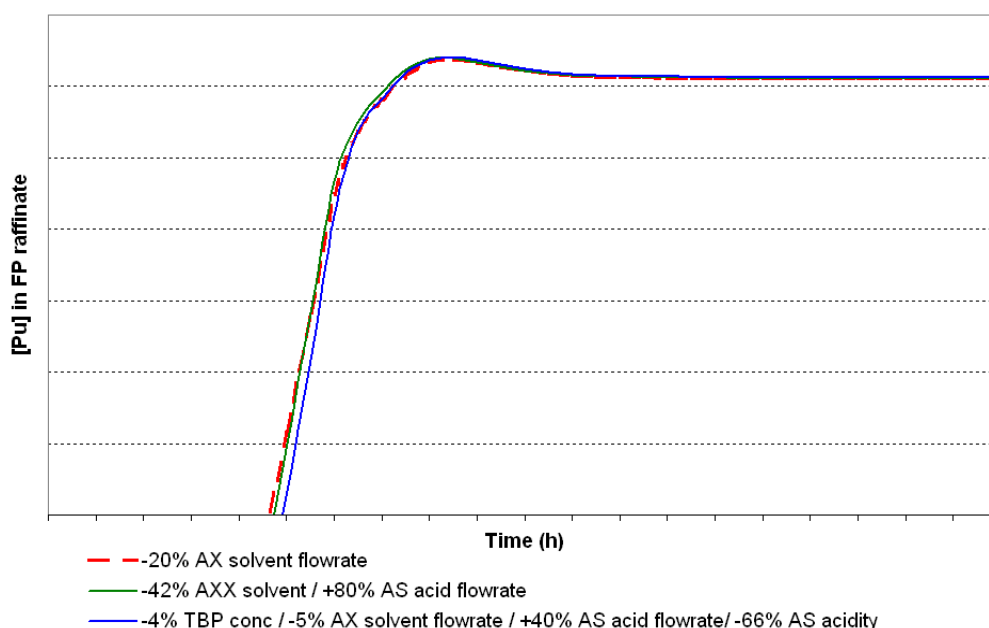


Fig. 5 : Dynamic evolution of [Pu] in FP raffinate for a 20% decrease of solvent flowrate and parameters combinations.

Utility for future safety analysis

For that kind of extraction-scrubbing operations, equivalence rules between process parameters disturbances are a convenient way to assess quite precisely the impact of various disturbances combination using available analyses results, either at steady state or in transient state.

III– OTHER PAREX APPLICATIONS AT LA HAGUE REPROCESSING PLANT

Apart from safety analysis which is the main use of PAREX code at La Hague reprocessing plant, there are other applications of PAREX code. Some of them are described below.

III-1 Procedures improvement

In the uranium purification cycle, thorium build-up occurs in the extraction section, just behind the uranium front (**Fig. 6**). Before shutdown, the cycle is fed with treated uranium to eliminate remaining impurities present in the extractors, like thorium. Thorium concentration was monitored during this procedure, giving evidence of the decrease of thorium build-up in the extractor. Uranium batches corresponding to the shutdown procedure must then be treated at cycle starting up as it is polluted with Thorium, leading to production time loss.

A thorium extraction model was developed by the CEA and implemented in the PAREX process simulation code.[7] The code improvement has allowed us to study the optimization of the flush out procedure in order to avoid thorium pollution in shut down uranium batches.

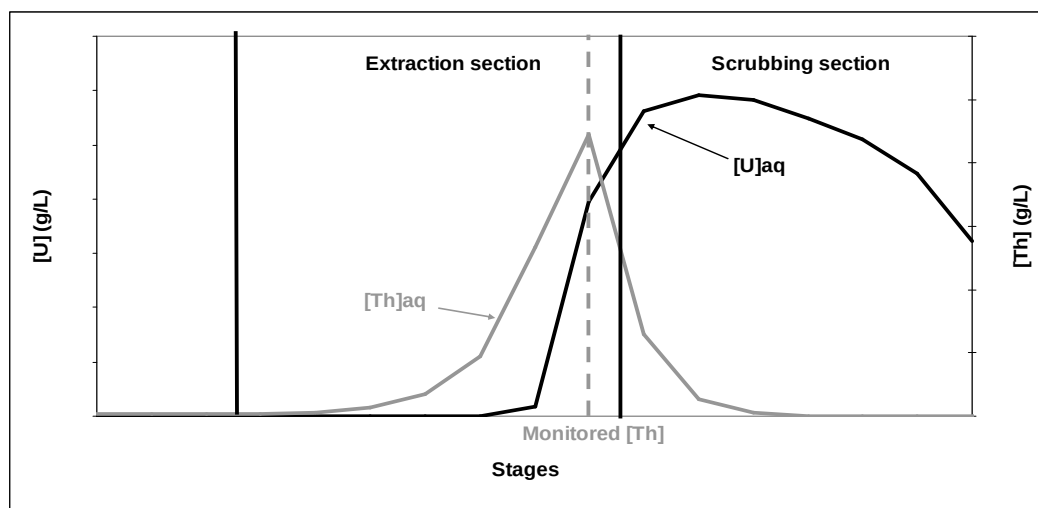


Fig. 6 : Accumulation of thorium, behind the uranium front, in extraction section of uranium purification cycle (steady-state).

III-2 Training simulator

A training simulator, derived from PAREX and named SIMULEX, offers the possibility of altering the operating conditions and displaying the resulting dynamic evolution of the process (concentration profiles in the extractors, change in concentration of a species over time at a point of the process). It was designed to give operators a better understanding of the facility behavior towards disturbances.

IV– CONCLUSION

This paper has shown how PAREX code is a powerful tool for La Hague plant operators, mainly for safety analysis which are essential to demonstrate process robustness to disturbances.

Constant improvements of the code features conducted by the CEA, with the financial support of AREVA, allow procedures improvement and are also essential for AREVA.

References

1. P. Baron, B. Boullis, Modelling of uranium/plutonium splitting in PUREX process. *I. Chem.*, Symposium series n°103, Extraction'87, p.323.
2. P. Baron, B. Dinh, J. Duhamet, F. Drain, F. Mèze, Ph. Lavanant, Plutonium purification cycle in centrifugal extractors : from flow sheet design to industrial operation. ISEC'08, Tucson.
3. B. Dinh, M. Montuir, P. Baron, Parex a numeric code for process design and integration. Global'13, Salt Lake City.
4. C. Sorel, M. Montuir, C. Balaguer, P. Baron., B. Dinh, X. Hérès, V. Pacary, H. Roussel, A powerful tool to model and simulate solvent extraction operations, Solvent Extraction Conference, ISEC'11, Santiago- Chili.
5. P. Baron et al., Extraction cycles design for La Hague plants. Global '93, Seattle.
6. F. Drain et al., Uranium plutonium separation in annular pulsed column. Global '97, Yokohama.
7. S. Michaud, M. Miguiditchian, G. Deblonde, B. Dinh, X. Hérès, G. Andreoletti, Modelling of thorium extraction by TBP. Atalante'12, Montpellier.

Investigation of Heat of Formation of Reverse Micelles using Isothermal Titration Calorimetry and Temperature Dependent Extractions

*A.S. Jackson¹, P.R. Zalupski², M. Nilsson^{*1}*

This work examines the thermodynamics of formation of reverse micelles using isothermal titration calorimetry (ITC) and the temperature dependence of the extraction of Dy^{3+} in a system of mixed extractants. A more complete understanding of how reverse micelles form in solvent extraction systems such as those in use for used nuclear fuel separation is of importance for reducing potential disruptions in the processes. ITC is used here to probe a classic surfactant, bis-2-ethylhexyl sodium sulfosuccinate, in non polar diluents. Temperature effect on the extraction of Dy^{3+} is used to examine the system combining tri-n-butyl phosphate and dibutyl phosphoric acid.

Introduction

Solvent extraction systems, such as those utilized for the separation of used nuclear fuel, contain extraction reagents which facilitate the transport of desired solutes between an aqueous and an organic phase. These reagents often have surface active properties. Under certain conditions, it has been shown that these reagents may form aggregates of reverse micellar type in the organic phase and produce a heavy organic phase (third phase) [1, 2] which can cause disruptions in separation processes. It follows that an increased understanding of the role that aggregates play in the organic phase would be invaluable.

Previous studies by Mukherjee and Moulik[3] and Majhi and Moulik[4] have used isothermal titration calorimetry (ITC) to probe systems of reverse micelles similar to the ones studied in our work, as detailed below, and have reported the existence of a critical micelle concentration (CMC) for such systems. Other studies [5-7] have examined the temperature dependence of metal ion extraction to further the understanding of the thermodynamics of extraction though not necessarily to better understand the aggregate formation that may take place.

The work presented here examines the formation of reverse micelles and the thermodynamic driving forces present. Two well documented methods have been used to probe two different systems: ITC and temperature dependent extractions. We have examined the heat of formation of reverse micelles formed by bis-2-ethylhexyl sodium sulfosuccinate (AOT) in nonpolar diluents using ITC as well as performed temperature dependent Dy^{3+} extractions combining tributyl phosphate (TBP) and dibutyl phosphoric acid (HDBP). The combination of these two reagents has been shown, in previous studies from our lab[12], to exhibit extraction synergy as well as the formation of reverse micelles.

* Corresponding Author, Tel.: +1-949-824-2800; fax: +1-949-824-2541. Email address: nilssonm@uci.edu

¹ University of California Irvine, Department of Chemical Engineering and Materials Science, Irvine, CA 92697-2575, USA

² Idaho National Laboratory, Aqueous Separations and Radiochemistry Department, Idaho Falls, ID, USA

Methods

ITC

All calorimetric measurements were done in a TA Instruments NanoITC with 24 carat gold sample and reference cells and a nominal sample cell volume of 1mL. AOT, n-dodecane and n-octane were obtained from Sigma Aldrich. All were $\geq 99\%$ pure and the solvents were anhydrous. The chemicals were all used as received. Water was of HPLC grade and from either Sigma Aldrich or EMD Chemicals. Solutions were prepared by mass using an analytical balance. Water content of organic solutions was checked by Karl Fisher titration.

The general experimental procedure was similar to that reported elsewhere[4, 8]. This procedure involved injecting a solution of concentrated reverse micelles in a selected diluent into the sample cell which was initially filled with pure diluent. Concentration of the injected solution as well as number and size of injections was chosen such that reverse micelles would be formed during the course of the experiment. The temperature of the cells was held constant for all runs at 25°C and was allowed to equilibrate before injections began. Data was recorded using NanoITC Run and analyzed using NanoAnalyze software from TA Instruments.

Temperature Dependent Extractions

Liquid-liquid extractions using TBP and HDBP were carried out at temperatures ranging from 10-40°C in a Norlake Scientific temperature controlled room. An aqueous solution of 10^{-4}M Dy^{3+} in 0.2 M HNO_3 was prepared from stock solutions. Dy^{3+} stock solution was prepared from dissolving Dy_2O_3 , obtained from Michigan Metals and Manufacturing at 99.999%, in HNO_3 . Organic solutions contained total 1 M extractant (TBP+HDBP) with molar ratios (TBP:HDBP) varying from 4:0 to 0:4. TBP was obtained at $>99\%$ and HDBP at $>97\%$, both from Sigma Aldrich. These were used without any further purification. The aqueous phase was pre-equilibrated by contacting with an equal volume of n-dodecane for 15 minutes. The organic phase was pre-equilibrated by contact with a 0.2 M HNO_3 phase for 15 minutes. Both pre-equilibrations were followed by centrifugation prior to the extraction. Equal volume samples of pre-equilibrated organic and aqueous phases were then contacted for 15 minutes on a vortex mixer followed by 5 minutes of centrifugation. Samples of each phase were then collected and analyzed using neutron activation analysis. This analysis was performed using the UC Irvine 250 kW TRIGA[®] reactor. Dysprosium was activated to produce ^{165}Dy and the samples were then measured using a Canberra HPGe detector.

Results

ITC

The results from calorimetric experiments are shown in Fig. 1. As is shown, the reverse micellar system, Fig. 1a, shows no sharp transition in heat signal, which is indicative of the absence of a CMC. For comparison, a plot of a normal micellar system is shown in Fig. 1b depicting the sharp transition in heat signal which signifies presence of a CMC. Similar results are presented for n-dodecane in Fig. 1c.

Differences in concentrations between n-octane experiments and n-dodecane experiments are accounted for in the expected CMC. N-octane experiments were done in an attempt to reproduce earlier work[4] so similar concentrations were used. No previous results were found for n-dodecane though trends suggested a lower CMC may be expected[3].

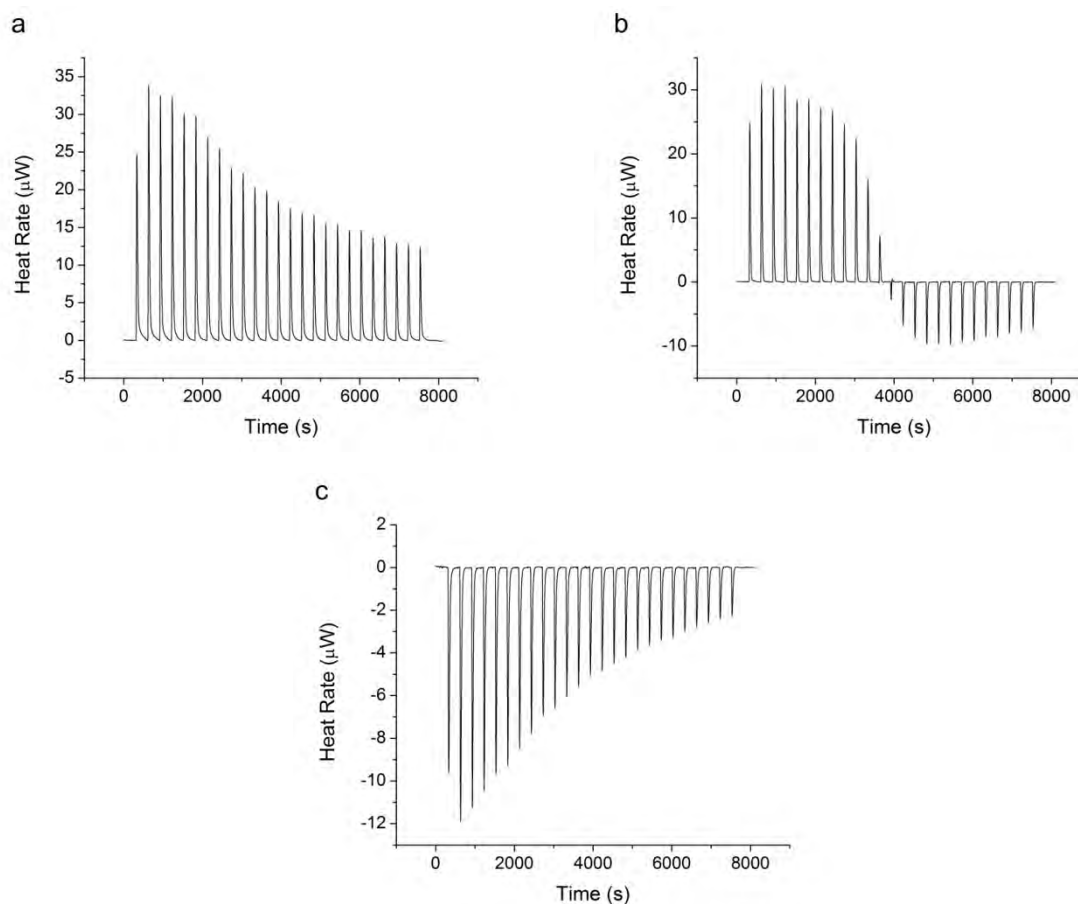


Figure 1:(a) Plot showing heat rates for 30mM AOT in n-octane injected into n-octane at 25°C (b) for comparison with reverse micelle systems, heat signals for 25mM AOT in water injected into water at 25°C (c) 4mM AOT in n-dodecane injected into n-dodecane at 25°C.

Temperature Dependent Extractions

Temperature dependent extraction results are shown in Fig 2. Fig. 2a depicts Van't Hoff plots of distribution ratio versus temperature. A resulting linear fit would be expected to conform to equation 1, where the slope would give the sign and value of the enthalpy of extraction. A representative distribution ratio plot is depicted in Fig. 2b for comparative purposes with previously published results on the TBP and HDBP extraction system[9].

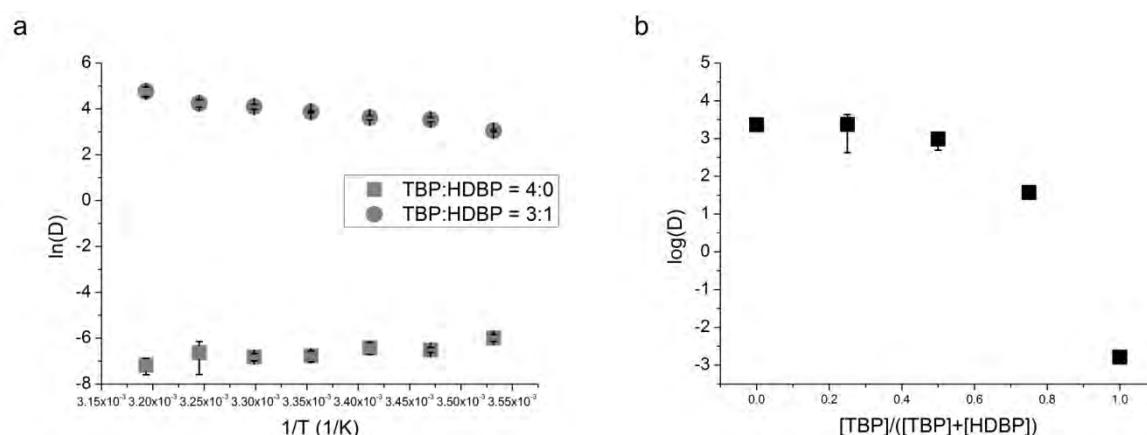


Figure 2:(a)Van't Hoff plots for given TBP:HDBP ratios in the extraction of Dy^{3+} from 0.2M HNO_3 . (b)representative distribution plot of data used to construct van't Hoff plots. All uncertainties represent one standard deviation from triplicate measurements. All plots show total 1M extractant (TBP+HDBP) concentration.

Discussion

Previous studies reported the presence of a reverse CMC for AOT in n-alkanes through the use of ITC[3, 4]. Our data (Fig1a,c) do not show the same relationship that was reported under very similar experimental conditions. We show instead the absence of a CMC for reverse micellar systems in line with what others have reported[10, 11]. The absence of a well defined CMC (a well defined CMC is shown in Fig. 1b) suggests large aggregates are not formed at distinct concentration, as in a normal micelle system due to the hydrophobic effect, but rather that aggregates grow slowly as the concentration of surfactant is increased.

$$\ln(D) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

Past work has shown that aggregates of reverse micellar type do exist in systems used in nuclear fuel separation processes[1, 2] though difficulty in measurement by ITC may be a hindrance to our study of the thermodynamics of these reverse micelles. Fig. 2 shows results from temperature dependent extractions of Dy^{3+} in a system combining TBP and HDBP. It is clearly shown that while TBP alone extracts Dy^{3+} exothermically (see equation 1), the addition of even a small amount of HDBP results in an extraction that is endothermic. This suggests that the extraction mechanisms for combining TBP and HDBP is very different compared to pure TBP. The nature of the extraction mechanism is still under evaluation but it has been shown that reverse micelles may play a role in the extraction of metal ions under these conditions [12]. The exothermic extraction of Dy^{3+} has been shown previously[5] and our results for that extraction are similar to those observations.

Conclusion

Isothermal titration calorimetry proves difficult in measuring heats of formation for reverse micelles shown by AOT in n-alkane solvents. In an effort to study the formation of micelles in synergistic extraction system comprising TBP and HDBP, extractions at different temperatures were carried out to probe the nature of the

reverse micelles formed in this system. A significant change in the enthalpy of extraction for TBP alone and in combination with HDBP suggest that there is a fundamental change in the extraction mechanism. The exact role that TBP plays in aggregate formation in systems where HDBP is present is yet to be determined.

Acknowledgements

The authors wish to thank the U.S. Department of Energy through the Nuclear Energy University Program, NEUP Contract No. 120569 and DE-NE0000156 for financial support for the experiments and the HPGE detector, respectively. The authors wish to thank the UC Irvine TRIGA[®] Reactor Facility for use of the reactor for neutron activation analysis.

References

1. Chiarizia, R., et al., *Third Phase Formation Revisited: The U(VI), HNO₃-TBP, n-Dodecane System*. Solvent Extraction and Ion Exchange, 2003. **21**(1): p. 1-27.
2. Osseo-Asare, K., *Aggregation, reversed micelles, and microemulsions in liquid-liquid extraction: the tri-n-butyl phosphatediluent-water-electrolyte system*. Advances in Colloid and Interface Science, 1991. **37**(1-2): p. 123-173.
3. Mukherjee, K. and S.P. Moulik, *Thermodynamics of Micellization of Aerosol OT in Polar and Nonpolar Solvents. A Calorimetric Study*. Langmuir, 1993. **9**(7): p. 1727-1730.
4. Majhi, P.R. and S.P. Moulik, *Microcalorimetric Investigation of AOT Self-Association in Oil and the State of Pool Water in Water/Oil Microemulsions*. Journal of Physical Chemistry B, 1999. **103**(29): p. 5977-5983.
5. Fidelis, I., *Temperature effect on the extraction of lanthanides in the TBP-HNO₃ system*. Journal of Inorganic and Nuclear Chemistry, 1970. **32**(3): p. 997-1003.
6. Bagawde, S.V., et al., *The effect of temperature on the extraction of uranium(VI) from nitric acid by tri-n-butyl-phosphate*. Journal of Inorganic and Nuclear Chemistry, 1978. **40**(11): p. 1913-1918.
7. Kalina, D.G., G.W. Mason, and E.P. Horowitz, *The Thermodynamics of Extration of U(VI) and Th(IV) From Nitric Acid by Neutral Phosphorus-Based Organic Compounds*. Journal of Inorganic and Nuclear Chemistr, 1981. **43**(1): p. 159-163.
8. Paula, S., et al., *Thermodynamics of Micelle Formation as a Function of Temperature: A High Sensitivity Titration Calorimetry Study*. Journal of Physical Chemistry, 1995. **99**(30): p. 11742-11751.
9. Ellis, R.J., et al., *A SAXS study of aggregation in the synergistic TBP-HDBP solvent extraction system*. J Phys Chem B, 2013. **117**(19): p. 5916-24.
10. Ruckenstein, E. and R. Nagarajan, *Aggregation of Amphiphiles in Nonaqueous Media*. Journal of Physical Chemistry, 1980. **84**(11): p. 1349-58.

11. Ravey, J.C., M. Buzier, and C. Picot, *Micellar structures of nonionic surfactants in apolar media*. Journal of Colloid and Interface Science, 1984. **97**(1): p. 9-25.
12. Anderson, T.L., et al., *Synergistic Extraction of Dysprosium and Aggregate Formation in Solvent Extraction Systems Combining TBP and HDBP*. Solvent Extraction and Ion Exchange, 2013. **31**(6): p. 617-633.

Extraction Chromatographic Separation of Am(III) and Eu(III) by Porous Silica coating TPPEN-NIPA Gel (1) ---- Gel Synthesis and Temperature Effect ----

Kenji Takeshita and Yusuke Inaba, Tokyo institute of Technology, Tokyo, Japan;
Tsuyoshi Yaita and Shin-ichi Suzuki, Japan Atomic Energy Agency, Tokai, Japan;
Atsunori Mori, Kobe University, Kobe, Japan

N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) is a podand-type ligand with six nitrogen-donors and recognizes the slight difference in the softness between trivalent MA (minor actinide) and Ln (lanthanide). Co-polymer gels with a TPEN derivative, *N,N,N',N'*-tetrakis(4-propenyloxy-2-pyridylmethyl)ethylenediamine (TPPEN), and acrylic monomer were applied to the separation of MA from Ln. Four copolymer gels with different acrylic monomers, such as *N*-isopropylacrylamide (NIPA), acrylic acid (AAc), methyl methacrylate (MMA), and *N,N*-dimethylacrylamide (DMAAm), were synthesized. The chemical structures of TPPEN and the acrylic monomers were shown in Fig.1. The batch extraction tests of typical trivalent MA ($^{241}\text{Am(III)}$) and Ln ($^{152}\text{Eu(III)}$) into these gels were carried out, as shown in Fig.2. In weakly acidic solutions at pH 4 to 5, TPPEN-NIPA gel and TPPEN-DMAAm gel showed high separation factors of Am(III) over Eu(III), which were evaluated to be 26 and 18, respectively. These results indicate that the MA separation performance is improved by using poly-acrylamide as a backbone polymer and TPPEN-NIPA gel is the most suitable for the MA/Ln separation.

TPPEN-NIPA gel is a thermosensitive polymer (LCST: 32°C), which is swollen at 298K and shrunken at 313K. To understand the extraction behavior of metal ion in the gel, the temperature dependence of the extraction of metal ion into TPPEN-NIPA gel was studied by both the batch extraction tests and the X-ray absorption fine structure (XAFS) analysis. The complexation of metal ion with TPPEN was very weak at 298K, because of the hydration complex formation of metal ion. Eu(III) was not interacted with TPPEN and only Am(III) was complexed weakly. On the other hand, the complexation of metal ion with TPPEN was improved at 313K. Then Eu(III) was complexed weakly with TPPEN and Am(III) made a strong complex with TPPEN. The unique temperature effect of TPPEN-NIPA gel, which occurs by the hydration and dehydration of poly-NIPA, is available for the establishment of a new MA/Ln separation process with temperature operation. Temperature above LCST can be used for the recovery of MA from waste solution and that below LCST for the isolation of MA (i.e. the purification of MA).

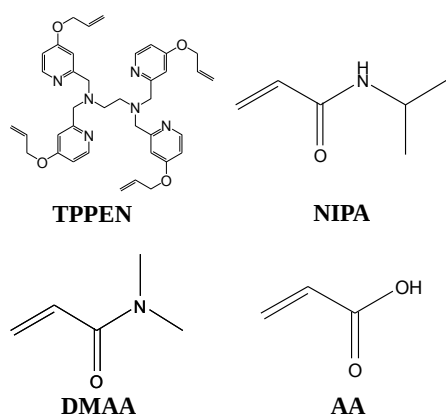


Fig.1 Chemical structure of monomers.

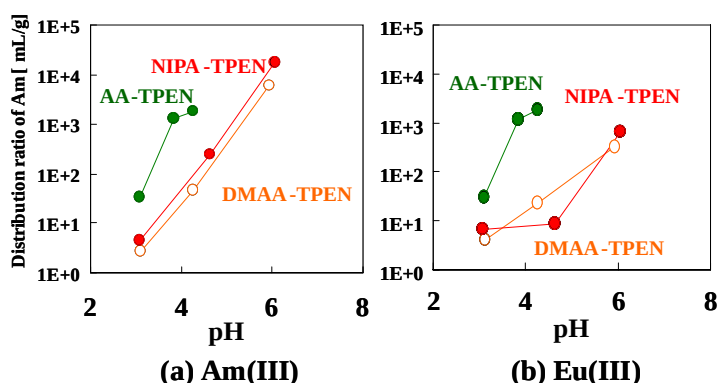


Fig.2 Extraction of Am(III) and Eu(III) with TPPEN gels.

Development of a TODGA-based Liquid-Liquid Extraction System for the Separation of Americium(III) from a Simulated PUREX Raffinate using Hydrophilic Complexing Agents.

P. Kaufholz^{1,*}; A. Wilden¹; G. Modolo¹; F. Sadowski¹; S. Lange¹; D. Bosbach¹; L.M. Harwood²; A. W. Smith²

¹Forschungszentrum Jülich GmbH, Institut für Energie und Klimaforschung-Nukleare Entsorgung und Reaktorsicherheit (IEK-6) Jülich, Germany, *p.kaufholz@fz-juelich.de

²Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, United Kingdom

Abstract

The heterogeneous recycling of minor actinides (MA) within the P&T concept requires high MA concentrations in specific targets. However, because of the high heat decay and neutron emission of curium, any dry or wet fabrication process will require special shielding and handling requirements. Therefore, an effective method for separating Am from Cm prior to re-fabrication is a major prerequisite for the discussion of further fuel cycle scenarios. One option would be to recycle solely the americium directly from the PUREX raffinate in a single cycle process, such as in the EXAm process developed in France¹. In the present study an alternative approach was studied within a laboratory study.

An i-SANEX process based on a 16 stage An(III)+Ln(III) extraction from a simulated PUREX-raffinate with 0.2 M TODGA in a mixture of TPH with 5% of 1-Octanol was recently demonstrated at Forschungszentrum Jülich². The extraction of some challenging fission products (e.g. Zr, Pd) was suppressed using CDTA in Feed- and Scrub solutions as well as Oxalic acid in the scrubbing step².

In this study, the loaded organic phase out of this spiked test was used to study the behavior of hydrophilic americium alone stripping agents under conditions close to test conditions. A novel

hydrophilic complexing agent, developed at the University of Reading and tested by CTU Prague³, was found to selectively strip Am(III) from the TODGA based process solvent. Batch tube tests with trace amounts of Am(III) and Cm(III) in aqueous nitric acid were recently carried out showing good results with high separation factors ($SF_{Am/Cm}$ up to 3.5). Furthermore, an excellent separation from Ln(III) was achieved, which will be separated together with Cm(III) in a consecutive stripping step.

Based on these results, a tentative process flow-sheet was developed and an Am(III) selective spiked separation process will be tested in the Jülich counter current centrifugal contactor rig.

1. Rostaing, C., Poinssot, C., Warin, D., Baron, P., Lorrain, B., Development and validation of the EXAm separation process for single Am recycling. ATALANTE 2012 International conference on nuclear chemistry for sustainable fuel cycles, Procedia chemistry: Montpellier, 2012; Vol. 7, pp 367-373.
2. Modolo, G., Wilden, A., Geist, A., Magnusson, D., Malmbeck, R., A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate. Radiochim. Acta 2012, 100(8-9, Plutonium Futures), 715-725.
3. Harwood, L.M., John, J., Distler, P., Unpublished Results,
The research leading to these results is being performed in the ACSEPT and SACSESS projects funded by the European Atomic Energy Community Seventh Framework Programme under grant agreement No. 211267 and No. 323282.

New Actinide Recovery Process using *N,N*-dialkylamide and Phenanthroline amide

S. Suzuki, T. Kobayashi, T. Yaita,*

Quantum Beam Science Directorate (QuBS), Japan Atomic Energy Agency (JAEA)

2-4 Shirakatashirane, Tokai-mura, Naka-gun, Ibaraki 319-1195, JAPAN

We proposed uranium isolation process using branched *N,N*-dialkylamide(BAMA). One of the most bulky BAMA, *N,N*-di-(2-ethyl)hexyl-2,2-dimethylpropanamide(D2EHDMPA), showed poor loading capacity of hexavalent uranium. To improve loading capacity of U(VI) with BAMA, we synthesized *N,N*-di-octyl-2-ethylbutanamide(DO2EBA), and investigated extraction property of U(VI), Pu(IV), Np(VI), Np(IV), and FP's, extracted structure using EXAFS(Extended X-ray Absorption Fine Structure) and stability for radiation. Furthermore, we studied recovery of degradation products from amide using solid-phase extraction. *N,N*-dialkylamides main degradation products is secondary amine and carboxylic acid. This carboxylic acid was very easy removed with alkaline scrubbing. However, secondary amine recovery methods have never proposed. This secondary amine extracted palladium which decreased decontamination factor. So we tested removal secondary amine from amide. The secondary amine was generated by radiation of amide, diamide, diglicolamide, and phenanthroline amide, that was important to selective separation of actinides from spent nuclear fuels.

After treatment of U(VI) isolation, we must recover other actinide from high level liquid solution. In ARTIST process, we used diglicolamide(DGA) for actinides recovery from HLLW. These DGA compounds had an affinity to lanthanides. Therefore 4f/5f separation process was necessary. In this study, we proposed raffinate treatment using hetero donor ligand, phenanthroline amide, which composed oxygen and nitrogen atoms. Phenanthroline amide extracted actinide like plutonium (IV), americium (III) from lanthanide at 1.0 M HNO₃ condition.

In this presentation, we will show the extraction properties of BAMA and PTA for actinide and fission products in acidic solutions, and the structural property with EXAFS study. In addition, we will propose new all actinide recovery process using BAMA and PTA to improve, 1) nuclear nonproliferation resistance, 2) economical efficiency, and 3) environmental load reduction.

Application of Annular Centrifugal Contactors in a Cold Test of a New Total Partitioning Process with Simulated High Level Liquid Waste

WuhuaDuan*, Jianchen Wang, and Jing Chen

Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China.

High level liquid waste (HLLW) produced from the reprocessing of the spent nuclear fuel still contains moderate amounts of transuranium (TRU) actinides and fission products such as Sr, Cs, etc., in addition to the slightly enriched uranium, which constitutes a permanent hazard to the environment. The partitioning and transmutation (P&T) strategy has increasingly attracted interest for the safe treatment and disposal of HLLW, in which the partitioning of HLLW is one of the critical technical issues. A new total partitioning process, including the TRPO process for the removal of actinides, the CESE (crown ether strontium extraction) process for the removal of Sr, and the calixcrown extraction process for the removal of Cs, has been developed to treat Chinese HLLW at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University, China. A cold test of the new total partitioning process was carried out using 74-stage 10-mm annular centrifugal contactors and simulated HLLW. The test results showed that the decontamination factors were $>1 \times 10^{-5}$, 1000, and 1000 for Nd, Sr, and Cs, respectively. Here Nd was used to simulate Am. During the test, 74-stage 10-mm-dia annular centrifugal contactors worked stable, continuously with no stage failing or interruption of the operation.

Keywords: Annular centrifugal contactor, Application, High level liquid waste, Total partitioning process

Transient extraction behavior analysis of plutonium in reprocessing

*G. Uchiyama^{*1} and H. Abe*

Summary

A simulation study and an experimental study were conducted for the consideration of a scenario of criticality accident at raffinate solution tanks in separation cycle in reprocessing plants.

In a simulation study, transient extraction behavior of Pu has been studied with the solvent extraction simulation code, ESSCAR to understand the effect of process parameters such as flow rate and Pu reductant concentration in separation cycle in reprocessing plants. It was found that the concentration of Pu in both organic and aqueous phases in the Pu washing step increases with decreasing of the flow rate of reductant solution having U^{4+} and increases with decreasing of the concentration of U^{4+} in the reductant solution.

In the experimental study, extraction behaviors of nitrous acid and dibutyl phosphate (DBP) which influence the extraction behavior of Pu in separation cycles were investigated by using a mixer-settler having 5 stages under a gamma-ray irradiation condition (exposure dose: 1×10^2 C/kg). It was found that the concentrations of nitrous acid in both organic and aqueous phases were less than 1×10^{-4} M and less than 2×10^{-5} M, respectively. The concentrations of DBP in both organic and aqueous phases were less than 5×10^{-4} M and 8×10^{-5} M, respectively.

Introduction

Japanese nuclear safety standards of reprocessing plant reflecting lessons learnt from the accident at the Fukushima Dai-ichi Nuclear Power Plants of Tokyo Electric Power Company (TEPCO) require serious accident management for the first time. Accidents such as criticality, boiling of high active liquid waste, fire of organic solvents, and explosion of hydrogen gas which occur beyond DBA (Design Basis Accident) conditions are included as serious accidents in reprocessing plants. Studies on scenarios and source terms of serious accidents in reprocessing plants are needed for the development of evaluation methods of effectiveness of accident management measures. For the consideration of scenario of criticality accident at raffinate solution tanks of separation cycle in a large scale reprocessing plant, a simulation study and an experimental study were conducted.

Several solvent extraction simulation codes such as SEPHIS and MIXSET have been developed to apply to process design, operator assistance and nuclear accountancy [1, 2]. In JAEA, the solvent extraction simulation code, ESSCAR (Extraction System Simulation Code for Advanced Reprocessing), was developed for the purposes of (1) evaluation of reprocessing for new type fuels, (2) simulation of steady and transient behaviors of individual nuclides, (3) simulation of new flow sheet, and (4) safety assessment with reasonable safety margin of anticipated transient extraction behavior in reprocessing plants [3, 4, 5].

^{*1} Nuclear Safety Research Center, Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan, e-mail address: uchiyama.gunzo@jaea.go.jp

In the simulation study, anticipated transient extraction behaviors of Pu and U have been studied with the ESSCAR code to understand the effect of process parameters in separation cycle in current large-scale reprocessing plants. In this paper the analytical results of transient extraction behavior of Pu in the separation cycle in reprocessing plant are mainly described.

Nitrous acid and DBP are radiolysis products of nitric acid and TBP, respectively in the separation cycle. Pu exists mainly Pu^{4+} and Pu^{3+} in Purex system. Pu reacts with nitrous acid. Pu valency state in nitric acid solution changes with concentrations of nitrous acid and nitric acid. Pu extractability by TBP solvent changes with Pu valency in the Purex system. Also Pu reacts with DBP and makes precipitates $\text{Pu}(\text{NO}_3)_2\text{DBP}_2$. So Pu extraction behavior in separation cycle changes with both nitrous acid and DBP concentrations. In the experimental study, extraction behaviors of nitrous and DBP were investigated in the nitric acid and 30%TBP/n-dodecane (nDD) system using a mixer-settler under gamma irradiation condition.

In this paper analytical results of transient extraction behavior of Pu in the separation cycle and the experimental results of extraction behaviors of nitrous and DBP are described in detail.

SIMULATION STUDY

Analytical procedure

The ESSCAR code is able to simulate steady and transient extraction behaviors of not only major components, such as UO_2^{2+} , U^{4+} , Pu^{3+} , Pu^{4+} , PuO_2^{2+} , HNO_3 , HNO_2 , HAN and N_2H_5^+ , but also minor components such as Np^{4+} , Np^{5+} , NpO_2^{2+} , Tc and Zr in a given extraction process flow sheet which may be composed of an arbitrary number of pulsed columns and mixer settlers.

The transient extraction behaviors of U, Pu and nitric acid in the separation cycle were analyzed with ESSCAR code. The separation cycle consists of 8 steps; co-decontamination, 1st and 2nd FP scrubbing, Pu scrubbing, U scrubbing, Pu washing and U back-extraction and auxiliary extraction steps. The contactors of the steps except for Pu washing, U back-extraction and auxiliary extraction are designed with criticality safety dimension. As for Pu washing and auxiliary extraction steps, Pu concentration is controlled from the criticality safety point. The contactors (TBP washing) and tanks for treatment of the raffinate solution from co-decontamination step are not designed with criticality safety dimension. The co-decontamination and Pu washing steps are barriers on the criticality safety control. The Pu leakage and Pu accumulation into the following steps have the possibility of critical excursion. The Pu concentration in the aqueous phase at the bottom of pulsed column in co-decontamination step is monitored to prevent from the leakage of Pu into the TBP washing step and tanks. So, in this study the Pu extraction behavior was analyzed in

the abnormal operations which allowed the increase of Pu concentration mainly in the Pu washing step in the separation cycle. The analytical procedure is as follows:

The extraction contactors in the separation cycle with steady state concentration profiles of U, Pu and nitric acid were operated in the normal process conditions for 7,000 min. Then operation conditions such as the flow rate of reductant solution having U^{4+} of a reductant of Pu^{4+} and the concentrations of U^{4+} and nitric acid in the reductant solution, fed to the Pu scrubbing step in the separation cycle were changed suddenly in the range of 50% to 100% of normal values to simulate abnormal conditions. The time dependency of concentration profiles of Pu, U and nitric acid in the Pu washing step which is a next step to the Pu scrubbing step in separation cycle were calculated for 1,800 min after the operation condition changes.

Results and discussion

Effect of decrease of flow rate of reductant solution having U^{4+} The effect of decrease of flow rate of reductant solution having U^{4+} on the Pu extraction behavior in the solvent extraction cycle was analyzed. As shown in the Fig. 1, the concentration of Pu in the organic phase at 6th stage in the Pu washing step in the U purification cycle without criticality safety concern increases gradually at about 14 hr with time after the 100% reduction of flow rate of reductant solution. The concentration of Pu in organic phase at 6th stage is less than 1.0 g/l even in the case of -100%.

Effect of decrease of U^{4+} concentration in reductant solution

The effect of decrease of Pu reductant (U^{4+}) concentration in the reductant solution from 0% (150 g/l) to 100% (0 l/hr) was analyzed on the Pu concentration in both organic and aqueous phases in 6 stages at the Pu washing step. As shown in the Fig. 2, the Pu concentration in organic phase at 6th stage increases slowly with time at about 14 hr after change of the reductant concentration in the reductant solution. The Pu concentration in organic phase in the Pu washing step is less than 2

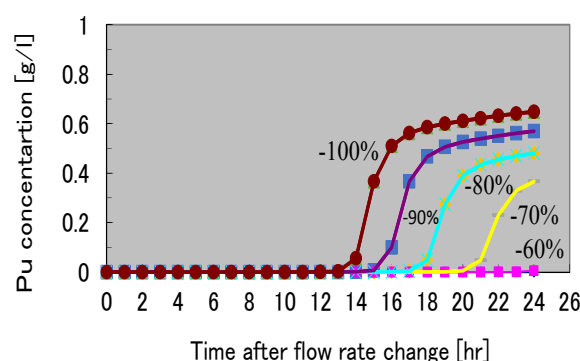


Figure 1 Time dependency of Pu concentration in organic phase at 6th stage in the Pu washing step in the case of flow rate reduction change of reductant solution -50% (20 l/hr) to -100% (0 l/hr).

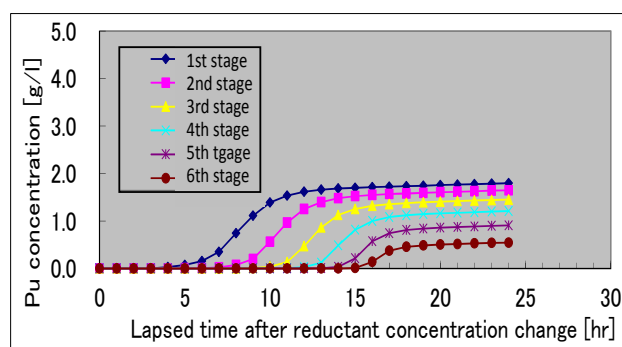


Figure 2 Time dependency of Pu concentration in the organic phase at stage 1 to 6th stage in the Pu washing step in the case of U^{4+} concentration change from 120 g/l to 0 g/l in the reductant solution.

g/l in the cases of U^{4+} concentration change from 120g/l to 0 g/l in the reductant solution.

Figure 3 shows the time dependency of concentrations of total Pu ($Pu^{4+} + P^{3+}$), U^{4+} , hydrazine and Pu^{4+} ratio to total Pu in aqueous phase at 1st stage in the Pu washing step in the case of concentration change of U^{4+} in reductant solution from 120 g/l to 0g/l. The concentration of U^{4+}

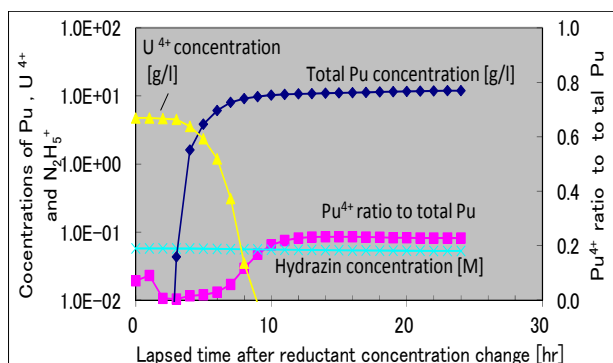


Figure 3 Time dependency of concentrations of total Pu, U^{4+} and hydrazine and Pu^{4+} ratio to total Pu in the aqueous phase at 1st stage in the Pu washing step in the case of concentration change of reductant solution from 120 g/l to 0g/l.

in aqueous phase at the 1st step in the Pu washing step decreased rapidly with time after the change of U^{4+} concentration and the total Pu concentration increased quickly with time. The Pu valency state changed from Pu^{3+} to Pu^{4+} with 3hr time lag. About 20 % of Pu in aqueous phase at 1st stage in the Pu washing step was oxidized to Pu^{4+} .

Effect of increase of nitric acid concentration of reductant solution

The effect of increase of nitric acid concentration of reductant solution from 2 M to 10 M was analyzed on the Pu concentration in both organic and aqueous phases in 6 stages at the Pu washing step. The Pu concentration at 6th stage increases slowly at about 10 hr with time after the change of nitric acid concentration in the reductant solution. The Pu concentration in organic phase in the Pu washing step is less than 2 g/l in the cases of nitric acid concentration change from 2 M to 10 M in the reductant solution.

These analytical results show that it takes longer than 10 hr that the Pu concentration in organic phase at 6th stage in Pu washing step increases after the occurrence of abnormal operation conditions of reductant solution. The Pu concentration in organic phase at 6th stage will not reach the nuclear safety limitation (7.5 g/l in this study). The earlier a recovery procedure is taken in a trouble, the more rapidly normal concentration profiles are recovered. It is required the recovery procedure manuals should be prepared for unexpected troubles or transient behaviors for appropriate measures without delay.

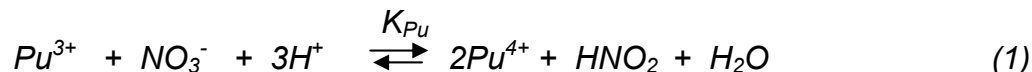
EXPERIMENTAL STUDY

Experimental

An extraction experiment was conducted by using a small scale mixer-settler equipment installed in a gamma cell for Co-60 irradiation. The volumes of the mixer and the settler sections having 5 stages were 12 ml and 57 ml, respectively. The organic solvent of 30% TBP and 70% n-dodecane mixture and the 3 M nitric acid solution were fed at stage 1 and stage 5 of the mixer-settler, respectively under irradiation of Co-60 gamma ray. The feed flow rate ratio of organic solvent to aqueous solution was 1.0. Nitrous acid was analyzed by a flow injection analysis method with N-(1-naphthyl) ethylenediamine. Dibutylphosphoric acid was analyzed by a liquid chromatography method. Nitric acid was analyzed by an alkalimetric titration method.

Results and discussion

The concentrations of nitric acid, nitrous acid and DBP in both organic and aqueous phases in the mixer-settler are shown in Fig.4. The concentrations of nitrous acid in both organic and aqueous phases were from 2×10^{-5} to 9×10^{-5} M and from 6×10^{-6} to 2×10^{-5} M, respectively. The ratio of the nitrous acid concentration in organic phase to that of aqueous phase is about 10, which is almost the same as distribution ratio of nitrous acid in 3 M nitric acid and 30 % TBP/nDD system [6]. The concentration of nitrous acid was very low under the experimental gamma irradiation conditions. The valency state of Pu seems to be Pu^{4+} in the both phases considering the equilibrium constant of Eq. (1) $K_{\text{Pu}} = 1.0 \text{ M}^{-1.5}$ at 3M HNO_3 [7].



The concentration of DBP in both organic and aqueous phases was less than 5×10^{-4} M and 8×10^{-5} M, respectively. The concentration of DBP in organic phase was less than 1/1,000 of that of TBP.

These experimental data on the extraction behaviors of nitrous acid and DBP are used to improve the ESSCAR code having a simulation function of radiolysis products of HNO_3 and TBP as a further study.

The extraction behavior of nitrous acid counter current mixer-settler under the gamma irradiation condition was obtained. Further experimental studies using a feed solution containing U and Pu under gamma irradiation is required

to evaluate the G-values of nitrous acid and DBP and to investigate the extraction behaviors of U and Pu under the these experimental conditions.

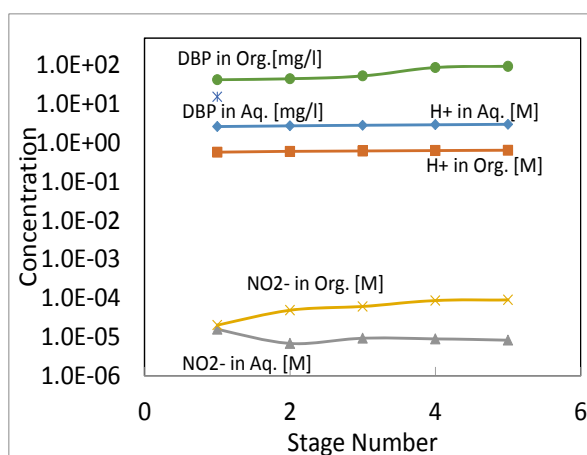


Figure 4 Concentration profiles of nitric acid, nitrous acid and DBP in both organic and aqueous phases in mixer-settler.

CONCLUSIONS

In the simulation study, the transient extraction behavior of Pu in separation cycle has been analyzed with the ESCCAR code beyond DBA conditions. The analytical result of Pu in the separation cycle is summarized as follows:

/The concentration of Pu in both organic and aqueous phases in the Pu washing step increases with decreasing of flow rate of reductant solution having U^{4+} . This will cause the leakage of Pu from the separation cycle to the U purification cycle.

/The concentration of Pu in both organic and aqueous phases in the Pu washing step increases with decreasing of the concentration of U^{4+} in the reductant solution.

In the experimental study, extraction behaviors of nitrous acid and DBP in the 3M nitric acid and 30% TBP/nDD system were investigated under a gamma-ray irradiation condition (exposure dose: 1×10^2 C/kg) The concentration of nitrous acid in both organic and aqueous phases was less than 2×10^{-5} M and less than 1×10^{-4} M, respectively. The concentration of DBP in both organic and aqueous phases was less than 5×10^{-4} M and 8×10^{-5} M, respectively.

REFERENCES

- Mitchell, A. D. (1979), A comparison between SEPHIS-MOD4 and previous models of the PUREX solvent extraction system, Oak Ridge National Laboratory Report QRNL/TM-6565 [1].
- Naito, M., Suto, T., Asakawa, T. (1999), MIXSET-X: A Computer Code for Simulating the PUREX Solvent Extraction Process, JNC-TN8400-99-005, [in Japanese] [2].
- Goto, M., Motoyama, S., Uchiyama, G., Fujine, S., Iwakami, T. (1999), Analysis of plutonium purification process and restrict conditions at the process, Proceedings of the 2nd NUCEF International Symposium NUCEF '98, JAERI-Conf 99-004 (Part II), pp. 536 – 542 [3].
- Department of Fuel Cycle Safety Research Center (2001), Handbook on process and chemistry of nuclear fuel reprocessing, JAERI-Review 2001-038 pp.548-578 [4].
- Asakura, T., Hotoku, S., Ban, Y., Matsumura, M. and Morita, Y. (2005) Technetium Separation for Future Reprocessing, Journal of Nuclear and Radiochemical Sciences, Vol. 6(3), pp. 271-274 [5].
- Uchiyama, G., Hotoku S. and Fujine S. (1998), Distribution of nitrous acid between tributyl phosphate/n-dodecane and nitric acid, Solvent Extraction and Ion Exchange; 16(5):pp.1177-1190 [6].
- Koltuvov.V.S. and Marchenko.V.I, (1973) Rdiokhimia,15, pp.748 [7].

Application of Annular Centrifugal Contactors in a Cold Test of an Improved Total Partitioning Process for High Level Liquid Waste

Wuhua Duan*, Jianchen Wang, Shuwei Wang, Jinghui Wang, Jing Chen,

Summary

The partitioning and transmutation (P&T) strategy has increasingly attracted interest for the safe treatment and disposal of high level liquid waste (HLLW), in which the partitioning of HLLW is one of the critical technical issues. An improved total partitioning process, including a TRPO process for the removal of actinides, a CESE (crown ether strontium extraction) process for the removal of Sr, and a calixcrown extraction process for the removal of Cs, has been developed to treat Chinese HLLW. A cold test of the improved total partitioning process was carried out using 74-stage $\phi 10$ mm annular centrifugal contactors and the simulated HLLW. The test results showed that the decontamination factors were $>1 \times 10^{-5}$, 1000, and 1000 for Nd, Sr, and Cs, respectively. Here Nd was used to simulate Am. During the test, 74-stage $\phi 10$ mm annular centrifugal contactors worked stable, continuously with no stage failing or interruption of the operation.

Keywords: Annular centrifugal contactor, Application, High level liquid waste, Total partitioning process

INTRODUCTION

The partitioning and transmutation (P&T) strategy for converting long-life nuclides from high level liquid waste (HLLW) into short-life radioactive or stable species constitutes an advanced nuclear fuel cycle, and has increasingly attracted interest for the safe treatment and disposal of HLLW^[1]. The partitioning of HLLW is one of the critical technical issues of the P&T strategy. Various advanced processes based on solvent extraction have been developed for the partitioning of HLLW^[2,3].

An improved total partitioning process, including a TRPO (tri-alkyl phosphine oxide) process for the removal of actinides, a CESE (crown ether strontium extraction) process for the removal of Sr, and a calixcrown extraction process for the removal of Cs, has been developed to treat Chinese HLLW, based on the old total partitioning process at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University, China^[4]. The main improvements include that DtBuCH18C6 as extractant is used to replace DCH18C6 in the old process for the removal of Sr, and the calixcrown extraction process with iPr-C[4]C-6 as extractant is used to replace the ion exchange process with KtiFC as the ion exchanger for the removal of Cs.

In the present work, a cold test of the improved total partitioning process for HLLW using 74-stage $\phi 10$ mm annular centrifugal contactors (ACCs) and the simulated HLLW was carried out, and the test results were reported.

EXPERIMENTAL

Chemicals

TRPO (commercial name Cyanex 923) was purchased from CYTEC, USA. TRPO was diluted with saturated kerosene to 30% TRPO-kerosene (v/v) for the removal of actinides. DtBuCH18C6 was synthesized at the INET, and diluted with *n*-octanol to 0.1 mol/L DtBuCH18C6-*n*-octanol, and then pre-equilibrated with nitric acid for the removal of Sr. iPr-C[4]C-6 was also synthesized at the INET, and diluted with *n*-

* Corresponding Author, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China. E-mail address: dwh203@mail.tsinghua.edu.cn

octanol to 0.025 mol/L iPr-C[4]C-6-*n*-octanol, and then pre-equilibrated with nitric acid for the removal of Cs. Other reagents were all analytical reagents. Table 1 gives the composition of the simulated HLLW. Based on their similar extraction behaviors in the TRPO processes, Nd and Zr were used to simulate Am and Pu, respectively ^[5].

Table 1 The main composition of the simulated HLLW

Element	Concentration (mg/L)	Element	Concentration (mg/L)	Element	Concentration (mg/L)
Na	4560	Ru	1880	Cs	2000
Fe	968	Rh	308	Ba	1555
Cd	164	Zr	309.3	Cr	240
Ni	200	Mo	1897	Nd	7866
Pd	1261	Sr	619.6	HNO ₃	1.13 mol/L

The $\phi 10$ mm Annular Centrifugal Contactor

The $\phi 10$ mm annular centrifugal contactor (ACC) was made at the INET. The inside diameter of its rotor is 10 mm, and its suggested rotor speed is from 4000 r/min to 5000 r/min, and its hold-up volume is about 4 mL. The $\phi 10$ mm ACC is made up of two modules as shown in Figure 1 ^[3]. Modules are installed together to form a complete ACC by simply inserting one module into the other module, and the modules are fitted without screws and nuts. In this way, it is much easier to manipulate ACCs. Moreover, to further reduce the liquid hold-up volume of ACCs, the multi-stage group housing structure that is a housing system containing multiple stage housings (e.g. 4, 3 or 2 stages) in a set has been adopted as shown in Figure 1. The principal part of the set is a whole stainless steel block, which consists of heavy phase collecting rings, light phase collecting rings, and inside interstage lines. The advantage of the set is no outside interstage lines between two stages in the set, therefore has very small liquid hold-up and no risk of leakage in interstage lines. The multi-stage group housing also make multi-stage cascade unit more compact for multi-stage processes.



Figure 1 The $\phi 10$ mm annular centrifugal contactors.

The Cold Test

The cold test of the improved total partitioning process as shown in Figure 2 was carried out using 74-stage $\phi 10$ mm ACCs and the simulated HLLW. The test system is shown in Figure 3. The process parameters are presented in Table 2. All feed solutions in the test were pumped by miniature MSP1-C1 syringe pumps (Baoding Longer Precision Pump Co., Ltd., China). The real flow rate of each stream was determined through the change of feed weight (the density of each feed was

determined beforehand) monitored by electronic balances. The operating parameters, for example, the pumping rate and the rotor speed of each ACC were monitored and controlled by a process-control system, which was designed at the INET. Samples from the outlets (product and raffinate) were taken in a timely manner for metal ions and HNO_3 concentrations analysis during the whole cold test. The decontamination factor of each metal ion (DF_M) was obtained as the ratio of the quantity of the metal ion (concentration multiplied by volume) in the product stream to that left in the final raffinate. After the completion of the test, all pumps and centrifugal contactors were stopped. The hold-up liquid in each stage ACC was also sampled for metal ions and HNO_3 concentrations analysis. Sr was determined by flame atomic absorption spectrophotometer (AAS, Hitachi Z-2000, Japan). Cs was determined by flame atomic emission spectrophotometer (AES, Hitachi Z-2000, Japan). Other elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Jarrell Ash IRIS Advantage, USA) or ICP-mass spectroscopy (ICP-MS, XSERIES 2, Thermo Fisher Scientific). The concentration of HNO_3 was determined by standard acid-base titration with potassium oxalate added in the solution to eliminate the influences of the hydrolysis of metal ions.

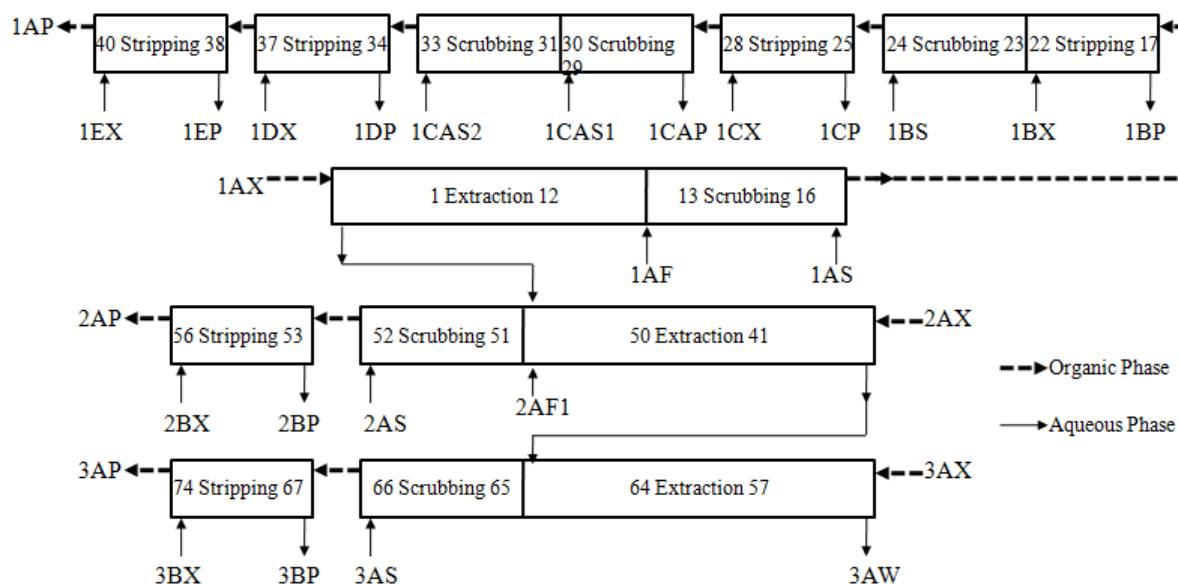


Figure 2 The total partitioning process



Figure 3 The demonstration test system

Table 2 The process parameters

Effluent	Composition	Flow Rate (mL/h)	Effluent	Composition	Flow Rate (mL/h)
1AF	Simulated HLLW	65	1EX	H ₂ O	70
1AX	30%TRPO-kerosene	70	2AX	0.1 mol/L DtBuCH18C6/ <i>n</i> -octanol	80
1AS	1.2 mol/L HNO ₃	15	2AF1	8 mol/L HNO ₃	15
1BX	5.5 mol/L HNO ₃	56	2AS	1.0 mol/L HNO ₃	14
1BS	0.1 mol/L HNO ₃	14	2BX	0.0001 mol/L HNO ₃	80
1CX	0.6 mol/L H ₂ C ₂ O ₄ + 0.1 mol/L HNO ₃	70	3AX	0.025 mol/L iPr-C[4]C-6/ <i>n</i> -octanol	112
1CAS1	5.5 mol/L HNO ₃	28	3AS	0.1 mol/L HNO ₃	20
1CAS2	0.05 mol/L HNO ₃	42	3BX	0.0001 mol/L HNO ₃	112
1DX	5% (NH ₄) ₂ CO ₃	70			

RESULTS AND DISCUSSION

The TRPO Process

The TRPO process includes 12 stages of extraction, 4 stages of scrubbing, and 24 stages of stripping. The concentration distribution of Nd in stages 1-24 is shown in Figure 4. As the organic phase flowed through stage 1 to 12, the loaded Nd concentration increased gradually, and then became stable in the scrubbing section, and lastly started to decrease when it passed through the stripping section. 30% TRPO-kerosene is a very good extractant for tri-valent Am (Cm) (here Nd was used to simulate them) at low and moderate HNO₃ concentration (<2 mol/L). However, the extraction ability of 30% TRPO-kerosene for Sr and Cs is very poor. In the cold test, the HNO₃ concentration was 1.13 mol/L, so Nd was well extracted by 30% TRPO-kerosene. When 5.5 mol/L HNO₃ was used to strip Nd, there is no any stripping difficulty for Nd loaded in the organic phase. These results are agreement with those of the previous tests [5].

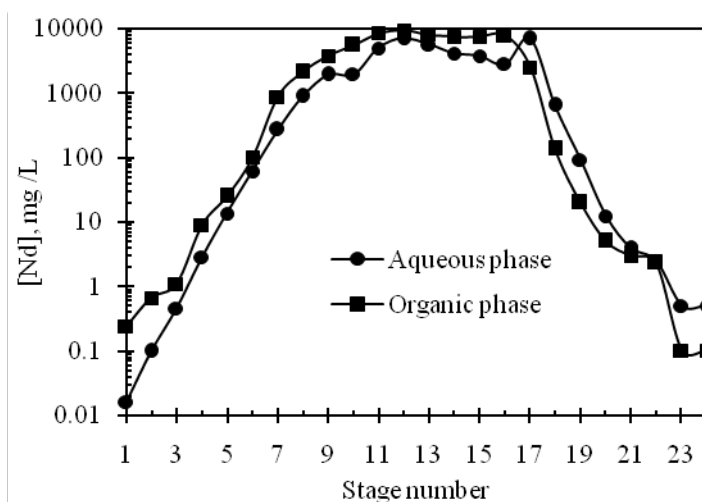


Figure 4 The concentration distribution of Nd in stages 1-24 after equilibrium.

The concentration distribution of Zr in stages 1-28 are shown in Figure 5. From stage 1 to stage 12, the concentration of Zr in the organic phase is increased, which shows that 30% TRPO-kerosene is highly extractable for Pu and Zr (here Zr was used to simulate Pu) in the nitric acid solution. From stage 12 to stage 24, the concentration of Zr in the organic phase keeps constant, which shows that Zr loaded in the organic phase is not stripped by the HNO₃ solution (the acidity >1 mol/L). When 0.6 mol/L H₂C₂O₄ + 0.1 mol/L HNO₃ is used to strip Zr loaded in the organic phase (stages 25-28), high stripping efficiency is obtained.

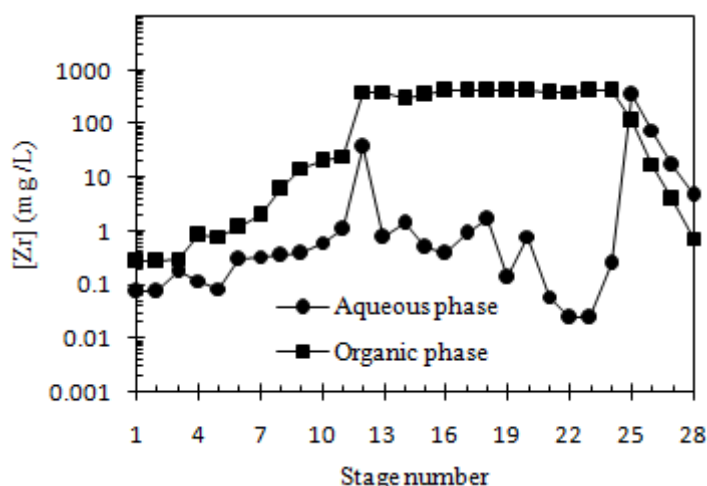


Figure 5 The concentration distribution of Zr in stages 1-28 after equilibrium

The CESE Process

The CESE process includes 10 stages of extraction, 2 stages of scrubbing, and 4 stages of stripping. The concentration distributions of Sr and Ba in each stage of the CESE process are shown in Figure 6. Both metals show similar distribution patterns due to the similar extractability of DtBuCH18C6 towards them. The composition of the aqueous solution coming out of stage 53 (2BP, Sr product) was also monitored during the whole test. Other metals except Ba were not obviously detected in the Sr product. Most of Ba was co-extracted into the final product because of the high affinity of DtBuCH18C6 to Ba. As the solvent flowed through stage 41 to 50, the loaded Sr concentration increased gradually. The Sr concentration in the solvent became stable in the scrubbing section and then started to decrease when it passed through the stripping section. In addition, about 0.39% of Cs was extracted and stripped with Sr.

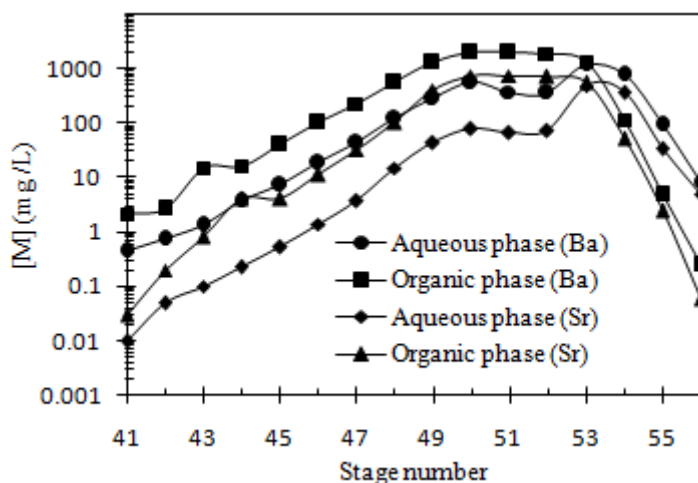


Figure 6 The concentration distributions of Sr and Ba in each stage of the CESE process

The Calixcrown Ether Extraction Process

The calixcrown ether extraction process includes 8 stages of extraction, 2 stages of scrubbing, and 8 stages of stripping. The concentration distribution of Cs in each stage of the CESE process is shown in Figure 7. As the solvent flowed through stage 57 to 64, the loaded Cs concentration increased gradually. The Cs concentration in the solvent became stable in the scrubbing section and then started to decrease when it passed through the stripping section.

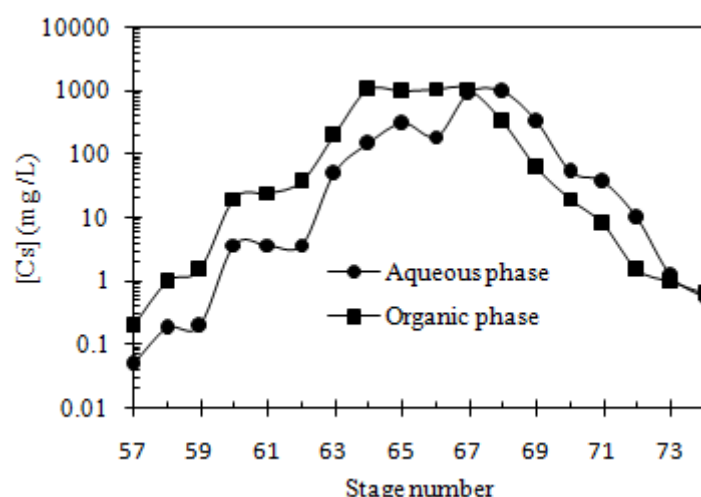


Figure 7 The concentration distribution of Cs in each stage of the calixcrown extraction process

The Removal Efficiency of Nd, Zr, Sr, and Cs

The decontamination factors (DFs) of Nd, Zr, Sr and Cs are shown in Table 3. The DF of Nd was 1.23×10^6 , and that for Zr was 1100, and those for Sr and Cs were 4600 and 7500, respectively, well within our expectation. It is found that all experimental DFs are more than the required ones which meet the removal requirement to change the HLLW into a non- α , and intermediate level liquid waste.

Table 3 Experimental and required decontamination factors

Element	DF _{ex}	DF _{re} [*]
Nd	1.23×10^6	1000
Zr	1100	1000
Sr	4600	2000
Cs	7500	2000

* The requirements is to change HLLW into a non- α and intermediate level liquid waste

CONCLUSIONS

A cold test of the improved total partitioning process for partitioning of HLLW was carried out with 74-stage $\phi 10$ mm ACCs. The test demonstrated that the improved total partitioning process was a promising process for partitioning of the Chinese HLW. The test was run for 5 hours. During the whole testing duration, 74-stage $\phi 10$ mm ACCs worked stable, without any observation of overflow, and continuously with no stage failing or interruption of the operation.

REFERENCES

1. Choppin, G.R. Technology for nuclear reprocessing: present and future directions. Sep. Sci. Technol., 2006, 41: 1955.
2. Nash, K.L.; Madic, C.; Mathur, J.N.; Lacquement, J. Actinide separation science and technology, in: Morss, L.R.; Edelstein, N.M.; Fuger, J. (Eds.), The Chemistry of the Actinide and Transactinide Elements. Springer, The Netherlands, 2008.
3. Duan, W.H.; Zhao, M.M.; Wang, C.Q.; Cao, S. Recent advances in the development and application of annular centrifugal contactors in the nuclear industry. Solvent Extr. Ion Exch., 2014, 32: 1-26.
4. Song, C.L.; Jin, G.Y.; Wang, J.C.; Zhu, Y.J. Treatment of Chinese HLLW by partitioning. Tsinghua Sci. Technol., 1996, 1: 81-85.
5. Wang, J.C.; Tian, G.X.; Chen, J.; Song, C.L. Application of miniature centrifugal contactors for treating high-level liquid waste. Sep. Sci. Technol., 2001, 36: 2983-2996.

Process for Uranium Recovery from Mixed Sulfate/Chloride Media

*James Quinn¹ and Karin Soldenhoff^{*2}*

Sulfuric acid leaching, followed by solvent extraction with tertiary amines, is well established technology for uranium recovery. In many locations, good quality water is in short supply and the use of sea water or saline bore water could provide an attractive option. However, the presence of chloride above 3 g/L has a negative impact on uranium loading, thus ruling out the use of water with high salinity. This work assesses alternative mixed organophosphorus (DEHPA and Cyanex 272) and tertiary amine (Alamine 336) reagents and proposes a process to allow for uranium recovery from liquors containing 20 g/L chloride, with performance comparable with current technology.

Introduction

Solvent extraction is used industrially to purify and concentrate uranium from sulfuric acid leach liquors. The most commonly used reagents are tertiary amines, which extract negatively charged uranyl sulfate complexes. Chloride, if present in the leach liquor, has a deleterious effect on the process. In practice, the chloride concentration in the leach liquor is generally controlled at concentrations below 3 g/L chloride. This places restrictions on the quality of make-up water used in the process and precludes the use of water sources containing high salinity, such as bore water or sea water.

A number of cationic liquid ion exchangers such as DEHPA (di-2-ethylhexyl phosphoric acid), are strong extractants for uranium and are not directly affected by chloride¹. However, these reagents also strongly extract ferric ion²⁻³. Mixtures of DEHPA and Alamine 336 (a mixture of octyl and decyl tertiary amines) suppress ferric ion extraction and allow for uranium extraction in the presence of both ferric ion and 20 g/L chloride⁴. However, uranium was found to be difficult to strip with acid, requiring at least 5.6 M H₂SO₄, which is higher than the 4 M H₂SO₄ acid concentration used in commercial amine processes using strong acid strip.

In this paper, we report on solvent extraction studies using Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), with and without the addition of Alamine 336, and compare its performance with DEHPA / Alamine 336 reagent mixture. The aim of this work was to propose a process to allow for uranium recovery from liquors containing 20 g/L chloride, with performance comparable with current technology. In particular, the objectives set out for this research were to:

- Ensure high uranium solvent loading in the presence of chloride;
- Prevent co-extraction of ferric ion; and
- Maximise stripping performance with sulfuric acid.

¹ James Quinn, Australian Nuclear Science & Technology Organisation, Sydney Australia,

^{*2} Karin Soldenhoff, Australian Nuclear Science & Technology Organisation, Sydney Australia, khs@ansto.gov.au

Experimental

Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, 90%) was supplied by Cytec. Alamine 336 (tri octyl/decyl amine, 99%) was supplied by Cognis. DEHPA (di-2-ethylhexyl phosphoric acid, 97%) was supplied by Shanghai Fopol. All extractants were used without purification. The molarity of all solvents was determined by potentiometric titration in ethanol/water (Cyanex 272 and DEHPA) or methanol (Alamine 336). Shellsol 2046, a commercial grade kerosene containing 17 % aromatics supplied by Shell, was used as the diluent in all experiments. Uranium stock solutions were prepared by dissolving an in house uranium peroxide solid in sulfuric acid. Iron (III) was added using analytical grade iron (III) sulfate or chloride salts. All other reagents were of analytical grade.

Experimental solutions were prepared as shown for each figure caption using uranium stock solution and analytical grade salts and acids. Liquors and solvents were contacted for 20 minutes (or 1-1.5 h if iron (III) was present) in separating funnels. The contact times were chosen to ensure that the system reached equilibrium. When controlling pH, the phases were instead mixed in a baffled beaker using an overhead stirrer, with pH controlled using concentrated ammonia or 5 M H_2SO_4 . Organic samples were stripped for analysis using 5 M H_2SO_4 for iron (and uranium in the case of Cyanex 272) and 1 M sodium carbonate for uranium. Feed and equilibrium aqueous and organic strip samples were analyzed using ICP-MS for uranium and ICP-OES for iron. Mass balances were generally correct to $\pm 5\%$.

Results and Discussion

Effect of pH on extraction of uranium and iron by Cyanex 272 and DEHPA with addition of Alamine 336

Uranium is strongly extracted by organophosphorus acids such as DEHPA and Cyanex 272, exhibiting very high distribution coefficients in the pH range (1-2) used for acid leaching of uranium. Therefore, extraction of uranium was measured at relatively high equilibrium acidities ranging from 0.5 to 8 M H_2SO_4 . The data for Cyanex 272, presented in Figure 1A, shows increasing extraction with decreasing acidity, which is consistent with a cation exchange extraction mechanism typical for uranium extraction with this type of reagent⁵. Extraction with Alamine 336 also decreases with increasing acid concentration, but this is due to increased extraction of bisulfate by the protonated amine as the sulfuric acid concentration increases, effectively competing with extraction of anionic uranyl sulfate⁶. Synergism was observed with the addition of 0.01 M Alamine 336 to 0.1 M Cyanex 272, shifting the uranium extraction curve to higher acidities, beyond what would be expected from the contribution of each individual reagent. While beneficial in extraction, this effect impacts negatively upon sulfuric acid stripping.

A similar trend of increasing uranium extraction with decreasing acidity was found for mixtures of DEHPA/Alamine 336 (Figure 1B). It is apparent from this data that

uranium extraction occurs at higher acidities compared with Cyanex 272, which is expected by virtue of DEHPA's lower pKa (1.27 compared with 3.73)⁷.

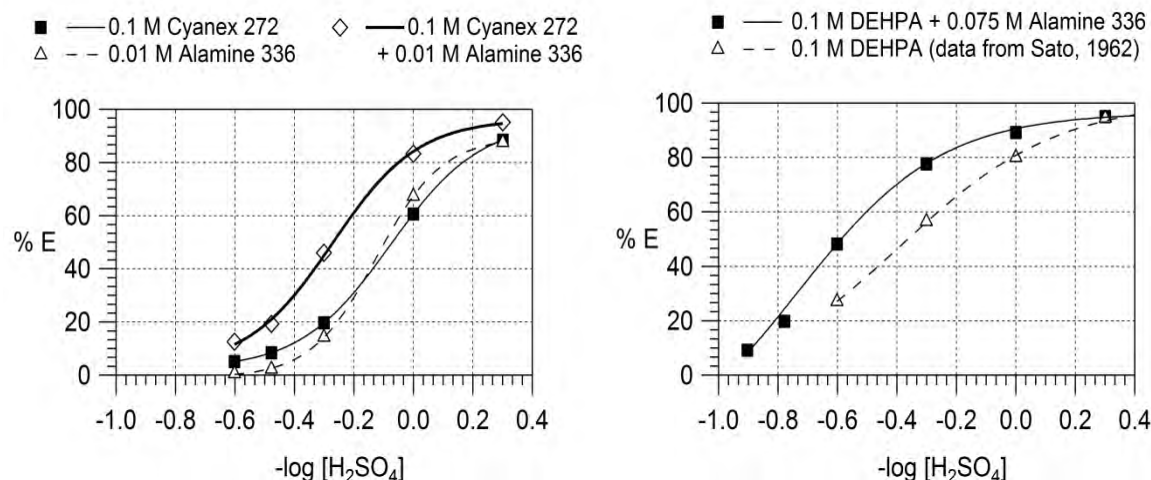


Figure 1: Impact of acidity on uranium extraction with Cyanex / DEHPA/ Alamine 336

1A(left): Aq: 50 mg/L U, 0.5-4 M H_2SO_4 Solvent: 336 as indicated; A/O=1.

1B (right): Aq: 5.8 g/L U, 0.5-8 M H_2SO_4 Solvent: 0.1 M DEHPA + 0.075 M Alamine 336, A/O=2. Also shown, data from Sato, 1962⁵.

The impact of pH on the extraction of ferric ion with Cyanex 272 with and without addition of Alamine 336, is presented in Figure 2A. An antagonistic effect was observed for equilibrium pH values >1 , but this was reversed at higher acidities. A more pronounced antagonistic effect has previously been reported for a mixed DEHPA/Alamine 336 mixture (Figure 2B). The interesting aspect highlighted by this work is that whilst the addition of Alamine 336 is essential for the suppression of ferric ion extraction by DEHPA, this is not the case for Cyanex 272. Cyanex 272 is a much weaker acid than DEHPA⁷ and ferric ion extraction can be prevented by judicious control of pH.

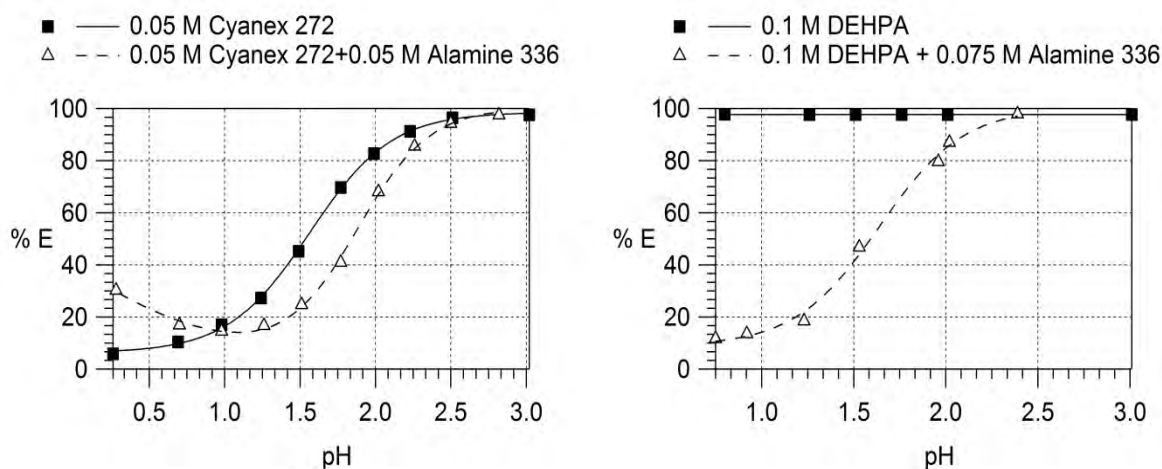


Figure 2: Effect of pH on extraction of iron (III) by Cyanex 272/ Alamine 336/DEHPA

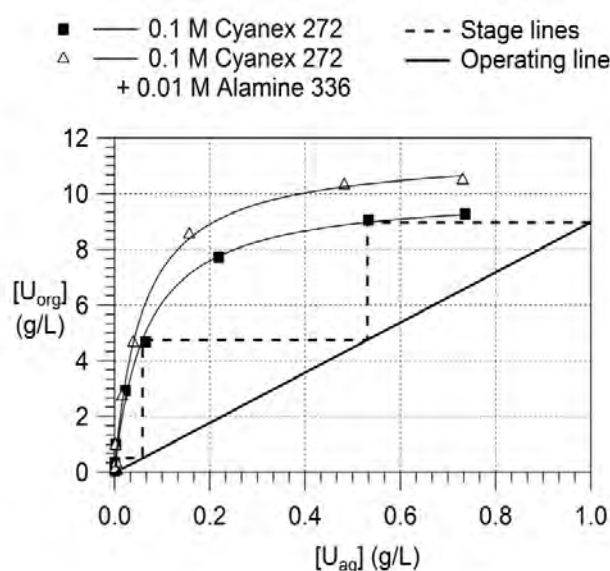
2A(left): Aq: 50 mg/L Fe(III), 0.5 M SO_4 , 20 g/L Cl, Solvent: as indicated; A/O=1.

2B (right): Aq: 50 mg/L Fe(III), 0.6 M SO_4 , 20 g/L Cl, Solvent: as indicated, A/O=1.

Uranium Loading Characteristics

Uranium extraction isotherms for two solvent compositions, Cyanex 272 and a Cyanex 272/Alamine 336 mixture are shown in Figure 3. The aqueous composition is fairly typical of a tank leach liquor, (pH 1.75 and 2 g/L iron (III), 1 g/L U, 0.5 M SO₄), but in addition NaCl was added in order to simulate the presence of chloride. The chloride concentration was 20 g/L. The Cyanex 272 concentration was chosen to achieve acceptable uranium loading, but would need to be optimised to suit a specific liquor composition. The addition of Alamine 336 was kept low to minimise the amount of acid required for stripping.

Favourable equilibrium loading isotherms were measured for both Cyanex 272 and the mixed solvent, with uranium solvent loadings reaching 9.3 and 10.5 g/L respectively. This loading is comparable with existing plant operations using conventional tertiary amine circuits⁸. As expected, the synergistic solvent mixture reached a higher loading than Cyanex 272 alone. A McCabe-Thiele construction using the 0.1 M Cyanex 272 data indicates that 3 to 4 stages of extraction would be sufficient to achieve uranium concentrations of <10 mg/L, given a 1 g/L U concentration in the feed. The maximum iron (III) loading was similar for both solvents, reaching ~1.3 g/L Fe. However, as the uranium loading increased, the iron (III) loading decreased to 0.2 g/L, as detailed in Table 1. When the uranium loading increases, the concentration of free extractant is lowered, resulting in a decrease in distribution ratios for uranium and iron (III). This crowding effect, combined with a dilute acid scrub to selectively strip Fe from the loaded solvent, can be used to effectively control Fe concentrations in the uranium loaded strip solution.



0.1 M Cyanex 272	
[U _{org}] (g/L)	[Fe _{org}] (g/L)
0.051	0.1
0.11	0.18
0.33	0.48
0.99	1.03
2.93	1.3
4.68	1.13
7.72	0.34
9.06	0.19
9.27	0.2

Figure 3 (left): Equilibrium Extraction Isotherms for Uranium at pH 1.74 and 21 °C.

Aq: 1 g/L U, 2 g/L Fe (III), 0.5 M SO₄, 20 g/L Cl. Solvent: as indicated. A/O of 0.1 to 40. McCabe Thiele Construction: Aq: 1 g/L U at pH 1.74, Org: 0.1 M Cyanex 272, 3 stages, A/O of 9.

Table 1 (right): Solvent U and Fe concentrations measured in 0.1 M Cyanex 272 extraction isotherm.

Uranium Stripping Characteristics

Conventional tertiary amine solvents can be stripped using a variety of reagents, including NaCl, $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4$, Na_2CO_3 and 4 M H_2SO_4 . For Cyanex 272, the first two options are not applicable because of the extraction reaction mechanism. Sodium carbonate can strip the uranium effectively⁹, however, a modifier is required to prevent third phase formation. In addition, the presence of even low concentrations of iron (III) in the loaded solvent are a likely source of crud formation. For these reasons, we have concentrated our efforts on sulfuric acid stripping. The advantages of using sulphuric acid are that it is relatively cheap, would already be used in a commercial leaching circuit, and does not present as many environmental issues as ammonium sulphate. In addition, we did not encounter any issues with third phase.

Sulfuric acid stripping isotherms for the two solvents previously examined are presented in Figure 4A. For 0.1 M Cyanex 272, stripping with 4 M H_2SO_4 produced a reasonably favourable isotherm. A similar tests was carried out with the mixed Cyanex 272/Alamine 336 system, and it is apparent that stripping is not as favourable. It was found that addition of just 0.01 M Alamine 336 to 0.1 M Cyanex 272, depressed stripping with 4 M H_2SO_4 by about 50%. This is due to the synergistic effect discussed earlier, which is more pronounced at high acidity. For comparative purposes, a stripping isotherm obtained with a mixed DEHPA/Alamine 336 system is also presented in Figure 4A and it is evident that uranium stripping is poor even at a relatively higher acid concentration of 5 M H_2SO_4 .

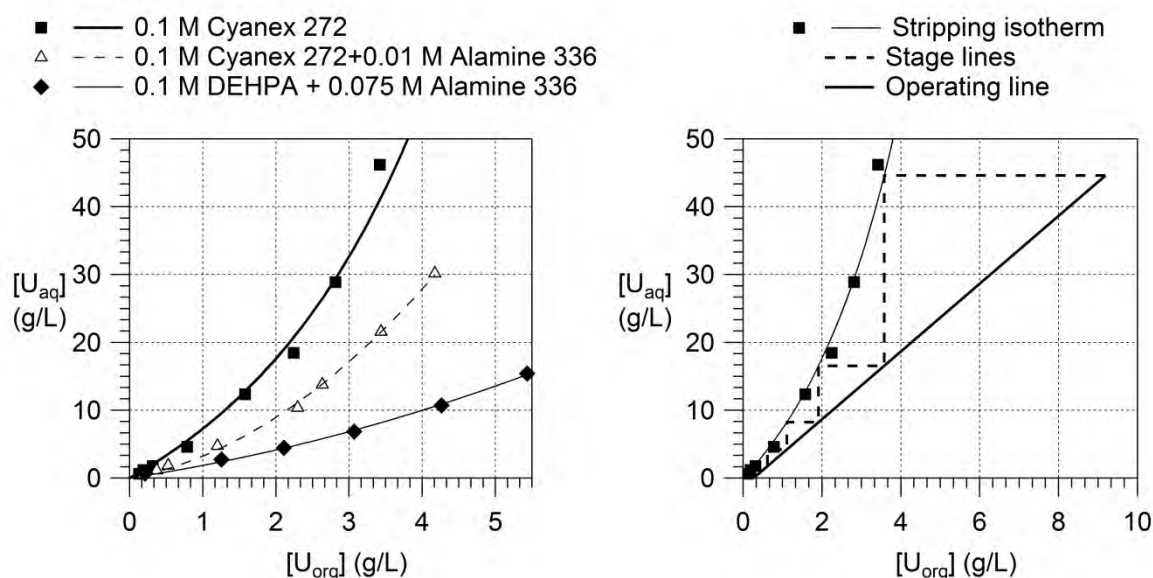


Figure 4 Stripping of Uranium with Sulphuric Acid

4A (left): Aqueous: 5 M H_2SO_4 for DEHPA solvent and 4 M H_2SO_4 for Cyanex solvents. Feed solvent: 6.6 g/L U for DEHPA solvent and 5.7 g/L for Cyanex 272 solvents. A/O: 0.05 to 10.

4B(right): MaCabe-Thiele Construction Aqueous: 4 M H_2SO_4 . Solvent: 0.1 M Cyanex 272. 5 stages, A/O: 0.2.

Sulfuric acid stripping of conventional amines targets 4 M H_2SO_4 and can achieve loaded strip liquor concentrations of 100 g/L U¹⁰. A MaCabe-Thiele construction of

the 0.1 M Cyanex 272 stripping isotherm indicates that a 4-5 stage 4 M H₂SO₄ acid strip circuit can achieve uranium concentrations of ~ 45 g/L in the loaded strip, which is considered quite competitive.

Conclusion

This work has shown that uranium was extracted by Cyanex 272, exhibiting very high distribution coefficients at pH 1. Extraction of iron (III) was much weaker ($\beta_{U/Fe}=129$). Addition of Alamine 336 resulted in antagonism for iron (III) extraction at pH > 1 and synergism at higher acidities. Synergism was observed in the extraction of uranium, which resulted in an increase in the concentration of sulfuric acid required for stripping. Therefore it was concluded that addition of Alamine 336 to Cyanex 272 provided no advantage, from a uranium processing point of view. McCabe-Thiele analysis of extraction and stripping isotherms showed that 9.2 g/L uranium could be loaded on the solvent using 0.1 M Cyanex 272 at pH 1.75 in 4 stages of extraction, and 4 stages of stripping using 4 M H₂SO₄ produced a solution containing 45 g/L uranium.

Compared with DEHPA/Alamine 336 mixed reagent, Cyanex 272 on its own was found to be a better option for extraction of uranium in the presence of high concentrations of both iron (III) and chloride, resulting in higher uranium loadings and lower requirement of acid for stripping. The suggested process allows for the use of sea water or saline bore water for leaching.

References

1. Sato, T., The extraction of uranium (VI) from hydrochloric acid solutions by Di-(2-ethylhexyl)-phosphoric acid. *Journal of Inorganic and Nuclear Chemistry* **1965**, 27 (8), 1853-1860.
2. Sato, T.; Nakamura, T.; Ikeno, M., The extraction of iron(III) from aqueous acid solutions by di(2-ethylhexyl)phosphoric acid. *Hydrometallurgy* **1985**, 15 (2), 209-217.
3. Biswas, R. K.; Singha, H. P., Purified Cyanex 272: Its interfacial adsorption and extraction characteristics towards iron(III). *Hydrometallurgy* **2006**, 82 (1-2), 63-74.
4. Quinn, J. E.; Wilkins, D.; Soldenhoff, K. H., Solvent extraction of uranium from saline leach liquors using DEHPA/Alamine 336 mixed reagent. *Hydrometallurgy* **2013**, 134-135 (0), 74-79.
5. Sato, T., The extraction of uranium (VI) from sulphuric acid solutions by di-(2-ethylhexyl)-phosphoric acid. *Journal of Inorganic and Nuclear Chemistry* **1962**, 24 (6), 699-706.
6. Coleman, C. F.; Brown, K. B.; Moore, J. G.; Crouse, D. J., Solvent extraction with alkyl amines. *Industrial & Engineering Chemistry* **1958**, 50 (12), 1756-1763.
7. Kolarik, Z., Review: Dissociation, Self-Association, and Partition of Monoacidic Organophosphorus Extractants. *Solvent Extraction and Ion Exchange* **2010**, 28 (6), 707-763.
8. Ritcey, G. M., *Solvent Extraction, Principles and Applications to Process Metallurgy*. Revised Edition ed.; G.M. Ritcey and Associates Inc.: 2006; Vol. 2, p 505-573.
9. Rajeswari, B.; Dhawale, B.; Bangia, T.; Mathur, J.; Page, A., Role of Cyanex-272 as an extractant for uranium in the determination of rare earths by ICP-AES. *Journal of Radioanalytical and Nuclear Chemistry* **2002**, 254 (3), 479-483.
10. Morais, C. A.; Gomiero, L. A.; Filho, W. S.; Rangel Jr, H., Uranium stripping from tertiary amine by sulfuric acid solution and its precipitation as uranium peroxide. *Minerals Engineering* **2005**, 18 (13-14), 1331-1333.

Probing Ligand Exchange Kinetics in Actinide/Lanthanide Solvent Extraction Systems using NMR Spectrometry

Elizabeth O. Krahn^{*1}, Cécile Marie² and Kenneth L. Nash¹

Summary

Though the technique has been rarely applied for this purpose in solvent extraction systems, NMR spectrometry (³¹P) has great potential for application in improving understanding of ligand exchange kinetics of organophosphorus extractant molecules. In this report, features of ligand exchange dynamics of lanthanide complexes with (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester (HEH[EHP]) and di-(2-ethylhexyl) phosphoric acid (HDEHP) non-polar organic extractant solutions are studied.

Background

Closed nuclear fuel cycles are those in which used fuel is physically and chemically processed to remove fissile material for recycle and transmutation. State-of-the-art technology utilizes liquid-liquid extraction as the main separation process to isolate the reusable metals of interest. A key to the long-term viability of this design process is the continued development and refinement of fundamental understanding of the interactions between molecules, ions, and metals in the organic phase, aqueous phase, and at the interface of extraction systems. Investigation of the solvent exchange kinetics and complex formation occurring in the two phases can lead to an improved understanding of the mechanisms involved in the overall pathway of extraction. A more complete understanding of these interactions in already implemented separation processes could lead to improved separation schemes. Various spectroscopic techniques have been used to probe these interactions.

In this report, ³¹P Nuclear Magnetic Resonance (NMR) spectrometry is employed to develop an improved understanding of ligand exchange dynamics for the lanthanides, which are important elements that are extracted in used nuclear fuel separations. Many of the ligands used in these systems are organophosphorus extractants, making them well-suited for study through direct analysis of the phosphorus atom by ³¹P NMR. In a recent study, this technique has been applied to characterize the binary complex formed between lanthanides and the cation exchange ligand, di-(2-ethylhexyl) phosphoric acid (HDEHP), used in the TALSPEAK process. Marie *et al.*¹ offered evidence for the presence of ternary complexes observed when the lactic acid buffer was introduced into the system in the form of (Ln(Lac)_n(DEHP·HDEHP)_{3-n}). In the present work, features of the ligand exchange dynamics and paramagnetic

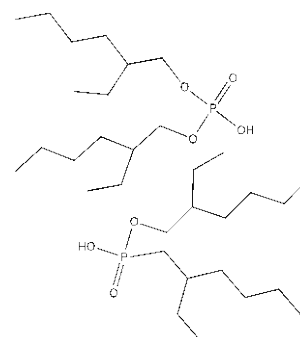


Figure 1. HDEHP (top) and HEH[EHP] (bottom)

^{*1} Washington State University, Department of Chemistry P.O. Box 644630, Pullman, WA 99164-4630, email: elizabeth.krahn@wsu.edu

² CEA Marcoule, DRCP/SMCS/LEPS – Bât. 399 – BP 17171 30207, Bagnols-sur-Cèze Cedex, France

shifts of lanthanide-HDEHP complexes are compared with parallel data on the less acidic phosphonic acid cation exchange ligand (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester, HEH[EHP]. The latter extractant is of interest in lanthanide process chemistry but also as an extractant in an Advanced TALSPEAK process² (Figure 1).

Experimental Methods

Reagent Preparation

HDEHP was purchased from Sigma-Aldrich (97% purity) and purified to > 99% using the copper precipitation method.³ HEH[EHP] was purchased from Yick-Vic Chemicals and Pharmaceuticals Ltd. and purified to > 99% using the third phase formation procedure.⁴ The purity was verified using ³¹P NMR spectrometry and potentiometric titration. The diluent 1,3-diisopropylbenzene (1,3-dipb) was purchased from Alfa Aesar (97%) and used as received. The lanthanide nitrate stock solutions were prepared from lanthanide oxides (99.9999%) purchased from Arris International and standardized for metal, nitrate and H⁺ concentrations. Lanthanide concentrations in the aqueous phase were determined using an HP Agilent 7500 ICP-MS instrument.

To prepare the extracted complex samples, aqueous lanthanide nitrate solutions were contacted (vortex mixing) for 20 minutes with organic solutions containing HDEHP 0.1 mol L⁻¹ or HEH[EHP] 0.1 mol L⁻¹ in 1,3-dipb. The two phases were carefully separated after centrifugation. The organic phase was used directly for ³¹P NMR studies. The aqueous phase was diluted for ICP-MS analysis of metal content.

³¹P NMR

The ³¹P NMR spectra were collected on a Varian VNMRS 600 MHz, Oxford 14.1 T 51 mm bore magnet, spectrometer with a 5 mm broadband probe. The metal loaded organic phases were analyzed using a 5 mm NMR tube. A coaxial insert was filled with acetone-d₆ (99.9 atom-% D) as the lock solvent for low temperature work, (< 22°C) or DMSO-d₆ (99.9 atom-% D) as the lock solvent for high temperature work (> 22°C). A chemical shift reference of 0.1 mol L⁻¹ phosphoric acid (Fisher Chemicals, 85%) was used for room temperature spectra. The temperature was calibrated using an RTD digital thermometer inside an NMR tube, or by running methanol (< 22°C) or ethylene glycol (> 22°C) calibrations.

Results and Discussion

HDEHP and HEH[EHP] exist predominately as dimers in non-polar organic phases.⁵ Slope analysis experiments indicate that three of the dimers coordinate to the Ln(III) cation upon extraction from the aqueous phase via the reaction shown in Eqn. 1. In both systems, the cation coordination environment is presumed to be a pseudo-octahedral arrangement of six oxygen donors from each of three extractant dimers.⁶



Initial characterization of the ligands in the non-polar organic phase, 0.1 mol L⁻¹ HDEHP or 0.1 mol L⁻¹ HEH[EHP] were contacted with an aqueous phase containing a single Ln³⁺ as the nitrate. The post-contact organic phase was analyzed by ³¹P NMR at room temperature (22°C). The room temperature ³¹P resonance of free HDEHP was found at -1.51 ppm, and for free HEH[EHP] at 35.9 ppm (Figure 2A & D). When the ligands were complexed to the diamagnetic La³⁺ ion, a single, broad peak was observed for both HDEHP and HEH[EHP] at -3.95 ppm and 29.9 ppm, respectively (Figure 2B & E). The single peak is a composite peak of free and bound ligand, indicating rapid exchange (on the NMR time scale). A representation of ³¹P NMR spectra for HDEHP bound to the paramagnetic Ln³⁺ ions across the series is shown in Figure 3. The rate of ligand exchange at room temperature slows as the cation radius decreases (with increasing atomic number), likely due to the stronger electrostatic interactions between the cation and HDEHP donor atoms.

For the paramagnetic Ln complexes, two peaks are observed at room temperature. The peak located at -1.51 ppm corresponds to the bulk HDEHP, all other peaks correspond to the respective Ln complexed to HDEHP. The lighter paramagnetic lanthanides (Ce to Nd) induce a downfield shift, while the bound ligand signals are shifted upfield for complexes of heavier lanthanides (Sm to Tm) in both the HDEHP and HEH[EHP] systems. The magnitude of the paramagnetic shift is a combination of contact shift (through bond interactions) and dipolar shift (through space interactions). The contact shift will depend on spin expectation values $\langle S_z \rangle$ and dipolar shift on magnetic susceptibilities of lanthanide cations.^{7,8} Those intrinsic nuclear properties of lanthanides explain more important variations observed along the Ln series. A comparison between the magnitude of the chemical shift from the bulk ligand to the ligand coordinated lanthanide is seen in Table 1. In general the paramagnetic Ln complexed with HEH[EHP] causes a smaller change in the chemical shift relative to that of HDEHP complexes. The small shift that is seen for Sm³⁺ complexes correlates with the low magnetic susceptibility of this ion.

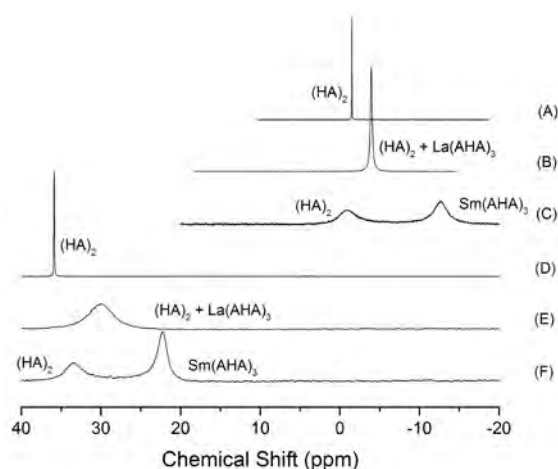


Figure 2. ³¹P NMR spectra at room temperature (22°C) of (A) Free HDEHP; (B) HDEHP after equilibrium with La(NO₃)₃; (C) HDEHP after equilibrium with Sm(NO₃)₃; (D) Free HEH[EHP]; (E) HEH[EHP] after equilibrium with La(NO₃)₃; (F) HEH[EHP] after equilibration with Sm(NO₃)₃.

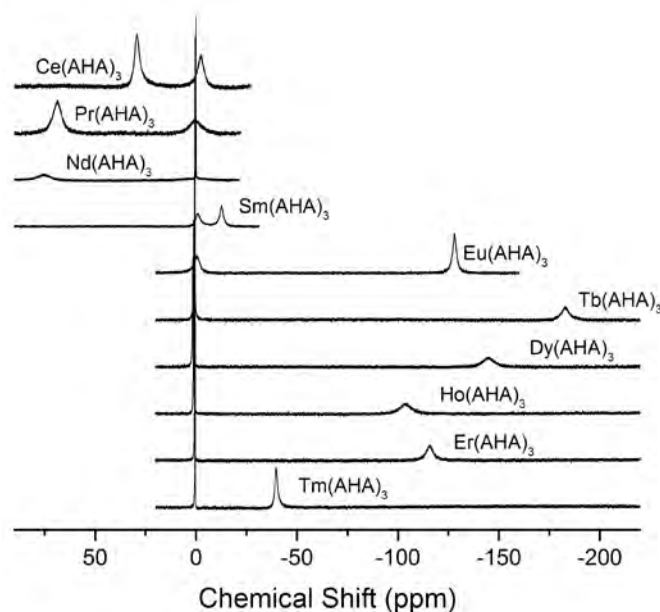


Figure 3. ^{31}P NMR spectra of 0.1 mol L^{-1} HDEHP at 22°C after equilibration with respective lanthanide.

Table 1 Change in chemical shifts for the paramagnetic Ln.

Extractant	$\Delta\text{ppm relative to free extractant peak}$									
	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}
HDEHP	+30	+69	+75	-13	-128	-182	-149	-104	-116	-40
HEH[EHP]	+18	+41	+42	-11	-69	-53	-38	-20	-53	-15

La^{3+} is most interesting ion for ligand exchange kinetic studies because it is diamagnetic and the single composite peak could potentially be resolved to the separated bulk and coordinated peaks by decreasing the temperature. Sm^{3+} is paramagnetic, however its nuclear charge is relatively low hence the paramagnetic shifts are small.⁹ The incomplete resolution of the free and bound peaks (-3.86 ppm and -14.27 ppm for HDEHP and 33.5 ppm and 22.3 ppm for HEH[EHP], Figure 2C & F), indicates that ligand exchange rests in a convenient range to probe using ^{31}P NMR. These two Ln have been studied in the HDEHP system.¹ In this report, the earlier results are compared to those obtained for the HEH[EHP] system.

An example of experimental and simulated ^{31}P NMR spectra for the Ln^{3+} HEH[EHP] system is shown in Figure 4. Spectra were collected at different temperatures and a complete band shape analysis, using general equations for an uncoupled two-site exchange described by Rogers and Woodbrey¹⁰ was employed to determine the mean lifetime of the ligand in its metal-coordinated form (τ). The exchange rate, k_{ex} , was determined using Eqn. 2, where p_A and p_B are the fractional populations of nuclei in the free (A) and coordinated (B) states, respectively.

$$\tau = p_A / k_{\text{ex}} (p_A + p_B = 1) \quad (2)$$

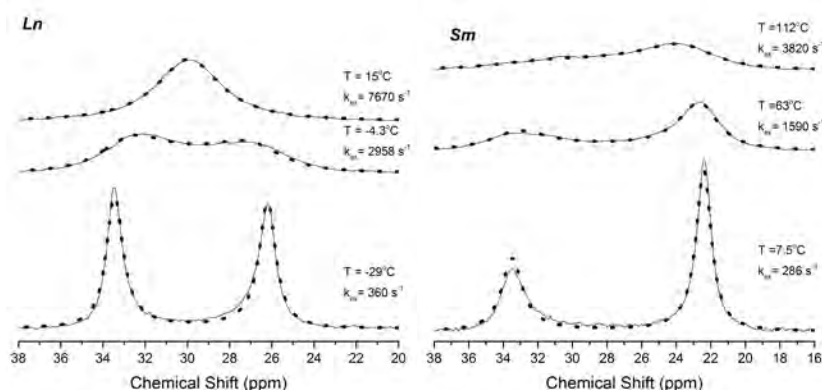


Figure 4. Representative variable temperature ^{31}P NMR experimental (solid) and calculated (dots) spectra of HEH[EHP] exchanging on La^{3+} (left) or Sm^{3+} (right)

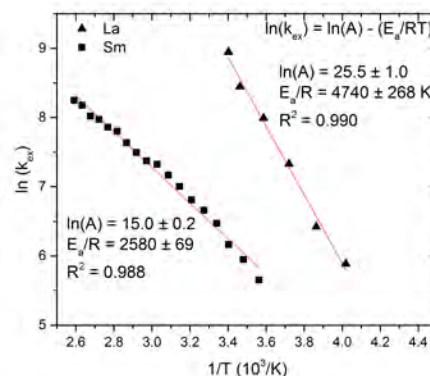


Figure 5. Arrhenius plot for HEH[EHP] exchange on La^{3+} or Sm^{3+}

The Arrhenius law was applied to data collected over the temperature range of -29°C to 15°C for La and 7.5°C to 112°C for Sm (Figure 5). From these data, the activation parameters were calculated for comparison to those determined for HDEHP complexes (Table 2). In the HDEHP system, Marie *et al.*¹ found the ligand exchange on Sm^{3+} was about 70 times slower ($k_{\text{ex}} \approx 1.8 \times 10^3 \text{ s}^{-1}$) than the HDEHP exchange on La^{3+} ($k_{\text{ex}} \approx 1.3 \times 10^5 \text{ s}^{-1}$). HEH[EHP] ligand exchange on Sm^{3+} ($k_{\text{ex}} \approx 5.8 \times 10^2 \text{ s}^{-1}$) or La^{3+} ($k_{\text{ex}} \approx 1.4 \times 10^4 \text{ s}^{-1}$) are about 25 times slower. A comparison of the ligand exchange from the La^{3+} metal center proceeds about 9 times slower with HEH[EHP] than HDEHP, and 3 times slower on Sm^{3+} with HEH[EHP] than HDEHP.

The activation parameters presented in Table 2 may offer insight into a mechanism of the ligand exchange reaction. Marie *et al.*¹ suggested that the reaction should occur *via* a dissociative interchange mechanism for the HDEHP on La^{3+} complex. As the cationic radius decreases from La^{3+} to Sm^{3+} , the mechanism changes to that of an associative mechanism. A similar trend can be seen with the HEH[EHP] exchange on La^{3+} and Sm^{3+} . The activation entropy characterizing the exchange of HEH[EHP] on La^{3+} do not suggest the dissociative interchange rather suggesting a more associative processes. The HEH[EHP] ligand exchange on Sm^{3+} (nearly identical with those for HDEHP) are also suggestive of a more strongly associative process.

Table 2 Activation parameters for extractant exchange in $\text{Ln}(\text{AHA})_3$ complexes ($\text{Ln}=\text{La}$ or Sm) at 25°C

Extractant	Ln^{3+}	$[\text{Ln}^{3+}]_{\text{org}}$ (mmol L^{-1})	k_{ex} (s^{-1})	E_a (kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$)
HEH[EHP]	La^{3+}	7.4 ± 0.2	$1.4 (\pm 1.8) \times 10^4$	39.4 ± 2.2^a	36.9 ± 2.2^a	-41 ± 13^a
HDEHP ¹	La^{3+}	8.7 ± 0.3	$1.3 (\pm 1.1) \times 10^5$	50.8 ± 1.6^a	48.3 ± 1.6^a	15 ± 6^a
HEH[EHP]	Sm^{3+}	9.1 ± 0.3	$5.8 (\pm 1.8) \times 10^2$	21.5 ± 0.2^a	19.0 ± 0.2^a	-128 ± 3^a
HDEHP ¹	Sm^{3+}	9.9 ± 0.1	$1.8 (\pm 0.7) \times 10^3$	19.5 ± 0.9^a	17.0 ± 0.9^a	-126 ± 3^a

^aQuoted error corresponds to standard deviation obtained from the linear regression fit of experimental data to Arrhenius equation

These results give some insight into the mechanism of exchange of the ligand on the metal, however, a more complete interpretation of those results will require further study. In general, slower exchange correlates with stronger bonding interaction with the O-donor atoms of HEH[EHP] and the Ln ion when compared to those formed with the HDEHP ligands. The shift in mechanism from one of dissociative-interchange character to one that most resembles an associative process is intriguing. Since Sm is a stronger Lewis acid, it exhibits a stronger interaction with O-donors than La. One possible explanation for this trend might be to suggest an intermediate state with an increased number of O-donors directly coordinated to the metal center. An interesting concept to consider is whether intact dimers or monomeric extractant molecules might be mechanistically important in these systems.

Conclusions

The $\text{La}^{3+}/\text{Sm}^{3+}$ results presented in this report demonstrate that the expected stronger electrostatic interaction correlates in general with the rate of observable ligand exchange dynamics ($k_{\text{LaHDEHP}} > k_{\text{LaHEH[EHP]}} > k_{\text{SmHDEHP}} > k_{\text{SmHEH[EHP]}}$). The activation parameters for this limited set of observations indicate a possible change in the mechanism of exchange changes from dissociative-interchange character to more of associative character when the Ln ion is changed from La^{3+} to Sm^{3+} . Research will continue toward developing a more complete picture of the organic phase in Advanced TALSPEAK processes. Varying the ratio of bulk to coordinated ligand will offer further information to any mechanistic changes in the system. A study on the exchange kinetics when the ligand is in a more polar diluent will be conducted to help elucidate the cause of the observed changing mechanism.

References

1. Marie C, Hiscox B and Nash KL, *Dalton Transactions*, **41**, 1054 (2012).
2. Braley JC, Grimes TS and Nash KL, *Ind. Eng. Chem. Res.*, **51**, 629 (2012).
3. Partridge JA and Jensen RC, *J. Inorg. Nucl. Chem.*, **31**, 2547 (1969).
4. Hu Z, Pan Y, Ma W and Fu X, *Solvent Extr. Ion Exch.*, **13**, 965 (1995).
5. Miralles N, Sastre A, Martinez M and Aguilar M, *Anal. Sci.*, **8**, 773 (1992).
6. Peppard DF, Mason GW, Driscoll WJ and Sironen RJ, *J. Inorg Nucl. Chem.* **7**, 276 (1958).
7. Golding RM, Halton MP, *Aus. J. Chem.*, **25**, 2577 (1972).
8. Bleaney B, *J. Magn. Res.*, **8**, 91 (1972).
9. Huray PG and Nave SE, *J. Less-Common Met.*, **93**, 293 (1983).
10. Rogers MT and Woodbrey JC, *J. Phys. Chem.*, **66**, 540 (1962).

Intensification of liquid-liquid mass transfer with gas agitation for the preparation of caprolactam

Jisong Zhang, Kai Wang, Xiyan Lin, Yangcheng Lu and Guangsheng Luo,
The State Key Laboratory of Chemical Engineering, Department of Chemical
Engineering, Tsinghua University, Beijing 100084, China*

The Beckmann rearrangement of cyclohexanone oxime in oleum for the production of caprolactam is a fast exothermic liquid-liquid reaction. The mass and heat transfer performances and the uniform flow conditions determine reaction rate and selectivity. To reach the ideal reaction conditions an adiabatic multiphase microchemical system consisting of a micro-sieve dispersion mixer, a delay loop and a microhydrolyzer is specially designed (Figure 1). Cyclohexanone oxime is dissolved in n-octane as the continuous phase and oleum as the dispersed phase. Microbubbles as gas agitation elements are introduced into the microsystem to enhance the mass and heat transfer and reaction as well. The effects of gas agitation on dispersion performance and mass transfer rate have been investigated. The acid droplets diameters range from about 44 μm to 20 μm , decreasing with the increase of the gas flow rate. The overall volume mass transfer coefficient in the microsystem ranges from 0.16 to 0.74 s^{-1} , 1.5~3.8 times larger than that without gas agitation. The reaction performance is evaluated under different conditions. Reaction rate is found to be increased only if the gas agitation is intense enough to prevent the coalescence of rearrangement mixture. However, the selectivity is greatly improved with gas agitation and less side reaction of carbonization occurs. The introduction of gas agitation is proven to be very useful for enhancing the mass and heat transfer rate and improving safety for reliable design of Beckmann rearrangement process.

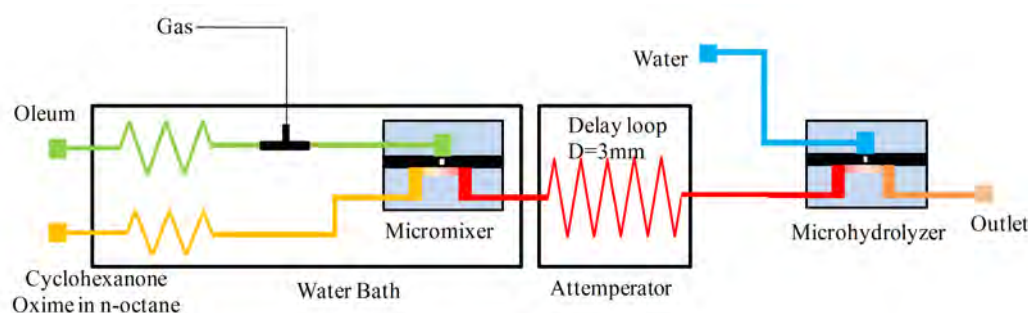


Figure 1. The schematic overview of the experimental setup.

Liquid membranes to improve resource efficiency in the surface treatment industry

Eugenio Bringas, Ane Urtiaga, Inmaculada Ortiz*

Dept. Chemical and Biomolecular Engineering, University of Cantabria, Spain

() Corresponding author Phone: +34 94220931 e-mail: bringase@unican.es*

An increase of the resource efficiency will bring major economic opportunities, improve productivity, drive down costs and boost competitiveness. In particular, surface treatment processes contribute to the consumption of water and raw materials especially metals and mineral acids, and to the generation of liquid and solid wastes which limit the eco- efficiency of this industrial sector. Surface treatment zinc-based processes (hot-dip galvanizing and electroplating processes) produce large volumes of hazardous wastes and spent baths containing important amounts of valuable materials such as zinc. The development of eco-efficient and selective separation processes is a demand of this sector to achieve the recovery of valuable materials from waste waters streams and have the longest possible service life of process baths avoiding the waste generation. In this work, the membrane-based solvent extraction (MBSX) technology is analyzed as a suitable alternative to improve the resource efficiency of two different problems in the framework of the surface treatment industry: i) the regeneration of Cr^{3+} passivation baths in nitrate acidic media by the selective removal of Zn^{2+} and Fe^{3+} and, ii) the management of spent pickling solutions (SPS) generated in hot-dip galvanizing process with high concentrations of Fe^{2+} and Zn^{2+} in HCl media.

Introduction

Membrane operations have the potential to replace conventional energy-intensive techniques, accomplish the selective and efficient transport of specific components, and, ultimately, provide reliable options for a sustainable growth [1]. In addition membrane processes can be beneficially integrated at different levels because of their several advantages over conventional processes: compactness, easy scale-up and automation. In particular, liquid membrane technology incorporating selective carriers is strongly related to the process intensification strategy due to the benefits derived from the facilitated transport of a solute resulting from the coupling between chemical reaction and mass transport phenomena [2]. The development of membrane-based solvent extraction (MBSX) processes based on the combination of liquid membranes and membrane contactors is a suitable strategy to increase the process competitiveness due to the following reasons: i) the high ratio between the interfacial mass transfer area and the equipment size, ii) the known and constant effective contact area, iii) the independent flow rates of the fluid phases, iv) the non-dispersive contact between the fluid phases avoiding additional separation stages, v) the modular design that simplifies the process scale-up and allows to operate over a wide range of capacities [3].

Two different MBSX process configurations are usually employed: Non-Dispersive Solvent Extraction (NDSX) and Emulsion Pertraction Technology (EPT). As depicted in Figure 1, in NDSX the extraction (EX) and back-extraction (BEX) of the targeted compounds are conducted in two different membrane modules. The contactors allow the non-dispersive contact between the feed and the organic solutions and between the organic and the stripping solutions. In EPT, the EX and BEX stages are performed in a single membrane module. Further, a pseudo-emulsion is prepared by dispersing the stripping solution into the organic solution in order to improve the interfacial area between both liquids. The contact between the feed and the emulsion is non-dispersive.

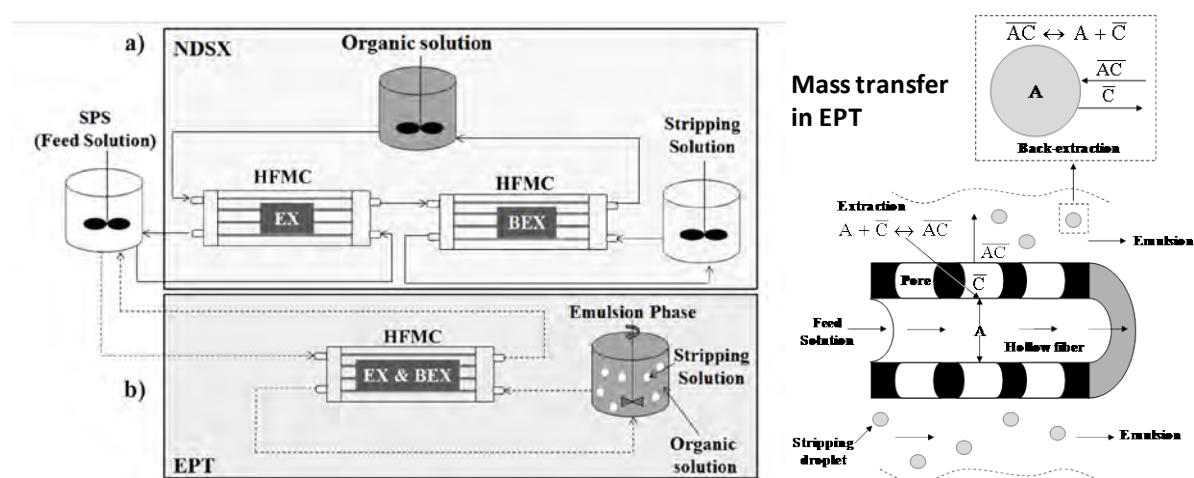


Figure 1. Configurations of MBSX processes: a) NDSX; b) EPT.

In order to move towards a European industry with a high level of resource efficiency, the Waste Management Hierarchy must be carefully considered. Resource efficiency by means of valorization practices is the key strategy to reduce the environmental impact of processes that utilize hazardous materials and produce hazardous effluents. The recovery of zinc from effluents and spent baths generated by zinc-based surface treatment processes decreases the need for virgin material, which market value is 1600 €/ton in 2013, and reduces the toxicity of those streams.

In this work, the performance of MBSX technology is analyzed through two different case studies defined in the context of the zinc-based surface treatment industry: i) the application of the EPT technology to perform the regeneration of Cr^{3+} passivation baths in nitrate acidic media by the selective removal of Zn^{2+} and Fe^{3+} impurities derived from the zinc electroplating process and, ii) the comparison of EPT and NDSX configurations to carry out the treatment of spent pickling solutions (SPS) generated in hot-dip galvanizing process with high concentrations of Fe^{2+} and Zn^{2+} in HCl media with the aim of obtaining a raffinate enriched in iron and chloride to be reprocessed as coagulant (FeCl_3) and a zinc concentrated solution with minimum contents of iron and chloride. In both case studies the search of a high selectivity is of

outstanding importance in order to attain the final goal of the electrolytic recovery of zinc.

2. Regeneration of chromium-based passivation baths with zinc recovery

Electroplating is one of the typical galvanic operations, used for the corrosion protection of metallic components. Chemical passivation usually follows the electroplating step with the aim of enhancing the corrosion protection. However, the new coatings based on trivalent chromium, are more sensible to the presence of zinc and iron impurities and thus, their lifetime is significantly reduced with respect to the previously employed baths formulated with hexavalent chromium, now banned due to their environmentally hazardous properties. The long-term accumulation of zinc and iron produces the loss of efficiency in the passivation process which finally causes the generation of spent passivation baths with the typical composition reported in Table 1 [4].

Table 1. Physical-chemical properties of spent chromium-based passivation baths.

Parameter	Value
pH	1.8-2.5
Zn ²⁺ (mg L ⁻¹)	2500-11780
Fe ³⁺ (mg L ⁻¹)	20-90
Cr ³⁺ (mg L ⁻¹)	4500-9350
NO ₃ ⁻ (mg L ⁻¹)	67520

Figure 2 depicts the separation and recovery objectives to be achieved by the application of EPT to the treatment of spent passivation baths: i) the in-situ regeneration of Cr³⁺-based passivation baths by the selective removal of iron and zinc up to the limits required for bath reuse and ii) the generation of a zinc concentrate with the lowest possible concentration of iron allowing the recovery of metallic zinc.

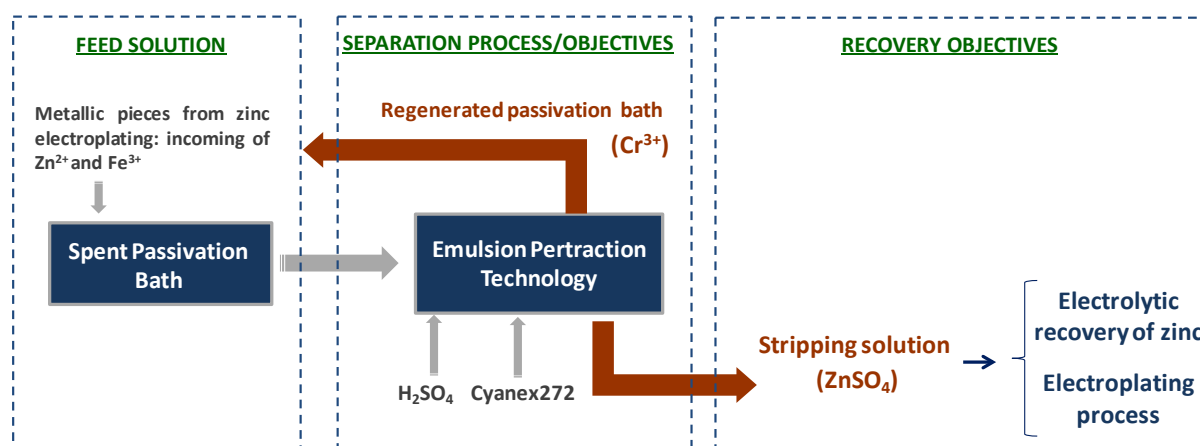


Figure 2. Regeneration of chromium based passivation baths by EPT with zinc recovery.

The commercial selective carrier bis(2,4,4- trimethylpentyl) phosphinic acid (Cyanex272) was selected as a suitable reagent to formulate the liquid membrane due to its capacity to selectively separate Fe³⁺ and Zn²⁺ (tramp ions) from chromium

under the typical pH conditions of the passivation baths. Sulphuric acid was selected as stripping agent [5].

The efficiency of the EPT process to carry out the regeneration of real passivation baths is demonstrated in Figure 3 which shows reductions in the zinc and iron contents higher than 80% after 3 hours of experimental running with an almost negligible variation of the chromium concentration. Furthermore, zinc is selectively recovered in the stripping solution (concentration >35 kg m⁻³) being the concentrations of iron (<0.45 kg m⁻³) and chromium (<0.003 kg m⁻³) almost negligible [5-8].

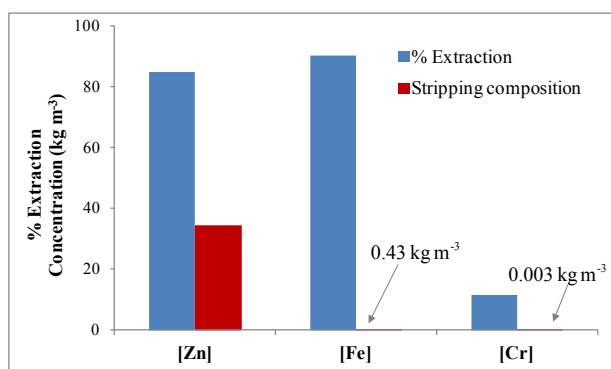


Figure 3. Extraction percentages and concentrations in the stripping solution after 3 hours of EPT regeneration of spent passivation baths using Cyanex272 as selective extractant ($C_{Zn, initial}=7 \text{ kg m}^{-3}$; $C_{Fe, initial}=0.04 \text{ kg m}^{-3}$; $C_{Cr, initial}=4.5 \text{ kg m}^{-3}$).

3. Management of spent pickling effluents with zinc recovery

Hot-dip galvanizing is the most extensively used surface treatment to protect steel pieces against corrosion. The treatment consists of the following steps: alkaline or acidic degreasing, rinsing with water, pickling with dilute hydrochloric or sulfuric acid, rinsing with water, fluxing in aqueous ZnCl₂/NH₄Cl baths, and finally dipping into molten zinc at temperatures of about 450 °C for a defined period [9]. The process generates a significant amount of spent pickling solutions (SPS), which are of environmental concern because of their hazardous composition that is reported in Table 2

Table 2. Physical-chemical properties of spent pickling solutions.

Parameter	Value
[H ⁺] (mol L ⁻¹)	1.1
[Zn ²⁺] (g L ⁻¹)	122
[Fe] (g L ⁻¹)	95.6
[Fe ²⁺] (g L ⁻¹)	92.6
[Fe ³⁺] (g L ⁻¹)	3
[Cl ⁻] (g L ⁻¹)	301

Figure 4 shows the objectives to be achieved by the application of MBSX in the treatment of SPS: i) to obtain a retentate enriched in iron to be reuse as coagulant

FeCl_3 and ii) to recover zinc in the stripping solution which can be further processed to obtain metallic zinc.

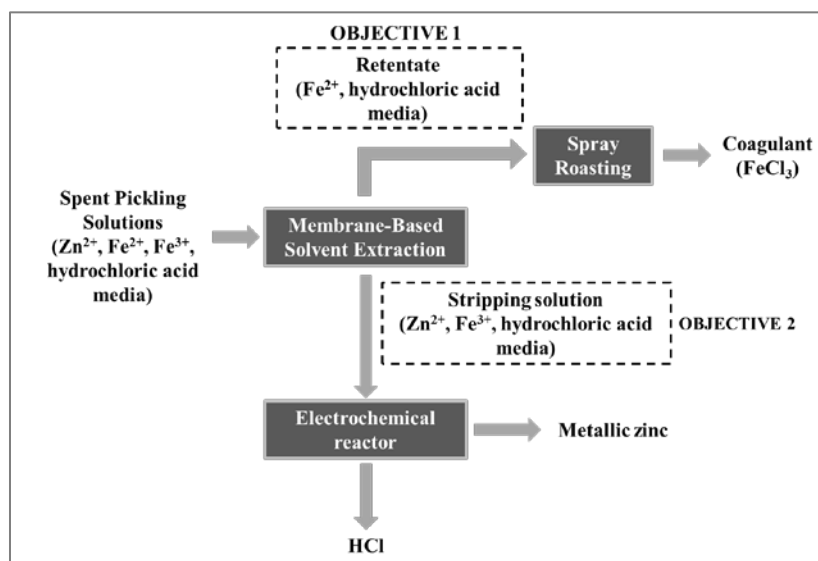


Figure 4. Regeneration of chromium based passivation baths by EPT with zinc recovery.

Under the usual composition of SPA zinc forms anionic chlorocomplexes (ZnCl_4^{2-} and ZnCl_3^-) while iron is present in the form of neutral or cationic compounds [9]. Tributyl phosphate (TBP) and water are reported as the most suitable extraction and back extraction reagents enabling the selective separation and concentration of zinc with minimum iron extraction [10].

As a proof of concept Figure 5 shows the kinetic results obtained when SPS are treated by EPT employing TBP and water. It is concluded that the EX percentages of zinc and iron, when chemical equilibrium conditions are reached, are respectively, 79% and 23%. Under these operation conditions, the maximum value of selectivity of zinc over iron in the stripping solution is 15 kg of Zn/kg of iron [8, 11-14].

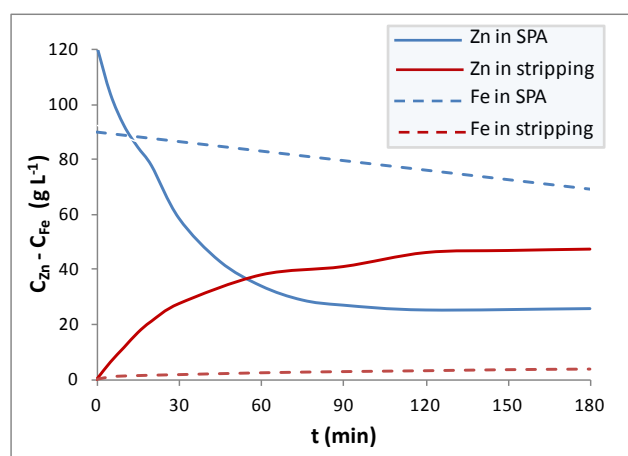


Figure 5. Evolution with time of iron (discontinuous line) and zinc (continuous line) concentration in the SPS and stripping solution (0.5 L of SPS with the composition indicated in Table 2; 1 L of Organic solution containing 50% v/v TBP in Shellsol D70; 1 L of tap water).

In addition the influence of the listed several variables on the process kinetics and on the selectivity of the process towards zinc over iron was analyzed: (i) the process configuration, NDSX versus EPT (ii) the concentration of TBP (iii), the volume ratio between the fluid phases organic and aqueous ($V_{\text{organic}}/V_{\text{aqueous}}$) and between the stripping and aqueous phase ($V_{\text{stripping}}/V_{\text{aqueous}}$).

4. Conclusions

According to the previous promising results, MBSX processes are prepared to be managed as common chemical engineering processes allowing their application to new scenarios where valuable compounds are possible to be recovered. However, their future development will require research and development activities in the following areas:

1. Determination of the optimal operational conditions to: i) maximize the extraction and back-extraction kinetics and ii) achieve maximum values of selectivity which permit the exploitation of the different process streams generated after the application of the EPT process.
2. Analysis of the long-term performance of the separation process to evaluate the stability of the selective carrier which guarantees the process economic viability.

Acknowledgments

Support from projects TIGI (GA 218390; 7th FP European Commission), CTQ2008-00690(MICINN; Spain), CTQ2012-31639 (MINECO; Spain-FEDER 2007-2013)) is gratefully acknowledged.

5. References

- [1] E. Drioli, E. Curcio, G. Di Profio, Trans. IChemE, Part A. Chem. Eng. Res. Des. 83 (A3) (2005) 223.
- [2] H.J. Bart, C. Drumm, M.M. Attarakih, Chem. Eng. Process. 47 (2008) 745.
- [3] Urtiaga, A.M., Ortiz, M.I., Salazar, E., Irabien, J.A., Ind. Eng. Chem. Res. 31 (1992) 1745.
- [4] Ortiz A., Fernández-Olmo I., Urtiaga A. and Ortiz I., Ind. Eng. Chem. Res. 48 (2009) 7448.
- [5] Urtiaga A., Bringas E., Mediavilla R., Ortiz I. J. Membr. Sci. 356 (2010) 88.
- [6] Bringas E., Mediavilla R., Urtiaga A., Ortiz I. Comp. Chem. Eng. 35 (2011) 918.
- [7] Diban N., Mediavilla R., Urtiaga A., Ortiz I. J Hazard Mater 192 (2011) 801.
- [8] Bringas E., San Román M.F., Urtiaga A.M., Ortiz I (2012). Chem. Eng. Process. 67 (2013) 120.
- [9] Regel M., Sastre A.M. and Szymanowski J. Environ. Sci. Technol. 35 (2001) 630.
- [10] Cierpezewski R., Miesiac I., Regel-Rosocka M., Sastre A.M., Szymanowski J. Ind. Eng. Chem. Res. 41 (2002) 598.
- [11] Ortiz I., Bringas E., San Román M.F., Urtiaga A.M. Sep. Sci. Technol. 39 (2004) 2441.
- [12] Samaniego H., San Román M.F., Ortiz I. Sep. Sci. Technol. 41 (2006) 757.
- [13] Samaniego H., San Román M.F., Ortiz I. Ind. Eng. Chem. Res. 46 (2007) 907.
- [14] Carrera J.A., Bringas E., San Román M.F. Ortiz I. J. Membr. Sci. 326 (2009) 672.

Ant colony optimization for sequencing of solvent extraction stages and optimization of their performance

*Fedor Vasilyev, Lappeenranta University of Technology, Lappeenranta, Finland;
Sami Virolainen, Lappeenranta University of Technology, Lappeenranta, Finland;
Tuomo Sainio, Lappeenranta University of Technology, Lappeenranta, Finland.*

Successful hydrometallurgical process synthesis requires identification of the most suitable combinations of purification methods to achieve the desired purification in the minimum number of steps and minimum costs. Considering design of a multistep process, identification, evaluation and comparison of promising process alternatives is a challenging task. The objective of this research was development of algorithm-based method for simultaneous sequencing of extraction-back extraction stages within and optimization of their operating conditions in a hydrometallurgical purification process.

Meta-heuristics can help to find approximate solutions of the process design problem in an efficient manner. Among meta-heuristic methods, ant colony optimization (ACO) algorithm was selected. The performance of alternative sequences of extraction-back extraction stages can be represented as a two-dimensional graph. An ACO based algorithm can be used for construction of purification process and its simultaneous optimization using this graph. Separation cost indicator (SCI) function, a tool for comparison of process alternatives on economic basis, can be used as an objective function for identification of the most promising process option.

The developed method was used for synthesis of hydrometallurgical processes for recovery of zinc from argon oxygen decarburization (AOD) dusts and for extraction of lanthanides from spent Ni-MH batteries. In the former case, new experimental data representing leaching, solvent extraction and stripping under different conditions were used. In the latter case, data for leaching, precipitation, solvent extraction and stripping were collected from literature sources. The process constructed for the recovery of zinc consists of leaching with sulfuric acid at final pH 3.4, solvent extraction with 20% D2EHPA extractant at pH 4.1, and stripping with sulfuric acid with volumetric phase ratio (O/A) of 1.6. The final purity of zinc sulfate was 99.97%. The process constructed for extraction of lanthanides consists of four steps: leaching with 1.3 M HCl, solvent extraction with 25% D2EHPA at pH 2.4 (O/A ratio 1:1), stripping with HCl at pH 2.4 (O/A ratio 3:1) and precipitation with oxalic acid at pH 1.1. The final purity of lanthanide oxalates was 99.44%.

It was shown that an ACO based algorithm using SCI function as the objective function is able to identify the most economic process alternative in an iterative manner. Its computation time increases slower than size of the process synthesis problem, what makes the method applicable for efficient solution of large problems. The developed method is well suited for early stages of experiment based development of hydrometallurgical purification process development.

Preventing the Introduction of Air from the Surface into Liquids in Baffled Mixing Vessels

*R. Sheinman^{*1}, Y. Kokotov¹, L. Braginsky¹*

Summary

The negative effects of surface air being incorporated into the emulsion of solvent extraction mixers are well known. A study of this phenomenon has shown that air ingestion from the surface in baffled mixing tanks occurs due to the formation of small scale turbulent vortices near the surface of the liquids. This happens when the local energy of turbulence is high enough to overcome the joint effect of surface tension and gravity. We describe a novel technical solution developed by Turbulent Technologies that virtually eliminates surface air entrainment even for intensive mixing. The device can be easily retrofitted to existing mixers, and is applicable for any liquid mixing application where air ingestion is undesirable. Experiments have shown that the device allows for much higher mixing energy inputs before air ingestion occurs.

Introduction

Many processes in the chemical industry cannot tolerate air ingestion by liquids in agitated vessels. Adverse effects of contact with air include reactant and product oxidation, contamination with by-products and change in the physical properties of liquids. For example, for many solvent extraction processes, air ingestion is generally associated with degradation of the expensive extractants and may lead to extensive crud formation (Ritcey, 1980).

Much effort is commonly applied to prevent air entrainment and to ward off the negative consequences of this phenomenon. Usually the impeller is placed in the lower part of the mixing tank to reduce disturbance at the surface and the mixing is tuned to be gentle. Both these actions sometimes cause partial phase separation inside the mixing tank, and even phase inversion. The low intensity mixing is often a compromise, requiring longer residence times and decreasing mass transfer rate. However, for numerous applications intensive mixing is highly desirable. Intensive mixing improves mass transfer between phases, prevents phase separation and dead zone formation and intensifies heat transfer. For example, Braginsky and Kokotov (1997) have shown that in the case of mixing of two immiscible liquids, intensive homogeneous turbulent mixing creates a narrower distribution of droplet sizes, which improves the subsequent separation of phases.

In this paper, we describe a novel system developed to suppress air bubble capture at the surface. The system allows aggressive stirring in almost the entire volume. It is shown that for any given mixing tank design, the impeller rotation speed where significant numbers of air bubbles begin to be captured (minimum aeration limit or MAL) is much higher using the new design. A mathematical model was developed to

^{1*} Corresponding Author, Turbulent Technologies Ltd., Jerusalem, Israel

¹ Turbulent Technologies Ltd., Jerusalem, Israel

estimate the increase of MAL as a function of the system design parameters and process characteristics. The model has been verified at laboratory scale in both batch and continuous flow systems.

An Approach to Minimize Air Ingestion

In unbaffled vessels the main mechanism of air entrapment via the liquid surface is by local turbulent vortices, and thus we expect that more intensive turbulence near the surface will correlate with more frequent capture of bubbles (Barabash et al., 1987). While theories of near-surface turbulence exist, we will simply state that it correlates with the turbulent dissipation in bulk, which will be used to describe the turbulence intensity.

Therefore, we wish to reduce the level of turbulence near the surface. In baffled vessels, the turbulence is transferred mostly by axial circulation. If we effectively divide the volume of the tank into two parts, the upper part with a lower level of turbulence, and a lower part with the desired level of mixing and higher turbulence, there will be no strong vortices near the surface, and the volume of air ingested into the liquid will be greatly reduced.

On the other hand, we wish to minimize the volume of the upper part of the tank where the turbulence is low, because we don't want to reduce the effective volume being mixed (or residence time for a continuous flow system). In addition, complete separation of the two volumes of the tank is undesirable for many other reasons – the upper part will tend to have a different temperature or concentrations of reactants, making side reactions significant, solids may build up etc. Hence, we desire that the baffle separating the two volumes shall only prevent intensive transfer of turbulence from in the lower to the upper part.

Our goal – reducing the turbulence in the upper zone – requires a custom design that depends on the specific properties of each mixing system: the physical properties of liquids being mixed, flow pattern, energy input and intensity of turbulence. Therefore, a robust mathematical model has been developed to make the processes of the design and scaling straightforward.

Mathematical Model of Turbulence Transfer

Assuming that the Kolmogorov model of homogeneous isotropic turbulence is applicable, we can write:

$$\varepsilon_1 = v_{p1}^3 / \lambda_1 \quad 1$$

where ε_1 is the local energy dissipation rate, W/kg. The method of calculation of energy dissipation rate is presented in Braginsky and Kokotov (1997); v_{p1} is the velocity of turbulent pulsations at the scale λ_1 ; λ_1 is the characteristic length. The characteristic length is proportional to the width of peripheral zone B when the coefficient equals to 0.4 (Braginsky et al., 1984). For baffled mixing tanks $B = 0.3R$,

therefore the value of the characteristic length is $\lambda_1 = 0.4 \cdot (0.3R) = \xi R$. The constant ξ can be adjusted using experimental data for this specific application, if necessary.

For the sake of simplicity we suppose that the level of turbulence in the upper zone is substantially lower than in the lower zone. Below we summarize the turbulent energy entering the upper zone. The total energy transfer through the hole in the separating baffle equals the total energy dissipation in the upper zone which is:

$$F_{T1} + F_{R1} + F_{C1} = V_2 \varepsilon_2 \quad 2$$

Where $F_{T1} = T_1 \cdot (Q + s \cdot v_{p1} / 2)$ is the turbulent energy transfer due to convection and turbulent pulsations; and $T_1 = \rho v_{p1}^2 / 2$ is the kinetic energy of pulsations; $F_{R1} = 0.5 \rho v_{\tau}^2 \cdot (Q + s \cdot v_{p1} / 2)$ is the energy of tangential motion transfer due to convection and turbulent pulsations; $F_{C1} = \rho v_c^2 / 2 \cdot Q$ is the kinetic energy of the flow via the hole; $v_c = Q / s$ is the linear velocity at the hole.

Therefore, the mean energy dissipation rate in the upper zone is

$$\varepsilon_2 = \frac{2}{\pi h_2 D^2} \left[\left(Q + \frac{1}{2} s \cdot v_{p1} \right) (v_{p1}^2 + v_{\tau}^2) + \frac{Q^3}{s^2} \right] \quad 3$$

Let's define $A = \pi D^2 / 4$ area of horizontal cross-section, $K = 1 + v_{\tau}^2 / v_{p1}^2$ and $w = Q / A$ superficial velocity. Rotational velocity v_{τ} and consequently K can be calculated according to the hydrodynamic model described by Braginsky et al. (1984). Applying Equation 1 we derive the ratio of dissipation energies in upper and lower zones:

$$\frac{\varepsilon_2}{\varepsilon_1} = \frac{\xi D}{4 h_2} \left[K \left(\frac{w}{v_{p1}} + \frac{1}{2} \frac{s}{A} \right) + \left(\frac{w}{v_{p1}} \right)^3 \left(\frac{A}{s} \right)^2 \right] = \frac{\xi D}{4 h_2} f_2 \left(\frac{s}{A}, K, \frac{w}{v_{p1}} \right), \quad f_2 = \frac{\varepsilon_2}{\varepsilon_1} \frac{4 h_2}{\xi D} \quad 4$$

In Figure 1 below we show the influence of the area of the hole in the separating baffle on the dissipation energy ratio. As we see, $\varepsilon_2 / \varepsilon_1$ depends significantly on the ratio s / A , and the parameters of this dependence are $K, w / v_{p1}$ and $\xi D / (4 h_2)$. As illustrated by the Figure 1, the curve has a minimum for continuous processes. This means that there exists an optimal size of the opening that minimizes turbulence near the surface for any given configuration of the process and the mixing system.

For batch processes the theoretical optimal solution is a fully closed cover ($s/A = 0$ at $w = 0$). In many cases this is impossible in practice.

In practice one will trade-off between process demands, equipment cost and minimization of the air intake.

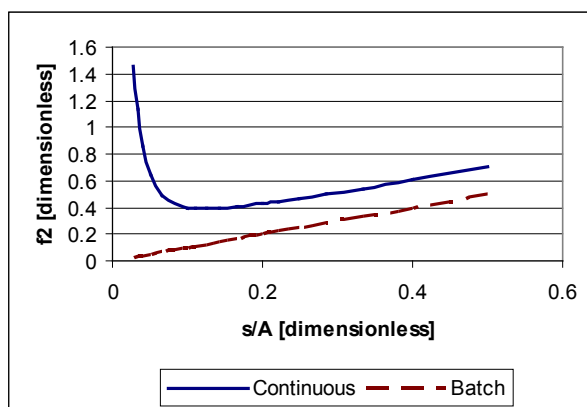


Figure 1: Illustration of dependence of the dissipation energy ratio on the hole area. For this calculation the following data were used: $w/v_{p1} = 0.1$ for continuous flow and $w/v_{p1} = 0$ for batch operation, $v_{\tau}/v_{p1} = 1$, $K = 2$.

Condition and corresponding value of minimum energy dissipation in the upper zone that can be achieved for the specific parameters of mixing and volume of the upper

zone are $\left. \frac{s}{A} \right|_{\varepsilon_2 \rightarrow \min} = \left(\frac{4}{K} \right)^{1/3} \frac{w}{v_{p1}}$; $\frac{\varepsilon_{2,\min}}{\varepsilon_1} = \frac{\xi D}{4 h_2} K^{2/3} \frac{w}{v_{p1}} [K^{1/3} + 2^{-1/3} + 2^{-4/3}]$.

Description of the Experiment

The experimental system is shown in Figure 2. The system has a glass mixing vessel (143 mm internal diameter and 200 mm height) Up to 6 cylindrical baffles (16.5 mm diameter and 140 mm height) can be installed in the mixing vessel.

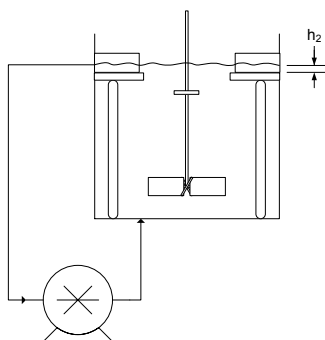


Figure 2: Scheme of experimental installation

Two impellers were used in the experiments: the first (A) was a 60° pitched blade turbine (diameter 63 mm, 70 mm width of blades, 20 mm length of the blades) and the second (B) was a 45° pitched blade turbine (diameter 69 mm, 13 mm width of blades, 20 mm length of the blades), see Figure 3. The impeller speed was controlled between 100 and 3,000 rpm. The liquid was fed continuously through the bottom, and collected near the surface by an outflow pipe (8 mm internal diameter). A positive displacement pump provided variable flow up to 1.3 L/min (residence time 1.5 minutes).



Figure 3: Impellers A and B

A removable “Less-Air” device was positioned above the baffles at 140 mm height above the floor of the tank, to separate the upper and the lower liquid volumes. The device is a cover with a 70 mm hole in the center (which makes s/A ratio equal to 0.24). Radial baffles were placed above the cover. A 40 mm diameter disk was fixed on the shaft.

In order to validate the mathematical model, a series of experiments were performed with different setups. The setup parameters were impeller type, quantity of baffles in the tank and the presence or absence of a surfactant (see Table 1). For each setup the height of the upper part (h_2) and the flow rate (Q) were varied. For each combination of parameters the impeller speed n at the minimum aeration limit was recorded for the systems with and without the Less-Air device in position.

	Setup 1	Setup 2	Setup 3	Setup 4	Setup 5
Impeller	A	A	A	B	B
Number of baffles	6	6	2	6	6
Surfactant added	Yes	No	No	No	Yes
Height of the upper zone, mm	9-40				
Flow rate, L/min	0-1.3	0-1.3	0	0-1.3	0-1.3

Table 1: Summary of different experimental conditions

All experiments were performed with purified water (HPLC grade). Surface tension was modified by adding Polysorbate 20 (Tween®-20).

Experimental Results

Our experiments have shown, that the Less-Air device is able to suppress air intake for impeller rotation at least twice the speed at which air is ingested without the device. The results of the experiments are shown Figure 4 below. The comparison of measured values of (n^*/n) and the values calculated using Equation 4 and are shown in Figure 4b. The power input to a stirred tank can be estimated (Harnby et al., 1997) as $P = K_p \rho n^3 d_{impeller}^5$, and thus $\varepsilon_*/\varepsilon = (n_*/n)^3$. It means that doubling the impeller

velocity ratio ($n_*/n = 2$) corresponds to an eight times increase in power input ($\varepsilon_*/\varepsilon = 8$), i.e. much more intensive mixing.

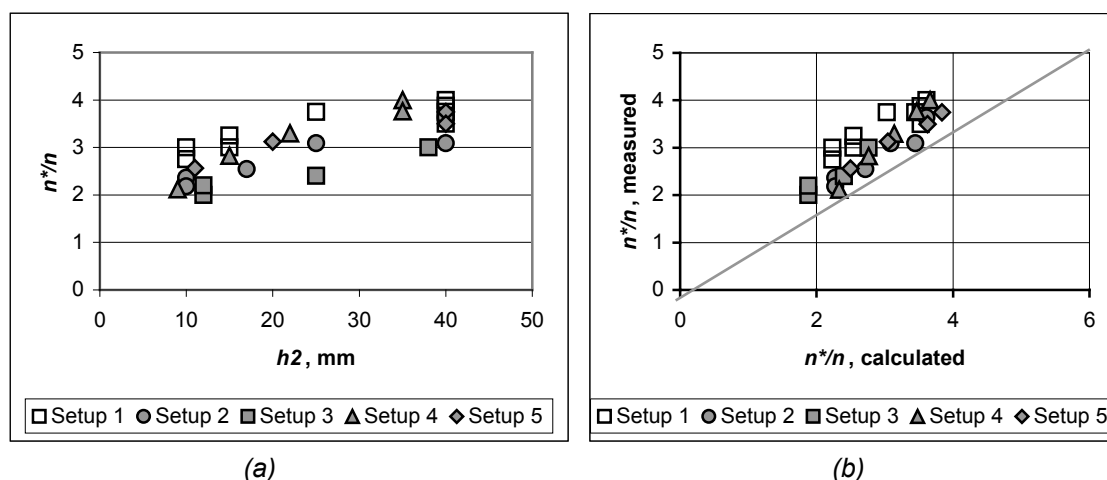


Figure 4: (a) – Experimental results; (b) – Measure n^*/n vs. calculated n^*/n values.

Conclusions

A novel system for the suppression of bubble capture from the surface of liquids in baffled mixing tanks, even under conditions of intensive mixing with high energy input has been developed enabling at least twice increase in the impeller rotation speed corresponding to the beginning of visible air bubbles capture (MAL).

The effect is achieved by a reduction of the level of turbulence near the surface. The volume of the tank is divided into two parts, the upper part with a lower level of turbulence, and a lower part with the desired level of mixing and higher turbulence.

The mathematical model developed to estimate the increase of MAL as a function of design parameters and process characteristics was verified in laboratory scale batch and continuous flow systems. We plan to continue to improve the model and to compare it to data from full scale implementation.

Literature

- Barabash V.M., Braginsky L. N. and Gorbacheva G. B. (1987) On analysis of gas holdup in agitated vessels. *Theor. Found. of Chem. Eng.*, 21(5) pp. 654-660
- Braginsky L. and Kokotov Y. (1997) Kinetics of Break-Up and Coalescence of Drops in Mixing Vessels. *International Symposium on Liquid-Liquid Two Phase Flow and Transport Phenomena*, Antalya, Turkey, 1997, pp.567-574
- Braginsky L.N., Begachev V. I., Barabash V. M. (1984) *Mixing of liquids. Theoretical basements and methods of technical calculation*. Himia Publishers, Leningrad
- Harnby N., Edwards M.F. and Nienow A.W. (1997) *Mixing in the Process Industries*. Butterworth-Heinemann, Oxford
- Ritcey, G. M. (1980) Crud in solvent extraction processing: review of causes and treatment. *Hydrometallurgy*, 5:97–107.

Study on preparation of KH_2PO_4 in microreactors by a reaction-extraction coupling process

F. Zhao, G.S. Luo, Y. C. Lu, K. Wang, The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, China

In this study, we developed a reaction-extraction coupling process for the preparation of KH_2PO_4 in microreactors, and achieved effective control of crystal size, shape and purity by controlling the liquid-liquid reaction and transport. The oil phase we used was the mixed extractant (a mixture of trioctylamine and n-octanol) with H_3PO_4 extracted from the wet-process phosphoric acid, and the aqueous phase we used was the solution of KCl. When the two phase contact with each other, liquid-liquid extraction and reaction take place, with HCl extracted into the oil phase and producing KH_2PO_4 in the aqueous phase, which is described as the reaction-extraction coupling process. We first studied the apparent kinetics of HCl extraction by the mixed extractant in the microreactors. Then we actualized the preparation of KH_2PO_4 in microreactors by the coupling process of reaction and extraction, and further, studied the apparent kinetics of this process and the variation of the selectivity of the extractant for HCl. Finally, we actualized the preparation of KH_2PO_4 crystals in microreactors by the coupling process of reaction, extraction and crystallization, and further, studied the effect of liquid-liquid reaction and transport on crystal size, shape and purity. This work paves the way for the modeling of the coupling crystallization process.

Impact of particle size distribution in packed bed for solid-liquid extraction for Montan wax

*Yan Wang^{*1}, Volker Herdegen¹, Jens-Uwe Repke¹*

In this work, Montan wax is extracted from granular brown coal with toluene as solvent. The particle size distribution of the raw material has a significant impact on the solid-liquid extraction process with packed bed extractor, but heretofore most of mathematical models of solid-liquid extraction without considering about it. To analyze the influence of the particle size distribution, CFD simulations are carried out with COMSOL 4.2a. A fundamental mathematical model of solid-liquid extraction is proposed based on systematic experimental investigations. The velocity field of solvent is computed and affects the time-dependent yield of extraction. The whole simulated extraction procedure is considered with different particle size distributions. Simulated results are validated by laboratory extraction experiment.

Introduction

Montan wax is a widely used intermediate product for cosmetics, paper, plastics and precision casting, etc. manufactory industry and is produced by means of solid-liquid extraction from brown coal. The kinetics and the influence of particle size distribution are investigated for solid-liquid extraction in this study. Solid-liquid extraction is a widely used separation technique nowadays for a selective gaining of components from solid phase or treatment of toxic components in solid material. A wide range of extractors in industry can be considered as packed beds, consisting of randomly packed particles. The packing itself affects the process in extractor/bed, thus some researches^{1,2} focus on the algorithm of generating random packing of granules. The flow behaviors with different shape of granule were investigated in CFD simulation of packed bed in different works. Investigation of specific arrangements of particles in random packed bed for heat transfer are contributed, such like 120-sphere with uniform particle size³, cylindrical particles in two different arrangements⁴, arrangement of circle packing with uniform particle size⁵, etc. However, there are a rare number of studies taken account of packed beds with different particle size distribution. In this study, an innovative approach to model and analyze the Montan wax extraction with packed bed is provided.

Implemental Method with 2-D simulation

In order to simulate the solid-liquid extraction process and investigate the impact of particle size distribution for extraction yield in this study, 2-D pseudo-homogeneous model with set packed bed porosity and particle size distribution is used. In the 2-D pseudo-homogeneous model the following assumptions were made: a) The 2-D slice is a simplified scenario for 3-D and the extracted yield has similar impact of particle size distributions in 2-D model and 3-D model. b) It has the same packed bed porosity as a real 3-D simulation. c) The particle numbers of different size are all

^{*1} Email: Yan.Wang@tu-freiberg.de, Institute of Thermal, Environmental and Natural Products Process Engineering, University of Technology Bergakademie Freiberg, Leipziger Street 28, 09596 Freiberg, Germany

charged in packed bed proportional comparing as a real 3-D simulation. d) Particles filled the packed bed randomly.

Geometric modeling

From the distribution of granule size, the proportional area of granule in class j in 2-D cross section area can be calculated, as following equation:

$$A_j = p_j(r) \cdot A \cdot (1 - \varepsilon) \quad (1)$$

There, A_j is the area of granule in class j in 2-D cross section, p_j is probability of sphere radii according to sieve analysis determined experimentally and represents the particle size distribution. During creation non-overlapping randomly packed bed of spheres, the ideal probability of random intersections for each granule is considered. Granules are spheres and their intersected circles are random dispersed within the cross section. In case of sphere particles, the probability of random intersections in corresponding size class can be computed by the well-known analytical expression

$$p_i(R_{i-1} < R < R_i) = \sqrt{1 - \left(\frac{R_{i-1}}{R_{max}}\right)^2} - \sqrt{1 - \left(\frac{R_i}{R_{max}}\right)^2} \quad (2)$$

The radii of circles of intersection are numbered in size class i , based on equal width $\Delta = \frac{R_{max}}{q}$, as given by

$$R_i = \Delta \cdot i \text{ and } R' = R/R_{max} \quad (3-4)$$

Here, R_{i-1} and R_i denote a lower and upper bound of a given size class respectively; p_i is probability of the radii of the corresponding circles of random intersection for spherical shape body; R_{max} is the maximum diameter of intersections in the specimen.

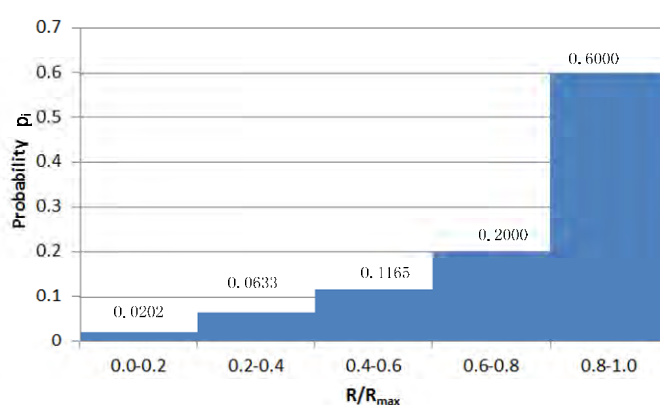


Figure 1. Probabilities of random intersection for spherical granule

The area of each size class j of spherical granules according to the circles in every size class i in cross section are given by

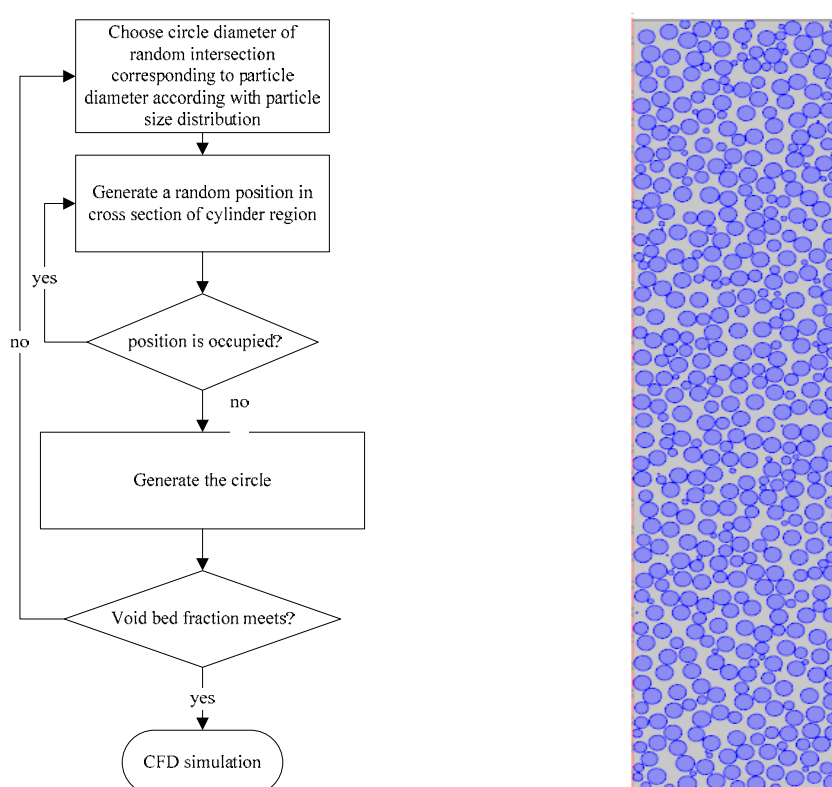
$$A_j = \sum_{i=1}^q N_A \cdot p_i \cdot \pi R_i^2 \quad (4)$$

Where N_A is the total number of circles of random intersection in entire range size classes $N_A = \sum_{i=1}^q n_i$; n_i is the number of circles of random intersection in size class i ; q is the number of size classes; r is the sphere radius; R is the radius of the corresponding circles of intersection; R' is dimensionless circle radius for intersection; the radii of spherical granules are numbered in class j . Using the probability of the radii of the circles of random intersection for sphere as shown in Figure 1, equation 5 is transformed to

$$N_A = (0.51424 * A_j) / R_{max}^2 \quad (5)$$

The circles number n_i in class i can be evaluated form N_A and p_i , as given by

$$n_i = N_A p_i \quad (6)$$



Left: Figure 2a. Flow chart of creating random packed bed; Right: Figure 2b. Example of a 2-D cross section of random packed bed (– an idealized model of the real 3D bed)

The circles of number n_i is drawn in every size class i one by one to meeting the bed void fraction ε . The programming of drawing random circles is illustrated in Figure 2a. Using the above-mentioned method, the random circles of cross section along with axial can be drawn out as Figure 2b, which illustrates non-overlapping circles randomly distributed in a cross section of packed bed with cylindrical shape. Using MATLAB software to establish the randomly circles in cross section along with the axis one by one. COMSOL loads the geometry and calculates the model numerically according to conversation of momentum and mass transfer. The most important parameters to define the geometry of random packed bed are size of packed bed, bed void fraction ε , particle size distribution p_j , probability of random intersection of corresponding sphere p_i .

Governing equations

In the work a solid-liquid extraction of Montan wax from brown coal in packed bed is investigated, using the governing equations from the conservation of momentum and mass. The simulation describes the flow and the mass transfer in packed bed with COMSOL with those equations.

Laminar flow

The force that drives the solvent flow is very low along with time and the rate of flow is relative low, therefore steady state flows by Navier-Stokes equations are considered in packed bed. The flow is assumed also incompressible and viscosity is constant.

$$\rho u \cdot \nabla u = -\nabla p + \mu \nabla \cdot \nabla u \text{ and } \nabla \cdot u = 0 \quad (7-9)$$

Transport of diluted species

Combining the velocity field calculated from the previously step, the mass transfer is considered with a convection, a diffusivity and a source item.

a. Mass balance in liquid phase

$$\frac{\partial C_f}{\partial t} + u \nabla C_f = S(r, z, t) + \nabla \cdot (D \nabla C_f) \quad (8)$$

$$S(r, z, t) = \frac{(1-\varepsilon)}{\varepsilon} \cdot k_f \cdot a \cdot (C^* - C_f) \quad (9)$$

Where S denotes the source item and source item equals to extracted solute from solid particles. Based on systematic experiments, a description for S is developed.

b. Mass balance in solid particles

$$\frac{\partial C_s}{\partial t} = D_e \left(\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right) \quad (10)$$

Initial conditions: $t=0$: $C_s = C_{s0}$; Boundary conditions: $r = R$, $D_e \left(\frac{\partial C_s}{\partial r} \right) = -k_f(C^* - C_f)$

c. Equilibrium relationship: Freundlich isotherm

$$C^* = \left(\frac{\bar{C}_s}{K} \right)^n \quad (11)$$

Inequality equation: $C^* > C_f$

The Freundlich isotherm is applied to describe the equilibrium condition. Effective diffusion coefficient in particles, film mass transfer coefficient and equilibrium parameter are identified as setting parameters from a laboratory extraction experiment by a stochastic optimization method.

Results and Discussion

In brown coal industry the Montan wax extraction based on the Graefe extraction is an established standard laboratory method^{6,7}. Briefly, the Grafe extraction represents solvent (toluene) cycles by means of evaporation and condensation to extract

Montan wax from brown coal. In the scope of our investigations, intensive extractions with different coals and grain size have been carried out. Experimental data (brown coal with mean particle size 1.3mm, moisture 18%, porosity 0.47) is used to validate the simulation of extracted Montan wax. The simulation is evaluated with COMSOL using the mathematical model (eq.10-13) with identified parameters k_f and n . The simulation fit the experimental data, as shown in Figure 3. It indicates that the CFD simulation has the relative correct result for solid-liquid extraction.

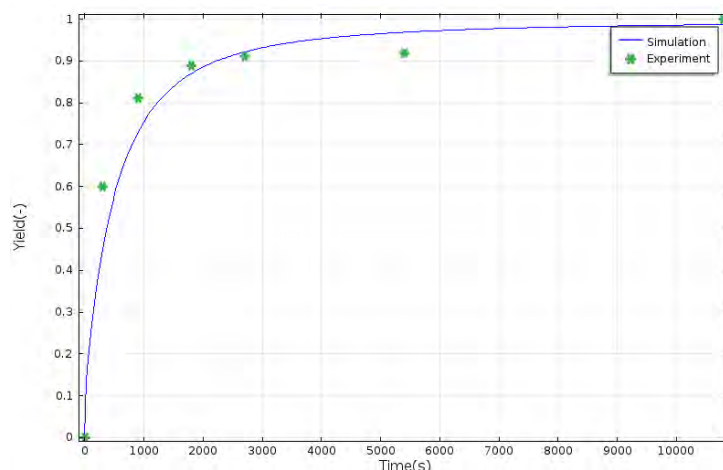


Figure 3. Comparison of experimental data^{6,7} and simulation by COMSOL of a packed bed

In order to compare the different particle size distribution, two types of distribution (normal distribution and uniform distribution) with same mean size are considered to generate random particle in packed bed, that establish pattern A (normal distribution $N(\mu, \sigma)$ with $\mu = 1.3, \sigma = 0.4$) and pattern B (uniform distribution from 0.3 to 2.3), respectively. It is assumed that the extraction process only with different particle size distribution but with the same other parameters and extraction conditions.

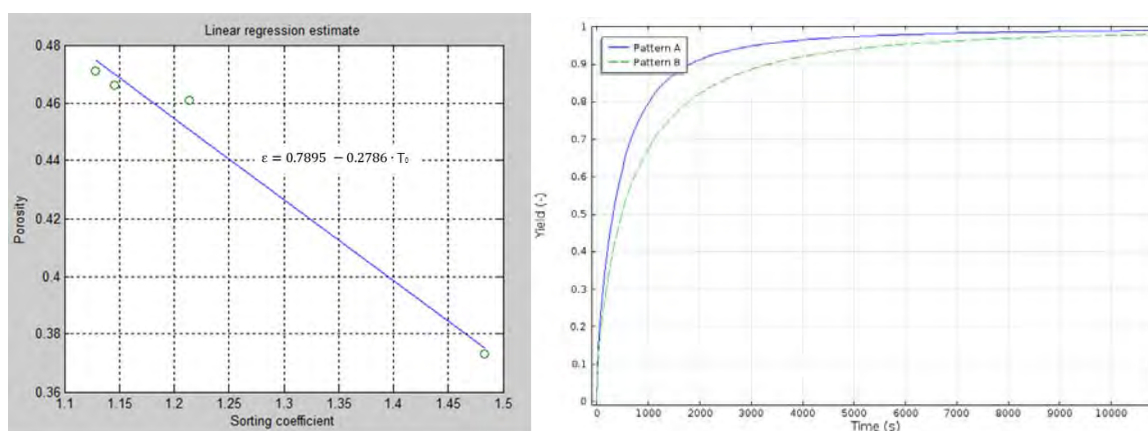
The porosity of packed bed corresponding to pattern A or B can be estimated from the particle size distribution theoretically. The porosity is independent of grains size but a function of sorting. The degree of sorting (grain size distribution) is expressed by the sorting coefficient (Trask Coefficient) T_0 , which is expressed as

$$T_0 = \left(\frac{d_{25}}{d_{75}} \right)^{1/2} \quad (12)$$

there, d_{25} = mesh size (grain diameter) at 25% of sample weight; d_{75} = mesh size (grain diameter) at 75% of sample weight. The measured porosities with different particle size distributions of brown coal are used to find out the correlation with sorting coefficient. The regression of porosity (ε) with sorting coefficient (T_0) gives the following linear correlation for the brown coal granules as shown in Figure 4a.

So according to regression equation, the porosity is 0.5087 for pattern A and 0.3774 for pattern B respectively. Using the porosity in simulation, the yield of Montan wax from simulations of pattern A and pattern B are illustrated in Figure 4b. Analyze the yields curve could give conclusion that distribution pattern A of particle size extracted rate is faster than distribution B. When extractions yield equal to 80%, pattern B used

nearly twice time of pattern A. Therefore in the pretreatment of the brown coal grain size should be one important adjustable parameter for an efficient and fast extraction process.



Left: Figure 4a. Regression equation from experiment data for packed bed porosity; right: Figure 4b. Comparison of time-dependent yield form Pattern A and Pattern B

Conclusions

CFD simulations were carried out to investigate the mass transfer in solid-liquid extraction of Montan wax. Using the developed model with different particle size distributions in packed bed, the simulations have been compared and discussed with own experiments. In condition of same mean particle size, the normal distribution has high extraction rate than the uniform distribution. The normal distribution accelerates the extraction and can describe the experimental data better. In further research, the difference of Montan wax simulated yield between 2-D and 3-D model will be considered. Furthermore, a scale-up extraction of the Graefe experiment with the developed model will be carried out.

References

- 1 Al-Raoush, R. and. A. M., Simulation of random packing of polydisperse particles. *Powder Technol.* **2007**,176, (1), 47.
- 2 Jodrey, W. S.; Tory, E. M., Simulation of random packing of spheres. *Simulation* **1979**,32, (1), 1.
- 3 Dai, X. G. R., Numerical simulation of flow and heat transfer in a random packed bed. *Particuology.* **2010**, (3), 293.
- 4 Motlagh, A. H. A.; Hashemabadi, S. H., 3D CFD simulation and experimental validation of particle-to-fluid heat transfer in a randomly packed bed of cylindrical particles. *Int. Commun. Heat Mass* **2008**,35, (9), 1183.
- 5 Guardo, A.; Coussirat, M.; Larrayoz, M. A.; Recasens, F.; Egusquiza, E., CFD flow and heat transfer in nonregular packings for fixed bed equipment design. *Ind. Eng. Chem. Res.* **2004**,43, (22), 7049.
- 6 Wollmerstädt, M.; Lohmeier, R.; Herdegen, V.; Schröder, H.-W.; Repke, J.-U. Influence of drying on the extraction of different processed lignites. *Eur. J. Lipid Sci. Technol.* **2014**, 116, 177–184
- 7 Repke, J.-U.; Naundorf, T.: Herausforderungen und Lösungswege bei der stofflichen Nutzung von Braunkohlen. Jahrestreffen der Fachgemeinschaft Fluidtechnik und Trenntechnik, 25.-27.9.2013, Würzburg, *Chem. Ing. Tech.* (85) **2013**, 1395

Extractive desulfurization of hexadecane using ionic liquid as a solvent

Babak Mokhtarani, Hossein Mansurzareh, Hamid Reza Mortaheb, Ali Sharifi*

Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran.

Summary

The suitability of 1-butyl 3-methylimidazolium nitrate ([Bmim][NO₃]) and 1-methyl 3-octylimidazolium nitrate ([Omim][NO₃]) as solvents for extraction of thiophene from hexadecane was investigated. Liquid – liquid equilibria (LLE) data for the ternary systems of hexadecane + thiophene + [Bmim][NO₃] or [Omim][NO₃] were determined at 298.15 K and atmospheric pressure. In order to determine the suitability of studied IL, the parameters of selectivity (*S*) and distribution ratio (*β*) were calculated. The experimental results show higher selectivity values for the ternary system of hexadecane + thiophene + [Bmim][NO₃] than those of the mixtures with [Omim][NO₃] but lower corresponded distribution coefficients. The experimental data indicated that the selectivity values are decreased by increase in the size of IL's cationic alkyl chain. This implies that the ILs with shorter alkyl chain are more suitable for desulfurization where the required amount of solvent, which can be recycled, is increased. The LLE data were correlated using the thermodynamic model of NRTL, in which the nonrandomness factor (*α*) was set to 0.3. The results show that the NRTL model can correlate the experimental data with a good accuracy.

1. Introduction

Emission of sulfur oxide, which is mainly originated from oil and gas refineries is a major environmental problem [1]. The hydro desulfurization units have been widely used in oil refineries to reduce the sulfur content of fuels. However, some constituents such as thiophenes cannot be removed efficiently by those units [2]. Extractive desulfurization is an alternative efficient process. The process is clean, cheap and facile. The appropriate solvent for extractive desulfurization must remove sulfur compounds selectively without affecting the octane number of fuel [2]. Several organic solvents have been used for this process while none of them can provide a perfect performance [2]. Ionic liquids (ILs) are promising replacements for those organic solvents. ILs are organic salts that are liquid below 100°C [3] having some advantages such as low vapor pressure, acceptable solubility, non-flammability, and high stability [4]. In recent years, attempts have been made to separate sulfur compounds by direct extraction using ILs [5-11].

* Corresponding author *E-mail:* mokhtarani@ccerci.ac.ir Tel.: +98 21 44580751; fax: +98 21 44580781.

In this study, extraction of thiophene from hexadecane are studied using 1-butyl 3-methylimidazolium nitrate [Bmim][NO₃] and 1-methyl 3-octylimidazolium nitrate [Omim][NO₃]. The nitrate-based ILs are halogen-free and more environmentally friendly than other types of ILs [12].

The liquid-liquid equilibrium (LLE) data for the ternary systems of [Bmim][NO₃] + hexadecane + thiophene and [Omim][NO₃] + hexadecane + thiophene are measured. The effects of cation's chain length on the extraction of thiophene from hexadecane are also investigated. Finally, the LLE data are correlated using NRTL model.

2. Materials and methods

Thiophene and hexadecane were purchased from Merck Company. Their purities were more than 99%. [Bmim][NO₃] and [Omim][NO₃] were synthesized in our laboratory. These ILs were prepared according to the procedure in literature [13]. The synthesized ILs were checked with nuclear magnetic resonance (NMR) spectroscopy. The mass fractions of the water in the synthesized ILs were less than 1×10^{-3} .

The mixture of IL + hexadecane + thiophene was prepared in glass vials. Each component was weighted by a laboratory balance with the precision of $\pm 10^{-4}$ g. The mixture in the glass vial was closed firmly with a cap and septum, and stirred by a shaker (IKA HS-260). The temperature of the mixtures was controlled using a water bath with a precision of ± 0.1 K (Julabo, FP50). After 24 h, the two phases in the glass vial were separated and analyzed. The composition of each phase was determined using gas chromatography (Varian, cp 3800) with a FID detector and capillary column (Chrompack, 30 m $\times$ 0.25 mm $\times$ 1.2 μ m). The analysis procedure was according to the previous works [12].

3. Results

Experimental data for ternary systems of [Bmim][NO₃] (1) + hexadecane (2) + thiophene (3) and [Omim][NO₃] (1) + hexadecane (2) + thiophene (3) at 298.15 K and atmospheric pressure are reported in Table 1. the parameters of selectivity (S) and distribution ratio (β) were calculated from experimental data as follow:

$$\beta = \frac{x_3^{II}}{x_3^I} \quad (1)$$

$$S = \frac{x_3^{II} x_2^I}{x_3^I x_2^{II}} \quad (2)$$

where x is the mole fraction, the superscripts II and I refer to the alkane- and IL-rich phase, and the subscripts 2 and 3 refer to hexadecane and thiophene, respectively.

Table 1. Experimental LLE for ternary systems of IL (1) + hexadecane (2) + thiophene (3) at 298.15 K and calculated distribution coefficient (β) and selectivity (S) values.

Feed			hexadecane rich phase		IL rich phase		β	S
x_1	x_2	x_3	x_2^I	x_3^I	x_2^{II}	x_3^{II}		
[Omim][NO ₃] (1) + hexadecane (2) + thiophene (3)								
0.441	0.472	0.087	0.924	0.076	0.019	0.098	1.29	61.81
0.417	0.415	0.168	0.851	0.149	0.022	0.185	1.24	48.53
0.397	0.363	0.241	0.786	0.214	0.024	0.262	1.22	40.36
0.378	0.317	0.305	0.725	0.275	0.023	0.327	1.19	37.51
0.359	0.275	0.366	0.666	0.334	0.021	0.387	1.16	36.84
0.345	0.238	0.417	0.615	0.385	0.020	0.436	1.13	35.72
0.332	0.202	0.465	0.561	0.439	0.018	0.478	1.09	33.34
0.319	0.170	0.511	0.516	0.484	0.017	0.523	1.08	32.10
0.306	0.140	0.554	0.473	0.527	0.017	0.563	1.07	29.60
0.294	0.117	0.589	0.415	0.585	0.015	0.591	1.01	27.43
[Bmim][NO ₃] (1) + hexadecane (2) + thiophene (3)								
0.503	0.418	0.079	0.924	0.076	0.012	0.082	1.07	83.21
0.478	0.371	0.151	0.851	0.149	0.015	0.152	1.02	56.59
0.452	0.324	0.224	0.777	0.223	0.016	0.225	1.01	48.01
0.439	0.287	0.273	0.725	0.275	0.016	0.272	0.99	44.07
0.422	0.251	0.327	0.666	0.334	0.015	0.324	0.97	43.90
0.403	0.217	0.380	0.611	0.389	0.014	0.375	0.96	42.87
0.388	0.185	0.427	0.556	0.444	0.013	0.419	0.94	40.02
0.375	0.157	0.469	0.499	0.501	0.012	0.455	0.91	39.37
0.361	0.130	0.510	0.449	0.551	0.010	0.494	0.90	38.78
0.347	0.108	0.546	0.379	0.621	0.008	0.518	0.83	37.86

From Table 1, increasing the thiophene concentration reduce the selectivity and distribution coefficient values. Moreover, the experimental data indicated that the

selectivity values are decreased by increase in the size of IL's cationic alkyl chain. This implies that the ILs with shorter alkyl chain is more suitable for desulfurization where the required amount of solvent, which can be recycled, is increased.

The LLE data were correlated using the NRTL thermodynamic model, in which the nonrandomness factor (α) was set to 0.3.

The energy parameters are calculated by minimization of differences between the experimental and calculated mole fractions of each component.

The minimization was performed with Solver in Excel software. the calculated energy parameters are given in Table 2 and the root mean square deviation is defined as follows:

$$rmsd = \left[\frac{\sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{X_{ijk}^{exp} - X_{ijk}^{cal}}{X_{ijk}^{exp}} \right)^2}{2mn} \right]^{1/2} \times 100, \quad (3)$$

where m is the number of the tie lines and n is the number of the components in the mixtures.

Table 2. The correlated binary interaction parameters (Δg) for NRTL model and the root mean square deviation (rmsd) for experimental ternary systems of IL + hexadecane + thiophene

Component i-j	NRTL parameter		rmsd
	Δg_{ij}	Δg_{ji}	
	/kJ. mol ⁻¹	/kJ. mol ⁻¹	
[Omim][NO ₃] (1) + hexadecane (2) + thiophene(3)			
1-2	15.251	-1.950	0.291
1-3	3.119	14.654	
2-3	4.252	16.757	
[Bmim][NO ₃] (1) + hexadecane (2) + thiophene(3)			
1-2	17.149	-2.538	0.345
1-3	2.433	15.273	
2-3	3.162	17.995	

As Table 2 is shown, rmsd values reasonable and there is a good agreement exist between the experimental and correlated results.

4. Conclusion

New Experimental data for extraction of thiophene from hexadecane were reported using [Bmim][NO₃] and [Omim][NO₃] as solvent at atmospheric pressure and 298.15 K. The selectivity and the solute distribution coefficient values were calculated from the experimental data. The length of IL's cationic chain has a great effect on the selectivity values. The selectivity values reduce with increase in the length of IL's cationic chain while the thiophene distribution coefficients increase. This implies that [Bmim][NO₃] is a more suitable solvent than [Omim][NO₃] for desulfurization of the studied systems although it requires a higher amount of the solvent. The experimental data were correlated using NRTL models. The results show that the NRTL model can correlate the experimental data with a good accuracy.

References

- [1] Wilfred, C. D.; Kiat, C. F.; Man, Z.; Bustam, M. A.; Mutalib, M. I. M.; Phak, C. Z., Extraction of dibenzothiophene from dodecane using ionic liquids. *Fuel Process. Technol.* **2012**, 93, 85.
- [2] Rodríguez-Cabo, B.; Soto, A.; Arce, A., Desulfurization of fuel-oils with [C2mim][NTf₂]: a comparative study. *J. Chem. Thermodyn.* **2013**, 57, 248.
- [3] Anantharaj, R.; Banerjee, T., COSMO-RS based predictions for the desulphurization of diesel oil using ionic liquids: Effect of cation and anion combination. *Fuel Process. Technol.* **2011**, 92, 39.
- [4] Seddon, K. R., Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, 68, 351.
- [5] Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Phase Behaviour of 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide with Thiophene and Aliphatic Hydrocarbons: The Influence of n-alkane Chain Length. *Fluid Phase Equilib.* **2008**, 263, 176.
- [6] Jiang, X.; Nie, Y.; Li, C.; Wang, Z. Imidazolium-Based Alkylphosphate Ionic Liquids—a Potential Solvent for Extractive Desulfurization of Fuel. *Fuel* **2008**, 87, 79.

- [7] Francisco, M.; Arce, A.; Soto, A. Ionic Liquids on Desulfurization of Fuel Oils. *Fluid Phase Equilib.* **2010**, *294*, 39.
- [8] Rodríguez-Cabo, B.; Francisco, M.; Soto, A.; Arce, A. Hexyl Dimethylpyridinium Ionic Liquids for Desulfurization of Fuels. Effect of the Position of the Alkyl Side Chains. *Fluid Phase Equilib.* **2012**, *314*, 107.
- [9] Li, F.-t.; Kou, C.-g.; Sun, Z.-m.; Hao, Y.-j.; Liu, R.-h.; Zhao, D.-s. Deep Extractive and Oxidative Desulfurization of Dibenzothiophene with $C_5H_9NO \cdot SnCl_2$ Coordinated Ionic Liquid. *J. Hazard. Mater.* **2012**, *205*, 164.
- [10] Domańska, U.; Lukoshko, E. V.; Królikowski, M. Separation of Thiophene from Heptane with Ionic Liquids. *J. Chem. Thermodyn.* **2013**, *61*, 126.
- [11] Królikowski, M.; Walczak, K.; Domańska, U. Solvent Extraction of Aromatic Sulfur Compounds from n-Heptane Using the 1-Ethyl-3-Methylimidazolium Tricyanomethanide Ionic Liquid. *J. Chem. Thermodyn.* **2013**, *65*, 168.
- [12] Mokhtarani, B.; Mansourzareh, H; Mortaheb, H. R., Phase behavior of nitrate based ionic liquids with thiophene and alkanes. *Indus. & Eng. Chem. Res.* **2014**, *53*, 1256.
- [13] Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular States of Water in Room Temperature Ionic Liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.