

SOLVENT EXTRACTION IN THE PROCESS INDUSTRIES

VOLUME 1

PROCEEDINGS OF ISEC '93

Edited by
D.H. Logsdail and M.J. Slater



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**SOLVENT EXTRACTION
IN THE PROCESS INDUSTRIES**

Volume 1

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Edited by

D.H. LOGSDAIL

SPS, AEA Technology, Harwell, UK

and

M.J. SLATER

Department of Chemical Engineering, University of Bradford, UK

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FOREWORD

Solvent extraction is now a most powerful separation and purification tool in the process industries. It is used commercially in hydrometallurgy (including the nuclear industry) and widely within the chemical industry including organic chemicals, petrochemicals and pharmaceuticals. That the technique has risen to prominence in only a few decades is undoubtedly due to the vast amount of research and development carried out not only into reagents, their extraction chemistry and performance in a wide variety of systems, applications and process development but also in the development of appropriate equipment for the process without which process development would be impossible. The scientific literature is rich in papers from fundamental solvent extraction studies on basic physical chemistry, coordination chemistry, extraction chemistry, chemical kinetics to process development through to the chemical engineering fundamentals and design required to understand the process of solvent extraction and to permit design and engineering of processes and equipment. Solvent extraction must be one of the most well documented unit processes ever. Solvent extraction is also a truly outstandingly successful commercial process which says much for all the research and development effort that has gone into this one unit process over the years.

As a hydrometallurgist, my own involvement in solvent extraction has of course been with metals and it has been my privilege to see the subject grow from a relatively unknown process restricted to the nuclear field, some less common metals and the analytical laboratory into the hugely successful and one of the most important unit processes in hydrometallurgy for the separation, purification and concentration of metal ions and inorganic salts. It is to this area that I therefore address myself here.

It is nowadays almost easier to say which metals solvent extraction is not used for than to list all the metals it is used for in commercial operations somewhere in the world. It has transformed the copper industry with respect to low-grade oxidic ores, revolutionised the processing of the platinum group metals, provided relatively easy access to high purity individual rare earths and is used in the hydrometallurgical processing of nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, zirconium, hafnium, niobium, tantalum, boron, the purification of wet process phosphoric acid and of course in the reprocessing of nuclear fuels. Throughout the development of the commercial application of solvent extraction in hydrometallurgy there ran in parallel intensive work on the

underlying chemistry, physics and chemical engineering aspects of the process, thus ensuring that the processes involved were well understood and therefore that there were no really nasty surprises in store when particular processes were commercialised. This I believe has generally worked very well. In fact one might assume that, with all the effort expended on solvent extraction research, there was little left to do. Indeed I understand that a similar remark was made at the International Solvent Extraction Conference held in Israel in 1968. Nothing could be further from the truth! The investigation in recent years of phenomena such as reversed micelles, microemulsions and lyotropic liquid crystals will keep us busy for a long time yet, to say nothing of the continuing search for a truly direct method of studying the interfacial reactions involved in many solvent extraction systems and direct identification and characterisation of the interfacial species.

Liquid membranes also continue to command significant attention but have not found any real commercial application within hydrometallurgy for either mainstream or pollution control applications. This process, in its supported membrane mode, still offers a solution to solvent-in-pulp processing. It is possible that commercialisation of liquid membranes will take place in the pharmaceutical industry before hydrometallurgy. For hydrometallurgy there remain considerable barriers to commercial exploitation and, while exhortations to identify these have borne some fruit, similar exhortations to remove them remain largely unfulfilled.

With regard to equipment for solvent extraction in hydrometallurgy the workhorse remains the mixer settler but with refinements and improvements that now provide performances that were not dreamed of twenty or thirty years ago. Columns remain far less popular in hydrometallurgy than, say, in the petrochemicals industry. Are there still more developments to come and/or new ways of contacting immiscible phases and achieving rapid mass transfer? The ISEC conferences in the future will no doubt reveal all.

What then of the ISEC conferences? The ISEC-type series of conferences started within the nuclear industry at Gatlinburg in 1962 but the first ISEC proper was held in The Hague in 1971. This was organised by the Society of Chemical Industry just as ISEC '93 is. The ISECs have been a unique series dedicated to providing fora for the presentation of new research, reports of applications, process and equipment development, topical reviews, plenary and keynote papers in various sectors of research, applications and future prospects across the whole spectrum of activities wherein solvent extraction science and technology is practised. The ISECs quickly became the premier international solvent extraction conference and the event which all solvent extraction chemists, technologists and engineers in academe and in industry wished to attend not only for the formal sessions but also for the informal discussions with old friends and colleagues and the making of new acquaintances and enjoying the social functions which have always been a feature. The ISECs are truly international with ISECs subsequent to The Hague conference being held in Lyon, France (also organised by the SCI); Toronto, Canada; Liège, Belgium; Denver, USA; Munich,

Germany; Moscow, Russia; and Kyoto, Japan. Now ISEC comes to the UK for the first time. In planning ISEC '93 the Organising Committee selected as the conference theme "Solvent Extraction in the Process Industries" noting that, while solvent extraction continues to develop improved processing, yields, separations and reduced costs, it was timely to seek to answer the questions: "How does this technology measure up in today's environmentally aware world? Where should new developments be? What should the goals be now for workers in both solvent extraction and liquid membranes?" We hope that these conference volumes with the plenary paper, all oral papers and most of the poster papers will provide partial if not complete answers to these questions. We certainly believe that there is something for everyone in these Proceedings and that they add to the reputation of the ISECs down the years.

I would like to record my very sincere appreciation to all the members of the Organising Committee for their very hard work, without which this Conference would not have been possible. To mount such an international event takes a very large amount of work. The backing, help and office support of the SCI, in particular the Conference Office, and all staff have been invaluable in this respect. I also thank most sincerely the corresponding members of the SCI Solvent Extraction and Ion Exchange Group and the members of the International Committee for Solvent Extraction for their help, contributions and advice which has been so welcome throughout the preparations that began back in Kyoto at the time of ISEC '90.

The Organising Committee wish to express their sincere appreciation to all authors for their contributions to the Conference and to these volumes and to all attendees. Without you there would be no conference.

Welcome to York and have a wonderful and memorable conference.

Professor D S Flett
Chairman, Organising Committee

PREFACE

Reading maketh a full man; conference a ready man; and writing an exact man.

Francis Bacon

The Editors wish to express their appreciation of the efforts made by authors to produce manuscripts in the style requested and within the restricted number of pages allowed. We were aware that not every author was in a position to comply with these requirements; however, it seems probable that in the foreseeable future a uniform style should be able to be achieved, making it easier to produce Proceedings of high quality for future conferences.

It was not possible in the time available to make editorial changes to manuscripts modified by authors according to reviewers' comments, so perfection eluded us! We acknowledge that most authors were writing in a foreign language and we greatly applaud their skills. We are indebted to the many reviewers who have ably assisted in ensuring a high standard of papers, one of the aims of the Organising Committee.

The Index has been constructed on the basis of authors' keywords and although therefore not totally consistent it should prove helpful in locating information.

A number of papers were presented as posters at ISEC '93 which were not printed in the Proceedings due to late submission.

We also wish to record our thanks to Mrs L M Heald, SCI Managing Editor, and Mrs H A Freeman, SCI Publications Office.

D H Logsdail
M J Slater

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RECOMMENDED NOMENCLATURE

SI UNITS

a	specific interfacial area
a_p	specific area of a drop
A	column cross-sectional area
A_p	amplitude of pulse or oscillation (stroke= $2A_p$ for reciprocating plates)
b	exponent
c	concentrations
C	coefficients ($C_1, C_2, \dots$)
C_o	orifice discharge coefficient
C_d	drag coefficient
d	drop size
d_p	packing size
d_h	horizontal diameter
d_v	vertical diameter
D	distribution ratio or diameter
D_N	nozzle diameter
D_o	orifice diameter in plate
D	diffusion coefficient
e	voidage or free area
E	axial mixing coefficient
E	degree of extraction (fraction extracted)
f	frequency
f_n	natural frequency
f_v	volume fraction
F	flow rate (volumetric)
F_s	shaft force
g	gravitational coefficient
h	height
H	compartment, stage or dispersion height
I	intensity of agitation
J	flux

i	class number
I	intensity of reciprocation
k	rate coefficient (m/s) or constants
k_B	Boltzmann constant
K	equilibrium constant
K_{oc}	overall rate coefficient
L	length
l_s	shaft displacement
L	total column length or fluid thickness
m	equilibrium line slope, (solvent/aqueous or continuous/dispersed) or exponent
M	molecular weight
n	number of drops or exponent
n_p	number of plates or stages
N	agitator speed or number of transfer units or total number of stages
p	drop breakage probability
P_s	power per disc or turbine or stage
ΔP	pressure drop
r	distance in radial direction
r_o	radius
R	flow ratio, dispersed/continuous
R	internal enhancement factor for mass transfer
s	Laplace variable
t	time
T	temperature
U	Velocity other than superficial phase velocity (in drops, circulation, turbulent etc.)
U_s	shaft displacement velocity
v	volume
V	superficial phase velocity
V_T	terminal velocity
V_o	characteristic velocity
V_k	" "
V_{slip}	slip velocity
w	mass or width

x	dimensionless aqueous concentration or distance in x direction
X	dimensionless distance x
y	dimensionless solvent concentration, or distance in y direction
Y	dimensionless distance y
z	fraction length
z	valency

GREEK

α	backflow ratio
δ	film or plate thickness
γ	interfacial tension
σ	surface tension or second moment
τ	a specific time
θ	reduced time or angle from drop front
ϕ	fraction or hold-up of dispersed phase
ρ	density
$\Delta\rho$	density difference
ε	specific energy or power (W/m^3)
ε_m	power per unit mass (W/kg)
μ	viscosity or first moment
λ	extraction factor $mF_{\text{solv}}/F_{\text{aq}}$ or coefficient
ψ	function
κ	viscosity ratio (dispersed/continuous)
η	efficiency
Γ	surface concentration of contaminant
v	number of daughter drops

GROUPS

Ar	Archimedes	$\Delta\rho \rho_c d^3 g / \mu_c^2$
Bi	Biot	$d k m / D$
Bo	Bond	$g d^2 \Delta\rho / \gamma$
Eö	Eötvös	$g d^2 \Delta\rho / \gamma$

Fr	Froude	$U^2 / g d$ or $N^2 D r / g$
Mo	Morton	$g \mu_c^4 \rho / \rho_c^2 \gamma^3$
Pe	Peclet	$Pe_d (d V / E)$ or $Pe_L (L V / E)$ or $d U / D$
Re	Reynolds(drop)	$\rho_c d V_T / \mu_c$
Sc	Schmidt	$\mu / \rho D$
Sh	Sherwood	$k d / D$
We	Weber	$\rho_c d U^2 / \gamma$ or $\rho_c N^2 D_R^3 / \gamma$

SUBSCRIPTS

a	aqueous
c	continuous phase
cr	critical
d	dispersed phase
e	effective value
f	flooding or formation
i	interface or <i>i</i> th value
j	jet
m	mean value
max	maximum
o	original (initial) value
p	plate
s	solvent
∞	bulk value or at infinite distance
C	column
I	inlet
M	molecular
N	nozzle
R	rotor
S	stator
T	tank (for mixer) or terminal

SUPERSCRIPT

*	equilibrium value
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PLENARY LECTURE

Pl.1

SOLVENT EXTRACTION IN THE PROCESS INDUSTRIES: QUO VADIS?

C. JUDSON KING

Department of Chemical Engineering and Lawrence Berkeley Laboratory
University of California
Berkeley CA 94720 U.S.A.

ABSTRACT

The past and present are analyzed to serve as a partial basis for prediction of the future of solvent extraction in those industries that involve organic solutes. Successful applications of solvent extraction have for the most part been cases where entire chemical classes of compounds are to be separated, differences in acidity or basicity are exploited, distillation is unworkable or disadvantaged, and/or relatively benign processing conditions are required. Some of the most important trends affecting opportunities for solvent extraction are environmental awareness; needs for recovery, recycle and reuse; new and specific pharmaceuticals; and the advent of production of both biologically active agents and commodity chemicals by biotechnology. Promising avenues for research, development and innovation are identified. These include a number of ways of making extraction less contaminating and/or less harmful to sensitive products, highly selective yet regenerable reagents, effective solvents or sorbents for sugars, starches, and other highly polar substances, economical methods of regeneration with large "swing" factors, and efficient, high-throughput contactors minimizing settling problems.

INTRODUCTION

The purpose of this talk is to pursue the goal that was urged by the organizers of ISEC'93: What is the future of solvent extraction in the process industries? This is a formidable and dangerous task. It is also one that requires definition and, of necessity, limitation. I have chosen to confine my remarks and conjectures to the industries where the product is organic, notably fuels, petrochemical, organic-chemical, pharmaceutical, food and biotechnology, along with environmental needs that relate to those industries. By doing so, I leave out such interesting areas as hydrometallurgy, processing related to nuclear energy, inorganic chemicals, and waste needs deriving from those industries. Others are far more knowledgeable than I am of those applications.

I shall also define solvent extraction rather broadly, so as to touch upon areas such as reactive sorbents and membranes, micellar and emulsion liquid membrane systems, and solvent leaching of solids. One cannot consider the future of solvent extraction in isolation from these related areas.

I will start by considering in a generic fashion the useful features, and then the drawbacks, of solvent extraction. Next I would like to analyze some of the factors that have led to past and current successes of extraction. Then I will seek to identify some of the trends and growing needs that have meaning for the future of solvent extraction. Finally, I will speculate on promising avenues for future research and development pertaining to solvent extraction and allied methods of separation.

What are the Useful Attributes of Solvent Extraction?

Chemical Specificity. The separation factor for a solvent extraction process is derived through interactions in each of two liquid phases. This means that solvation and chemical specificity contribute to, and indeed often dominate, the separation. Changing the solvent or extractant from one chemical class to another can very substantially change equilibrium distribution ratios and can change the order of extractability of different solutes. Solvent extraction affords a means of selectively removing a solute from other solutes of different chemical classes, as well as a way of separating multiple solutes of one chemical class from those of another class. A number of the most successful applications of extraction utilize this feature. However, it should also be noted that the degree of specificity attainable with extraction is, in general, not as great as can be obtained with separations involving solid phases, such as crystallization or adsorption with tailor-made adsorbents.

Lack of Dependence upon Volatility. Solute volatility is not a factor in extraction, unless it enters into regeneration considerations. Solvent extraction can therefore separate solutes which are not subject to distillation, because of either lack of volatility or closeness in volatility to other components of the mixture.

Countercurrency. Liquid-liquid extraction involves two fluid phases. Hence countercurrent contactors are readily used, in contrast with separations involving solids which operate best

with fixed or fluidized beds. True countercurrent contacting increases the degree of separation obtained with a given phase ratio.

Low Energy Consumption. Under the right conditions, solvent extraction can be a separation process with a relatively low energy consumption. The amount of energy consumed in the primary extraction step is usually small. In most cases the bulk of the energy consumption occurs in the solvent regeneration step; consequently, a low-energy method of regeneration leads to a low energy consumption overall.

A common method of regeneration is distillation, which suggests that the energy consumption for extraction regenerated by distillation might be comparable to that for separation by distillation alone. However, even when regeneration is by distillation, separation by solvent extraction can have a lower energy consumption than does separation by distillation if the equilibrium distribution ratio for the extraction is large, in which case the solvent flow and the flows in the distillative regeneration step will be low. Solvent extraction can also gain an energy advantage if the relative volatility for the regeneration is substantially higher than for the primary separation.

Suitability for Dilute Solutions. Finally, solvent extraction can gain an edge for separation of a solute from a dilute solution, especially if the solute of interest is less volatile than the main component(s) of the feed mixture and/or extraction provides a high equilibrium distribution ratio. Whereas distillation or evaporation would require expending energy to vaporize the entire major component(s), extraction removes the minor, desired component and as a result all downstream processing steps have lower flows and hence lower costs for both equipment and energy.

What Are the Drawbacks of Extraction?

Similar Phase Densities. The two liquid phases in a liquid-liquid extraction process have comparable densities, in contrast with vapor-liquid separation processes. Solvent selection is constrained by the need to afford a sufficient difference in densities to enable settling and/or countercurrent flow; however the use of suitable diluents can overcome this limitation. In some cases the order of densities of the phases can actually invert as solute is transported from the feed stream to the extract, making extraction unworkable.

The similarity of phase densities promotes and compounds problems of slow settling and/or emulsification. This leads to extraction equipment being complex, so as to meet the simultaneous needs of phase dispersion to provide interfacial area and mass transfer rate, on the one hand, and settling and/or countercurrent flow, on the other hand. The similarity of phase densities also results in liquid throughputs per unit volume in an extraction contactor being substantially less than in a vapor-liquid contactor.

Need for Regeneration. Since extraction uses a mass separating agent (the solvent), it is necessary to regenerate the extract in order to isolate the extracted product and to recover the solvent for reuse. Depending upon the solute and the solvent, regeneration can be difficult and costly.

Partial Miscibility. Each liquid phase will dissolve in the other to some extent, causing contamination and solvent consumption, and thereby engendering needs for further separations for recovery of dissolved solvent from the raffinate and/or for separation of coextracted feed material (e. g., water) from the recovered product.

Environmental Issues. Solvent extraction can pose environmental problems in two ways. First, if the solvent is volatile it can contribute to releases of VOC's (Volatile Organic Compounds) to the atmosphere. Secondly, when solvent extraction is used to treat an aqueous effluent stream, there is likely to be a residual concentration of dissolved or emulsified solvent in the water, thereby creating a need for another separation process, e. g., carbon adsorption, to remove the solvent before the water can be released.

The balance among advantages and disadvantages of solvent extraction has so far worked out so that it is one of several methods of separation, including adsorption and crystallization, that are used in a number of applications for recovery and separations of organics, but which are not used anywhere near as much as distillation.

Successful Applications of Extraction

Table 1 lists a number of successful industrial applications. From the key to this list, it is apparent that the applications of solvent extraction for extraction of organics so far are largely

TABLE 1**SOME SUCCESSFUL APPLICATIONS OF SOLVENT EXTRACTION OF ORGANICS**

(Lo, et al., 1983; Thornton, 1992)

Petroleum Products and Petrochemicals:

- Separation of aromatics from aliphatics and naphthenes (1)*
- Lube oil refining (1)
- Acetic acid production (2,3)
- Recovery of caprolactam from Beckmann rearrangement mixture (2,3)

Caustic Washing :

- Removal of mercaptans and phenols from petroleum fractions (1,2)
- Recovery of coal tar acids (1,2)

Processing of Effluent Waters:

- Recovery of phenols and cresols (1,3)
- Recovery of acetic acid (1,2,3)

Pharmaceuticals and Fermentation Products:

- Penicillin (2,3,4)
- Macrolide antibiotics, e. g., erythromycin (2,3,4)
- Polyenes, e. g., nystatin, amphotericin (2,3,4)
- Anthracyclines (2,3,4)
- Citric acid (2,3)

Food Products:

- Decaffeination of coffee -- green, roast and ground, and coffee extract (1,3,4)
- Extraction and leaching of oils and flavors from natural products (4)
- Extraction of free fatty acids from triglyceride oils (1,2,3)
- Refining of orange and lemon oils by removal of terpenes (1,3,4)

-
- * - Key:
- 1 -- Separation of entire chemical classes of compounds.
 - 2 -- Separation on the basis of differences in acidity or basicity.
 - 3 -- Distillation is unworkable or disadvantaged.
 - 4 -- Relatively benign processing conditions are required.

cases where broad chemical classes of compounds are to be separated, differences in acidity or basicity are exploited, distillation is unworkable or disadvantaged, and/or relatively benign processing conditions (e. g., no heating) are required.

Trends and Growing Needs

The following are some of the trends affecting the uses and potential for industrial solvent extraction of organics:

1. Environmental awareness is heightening worldwide. Solvent extraction with conventional solvents has inherent problems of water and air pollution. Residual dissolved solvent in a discarded aqueous raffinate is a pollutant unless it is removed before release of the water. In the United States, stringent recent regulations control releases of volatile organic compounds (VOC's) to the atmosphere. Conventional volatile or moderately volatile solvents are VOC's.

2. In connection with environmental awareness, there is growing interest in recovery, recycle and reuse of waste substances. Solvent extraction works well with dilute feeds and is a recovery process. There are two circumstances where extraction should be attractive for recovery of organics from wastewater streams. In the first instance, the value of the recovered product exceeds the cost of carrying out the recovery step, including removal of dissolved solvent from the raffinate if needed. In the second, the removed and recovered substances are ones that would place a major, and perhaps excessive, burden on a conventional biotreatment system. Examples would be sugars and starches from corn wet milling, wineries, canneries, etc.

Cost trade-offs between recovery and degradation by biotreatment do not seem to be made often. Such considerations are hampered by the fact that costs of recovery processes are borne by plants, while costs of biotreatment are often borne by municipalities.

3. There is growing interest in drugs that act very specifically and topically, so as to avoid undesirable side-effects. This calls for new pharmaceuticals which are carefully tailored substances. In many cases there will be made by biotechnology. Very specific and selective recovery processes will be needed. Solvent extraction promises the specificity, but can be hampered by toxicity effects.

4. As the price of petroleum inevitably increases, there will be increased interest in producing commodity chemicals from renewable resources, e. g., by fermentation of various forms of biomass, such as corn starch. These fermentations produce dilute and complex solutions and reactive products, such as carboxylic acids, for which solvent extraction is well suited, again with attention to control of possible toxicity problems.

Opportunities for Innovation

Making Extraction Less Contaminating and Less Harmful to Sensitive Products. This is perhaps the greatest and most varied opportunity for improvements. Several quite different avenues are worthy of pursuit:

Benign solvents. Solvents are needed which do not contaminate reaction (e. g., fermentation) media or the environment, are not toxic to organisms, and/or which do not degrade sensitive solutes.

Much attention has been given recently to supercritical fluid extraction, although the number of cases where it is clearly superior to other methods of separation is still small. Among supercritical fluids, carbon dioxide has received the greatest attention. It now appears that the attraction of CO₂ may be not so much in the opportunity to work with the unusual solvent properties of the supercritical state, but more because it is an extremely benign, non-polluting solvent. It is not necessary to use carbon dioxide in the form of a supercritical fluid. Liquid CO₂ can readily be used for extraction, as has been reported, for example, by Schultz, et al. (1974) for various food materials. Liquid CO₂ can be used at much lower pressures than are required for the supercritical state.

Other benign solvents worthy of greater attention are liquid fluorocarbons, silicones and volatile hydrocarbons, such as *n*-butane and isobutane (Earhart, et al., 1977), which become liquid at ambient temperatures under moderate pressure. Solvents with the volatility of butane have the advantage that they are readily removed from water by stripping. For all but the most volatile extracted solutes it is necessary to take such solvents overhead during regeneration by distillation, with the concomitant energy costs; however, this has been done for years in various hexane extractions in the food industry. Also, latent heats of vaporization of the lighter hydrocarbons are relatively low.

Still another area with promise that has received some recent attention is uptake of solutes into micelles, which can then be retained by an ultrafiltration membrane (Dunn, et al., 1985; Hurter & Hatton, 1992). Such a process should have very low energy

consumption, but raises the issue of separation of the recovered solute(s) from the micelle-forming agent(s).

Aqueous systems with properties similar to, or improving upon, organic solvents and extractants. Aqueous extractants avoid the VOC problem. They can also fulfill needs for keeping the conformational properties of sensitive proteins and enzymes intact during processing. Several different approaches have been considered or proposed:

Two-aqueous phase extraction. Extractions involving two aqueous phases (e.g., aqueous polyethylene glycol solution and an aqueous solution of a salt, such as potassium phosphate) have been the subject of considerable recent study (Verrall, 1992). The advantages of such systems is that they can avoid denaturation of proteins and/or loss of activity of enzymes, which occur with most organic solvents. In addition to research leading to a fuller understanding of partitioning and immiscibility in such systems, there seems to be potential for the identification or synthesis of polymers that are more effective, more specific and/or less expensive in such systems.

Reverse micelles. Reverse micelles contain an aqueous interior and are suspended in an organic solvent, the reverse of ordinary micelles. The aqueous interior environment is benign toward proteins. This field has received substantial research over the past decade (see, e. g., Hatton, 1992a) and is now relatively well understood. Some unresolved issues pertain to the need for full separation and recovery of the surfactant used to form the reverse micelles, and the fact that an organic solvent is still involved.

Aqueous polymer solutions equivalent to organic solvents. Here the aim is to avoid the problem of contamination due to organic solvent loss during extraction of wastewaters. Approaches that have been suggested include the use of amphiphilic star block copolymers (Hatton, 1992b). To prevent mixing of the phases during extraction, they can be physically separated by an appropriate, thin, high-surface-area membrane, e. g., in a hollow-fiber form.

Means of overcoming problems of contamination from residual solvent. Perhaps the most straightforward approach to the problem of contamination of effluent waters is to remove dissolved or entrained solvent by means of an appropriate process.

Stripping is effective for sufficiently volatile solutes and has been used for this purpose, e. g., in the Phenosolvan process (Jauernik, 1960; Wurm, 1968). Another obvious method is adsorption onto activated carbon or a relatively inert, regenerable polymeric sorbent, such as macroreticular, styrene-divinylbenzene copolymer adsorbents. For waters that have been contacted with more soluble solvents, the residual solvent can be removed by extraction into a non-polar, readily regenerable solvent, such as a hydrocarbon (Earhart, et al., 1977). Another approach is to preclude dissolution of solvent into the aqueous phase by means of a membrane with appropriate wetting/non-wetting properties. Yet another approach is to alter the form of the extractant or solvent so that it cannot dissolve or be entrained. For example, one can turn to solid polymeric sorbents containing the same functional groups as an extractant or solvent of interest. Simple and economical means of solving the problem of contamination by residual solvent are appropriate goals for research.

Highly Selective, Yet Regenerable Extractive Reagents. In the biotechnology industry, there is often a need to "pluck" the desired product from reaction mixtures that are highly dilute and complex. This is true both for very high-value, low-volume products, where the challenge is often to find any feasible method of separation, and for lower-value, high-volume products (e. g., carboxylic acids and glycols) made by fermentation. Similar needs should abound in the pharmaceutical industry, as more specific and targeted drugs are sought. An extreme case is the need for separations of chiral mixtures to obtain a particular enantiomer, although in most cases chiral separations will probably be avoided by building chiral selectivity in the reaction process itself. In a sense, there is a general, growing need to enable for organic substances the sorts of very selective separations afforded for inorganic substances by agents such as crown ethers, which actually have the ability to fractionate uranium isotopes (Lerat, et al., 1984).

Such extreme selectivity is often obtained through steric effects, which may be implemented as well or better through reactive sorbents as through liquid extractants. One approach toward selective extractants is to use ion-pair extraction, where the cation (or anion) is chosen for its ability to complex selectively with the substance of interest, and the anion (or cation) is given a large organic weighting so as to hold it in the solvent phase. Another approach worthy of further investigation is ligand exchange, which has the capability of reversing the selectivity

between carboxylic and mineral acids, in comparison with more conventional amine extractants and sorbents (Zhu, et al., 1992).

Identification or Development of Effective Extractants or Sorbents for Removing Sugars, Starches, and Other Highly Polar Substances from Aqueous Solution. This is a major challenge, because these compounds have very high affinity for water. But there are numerous large-volume applications that await such an extractant. As one example, ethylene and propylene glycol are made in dilute aqueous solution from ethylene and propylene oxides, and the current, energy-intensive method of recovery is evaporation of the water. As a second example, there are many large wastewater streams containing sugars and starches, from corn wet milling, beet and cane sugar refining, canneries, wineries, distilleries, etc. An effective extractant or reactive sorbent could remove and recover these materials, and thereby greatly alleviate loads on waste-treatment systems.

Economical Methods of Regeneration with Large "Swing" Factors. Most of the energy consumption and much of the expense of extraction processes come from the regeneration step. When the solute is more volatile than the solvent and sufficiently so, it usually makes sense to recover the solute and regenerate the solvent by distillation or stripping. For non-volatile solutes, the appropriate path is less obvious. A volatile solvent can be removed from a solute of lesser volatility by distillation, evaporation or evaporative crystallization, but this consumes energy and does not separate the desired solute product from any other low-volatility components that may have been present.

One common approach to regeneration is to "swing" a thermodynamic variable which will cause the equilibrium distribution ratio to change sufficiently to favor back extraction, even though forward extraction had been sufficiently favored under the original conditions. The usual swing variables are pH, temperature, and less often the composition (i. e., the nature of a diluent) in the solvent phase. A swing of temperature is used to accomplish regeneration in a successful extraction process for citric acid (Baniel, et al, 1981). However, the amount of change in the equilibrium distribution ratio obtainable by changing temperature is limited.

The amount of change in equilibrium distribution ratio that can be obtained by temperature swing is directly related to the enthalpy change upon extraction, through the Clapeyron equation. Larger swings can therefore be gotten for larger enthalpy changes, and it may be

useful therefore to examine extractants giving large enthalpy changes without as large free energy changes.

A typical example of regeneration by a swing in pH would be extraction of a carboxylic acid solute from aqueous solution into an organic solvent, followed by back-extraction into aqueous NaOH. However, this produces the sodium carboxylate. To return the carboxylate to the carboxylic acid form, one would have to add a strong acid, e. g., sulfuric acid. The process thereby consumes an acid (H_2SO_4) and a base (NaOH) and produces a waste salt (Na_2SO_4). Although such processes have been used in the past, they are becoming less attractive because of the cost of chemicals and the need for disposal of the waste. One avenue toward overcoming these problems in a pH-swing process is to alter pH through addition of CO_2 , NH_3 or a volatile amine (Poole, et al., 1991). The resultant salt can then be decomposed thermally, giving the product solute and solvent ready for recycle.

Efficient, High-throughput Contactors Without Settling Problems. This need stems from the inherently similar densities of liquid phases, emulsification tendencies and occasional needs to minimize residence times for labile products. Phase dispersion is sought to provide large contact areas and efficient mass transfer. However, too much or the wrong kind of dispersion can cause emulsification and settling problems, as well as axial dispersion which lessens concentration driving forces for extraction. Perhaps the most successful extractors in the fields of interest here have been the Rotating Disk Contactor (RDC) and the Podbielniak centrifugal extractor. Both involve moving parts and problems of seals. The compartment stage efficiency in the RDC and the number of stages available in the centrifugal extractor are both limited.

Two recent developments that seek large interfacial areas without excessive dispersion are the use of structured packing and hollow-fiber contactors. The hollow-fiber contactor keeps the phases apart by means of thin, porous fiber membranes and avoids form drag, which creates pressure drop and energy consumption without providing mass transfer capability. The interfacial area per unit contactor volume can be quite high. There are several issues surrounding such contactors that warrant research (Sengupta, et al., 1992). One is the mass-transfer resistance attributable to the membrane itself. Another is the avoidance of channeling and the efficiency of phase flow and distribution within the contactor. Another

may be stabilization of the phase interface within the fiber pores throughout an entire contactor.

Other promising areas for research and development would seem to be other non-dispersive forms of contactor that give a high efficiency per unit volume, and contactors effective with very short phase residence times, e. g., improvements on the centrifugal extractor.

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SESSION 1

CONTACTING EQUIPMENT

1.1

AROMATICS EXTRACTION WITH THE KÜHNI COLUMN, AN APPLICATION REQUIRING AN EXTREME DESIGN FLEXIBILITY

Ulrich BÜHLMANN
Kühni Ltd.
Gewerbstrasse 28
CH - 4123 Allschwil
Switzerland

ABSTRACT

The design of liquid-liquid extraction contactors is in principle not straight forward. In many cases the situation is further aggravated by strongly varying system parameters. In particular physical properties as well as operational parameters may change significantly as extraction proceeds. Such applications require a contactor with a high design flexibility in order to achieve optimal capacity and efficiency.

Aromatics extraction with DMSO is characterized by extreme changes of densities, interfacial tension, flow rates and phase ratio. The Kühni contactor has been successfully used several times for this application.

The characteristics of the Kühni column, in particular the ability to vary the compartmental geometry, is explained and the specific application of aromatics extraction is used to illustrate the design flexibility of this contactor. Initial design requirements are presented as well as the final industrial design together with experience from plant operation.

INTRODUCTION

The design of liquid-liquid extraction equipment requires not only experience but also understanding of the complex two-phase system. There are many parameters which influence the hydrodynamics and mass transfer in liquid-liquid extraction. The most important are physical properties and operational parameters such as flow rates and phase ratio. It is not unusual in industrial extraction processes that the main influencing parameters will significantly change when extraction proceeds. Such applications call for special extraction equipment with a high design flexibility in order to maintain optimal conditions throughout the extraction and to achieve an overall high performance.

Aromatics extraction according to the French IFF process is presented as an industrial example. The extraction with DMSO combined with a backwash leads to extremely

varying conditions in most aspects. In such a situation pilot testing is inevitable. However it will be demonstrated that appropriate modelling of the hydrodynamics and understanding of the main influence of constructional parameters allows design and prediction of the internal varying extractor geometry.

THE KÜHNI EXTRACTION COLUMN

The Kühni extractor belongs to the group of mechanically agitated columns Mögli, Bühlmann (1982), Bühlmann (1990). The basic construction of each stirred compartment is shown on Figure 1. It offers the advantage of easily varying the relevant stage geometry. It is therefore possible to influence and to adjust the hydrodynamics stagewise, which makes the Kühni column an excellent tool for extraction processes with changing parameters.

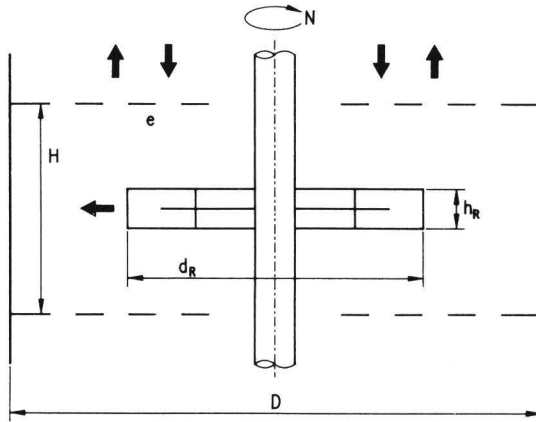


Fig. 1 Compartment of Kühni column

Stirring speed and column diameter are mostly kept constant over the column height because a variation is mechanically difficult and/or expensive. Stage height is usually not varied as well. The design variations concentrate on the mixing turbine and the stator plates, the two main elements of each compartment. Both have a direct and strong influence on hydrodynamics. Diameter and height are the two principal design parameters of the turbine. Free area of flow and to some degree also the hole arrangement characterize the design of the stator plates. The principal influence of the stage geometry on hydrodynamics is summarized in Table 1. Only the primary, direct influence is mentioned, neglecting any secondary influences.

TABLE 1
Geometrical parameters:
principal influence on hydrodynamics

· Turbine diameter	→ drop size, axial mixing
· Turbine height	→ radial discharge flow, radial mixing
· Fractional free area of stator plates	→ hold-up, throughput, axial mixing
· Compartment height	→ residence time, axial mixing

Some further explanations regarding the special turbine of the Kühni column are worth mentioning. It is a dual entry radial flow impeller which not only creates and maintains the two phase dispersion but also generates radial mixing. The latter aspect, characterized by the radial discharge flow is most important for scale-up in view of the decreasing relative stage height with increasing column diameter (Figure 2).

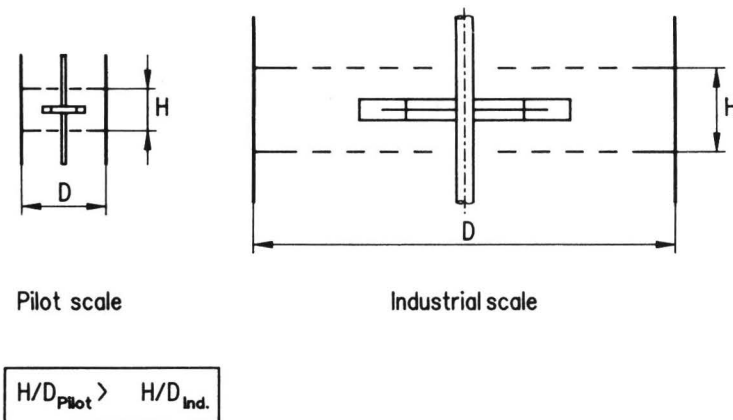


Fig. 2 Compartment geometry as a function of column size

IFP PROCESS FOR AROMATICS EXTRACTION

The IFP process is one of the successful processes in petroleum industry for aromatics recovery (benzene, toluene, xylene) from hydrocarbon mixtures produced by gasoline pyrolysis or naphtha reforming. The solvent used for this process is DMSO with a few percent of water. As reported in the literature Choffe et al. (1966), Raimbault (1968), the IFP process offers a series of advantages as extraction at ambient temperature, easy separation of solvent from product, use of mild steel for most equipment. The basic process scheme is shown in Figure 3. Unlike with other aromatics processes two extraction steps are being used thereby avoiding an extractive distillation step.

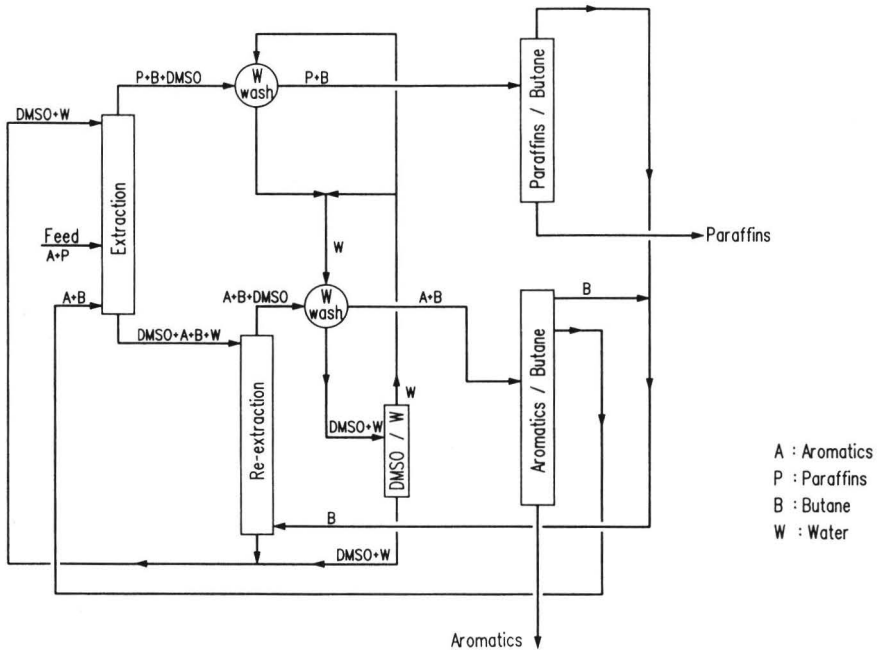


Fig. 3 Flowsheet of IFP process

The feed stream enters the first extraction column in the lower part. The solvent is chosen as the continuous phase and is fed into the column top. A backwash of butane is introduced into the bottoms to produce a high quality extract. In the second extraction column the solvent is regenerated by extracting the whole aromatic content with butane. Both extractors are operated at about 30-40°C and an elevated pressure.

The re-extractor does not give any unusual design problems, the only particular feature worth mentioning is the high specific throughput beyond 50 m³/m²h achieved with a

Kühni column. The first extraction step is however of particular interest. It is probably one of the most difficult design problems in the field of liquid-liquid extraction due to extreme changing physical properties and internal flow rates all along the column height.

DESIGN OF THE KÜHNI COLUMN

Typical profiles of the main physical properties and flow rates which govern the first extraction column show either a minimum or a maximum at the same location, at the main feed entry. Both interfacial tension and density difference between the two phases have a minimum, the internal flow rates have a maximum with a strong peak of the dispersed phase flow rate. The extreme values unfortunately do not compensate each other, but add up to an overall, highly unfavourable situation.

Already at early stages of the process development, pilot testing with the Kühni extractor has demonstrated that it can cope with the extreme situation described. Several large industrial columns have been built and operated successfully.

The design of the internal geometry, the most critical step of the extractor design is explained and illustrated with a recent new application of the process. The corresponding profiles of physical properties and flow rates are shown in Figure 4. Note the extreme changes between the feed location and the two column ends: approximately a factor of two for the interfacial tension and density difference, a factor of three to four for the dispersed phase flow rate !

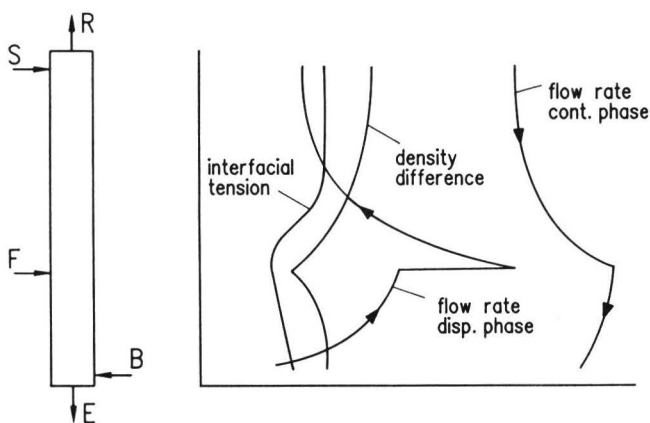


Fig. 4 Profiles of physical properties and flow rates

Due to the limited available time as well as the elevated operating pressure of 8 bars pilot testing was not possible. The main column dimensions (diameter, height, number of

compartments) were determined and derived from the operating industrial columns. The variation of the physical properties and flow rates, however, are different for each application. It was therefore necessary to resort to specific knowledge on hydrodynamics in order to allow the design of the varying internal geometry. The design concept was based on the following two basic assumptions:

- . constant drop size and hold-up
- . equal radial discharge flow of turbines

This allowed the following procedure for designing the turbine size and stator plates:

- . Turbine diameter
Use of drop size correlations as a function of physical properties and turbine diameter e.g. Fischer (1973)
- . Turbine height
Use of available correlations for radial flow rate e.g. Hody (1975)
- . Free area of flow of stator plates
Use of slip velocity equation assuming that slip velocity is proportional to terminal velocity and fractional free area. Use of available correlations for the terminal velocity.

Given a fixed geometry at one extractor end it was possible to calculate the variation of the internal geometry. Sample calculations have been carried out also for the existing running columns with the same procedure and gave in general a good agreement. Only the calculated variations of the turbine heights were found to be excessive and required a corresponding adjustment. The final profile used for manufacturing of the industrial column is shown in Figure 5.

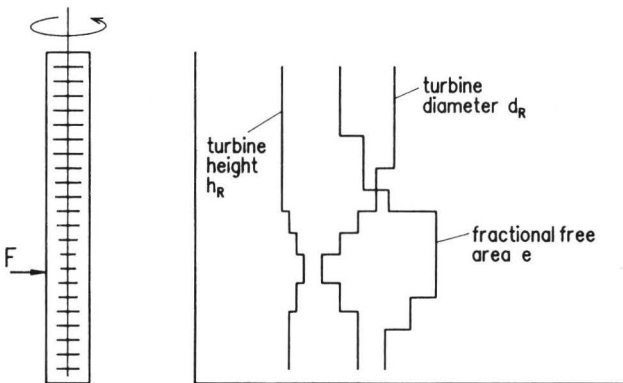


Fig. 5 Profile of compartment geometry

PLANT EXPERIENCE / CONCLUSIONS

The installed extraction columns of the design example are shown in Figure 6. Both have a diameter of above two metres. After commissioning the re-extractor gave immediately the guaranteed performance, whereas the first extraction column produced off-specification raffinate and extract. The reasons for the malfunction became evident after a detailed analysis: inadequate construction of the feed entry arrangement and wrongly calibrated flow meter for the solvent phase. After corrective actions the guaranteed values were reached and exceeded. It is interesting to mention that rotational speed strongly influences extractor performance, with values close to flooding giving the best performance.

The illustrated, extreme design example clearly demonstrates the capability of the Kühni column and confirms the concept of varying the internal extractor geometry to achieve optimal conditions regarding overall column performance.



Fig. 6 Installed extraction and re-extraction column (Enichem Anic)

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1.2

THE HYDRODYNAMIC AND MASS TRANSFER CHARACTERISTICS OF A HI-GEE SOLVENT EXTRACTOR

C.R. HOWARTH, J.G.M. LEE, C. RAMSHAW

Department of Chemical & Process Engineering

University of Newcastle-Upon-Tyne

Newcastle, NE1 7RU, U.K.

ABSTRACT

The use of Hi-Gee technology to intensify a process has been demonstrated in gas/liquid stripping duties producing considerable equipment size reduction. The extension of this technology to liquid/liquid systems needs fundamental data on the dispersed phase-packing interactions in centrifugal fields. Laboratory scale studies on wetting and non-wetting packings together with a Monte Carlo simulation to follow the droplet history have shown that the dispersed phase moves as discrete droplets in non-wetting packings, whilst in the wetting packing it is a combination of droplet and film flow.

Provisional mass transfer work on a pilot scale unit designed to remove organic contaminants from a large throughput of aqueous effluent has shown that non-wetting packings perform better and the Height of a Transfer Unit obtained is an order of magnitude less than those in a conventional packed column.

INTRODUCTION

Solvent extraction was the first commercial chemical process to use rotation to enhance the throughput and mass transfer performance of a single processing unit, the Podbielniak extractor being the first of its type, Podbielniak(1969). Since then this and other rotary extractors have found many applications in many areas, Hafez(1984), from effluent treatment to nuclear processing. When two phases are contacted in a rotary extractor centrifugal acceleration replaces gravitational acceleration in causing countercurrent flow of the two phases, which has two effects:

- (a) Firstly the settling velocity of the dispersed phase is increased, thereby increasing the continuous phase flow rate at which flooding occurs, reducing the cross sectional area of the contactor for given flow rates of both phases.
- (b) The second effect of rotation is to decrease the size of the dispersed phase droplets which leads to an increase in the interfacial area for mass transfer. The Podbielniak is a rotary sieve plate extractor in which droplets are formed on the surface of one plate, settle across the inter-plate gap and coalesce on the underside of the next plate, hence the size of the

droplets formed by the perforations in the plate is important in determining the interfacial area for mass transfer. For slow formation of droplets the size of the droplets is proportional to the inverse cubic root of the gravitational, or in this case centrifugal acceleration, $\omega^2 r$.

When droplets are formed from the break up of a liquid jet in a centrifugal field, Schilp & Blass(1984) found that the size of droplets produced by fragmentation of the primary droplets was proportional to the inverse square root of the centrifugal acceleration. Even with moderate rotational speeds ($\sim 1000 \text{ min}^{-1}$) the acceleration term is large giving rise to small droplets.

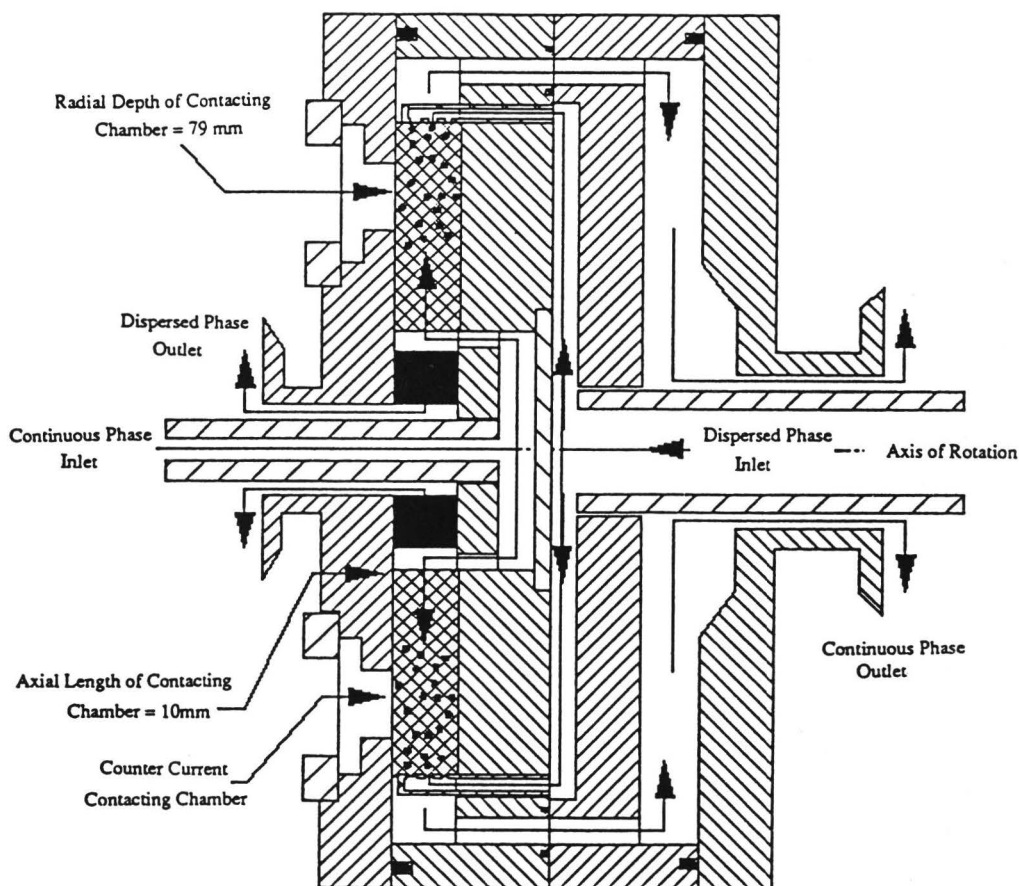


Figure 1 Section Through the Rotary Extractor

Ramshaw(1987) realised the advantages of rotation when used for a number of multiphase operations, his first machines being used for rotary distillation. Porter, Balasundaram &

Ramshaw (1989) developed these ideas further for use in a rotary gas stripper to remove oxygen from sea water. The high voidage plastic packing used in this machine ensured that the bulk fluid flow moved radially and also helped to maintain the size of the bubbles produced by the gas injectors, by bubble impact with filaments of the packing. A rotary solvent extractor based on the design of the sea water stripper has been described by Howarth, Lee & Ramshaw(1992). This extractor has a higher hydraulic capacity than a Podbielniak of similar size, Barson & Beyer(1953), whilst rotating at significantly lower speeds. This is due to the large area available for flow within the packing. This paper describes work undertaken to investigate the nature of the hydrodynamic processes within the packing, and the overall mass transfer performance of this rotary extractor.

Layout of the Rotary Extractor

Figure 1. shows a section through the extractor In this case the lighter of the two phases forms the dispersed phase, which enters the machine down the right hand shaft flowing outwards through a central chamber to the periphery where it is dispersed into the main counter current contacting chamber at the front of the machine. This main section is packed with porous plastic or ceramic packings. The continuous phase enters the machine down the left hand shaft and flows outward through the contacting chamber from where it flows out to the periphery whilst the dispersed phase settles inwards due to the rotation of the machine. On reaching the periphery of the contacting chamber the continuous phase flows through into a return chamber where it is returned to the axis of the machine ensuring that the contacting chamber is flooded with the continuous phase. The dispersed phase coalesces in a pool at the inner edge of the contacting chamber and flows over a weir into a stationary catch box.

DROPLET SIZE STUDIES

Hydrodynamic Modelling

Rigorous modelling of the behaviour of a droplet swarm is not possible due to the enormous number of individual droplets in the contacting zone. Statistical mechanical methods, Hulburt & Katz(1964), offer a better approach because it is possible to relate aspects of the hydrodynamic process to a probability function describing droplet breakage and/or coalescence rates, however the numerical solution of the resultant integro-differential equations is difficult for most realistic situations. Monte Carlo simulation, Levenspiel(1966) has been used as an alternative and is the method adopted here.

The most important aspect of the simulation is to derive an expression for the breakage frequency of the droplets, as a function of droplet size, velocity and packing dimensions. This frequency requires knowledge of the equilibrium droplet size, d_c , which represents the minimum size of droplet that can be obtained by impact breakage of the droplet with a filament of the packing material, Ramshaw(1963). d_c is found by performing a simple energy balance on a droplet immediately before and after collision with the packing. The droplet in Fig. 2 is assumed to be travelling at terminal velocity as it approaches the filament, after the

collision the two drops produced have zero velocity. The assumption that a droplet would attain terminal velocity before every collision has been validated by Schilp & Blass(1983). The energy losses and gains shown in Fig. 2 are written in terms of d_C . When the energy losses are equated to the energy gains this droplet size becomes the critical droplet size, which is the smallest sized droplet that has the energy to split into two daughter droplets and, is given by Lee(1992):

$$d_C = \frac{\sqrt{\rho_D^2 V_t^2 - 22.5 \Delta \rho \omega^2 r \gamma} - \rho_D V_t^2}{3.6 \Delta \rho \omega^2 r} \quad (1)$$

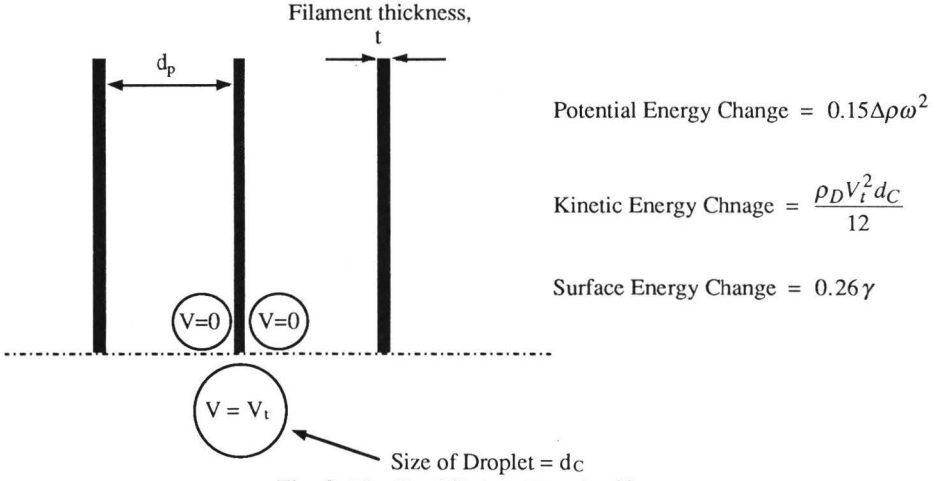


Fig. 2 The Equilibrium Droplet Size

The critical droplet size determines whether a droplet will split on collision with a filament of the packing. In order to determine the probability of a droplet hitting P_{hit} , and splitting P_{split} , a combined probability term is assumed, based on the area of a pore in the packing, the form area of a droplet and the thickness of the packing filament t , Howarth & Lee(1992). The complete expression for the probability of a droplet splitting is given by:

$$P_{break} = f(d_C) P_{hit} P_{split} = v(d - d_C) \left(\frac{d}{d_p} \right)^2 \left(1 - \frac{2t}{d} \right) \quad (2)$$

Using this concept droplet flow through the packing has been modelled for droplets from a nozzle, whose size has been measured experimentally. The droplet history was modelled in discrete time steps and discrete radial positions so that the droplets leaving the inner edge of the packing grid at every time step represent the predicted output distribution.

Experimental Droplet Size Studies

In parallel with the modelling, droplet size studies were carried using the apparatus shown in Fig. 3. The apparatus consists of a rotating bowl of 0.15m internal diameter, with a clear

Perspex lid, to allow visualisation of the droplet flow. A stationary continuous phase is contained as an annular pool while the machine rotates.

The dispersed phase enters the apparatus through a rotary union and flows out to the periphery, where it is injected through a 1mm diameter nozzle into packing material adjacent to the nozzle. The droplets travel radially inwards collecting as an annular pool at the centre of the apparatus from where they are scooped out. The packings used in experiments were a 25 pore/inch rigid wetting foam and a 20 pore/inch non-wetting foam.

The continuous phase was water and the dispersed phase dyed kerosene to enhance the contrast between droplets and the continuous phase. The strobe flash had a duration of $5\mu\text{s}$ which was short enough to 'freeze' the motion of both the rotating apparatus and droplets at speeds of 1200 min^{-1} . The images produced by the video camera were analysed using an image processor to yield a droplet size distribution to an accuracy of $\pm 100\text{ }\mu\text{m}$.

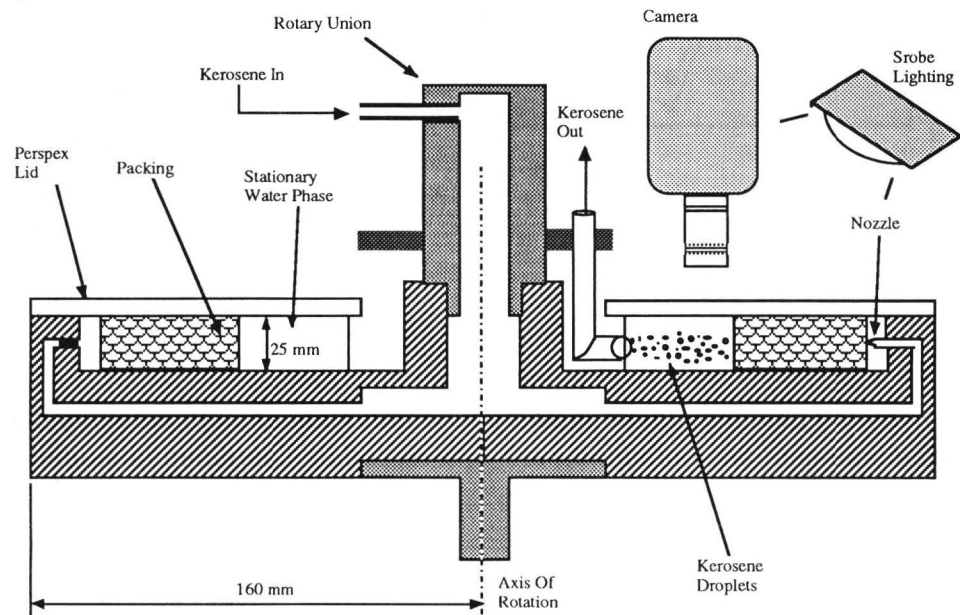


Fig. 3 Droplet Size Apparatus

Results from Droplet Size Studies

Fig 4. shows the effect of packing length for non-wetting packing material. It is clear that the increased speed decreases droplet size, but that after migrating through 40mm of packing, the critical droplet size is approached. If wetting packing is used the average size is larger as shown in Fig. 5. It was found that the wetting was easily wet by the kerosene hence the kerosene should flow as a film over each fibre of the packing with droplets forming at the inner edge. More likely however is a combination of droplet and film flow with less droplet splitting.

The simulation gives a log normal distribution of droplet sizes characteristic of a breakdown process, the shape of which agrees well with the experimental distribution of the non-wetting packing, whilst the experimental distribution obtained using wetting packing is more normal in shape suggesting a different process by which the dispersed phase migrates through the packing.

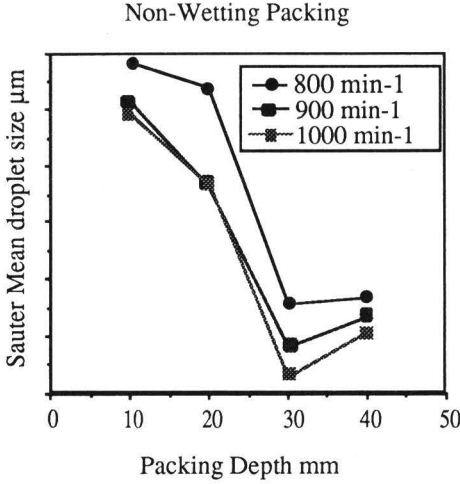


Fig 4 Variation of Sauter mean with radial packing depth

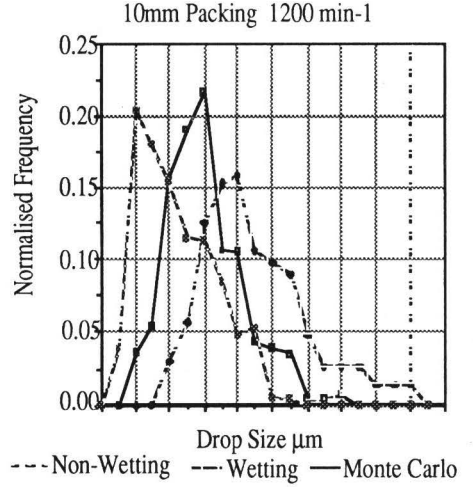


Fig 5 Comparison of Experimental and Monte Carlo Data

MASS TRANSFER STUDIES

Prediction of Mass Transfer Performance of the Rotor

In conventional gravity columns the height of a transfer unit remains more or less constant. In a rotary extractor the height of a transfer unit varies continuously with radius, the number or transfer units for dilute systems being given by:

$$N_{tOC} = \int \frac{dr}{H_{tOC}} \quad (3)$$

where the height of a transfer unit is given by eq.(4) for systems where the principal mass transfer resistance lies in the continuous phase:

$$H_{tOC} = \frac{R}{K_{OC} a (1 - x_C)_{OM} c_{Cav}} \quad (4)$$

For dilute systems $(1 - x_{Cav})_{OM}$ is essentially unity and c_{Cav} is the molar density of the continuous phase. The interfacial area a , was estimated by modifying the Monte Carlo simulation for counter current flow. By assuming plug flow of the continuous phase the droplet settling velocity can be estimated by:

$$V_S = V_t - V_C \quad (5)$$

The terminal velocity of the droplets was estimated using the correlation of Grace(1976) for ellipsoidal droplets with contaminated interfaces. The simulation gives the droplet size d , and hold-up ϕ , as function of the radius. The interfacial area is then given by:

$$a = \frac{6\phi}{d} \quad (6)$$

The continuous phase film coefficient, k_r was estimated from either penetration theory, Laddha(1976), the exposure time being taken as the time it takes a droplet to move a distance equal to its diameter or the correlation of Skelland(1973) for oscillating liquid droplets. The latter was found, Otillinger and Blass(1988), to be suitable for describing the continuous film coefficient, in their study of droplet mass transfer in centrifugal fields.

The mass transfer predictions could only be compared with results using from the non-wetting packing since the hydrodynamic simulation can only predict droplet sizes for non-wetting packings.

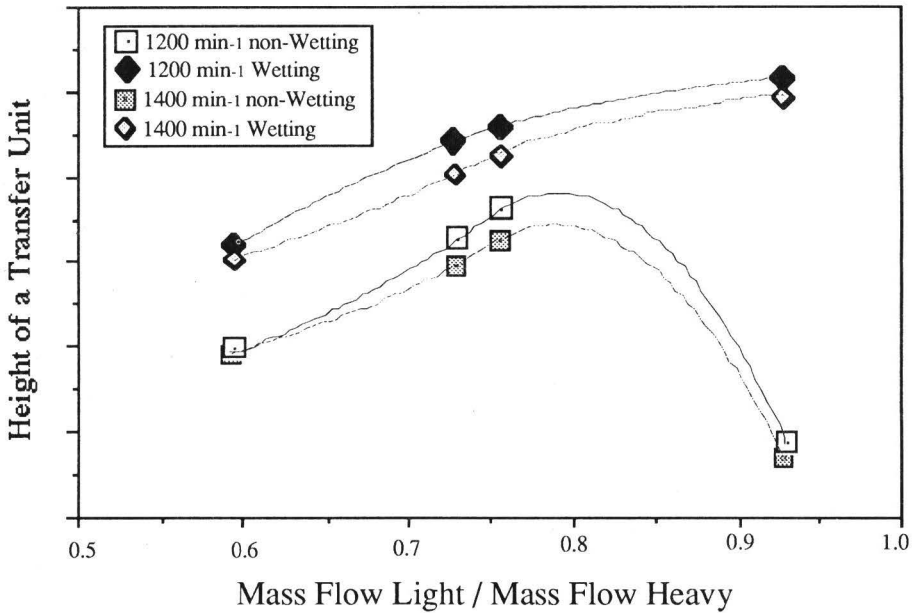


Fig. 6 (Data Confidential) Height of a Transfer Units vs. Mass flow Ratio

Mass Transfer Experiments

The mass transfer experiments were carried out on the apparatus shown in Fig. 1. The system studied consisted of water as the continuous phase contaminated with a chlorinated hydrocarbon in mg/L amounts, the solvent phase being a straight chain alkene with a high affinity (large m) for the contaminant. The speed varied from 900 min⁻¹ to 1400 min⁻¹, with solvent to aqueous flow ratios of 0.59 to 0.93. Samples of both phases were analysed using

gas chromatography. Fig. 6 shows a comparison between the height of a transfer units obtained with wetting and non-wetting packings.

CONCLUSIONS

Droplet studies have shown that the migration of a dispersed phase through an easily wet packing is by a combination of droplet and film flow.

Non-wetted packings give smaller droplet sizes and better mass transfer performance in rotary units

The height of transfer units in a rotating packed column is drastically reduced compared to those obtained in a conventional packed column.

Experimental heights of a transfer unit can be predicted with an accuracy of 25%, for the ceramic packing, using one of two expressions for the continuous phase film coefficient and Monte Carlo simulation of the droplet migration through the packing

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of the UK. SERC, ICI Chemicals and Polymers(Billingham) who provided additional sponsorship and Foseco Ltd.(Birmingham) who provided samples of packing for test purposes.

NOMENCLATURE

d_c	critical droplet size(m)
d_p	diameter of packing pore(m)
c_{Cav}	average concentration of all compounds in the continuous phase (kmol/m ³)
$(1 - x_C)_{OM}$	log mean concentration difference in the continuous phase
R	molar flowrate (kmols/ m ² s)
r	radius(m)
t	packing filament thickness(m)
$v()$	unit step function
ω	angular velocity (rads/sec)

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1.3

**THE USE OF A POWER FLUIDICS SOLVENT EXTRACTION CASCADE FOR
NUCLEAR FUEL REPROCESSING**

N.P.HANIGAN and J.W.STAIRMAND
Power Fluidics Department
AEA Technology
Springfields
Preston, PR4 0RR, UNITED KINGDOM

I.S.DENNISS
R&D Department
BNF plc
Sellafield, Seascale
Cumbria, CA20 1PG, UNITED KINGDOM

ABSTRACT

Power fluidics can be defined as the control and processing of fluids with devices which contain no moving parts in contact with the fluids. The technology utilises the principles of vortex formation, jet attachment and fluid entrainment. Since power fluidic devices contain no moving parts they are inherently reliable and require little or no maintenance.

Power fluidic equipment was initially developed and exploited within the nuclear industry, but in recent years has also found numerous applications within the pharmaceutical and fine chemical industries. A power fluidic solvent extraction system allows the stagewise, counter-current contacting and separating of two streams. It is analogous to a mixer-settler in which two streams are mixed to facilitate mass transfer and then separated.

This paper discusses a power fluidic solvent extraction system which would be suitable for the reprocessing of nuclear fuel. It describes the hydrocyclone and the four-diode pump, these being the fundamental components of such a system. It also gives the results of the trials carried out using a five stage experimental cascade; these demonstrate that a stable solvent/aqueous (S/A) profile and adequate mass transfer (both extract and backwash duties) can be achieved.

INTRODUCTION

A power fluidics solvent extraction cascade offers several advantages over rival systems for the reprocessing of nuclear fuel:

1. The system would contain no moving parts within the shielding, making it almost maintenance free.

2. It would be compact and hence the cost of shielding would be small when compared to the cost of shielding for a pulsed column.
3. The system would not suffer the residence time problems encountered with mixer settlers.

POWER FLUIDICS

Power fluidic technology utilises three fluid flow phenomena, namely entrainment, vortex flow and wall attachment. These can be used singly, or in combination, to pump and direct liquid streams and to control gas pressures and flows. Since they contain no liquid contacting moving parts, power fluidic components are inherently reliable and require little or no maintenance. The full range of fluidic components available has been described in detail by Etherington and Stairmand [1984, 1990].

Power fluidic valves, controllers and pumps have already been installed in the new THORP plant. Now a power fluidic solvent extraction cascade has been proposed for the reprocessing of nuclear fuel. A five stage experimental cascade has been built at Springfields to demonstrate the feasibility of such a system. This paper begins by describing the five stage cascade and its fundamental components, the hydrocyclone and the four-diode pump. It then gives the results of the solvent/aqueous concentration profiles and mass transfer trials carried out using the cascade.

THE VORTEX CASCADE SYSTEM

A flow diagram of the countercurrent vortex cascade system is shown in figure 1. This shows three vortex stages and one end purifier. These central stages are designed for a particular duty such as an extract or backwash. The end purifiers are a different design to the central units and produce either a pure organic or a pure aqueous stream, whereas the central stages produce two mixed streams. Each stage consists of a hydrocyclone and a four diode pump. The organic and aqueous phases are mixed in the diodes and charge vessels of the fluidic pumps where the turbulence within them facilitates mixing and produces a high superficial area for mass transfer. The mixed liquors are then discharged by the pump to the hydrocyclone for phase separation before passing to the next vortex stage.

HYDROCYCLONE

Hydrocyclones are the fluidic analogue to centrifuges and have been used for separation work for over 100 years as described by Svarovsky [1984]. A large amount of work on hydrocyclones for liquid/liquid separation was carried out in the 1950's in connection with nuclear applications. The idea was abandoned since the separation efficiencies

reported by Hitchon [1958] were low. The hydrocyclones installed in the vortex cascade have significant changes to their internal geometry which give much improved separation efficiencies.

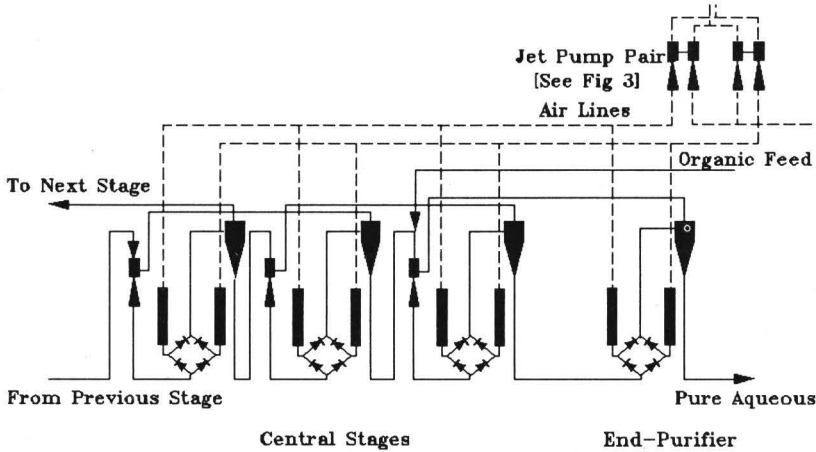


Fig. 1. Three stage vortex cascade

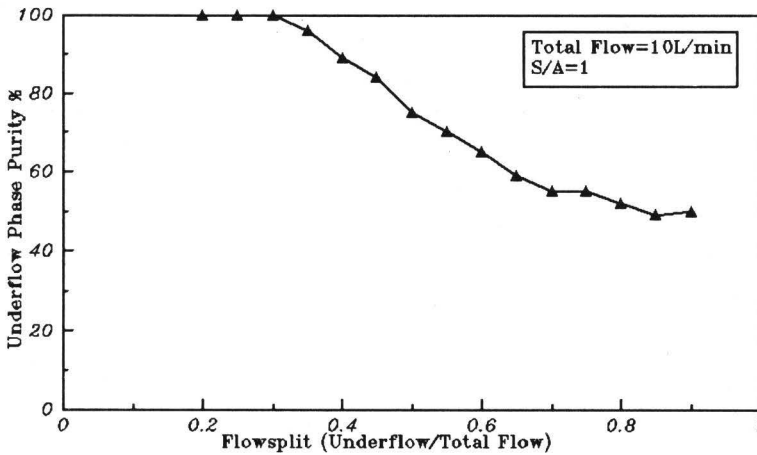


Fig. 2. Operating characteristics of an end-purifier

A mixture of solvent and aqueous enters the hydrocyclone tangentially and is caused to rotate about the central axis. The centrifugal action causes the heavier liquid (nitric acid) to migrate to the outer wall whilst the lighter liquid (Tributyl phosphate in odourless kerosene) moves to the central axis to form another vortex travelling in the opposite direction. The stream which is enriched in the heavier liquid exits the hydrocyclone from the underflow whilst the light phase enriched stream exits from the coaxially opposite overflow. It is not possible to obtain two pure streams from a

hydrocyclone but the flowsplit may be adjusted to give a single pure stream and a mixed stream. This is the concept of the end purifier hydrocyclones. Figure 2 shows the operating characteristics of an end purifier.

Experiments carried out at ambient temperature have indicated that reasonable separation efficiency may be obtained for an aqueous-rich mixture but that a solvent-rich mixture is more difficult to separate. Possible causes of poorer separation may include the difficulty of moving the aqueous droplets through the more viscous continuous phase and also inefficient coalescence of the drops due to film drainage effects. The viscosity of both phases may be reduced by increasing the temperature of the separation with a potential improvement in separation performance, particularly for the extract duty.

FOUR DIODE PUMP

The four diode pump is the fluidic equivalent of a double acting piston pump. It consists of a vortex diode bridge and two charge vessels which are analogous to the non-return valves and mechanical pistons of a piston pump respectively. The charge vessels are continually pressurised and evacuated with air to mimic a mechanical piston and the four diodes are interconnected such that a net forward flow is produced in the delivery line irrespective of which charge vessel is driving. The drive and suction of the charge vessels is effected by a dedicated jet pump pair whose air supply is controlled by solenoid/pilot air operated solenoid valves. Synchronization of the opening and closing of the valves, and hence drive/suction operational regimes, is directly controlled by a computer controller. Figure 3 shows a schematic of a four diode pump.

The controller receives information from pressure signals from two transducers connected to pneumercators which monitor the liquid level in the charge vessels.

EXPERIMENTAL PROGRAMME AND RESULTS

The vortex cascade system as described above and shown in Figure 1, was used for all experimental work. The rig consisted of five central stages and two end purifiers. The organic and aqueous phases were supplied from stock tanks via air operated pumps to the vortex cascade. The liquor flowrates and delivery pressures from the pumps were adjusted to simulate the flows and pressures from the preceding stages in the cascade. In this way the five vortex stages could simulate the intermediate stages within a large cascaded system. Sampling points were positioned at the inlets and outlets of the hydrocyclones to withdraw samples from which separation and mass transfer performances could be evaluated.

A single pair of jet pump pairs was used to simultaneously control all five pumps in the cascade. This resulted in each jet pump pair controlling the drive and suction phases of five charge vessels (one charge vessel from each fluidic pump). The five charge vessels

were interconnected by an air manifold to the relevant jet pump pair. There were thus two manifolds, each linking five specific charge vessels to a jet pump pair this corresponding to one half of the fluidic pump.

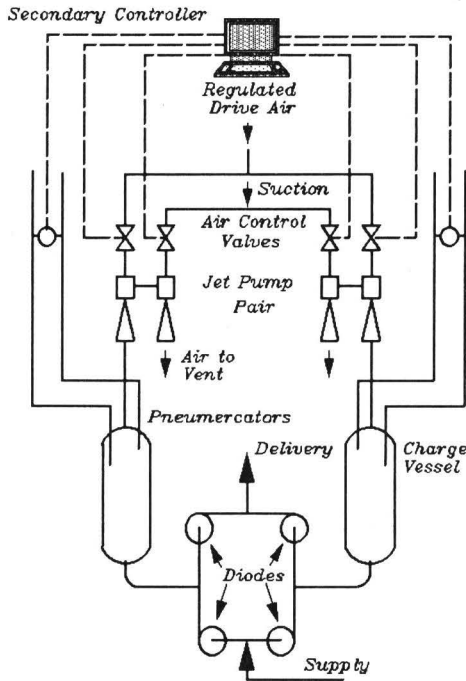


Fig. 3. Four diode pump arrangement

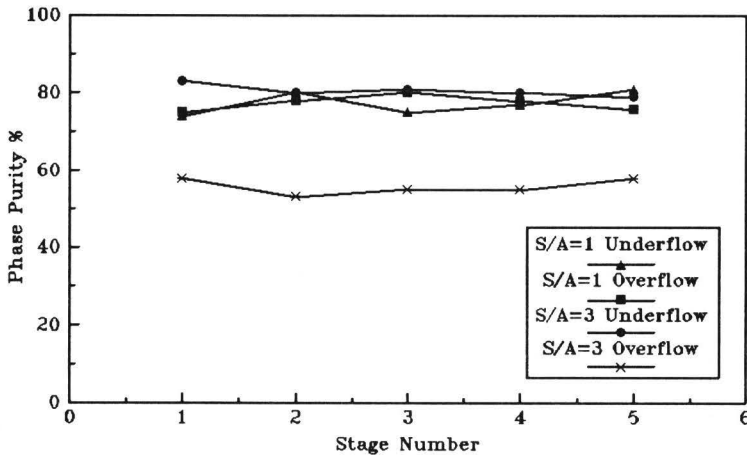


Fig. 4. Phase purity profile in a vortex cascade

All hydraulic tests on the vortex cascade rig were carried out with solvent (20% tributyl phosphate in odourless kerosene) and dilute nitric acid containing depleted uranium. Experimental tests on the rig were used:

- i) To determine whether it was possible to achieve a constant solvent/aqueous ratio being fed to each of the hydrocyclones along the vortex cascade.
- ii) To assess the mass transfer in a cascade of hydrocyclones and compare the results with those obtained by calculation.
- iii) To determine the ability of the system to break and reform entrainment in each stage and compare the results with a simple model based on the dilution of the aqueous phase in consecutive stages.

EQUAL SOLVENT/AQUEOUS FEEDS TO EACH HYDROCYCLONE

Known flowrates of aqueous and organic feeds were fed into the ends of the cascade to simulate two duties. The vortex cascade system was allowed to reach stable operation with no end purifiers operating. The outlet streams were then directed to the end purifiers and the flowsplit on the end purifiers altered allowing some flow to be redirected back into the cascade. This flowsplit was altered until a point was obtained when pure streams were exiting the cascade and the flow ratios in each of the central hydrocyclones was identical to the feed flow ratio. The phase purities at each stage in the cascade are given in Figure 4 for the two duties in question. The phase purity is given by:

$$P_o = V_o / V_a$$

Where P_o is the phase purity of the overflow and V_o and V_a are the volumes of the organic and aqueous in the overflow, respectively.

The separation efficiency of a hydrocyclone is given by:

$$E_o = P_o(1 + F) - F$$

Where E_o is the organic separation efficiency and R is the solvent/aqueous ratio.

The phase purities for the $R=1$ relate to separation efficiencies of 60%, whilst those for $S/A=3$ relate to efficiencies of 50%.

MASS TRANSFER TRIALS

Once it had been proved it was possible to operate a cascade with the flow ratios to each hydrocyclone equal to the feed flow ratio, the mass transfer was assessed. Extract and backwash duties were examined. Mass transfer data are given in Table 1.

TABLE 1
Mass Transfer in Vortex Cascade

Extract Duty - R=3, Acidity=1.6M					
Conc In g/L		Conc Out g/L (Experimental)		Conc Out g/ (Calculated)	
U org	U aq	U org	U aq	U org	U aq
0.68	2	1.55	0.11	1.31	0.125
0.68	10.89	3.87	0.15	4.27	0.135
0.68	18.4	8.78	0.13	6.77	0.143

Backwash Duty - R=1, Acidity=0.11M					
Conc In g/L		Conc Out g/L (Experimental)		Conc Out g/L (Calculated)	
U org	U aq	U org	U aq	U org	U aq
2.8	0.96	0.34	1.82	0.27	3.49
12.2	0.96	1.0	15.3	0.44	12.72
19.7	0.96	1.1	17.6	0.84	19.82

The feed tanks were filled with liquors containing known quantities of uranium. The loaded liquors were fed into opposite ends of the cascade and used to establish the profile for mass transfer. Once the profile had been established, the rig was left for a few hours to demonstrate the stability of the system before any samples were taken and analysed for uranium concentration. The mass transfer was assessed for an extract and a backwash duty. For both duties, three uranium feed concentrations were chosen. The results of the trials were compared with those obtained from a computer model which calculates the distribution of uranium in the vortex cascade system. The system showed good mass transfer as shown in Table 1.

BEHAVIOUR OF ENTRAINMENT

As stated earlier, hydrocyclones do not give pure streams when operating as the central units of a vortex cascade. Therefore, there is a certain amount of "wrong phase entrainment" depending on the separation efficiency of the central units. To determine whether the entrained phase was by-passing stages or being "equilibrated with the bulk", caesium nitrate was metered into the cascade at stage 4. The caesium is insoluble in the organic stream and hence its concentration in the aqueous stream through the cascade acts as a measure of the "back mixing" of aqueous phase between stages by Jenkins *et al* (1990). The results for R=3 are shown in Figure 5 along with the theoretical results predicted by the computer model.

Figure 5 shows good agreement between the experimental results and those predicted

by the model. The discrepancies are probably due to sampling techniques and a small amount of aqueous carry over in the organic outlet. From the graph it may be shown that the cascade rig is giving a decontamination factor (DF) of approximately 3 per stage. This indicates a DF of 3^{10} i.e. 5.9×10^4 over a ten stage cascade. The DF is for inextractable fission products entrained in the aqueous phase. From the tracer results it was concluded that the rig was performing as required with little concentration build-up or excessive wrong phase entrainment.

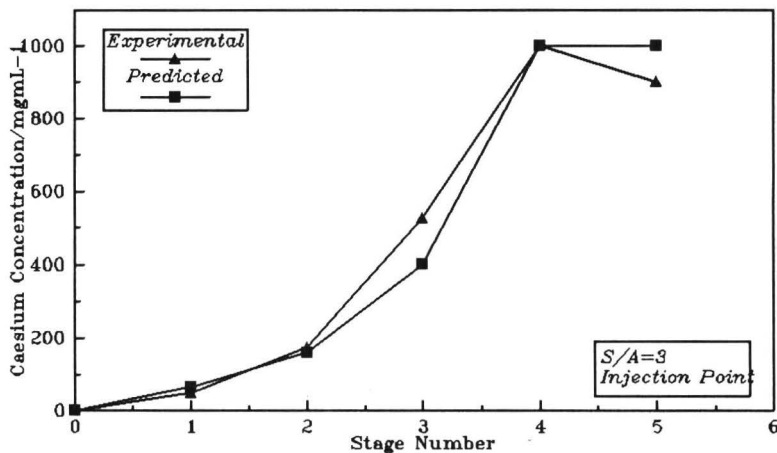


Fig. 5. Caesium distribution in cascade

CONCLUSIONS

A five stage experimental solvent extraction cascade has been described. Trials carried out using this cascade have shown that a stable flow ratio and adequate mass transfer can be achieved with no preferential carryover. These results have demonstrated that a larger cascade would make a viable solvent extraction system for the reprocessing of nuclear fuel.

The use of a power fluidics system removes the need for a large maintenance suite and involves only minimal cell penetration. In addition the system would be compact giving a reduced shielding cost. These factors make the power fluidics vortex cascade an attractive option.

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1.4

EXTRACTION DEMONSTRATION TEST OF ANNULAR PULSED COLUMN: I. CONFIRMATION OF EQUIPMENT PERFORMANCE

T.TSUYUKI, C.TANAKA*, H.SHIMAUCHI*, I.OKADA*, A.IDEGAMI*,
K.KITAMURA*, M.TOMITAKA*, K.KITADE*, F.DRAIN**

Japan Nuclear Fuel, Limited (JNFL)

1-2-10, Hirakawa-cho, Chiyoda-ku, Tokyo, 102 Japan

*Sumitomo Metal Mining Co., Ltd. (SMM)

2-7-17, Ikenohata, Taitoh-ku, Tokyo, 110 Japan

**Societe Generale Pour Les Techniques Nouvelles (SGN)

1, rue des Herons, Montigny-le-Bretonneux, 78182

Saint-Quentin-en-Yvelines, Cedex, France

ABSTRACT

The construction of the first Japanese commercial reprocessing plant is currently being prepared by JNFL. For the main process, French technology is adopted. Extraction demonstration test was planned not only to adapt the introduced technology to Japanese regulatory guides for licensing, technical standards and industrial standards, but also to confirm the performance of equipment and operation controllability of the system. Extraction Demonstration Test Facility (EDTF), which is composed of three annular pulsed columns (extraction, FP scrubbing and diluent washing columns) and their ancillary equipment, was constructed by the end of September 1990, and then the performance tests on equipment and the overall system have been carried out by JNFL and SMM with SGN's assistance.

This paper describes mainly the performance test results about each item of equipment. It is confirmed that the capacity and efficiency of annular pulsed columns are satisfactory and the efficiency of the baffle-plate annular column is much higher than that of a sieve-plate column.

INTRODUCTION

To cope with the future increase of spent fuels arising from nuclear power stations, JNFL is now preparing the construction of Japan's first commercial reprocessing plant with an annual capacity of 800 tonnage of LWR spent fuel at Rokkasho, Aomori prefecture in the northern part of Japan (Toyota, M., 1991). Under the policy to adopt one of the existing excellent technologies in the world, it was decided to introduce French technology for the main process. For the solvent extraction process, the codecontamination process features large-capacity and geometrically safe extractors, namely annular pulsed columns.

The extraction demonstration test was started in October 1988 to establish the reliability of introduced technology. Since then, the seismic soundness and fabrication technology of annular pulsed column has been confirmed (Tsuyuki, T. et al., 1991). The EDTF, which is a

large-scale uranium extraction test facility and composed of three annular pulsed columns (extraction, FP scrubbing and diluent washing columns) and their ancillary equipment, was constructed at Tokai Research Center of SMM by the end of September 1990 so as to confirm the performance of each item of equipment and the operation controllability of the overall system.

This paper describes the hydrodynamics and efficiency of extraction, FP scrubbing and diluent washing columns studied prior to the system test (Tsuyuki, T. et al., 1993, this conference).

TEST FACILITY

The simplified EDTF process flow diagram is shown in Fig.1. The objects of the test are three annular pulsed columns and their ancillary equipment (liquid transfer means, pulsation system and instruments installed in pulsed columns). They were installed within the 30m high building. Besides the annular pulsed columns, two cylindrical pulsed columns, several mixer-settlers and evaporators are also installed in the EDTF in order to recover and prepare the test solutions (uranyl nitrate, nitric acid, 30% TBP diluted in n-dodecane and so on).

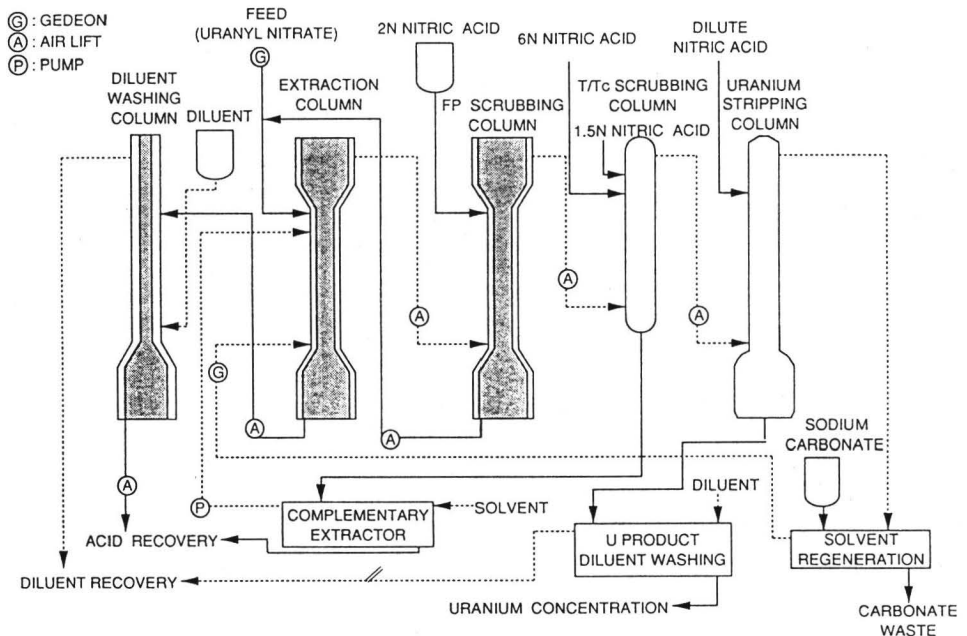


Fig 1 Simplified EDTF process flow diagram

EXPERIMENTAL PROCEDURES

The hydrodynamics of each annular pulsed column including dispersed phase hold-up characteristics and flooding behavior was investigated independently in the flowrate range of $\text{TSFn} \pm 50\%$ (here, TSFn is a nominal total specific flowrate at the daily capacity of 4 metric tons of spent fuel and corresponds to the flowrates indicated in Table 1), pulsation frequency of 30, 40, 60 cycles per minute (cpm) and pulsation pressure range from 20kPa to 80kPa. Aqueous and organic flowrates were increased stepwise under the constant pulsation condition.

TABLE 1
Standard feed condition

COLUMN	AQUEOUS FEED	ORGANIC FEED
EXTRACTION	177g-U/L, 3M HNO_3 0.9m ³ /h	30%TBP/n-dodecane 1.9m ³ /h
FP SCRUBBING	2M HNO_3 0.3m ³ /h	Loaded solvent from extraction column 1.9m ³ /h
DILUENT WASHING	Aqueous raffinate from extraction column 0.9m ³ /h	n-dodecane 0.02m ³ /h

An efficiency test was carried out in the flowrate range of $\text{TSFn} \pm 20\%$ and under the appropriate pulsation condition selected from the hydrodynamic test results. In the extraction column test, only the extraction column was operated and the uranium concentration of aqueous feed was decided taking into account the existence of returning solution from the FP scrubbing column in the extraction cycle. In the FP scrubbing column test, gadolinium (Gd) was used to mimic FP to evaluate the scrubbing efficiency. The distribution coefficient of Gd is about 6×10^{-3} at the nominal uranium concentration in the loaded solvent (about 80g-U/L). The extraction column was operated and Gd was added to aqueous feed solution at a concentration of 750mg/L. Besides the decontamination factor (DF) of Gd in the scrubbing column, that in the extraction column and the overall DF were also evaluated. In the diluent washing column test, the aqueous solution passed through the extraction column was fed into the diluent washing column.

The hydraulic situation in the columns was observed through the windows installed in the outer shell of columns. Samples were taken from the columns at intervals and provided the dispersed phase hold-up measurement and the concentration analysis of each element.

The structure of an annular pulsed column is shown in Fig.2. The column is made of stainless steel. Extraction and FP scrubbing columns have the same dimensions. The total height, outer and inner diameters are about 13m, 49cm and 31cm, respectively. The diluent washing column is slightly smaller in diameter; its dimensions are approximately 12m high, 41cm in outer dia. and 23cm in inner dia. Baffle plates are packed in the shaft portion. Compressed air is supplied and exhausted through a pulsation leg by means of a three-way type pulsation valve. Each column is operated in the organic continuous mode.

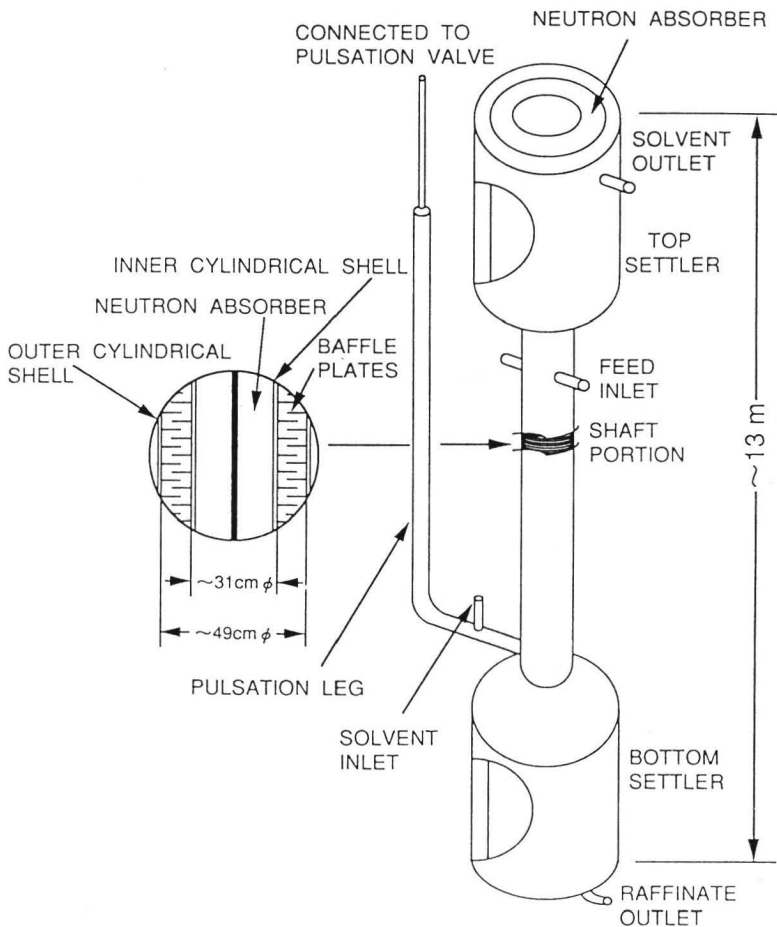


Fig .2 Structure of annular pulsed column
(Extraction column)

RESULTS AND DISCUSSION

Extraction column

From the hydrodynamic test, the stable operating region was determined and the capacity of the column was confirmed to be sufficient. Fig.3 shows the relation between dispersed phase hold-up and pulsation pressure at pulsation frequency of 40 cpm. It was found that flooding occurs at the upper part of the column when the dispersed phase hold-up exceeds 25% on average. Taking into account the flooding point, standard pulsation conditions of 40 cpm, 30kPa for the efficiency test were selected.

Extraction efficiency was examined under various operating conditions. Fig.4 shows the uranium concentration profile for the three different specific flowrates under the nominal pulsation condition. As can be seen from these data, the extraction efficiency is fully satisfactory. Mass transfer is almost completed in the upper column part of 3m length and the uranium concentration in the raffinate is below the detection limit (1mg/L) in every case. Similar results were obtained under the other operating conditions.

HETS (height equivalent to a theoretical stage) was evaluated by McCabe-Thiele diagram and averaged over the top three theoretical stages. The obtained HETS values under suitable operating conditions are in the range from 1.0 to 1.3m. In our experience of the 45cm diameter sieve-plate cylindrical column, extraction efficiency was poor because of a channeling effect. To overcome this drawback, redistribution plates (louver plates) were inserted, but HETS values for top theoretical stage(over 2m) were worse than those in the present study (Kobayashi, Y. et al., 1986).

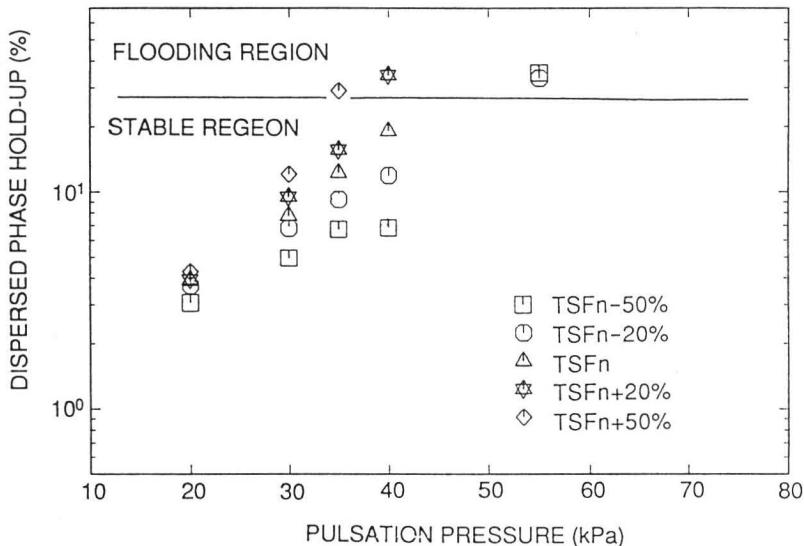


Fig. 3 Dispersed phase hold-up characteristics in extraction column
(Pulsation frequency : 40 cpm)

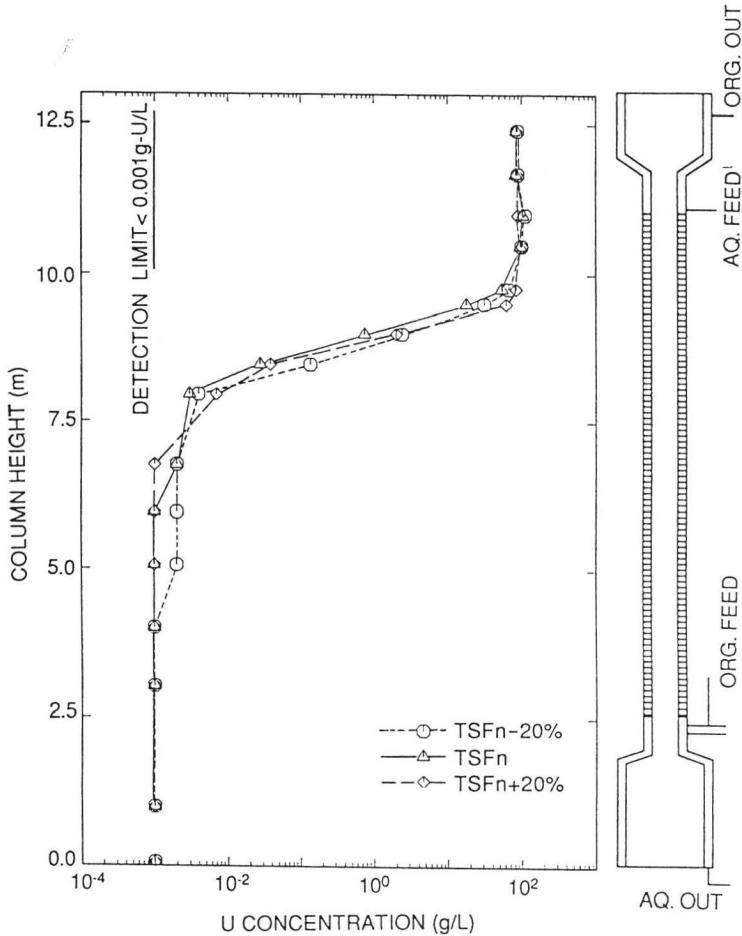


Fig. 4 Uranium concentration profiles in extraction column
(Pulsation condition : 40 cpm, 30kPa)

FP scrubbing column

In a similar way of thinking as the extraction column case, pulsation frequency of 40 cpm and pressure of 40kPa were selected as a standard condition for the efficiency test.

The results of Gd scrubbing tests are summarized in Table 2. Generally speaking, high scrubbing efficiency was achieved. DFs in the scrubbing column and the overall DFs reached the order of 10^3 and 10^5 , respectively, except for one low pulsation energy condition.

It is considered that the high efficiency of baffle-plate annular pulsed columns is brought about by the good radial mixing effect. In spite of the fact that no redistribution plate was installed in the column, a harmful channelling effect was not observed.

TABLE 2
Results of Gd scrubbing efficiency

Parameter	Flowrate			Pulsation Pressure		Pulsation Frequency	
Flowrate	TSFn	TSFn -20%	TSFn +20%	TSFn		TSFn	
Pulse condition							
Frequency (cpm)	40	40	40	40	40	30	60
Pressure (kPa)	40	40	40	30	45	40	40
Amplitude (cm)	2.7	2.7	2.7	2.2	3.1	5.2	1.7
Ave. dispersed phase hold-up (%)	10.4	4.8	11.7	2.8	9.4	12.8	6.9
DF for Gd							
Ex. column	6.3×10^1	6.9×10^1	5.7×10^1	5.9×10^1	4.8×10^1	7.5×10^1	5.6×10^1
Sc. column	$2.0 \times 10^3 <$	$1.8 \times 10^3 <$	$2.2 \times 10^3 <$	9.8×10^1	$2.5 \times 10^3 <$	$1.2 \times 10^3 <$	$2.6 \times 10^3 <$
Overall	$1.3 \times 10^5 <$	$1.2 \times 10^5 <$	$1.2 \times 10^5 <$	5.7×10^3	$1.2 \times 10^5 <$	$9.3 \times 10^4 <$	$1.5 \times 10^5 <$

Diluent washing column

In the case of this column, no flooding occurred and dispersed phase hold-up values were below 10% in the parameter range of hydrodynamic tests. These results can be attributed to large density difference between aqueous phase and organic phase ($\Delta \rho = 350 \text{ kg/m}^3$) and very low specific flowrate of continuous phase. It was confirmed that the column has no risk of flooding and has a wide operating region.

Fig.5 shows a typical plot of the change of TBP concentrations in the input and output streams with operating time. The time required to reach steady state is about 80 hours at least and much longer than those of extraction and FP scrubbing columns (3 and 5 hours, respectively). This time corresponds to one renewal of diluent in the column. The inlet aqueous solution coming from the extraction column contained only dissolved TBP at about 200mg/L and the content in the raffinate was reduced to less than 20mg/L. The efficiencies under the several operating conditions indicated the dependence on the dispersed phase hold-up and the lowest TBP content of about 10mg/L in the raffinate was obtained at the dispersed phase hold-up of 6.2%. These results are acceptable compared to the expected values.

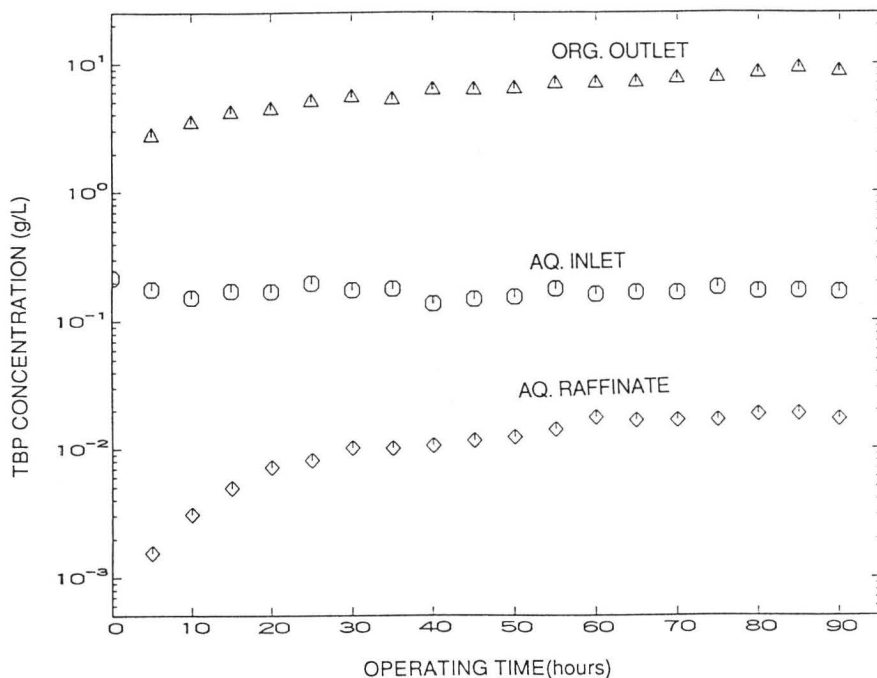


Fig. 5 TBP concentration change with operating time
(Pulsation condition: 40 cpm, 55 kPa, flowrate: TSFn)

CONCLUSIONS

The fundamental performance of annular pulsed columns was studied in the large-scale uranium extraction test facility (EDTF). It was confirmed that each of extraction, FP scrubbing and diluent washing columns satisfy the required capacity and efficiency. Moreover, the efficiency of baffle-plate annular columns is superior to that of sieve-plate cylindrical columns.

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1.5

A HIGH EFFICIENCY PACKING FOR LIQUID-LIQUID EXTRACTION

W.Y.FEI, X.M.WEN, S.H.FANG AND H.MAO
Department of Chemical Engineering, Tsinghua University
Beijing 100084, China

ABSTRACT

A new high efficiency packing-SMR (Super Mini Ring or QH-1) has been developed for liquid-liquid extraction. The performance of the SMR was studied using the butanol / succinic acid / water and 30% TBP (kerosene) / acetic acid / water systems in an experimental column of 0.10m in diameter.

An optical fiber chromometer and microcomputer data processing system was used for measurement of the axial mixing coefficients. The "true" Height of Transfer Unit was estimated from the measured concentration profiles of two phases based on the backflow model.

The comparison of the SMR packing, Intalox saddle, Pall ring and Mellapak shows that the SMR has superior characteristics for solvent extraction both in term of capacity and mass transfer efficiency.

INTRODUCTION

The packed column has found wide application in industrial practice for countercurrent liquid-liquid extraction for many years. Because the packing provides additional drop hold-up and lower axial mixing of the two phases, the packed column is more efficient than a spray tower and some other non-agitated extraction columns (Eckert, 1976, Laddha et al., 1983). It is favourable to choose a packed column for systems with low interfacial tension such as lube-oil refining while the large scale mechanical agitated columns often lose their efficiency because of the serious axial mixing suffered.

Several kinds of high efficiency packings, including random packings and structured packings, have been found to give high capacity and efficiency in distillation service. However, there is evidence that some kinds of structured packings do not perform well enough for liquid-liquid extraction (Holmes and Karr, 1987). Therefore, it is important to develop new high efficiency packings for liquid-liquid extraction service.

Many papers have been published on the hydrodynamics and mass transfer of packed extraction columns (Mackowiak et al., 1986, Seibert et al., 1987). However, most of the mass transfer data are based on the plug flow model. Axial mixing data for new

packings are still scarce, though their influence on extraction efficiency is critical. Thus, it is still difficult to design a commercial extraction column with confidence.

EXPERIMENTS AND DATA PROCESSING

The experimental column comprised a 0.10m (I.D.) flanged glass section with packing up to 1.0m height. The distributor for dispersed phase was located at about 0.15m below the packing support and had 19 holes of 3mm in diameter.

The geometrical characteristics of the packings studied in this paper are listed in Table 1. The SMR (or QH-1) are newly developed short rings with elaborate geometrical design to meet the needs of liquid-liquid extraction service (Fei et al., 1991). The small height-diameter ratio (about 0.3) ensures that the most of rings orient themselves at less than 30° from the horizontal in the column. The SMR has no flange and is divided into 4 spaces by three inside arc strips (Fig.1). These features of the new packing could enhance the dispersion-coalescence recycle and control the non-ideal flow of the two phases in the packing bed and therefore increase its capacity and efficiency.

TABLE 1
The geometric characteristics of the packings

packings	nominal size (mm)	bed gravity (kg / m ³)	specific area (m ² / m ³)	voidage (%)
Pall ring	16	615	239	92.8
Pall ring	25	427	219	94.6
Intalox	25	316	185	96.0
SMR	16	604	348	92.3
SMR	25	506	228	93.6
Mellapac	700y	395	700	95.0

TABLE 2
Physical properties of the test systems (20°C)

systems	ρ_x (kg / m ³)	ρ_y (kg / m ³)	μ_x (mPa · s)	μ_y (mPa · s)	γ (mN · m)	D_x (m ² / s)	D_y (m ² / s)
1	988	825	1.45	3.41	1.50	0.23	0.56
2	998	837	1.14	2.07	10.8	0.77	1.02

system 1--butanol / succinic acid / water; system 2--30% TBP / acetic acid / water

The n-butanol / succinic acid / water system of low interfacial tension and 30% TBP(kerosene) / acetic acid / water system of middle interfacial tension were used for simulating several industrial solvent extraction systems. The properties of the systems are listed in Table 2.

The equilibrium distributions of the systems at 20°C are:

$$C_y = 1.085C_x - 0.849 \times 10^{-3}C_x^2 - 0.162 \times 10^{-4}C_x^3 \quad (\text{system 1})$$

$$C_y = 0.657C_x - 0.357C_x^2 \quad (\text{system 2})$$

A data collecting and processing system consisted of two optical fibre probe chromometers (model PC-801) and a microcomputer. The unsteady state tracer method for measuring the axial mixing parameters based on the dispersion model was used (Misek and Rod, 1971). Using two probes in the column, the residence time distribution curves could be recorded. The least square fitting method in the time domain was applied to estimate the continuous phase axial mixing coefficients under both single and two phase flow conditions (Yang et al., 1982).

During the mass transfer experiments, the solutes were transferred from the continuous aqueous phase to the dispersed organic phase. Eight pairs of samplers were arranged along the column. The samplers for aqueous phase are stainless steel needles. As to the samplers for the dispersed phase, organic wetted polyethylene cups are attached to needles to obtain organic samples free from water. The acid concentrations of samples were analysed by an automatic digital titration system (model DTS-831, Radiometer Co, Denmark). The mass transfer and axial mixing parameters were evaluated from the measured solute concentration profiles based on the backflow model, using the Ricker-King algorithm, the maximum likelihood objective function and the Marquardt's optimization procedure (Rod, Fei and Hanson, 1983).

RESULTS AND DISCUSSION

Comparison of Single Phase Axial Mixing Coefficients

The measurement of continuous phase axial mixing coefficients from the residence time distribution curves for five kinds of packing were carried out under single phase (water) flow condition. Representative results are shown in Fig.2. The axial mixing coefficients of the 16mm SMR packing are the lowest among the packings. The axial mixing coefficients of the 25mm SMR packing are slightly higher than those of the 16mm SMR packing, but are still much lower than the others.

The Axial Mixing Coefficients under Two Phase Countercurrent Flow

Since the hydrodynamics of the two phase flow are different from those of the single phase flow, it is essential to measure the axial mixing coefficients under the real operation conditions. Fig.3 shows that the continuous phase axial mixing coefficients of two phase flow are much higher than those of single phase flow under the same flowrates of continuous phase. It is unwise, therefore, to use the single phase axial mixing

parameters for the scale-up of packed columns.

The Comparison of HTU_{oxp} of Different Packings

The apparent heights of transfer unit (HTU_{oxp}) were estimated from inlet and outlet concentrations of the two phases. The comparison of the HTU_{oxp} among packings are shown in Fig.4 and Fig.5. It is clear that for the Intalox saddles, their HTU_{oxp} is the highest among the packings tested with system 1 (i.e. the mass transfer efficiency of Intalox is the lowest one). Extensive coalescence of small droplets occurs under its flanges. The Mellapac did not perform as well as in distillation service. It is observed from the experiments that many droplets adhered to the packing surface and some film flow of the dispersed phase was formed. It is evident from Fig.5 that HTU_{oxp} values of SMR are the lowest for system 2, this was also found to be the case for system 1. The smaller the nominal diameter of the SMR, the higher the mass transfer efficiency.

The "True" Height of Transfer Units HTU_{ox}

The mass transfer and axial mixing parameters of the 25 mm SMR were simultaneously estimated from the measured concentration profiles. According to Miyauchi and Vermeulen (1963), the relationship among the "true", apparent and dispersion height of transfer unit is as follows:

$$HTU_{oxp} = HTU_{ox} + HTU_{oxd}$$

It is clear from the results that axial mixing is still important for packed extraction columns, especially for the low interfacial tension system (Fig.6).

The "True" Overall Mass Transfer Coefficients

In several experimental runs, the concentration profiles of both phases, drop size distribution and dispersed phase hold-up were measured simultaneously. The "true" overall mass transfer coefficients could consequently be calculated. A comparison between the experimental results and predicted values using different models was made and the modified oscillating drop model (Blass et al., 1986, Sherwood et al., 1975) seems to fit the results reasonably (Table 3). The experimental mass transfer coefficients (K_{oy}) are in the same range as single drop mass transfer data for regular packing arrays (Bahmanyar and Slater, 1990).

APPLICATION OF SMR

In order to use the SMR for revamp and new design of commercial packed extraction

columns, a reasonable design approach has been worked out as follows: the flooding velocities, mean drop size, hold-up of the dispersed phase and axial mixing coefficients are calculated with correlations proposed by the authors (Fang, 1990, Mao, 1992; Zhang et al., 1987, Wen et al., 1992) while the "true" mass transfer coefficients are estimated by the methods mentioned in this paper.

More than 10 SMR packed columns have been put into operation successfully since 1990. They are used for lube-oil refining, heavy aromatic extraction and stripping, waste water treatment etc. The largest SMR packed column in operation is 2.6m in diameter. The excellent performance of these commercial columns has demonstrated the superior characteristics and the reasonable scale-up approaches for the SMR.

CONCLUSION

The SMR (QH-1) packings have superior characteristics for liquid-liquid extraction. Its axial mixing is lowest while mass transfer efficiency is the highest among the packings tested in this paper.

Axial mixing is still important for packed extraction columns. The axial mixing data under the two phase flow conditions should be used for design purposes.

The "true" mass transfer coefficients of the SMR could be evaluated using the modified oscillating drop model.

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TABLE 3
 "True" mass transfer coefficients (system 2)

Run No.	U_x (mm/s)	U_y (mm/s)	Φ (%)	d_{32} (mm)	$(K_{ox})_{exp}$ $\times 10^3$ (l/s)	α_x	α_y	$(K_{oy})_{exp}$ (μ m/s)	$(K_{oy})_{cal}$ (μ m/s)
1	4.95	2.12	6.11	2.30	2.37	3.99	0.00	24.8	23.4
2	4.95	2.83	8.85	2.20	3.32	3.13	0.00	22.9	22.1
3	4.95	3.54	11.7	2.25	3.90	3.27	0.00	20.8	21.3
4	4.95	4.24	16.7	2.35	4.64	1.91	0.05	18.1	18.7
5	4.95	4.95	21.5	2.31	5.56	0.76	0.02	16.6	17.6
6	4.95	2.83	9.23	2.21	3.52	2.09	0.00	23.4	21.4
7	4.95	3.54	12.2	2.22	4.60	4.70	0.00	23.1	20.6
8	3.54	2.83	8.63	2.17	2.66	3.35	0.00	18.6	21.8
9	4.24	2.83	8.85	2.15	2.82	3.71	0.00	19.0	21.9
10	4.95	2.83	8.81	2.30	2.60	3.14	0.00	18.8	22.1
11	5.66	2.83	10.0	2.40	2.69	4.03	0.00	17.9	20.4
12	6.37	2.83	10.4	2.38	2.86	3.50	0.00	18.2	20.3
13	1.77	3.54	10.3	2.19	4.16	5.44	0.00	26.8	21.5
14	2.83	4.24	14.7	2.28	5.16	4.05	0.00	22.2	19.2

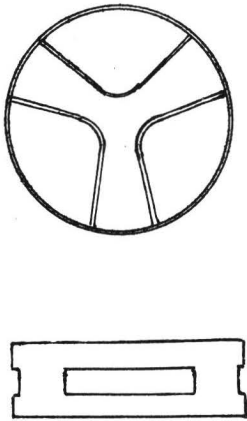


Fig.1 SMR packing

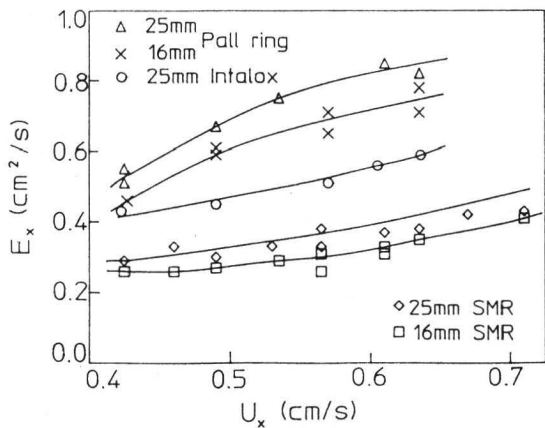


Fig.2 The comparison of axial mixing coefficients for different packings

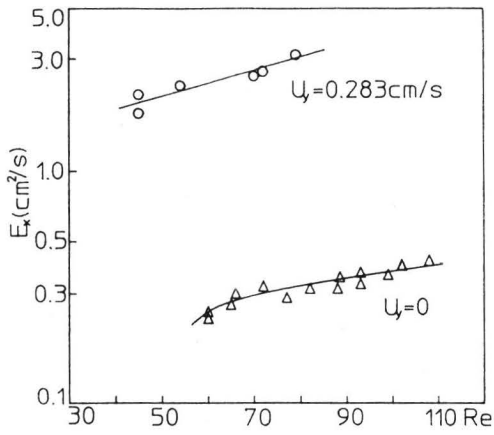


Fig.3 The comparison of axial mixing coefficients under single phase and two phase countercurrent flow without mass transfer (16 mm SMR)

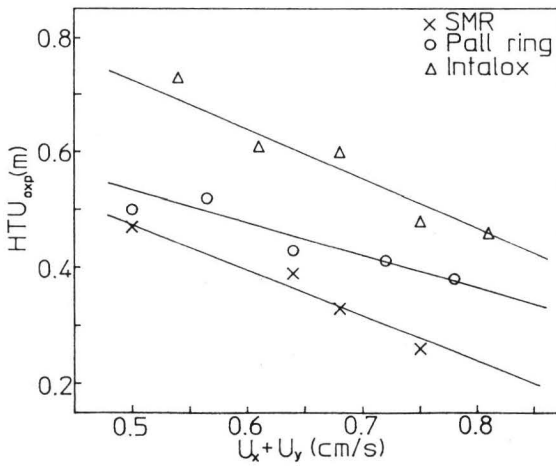


Fig.4 The comparison of HTU_{oxp} of different packings (system 1, 25 mm packings)

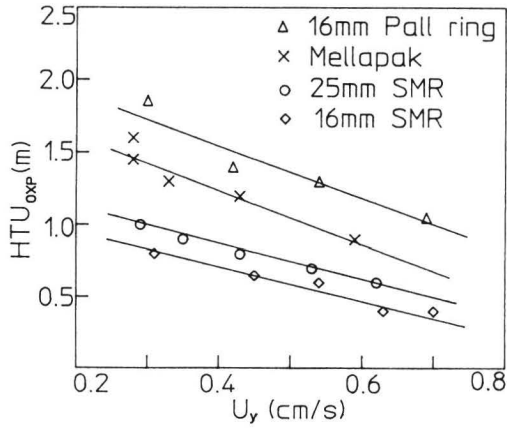


Fig.5 The comparison of HTU_{oxp} (system 2, $U_x = 0.32$ cm / s)

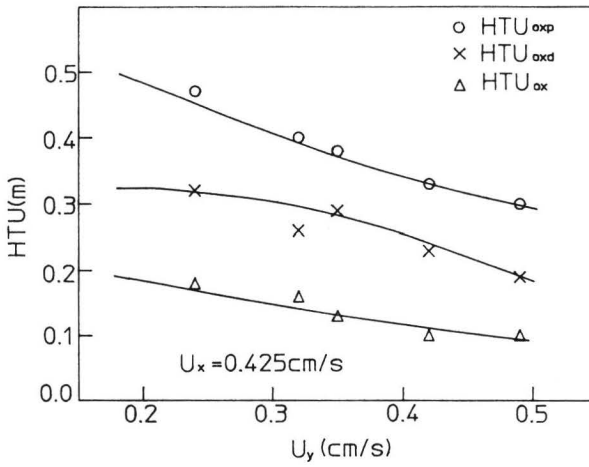


Fig.6 The Height of Transfer Unit (system 1, 25 mm SMR)

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MIXER-SETTLER EFFICIENCY IN DEHPA-EXTRACTION OF ZINC

L. STEINER, P. KENEZ and S. HARTLAND

Swiss Federal Institute of Technology
Dept. of Industrial and Engineering Chemistry
8092 Zürich, Switzerland

ABSTRACT

A novel type of compact mixer-settler has been developed to reduce the residence time to the minimum required by the process but virtually eliminating the time required to separate the phases. A small mixing chamber is incorporated into the lower part of a cylindrical settler, the pump-mixer discharging a rapid stream of the mixed phases into a coalescer, increasing its drop size considerably. Complete separation of the phases is achieved on the main interface in the middle of the settler, both phases being circulated back into the mixer. Runs with several test systems proved that the unit works with good mass transfer efficiency and short separation time.

INTRODUCTION

Mixer-settlers are characterised by long residence times which are necessary in many hydrometallurgical processes. Testing the performance of an apparatus consisting of several mixing stages is therefore time consuming, stabilisation of the operating conditions requiring frequently days and nights of continuous operation. The volume of the settlers being much larger than that of the mixers, most of the stabilisation time is lost for settling which does not contribute very much to the actual mass transfer process and may, therefore, be reduced by construction means without affecting the actual extraction. A novel apparatus has been developed to reduce the settling time by incorporating a small mixer into the settling chamber and providing means for a rapid circulation of both phases. The settling rate is enhanced by a coalescer so only a thin two-phase layer forms on the main interface.

Though a test with a nonreacting system (such as water, toluene and acetone) is useful, a proper evaluation of the performance requires a hydrometallurgical test system. In accordance with a proposal of the European Federation of Chemical Engineers zinc extraction by bis(2-ethylhexyl) phosphoric acid (DEHPA) has been used for this purpose. Unfortunately, the

behaviour of this system has not been investigated in full detail, especially in the region of higher concentrations. Both the equilibrium constant and the kinetics need further experimental work under conditions found in the industrial equipment.

THE APPARATUS

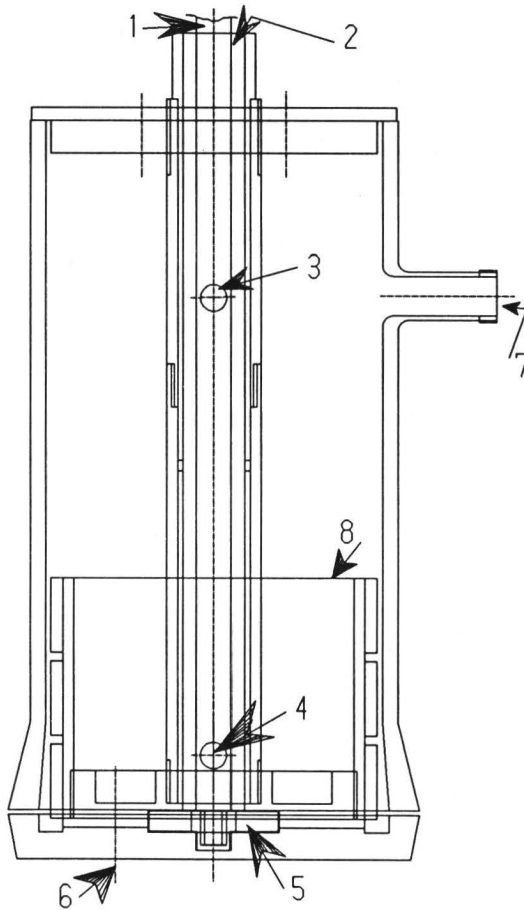


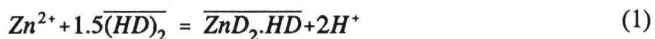
Figure 1: Compact Mixer-Settler: 1-Shaft, 2-Inlet of both phases, 3-Circulation, light phase, 4-Circulation, heavy phase, 5-Mixing chamber, 6-Outlet, heavy phase, 7-Outlet, light phase, 8-Coalescer.

A pilot-plant sized unit with a diameter of 150 mm and a height of 400 mm has been constructed as shown in Fig. 1. The main interface is maintained about 20 mm above the

upper level of the coalescer by an external overflow device, the level of the light phase being determined by the position of the outlet tube. A turbine agitator with a diameter of 60 mm in a tight casing in the lower part of the apparatus forms an efficient centrifugal pump. The agitator shaft is placed in a dual wall tube with circulation openings for both phases which may be independently opened or closed. The agitator discharges a mixture of both phases through four radial channels into the coalescer in the form of teflon ribs on the surface of a cylinder in the lower part of the settler. The mixture leaves the coalescer and proceeds to the main interface where the phases are completely separated. The circulation speeds being at least an order of magnitude higher than the phase throughputs, the concentrations in both liquid volumes inside the apparatus are nearly constant. The speed of agitation, circulation rates, phase throughputs and the position of the interface are independently controlled. The apparatus has been built into a common supply system with tanks and flow controls. Working with the DEHPA-system required an additional circuit with a small pump and a rotameter to maintain the pH value constant by continuously injecting an ammonium hydroxide solution into the mixing chamber. Additional small circulation circuits with peristaltic pumps transported the liquids into a sampling device and (in water phase) to a cell for pH measurement. Parts of these streams were directed into test tubes arranged on a revolving plate so that mean samples of both phases in 1 to 5 minute intervals were available, the sampling delay being few seconds only. The analysis was performed by standard methods on an atomic absorption spectrometer (SpectrAA-20 by Varian).

SYSTEM ZINC-DEHPA

The equilibrium between zinc in sulphate media and bis(2-ethylhexyl) phosphoric acid has been studied by Huang and Juang (1986) who found that the over-all stoichiometric equation is



Accordingly, DEHPA (abbreviated HD in the equations) is dimerised in kerosene solutions and the zinc complex contains one monomer molecule of HD. The equilibrium constant is then defined by eq. (2), its value being $0.00945 \text{ M}^{0.5}$. The concentration of the complex on the right hand side may be replaced by the measurable concentration of zinc in the organic phase and the concentration of free DEHPA in the denominator may be calculated from its

known original concentration and the concentration of zinc in the organic phase, i.e. $[(HD)_2] = [(HD)_2]_0 - 1.5[Zn]$.

$$K_{eq} = \frac{[ZnD_2 \cdot HD] \cdot [H^+]^2}{[Zn^{2+}] \cdot [(HD)_2]^{1.5}} \quad (2)$$

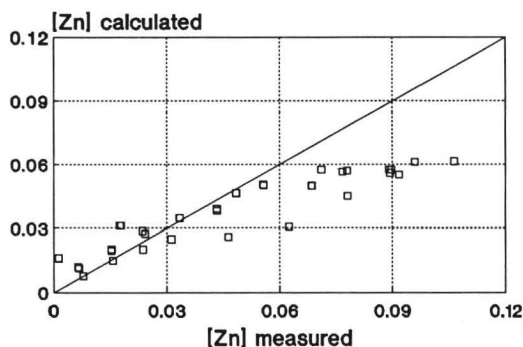


Figure 2: Comparison of Eq. (2) with experimental data of Xing (1991). Concentrations in mol/l, ca 10% DEHPA in kerosene.

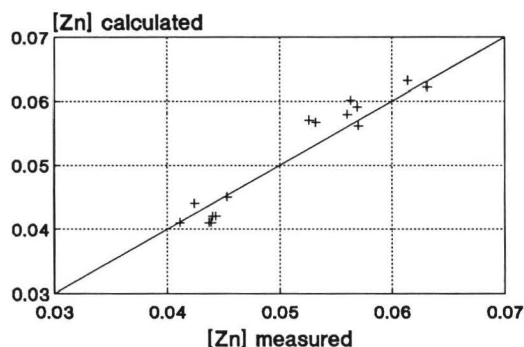


Figure 3: Comparison of eq.(2) to own data. Low Zn concentrations.

Checking the equation on data measured by Xing (1991) we found that eq. (2) is applicable in the region of low DEHPA saturation. The results shown in Fig. 2 indicate that with about 10% solutions of DEHPA in kerosene (corresponding to ca 0.28 mol/L of the dimer) the equation is applicable up to saturation of about 0.06 mol/L Zn.

A computer program has been written to calculate the distribution factor from eq. (2) taking into consideration the variable concentration of the free DEHPA. The ratio of zinc concentrations in organic and water phases was then calculated by iteration using Newton's method. The variability of the composition of the Zn-DEHPA complex has been further confirmed by measuring the maximum possible loading of DEHPA with zinc. Working with 0.28 mol/L of dimerised

DEHPA the maximum measured Zn concentrations were close to 19 g/L (=0.296 mol/L) which is slightly more than would correspond to the composition of ZnD_2 . It is possible that under these conditions some zinc dissolves physically. In this work we evaluated the equilibrium concentrations for all experiments experimentally, stopping the phase flows after

reaching the steady-state and taking samples after further 30 minutes of agitation. However, working with low zinc concentrations and low saturation of the DEHPA, eq. (2) proved suitable.

EFFICIENCY

In the steady-state operation the efficiency is defined by the common formula:

$$E = \frac{c_{in} - c_{out}}{c_{in} - c_{eq}} \quad (3)$$

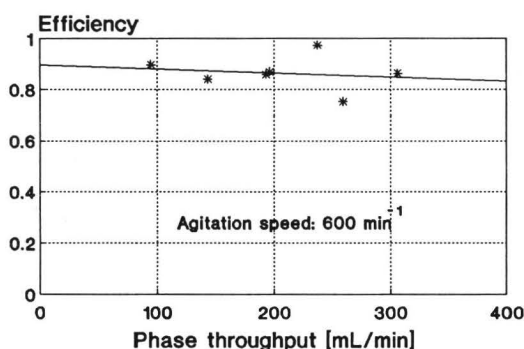


Figure 4: Influence of total phase throughput on efficiency. Steady-state method.

The measured values were between 80 and 100 % which is comparable to other types of mixer-settler. In the example in Fig.4 the efficiency decreases with the phase throughput (as expected). The total volume of the apparatus being 4000 mL, the mean residence time with a throughput of 300 mL/min was about 13.3 min. A comparable time would be necessary to approach the equilibrium in a large

mixer of the same volume. The advantage of our apparatus is that both reaction and complete phase separation are obtained in this time. Huang and Juang investigated the kinetics of the zinc extraction and found the interfacial transfer to be the controlling step. This is in agreement with our finding that the efficiency is improved by increasing the speed of agitation. With 900 min⁻¹ and 200 mL/min the efficiency of 98 % was measured. The output concentration was extremely sensitive to pH which had to be controlled to two decimal places to have reproducible results.

An unsteady-state method for determination of mixer efficiency was proposed by Wichterlová and Rod (1991) and improved by Weiss (1992). Both external flows are recirculated from outlet back to inlet and in a given time a short impulse of the solute is introduced into both phases respectively. The concentrations are measured at regular intervals and plotted in normalised form ($c^* = (c_w - c)/(c_w - c_0)$) against the time. The efficiency is then a function of mean residence times in both phases, the extraction factor and the areas between the

normalised curves for both phases. The distribution factor should be constant which, for the given system, is true only for very small concentration changes. We performed numerous efficiency measurements by this method, monitoring the concentrations in 2 min intervals. The results were comparable to or slightly higher than those obtained conventionally but the scatter was larger and the reproducibility poorer. Requiring only a short impulse of the solute (rather than stabilising a steady-state regime), the method has an advantage for investigation of production-scale units. In a pilot-plant scale the disadvantages such as multiplying the number of the analytical samples and increasing the scatter of the results prevail.

SIMULATION

A computer program for predicting the approach to equilibrium for a mixer with the volume equal to the total volume of our apparatus was written. The equilibrium being described by eq. (2) and with non-negligible change in the free DEHPA concentration the following differential equations had been solved by the Runge-Kutta method:

$$\frac{d\bar{c}}{dt} = \frac{\frac{K_{eq}}{[H^+]^2} \left([(HD)_2]_0 - \frac{3}{2}\bar{c} \right)^{3/2}}{1 + \frac{9}{4} \frac{K_{eq}c}{[H^+]^2} \left([(HD)_2]_0 - \frac{3}{2}\bar{c} \right)^{1/2}} \frac{dc}{dt} \quad (4)$$

and

$$\frac{dc}{dt} = \frac{1}{V} \left[Q(c_{in} - c) + \bar{Q}(\bar{c}_{in} - \bar{c}) - V \frac{d\bar{c}}{dt} \right] \quad (5)$$

The set is solved from initial values at time $t=0$ when the zinc concentrations in both phases are zero, the initial value of dc/dt being evaluated from eq.(2). The program is easily modified for efficiencies lower than 100 %.

A comparison of measured data to model predictions in Fig. 5 demonstrates a good agreement of steady-state concentrations. The transient period is slightly longer, especially in the water phase, which is explained by slower circulation between the mixer and the settler. The model assumes uniform concentrations in both phase volumes, since it is developed for a perfectly mixed stage with the volume equal to the total volume of the apparatus. In our case the mixing in the settlers is determined by the circulation rate which may be adjusted within broad limits. The experiment shown in Fig. 5 was carried out with

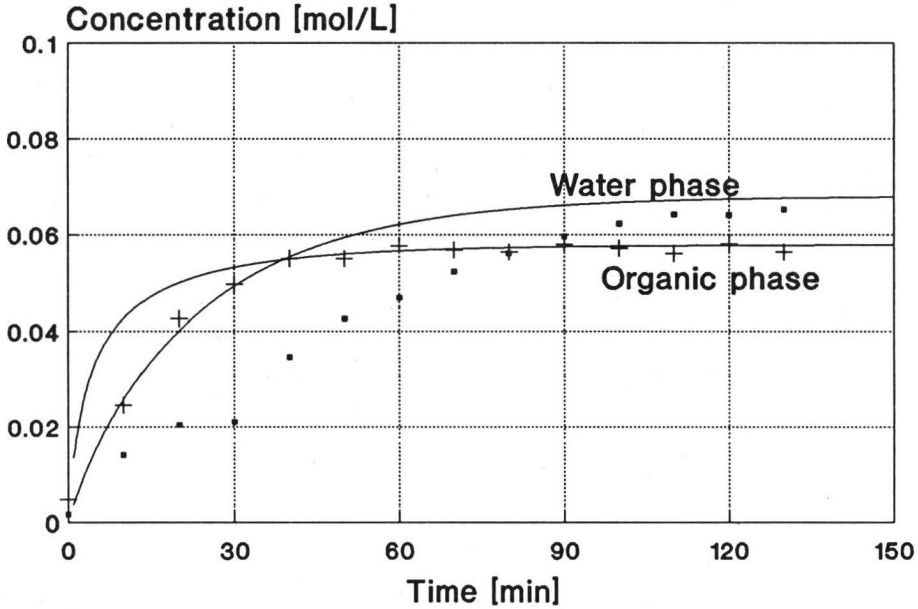


Figure 5: Comparison of simulated approach to steady state to experimental data. Agitation speed 900 min^{-1} , 120 mL/min . Circulation valve in water phase half closed.

the control valve in the organic phase fully open and the one in the water phase half closed. The measured points in the organic phase (marked by + in Fig. 5) are much closer to the predicted curve than the ones in the water phase (marked by ■). A special model taking into consideration the limited circulation rates is being developed.

CONCLUSIONS

Introducing a rapid circulation and an efficient coalescer into a compact mixer-settler apparatus reduces the residence time to a value comparable to that which would be necessary in a large mixer of the same volume from which, however, the phases would exit as a fine dispersion. The construction described guarantees a good phase separation in the same time. The system of zinc - DEHPA in kerosene - water is suitable for testing extraction equipment, the equilibrium at lower zinc concentration and low saturation of the organic phase is well described by the equation (2) of Huang and Juang. The measured exit concentration may be predicted by simulation assuming a single, well mixed stage with limited transfer rate.

NOMENCLATURE

E	Efficiency, def. by eq. (3)	indices:	
c	volumetric concentration [mol/L]	in	inlet
t	time [s]	out	outlet
V	volume [L]	eq	equilibrium
Q	volumetric throughput [L/s]	0	at zero time

The bar denotes property in organic phase.

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1.7

MIXER-SETTLER BASED ON PHASE INVERSION

D. HADJIEV, Y. AURELLE, G. CASAMATTA¹, C. GOURDON¹

Institut National des Sciences Appliquées, Département du Génie
des Procédés, Complexe Scientifique de Rangueil, 31077 Toulouse
Cedex, FRANCE

¹Ecole Nationale Supérieure d'Ingénieurs de Génie Chimique,
Chemin de la Loge, 31078 Toulouse Cedex, FRANCE

ABSTRACT

A new type of mixer-settler unit where coalescence is promoted by means of the phase inversion method is developed. Using alkaline etching solution and LIX 54 as extractant the influence of the intensity of mixing, the total flowrate and the hydrodynamic conditions upon the extraction and separation efficiencies is studied. A comparison between mixer-settlers with classic decanters and those based on phase inversion has clearly outlined the advantages of the latter where throughputs in the range 20 - 25 m³/m²h can be easily achieved.

INTRODUCTION

For many years, in the early development of solvent extraction as a unit process in hydrometallurgy, relatively few types of contactors were in use, and not many more were available. However, as a result of increasing use of solvent extraction processing the number and types of contactors have greatly increased. Major emphasis in the development of new equipment has been to increase throughput while maintaining efficiency, and also to increase efficiency without reduction of throughput Treybal (1963), Mattila (1974), Ritcey (1979).

The physical aspects of solvent extraction are primarily concerned with the dispersion of the two phases on mixing, the type of droplet formation, and the rate and completeness of phase disengagement or coalescence. Thus, these are important factors in the choice of suitable contacting equipment and the design and operation of the plant.

Over the past twenty years mixer-settlers have been widely used in hydrometallurgy and

many designs have been proposed with the general aim to decrease the area required while maintaining high throughput and efficiency. As is known, the rate of mass transfer across a phase boundary is a function, amongst other variables, of the drop size distribution or interfacial area between the phases. Up to a point, the smaller the drop-size the greater the rate of mass transfer. Coupled with increasing dispersion however, is increased coalescence time required, and therefore the settler size which becomes the critical factor in mixer-settler design. The size is governed by the throughput limitations imposed by the rate of coalescence of the dispersed phase. As settling problems related to solvent loss and/or entrainment were shown to be a major cost factor in the design, attempts have been made to increase the settling rate and therefore throughput, resulting in an increase in the overall economy Ritcey (1979). Finally in order to achieve good overall settling velocity together with good flexibility the settler has been found to require design with respect to such as trays or coalescing devices. Thus the rate of coalescence is increased by shortening the distance between the droplets and the interface or by increasing the drop-size which strongly affects velocity according to Stokes' law:

$$V_d = (\rho g d^2) / 18 \mu_c \quad (1)$$

indicating different parameters able to be varied in order to increase the rise velocity (V_d).

Usually the dispersed phase flows from the mixer into the settler as an emulsion band over the area of the interface. The thickness of this band characterizes the flow capacity of the settler and it increases exponentially with increasing flow. One attempt to increase the settling rate is the phase inversion method Hadjiev (1985, 1989), Aurelle (1990).

The mode of operation of a settler based on this principle, designed to separate an organic

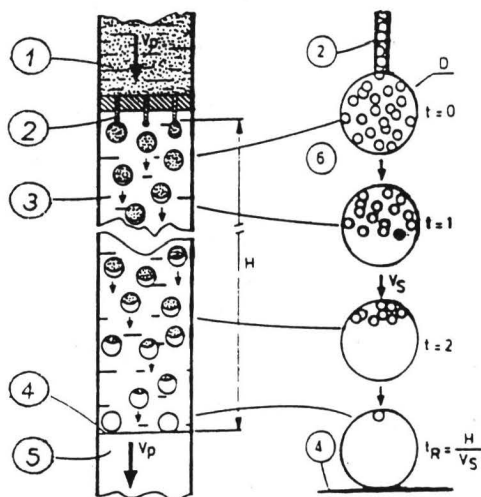


Fig. 1 Phase inversion principle

phase lighter than the aqueous one is given in Fig.1. Phase inversion can be easily realized by transforming the initial continuous phase (1) into drops (6) which are far larger than the droplets in the primary dispersion. For these purposes the mixture of both phases is forced through a perforated plate or another kind of dispersion device (2), and the drops are generated directly in an organic band (3), identical to the initial dispersed phase. During the movement through this layer these "carrier"

drops liberate the so called "carried" droplets. The latter tend to ascend in the carrier drop in the direction opposite to its movement and are concentrated in the upper part where coalescence takes place. The non-liberated droplets are released near the interface (4). As the results obtained have shown the advantages of the settlers based on phase inversion over ordinary settler units, our objective was therefore to design a new mixer-settler where coalescence is promoted by means of this method.

EXPERIMENTAL

Fig. 2 is a schematic diagram of the mixer settler. Both phases enter the mixing impeller (1) via a tube in the bottom of the mixing chamber (2). Mixing occurs in the impeller, which is a

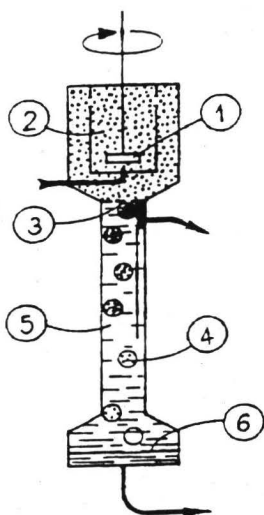


Fig 2. Diagram of the mixer-settler

four blade turbine designed to minimize the formation by shear of very fine droplets. These slow-settling droplets are the major cause of haze in the settler, giving rise to high organic losses in the raffinate. The mixed phases enter into the upper part of the settler and flow through the dispersion plate (3). The secondary drops (4) containing the fine droplets move through the organic band (5). During travel to the interface (6) part of them are separated. After coalescence on (6) the rest of the fine droplets are released near the interface and removed by simple decantation.

A diagram of the experimental facility is shown in Fig. 3. Both phases are forced through the mixer by means of centrifugal pumps (1, 2). The mixing chamber (3) is a glass tube 50 mm in diameter and 70 mm in height. The mixer impeller (4) 30 mm in

diameter is provided with a driving motor which allows a smooth increase in the impeller speed. Continuous phase flowrate is controlled by valve (5) and measured by the flowmeter (6). The extractant coming from tank (7) is pumped into the mixer after controlling and measuring (8, 9) its flowrate. The settling zone (10) is a glass tube 50 mm in diameter and 500 mm in height provided with a dispersion device (a perforated plate made of Teflon). The latter allows variations of the free surface and opening diameter. After separation both phases leave the device through the exits (11, 12).

The characteristics of the mixer-settler were studied using an industrial alkaline etching solution and LIX 54 as extractant. The initial copper concentration in the aqueous phase was 7 - 15 g/l copper and the pH - 9-10. The organic phase used was a 60% solution of the extrac-

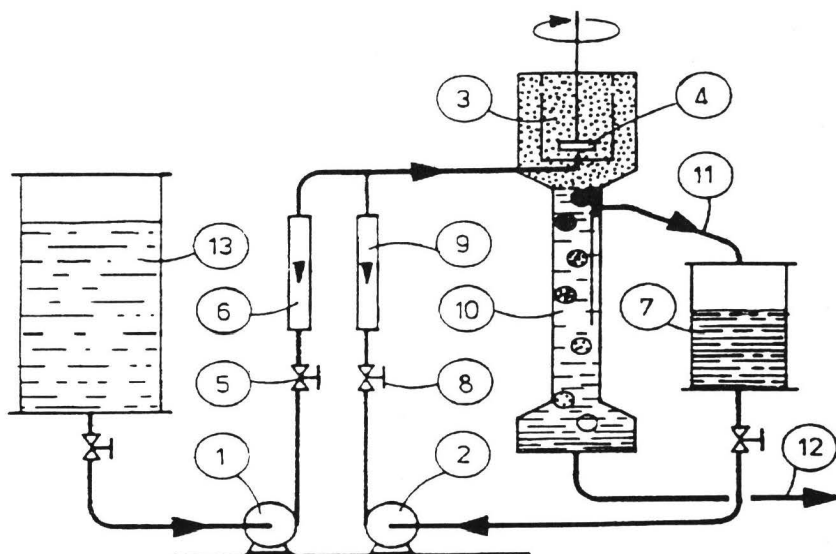


Fig 3. Scheme of the experimental installation

tant in kerosene. The analysis for the copper concentrations in the feed and raffinate solutions were performed on an AAS-3 spectrophotometer. Preliminary studies have shown the influence of pH, concentration of the extractant, initial copper content and Cl^- concentration upon the equilibrium in the system. Using the least-square method an equation has been determined which describes the equilibrium data within the experimental precision, and it was used to calculate the equilibrium copper concentration in the organic phase C^*_{org} . The extraction efficiency was then computed:

$$E = C^*_{\text{org}} / C_{\text{org}}$$

The quantity of entrained organic phase was determined using a standard CDO (Chemical Oxygen Demand) method - after boiling with 0,25 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of sulphuric acid and titration with 0,25 M solution of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The hold-up in the settling zone ($v_c/v_d + v_c$) was measured and the slip velocity ($V_{\text{slip}} = V_d + V_c$) in the latter zone was calculated according to Perrut (1972).

RESULTS

The influence of the intensity of mixing upon the extraction efficiency is shown in Fig. 4. The experiments are carried out at : feed concentrations - 7,8-14,3 g/l copper, phase ratio - aqueous to organic phase - 10:1 and total flowrate of 0,026 m^3/h . As can be seen, an important influence of this parameter on the extraction rate is observed at low mixing intensities -

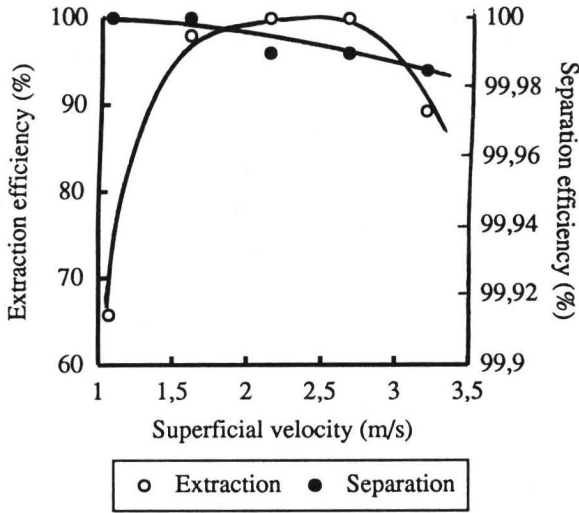


Fig. 4 Influence of intensity of mixing upon the extraction/separation efficiencies

below 1,5 m/s. From 1,5 up to 2,8 m/s the superficial velocity of mixing does not influence the extraction. Further increase in intensity decreases the extraction efficiency because of the formation of very fine droplets disturbing the mass-transfer between the phases. On increasing dispersion however, the entrainment of organic phase is not affected. Even at 3,2 m/s (the drop-size distribution shows at these conditions approximatively 15% of droplets 45 μm in diameter) it does not exceed 0,02% despite the fact that the total flowrate per unit surface is 13,24 $\text{m}^3/\text{m}^2\text{h}$.

Fig. 5 illustrates the influence of the total flow rate upon the extraction efficiency, as well as on the hold up and the relative velocity in the settling zone. The experiments are carried out using the same initial solutions and phase ratio, a superficial velocity of 1,6 m/s and total flowrate from 0,013 to 0,041 m^3/h . The free surface of the dispersion device is 3% and the openings are 1 mm in diameter. From the experimental data two regions can be outlined. The initial increase in flowrate decreases the residence time hence the extraction efficiency. Further increase however, increases this efficiency for a while. Evidently, on increasing the flowrate, the velocity through the nozzles of the scattering device is increased. An intensive internal motion is induced in the carrier drops. The circulations of the small droplets inside the drop accelerate the mass transfer and therefore the extraction process. Coupled with increasing flowrate however, the drop formation time is decreased and therefore a band of non-coalesced carrier drops begins to form near the interface i.e. the hold-up increases. On increasing the depth of the band, the residence time of the falling carrier drops increases, as

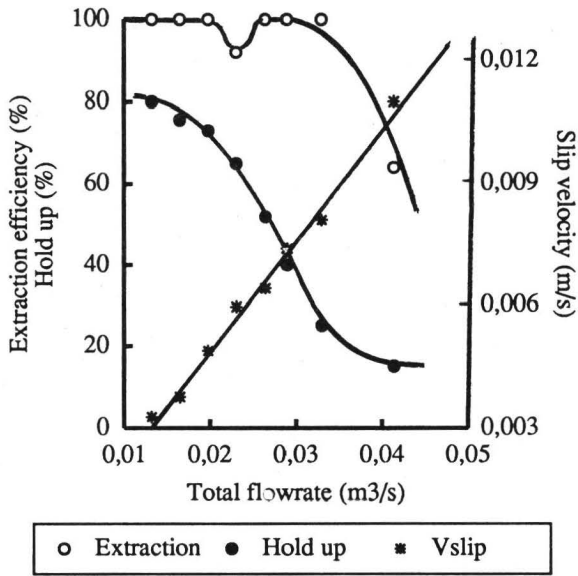


Fig. 5 Influence of the total flowrate upon the extraction efficiency, the hold-up and the slip velocity ($D_n = 1$ mm, $S = 3\%$)

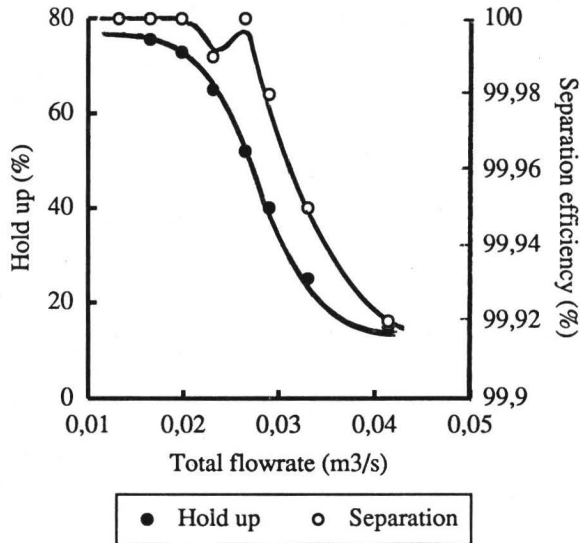


Fig. 6 Influence of the total flowrate upon the separation efficiency and the hold-up in the settling zone ($D_n = 1$ mm, $S = 3\%$)

well as the slip velocity between the phases. These effects compensate the decrease in the residence time in the mixer chamber and maintain the extraction efficiency relatively high. Further increase in the flowrate however, leads to less important changes in the hold-up and shorten considerably the residence time in the mixer and subsequently a decrease in the extraction efficiency is observed. The importance of these phenomena is determined by the physical properties of the system (interfacial tension and viscosity of both phases). The formation of this band of non-coalesced drops enhances the phase separation process and the separation efficiency is not altered. It still remains above 99,9% despite the fact that the total flowrate per unit surface has attained $20,88 \text{ m}^3/\text{m}^2\text{h}$ ($F = 0,043 \text{ m}^3/\text{h}$). The results can be seen in Fig. 6.

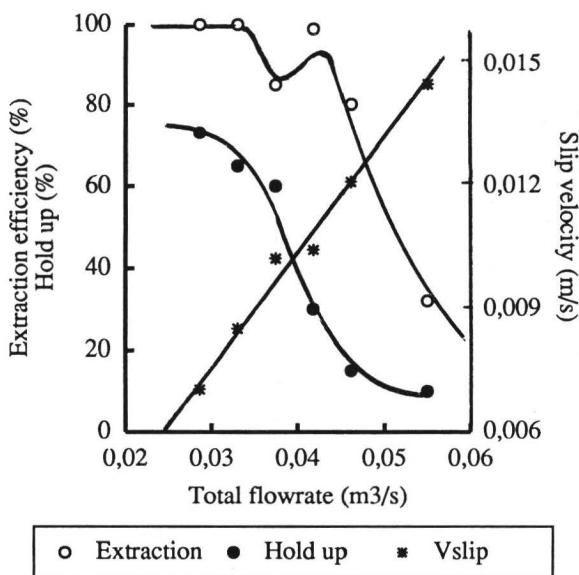


Fig. 7 Influence of the total flowrate upon the extraction efficiency, hold-up and the relative velocity ($D_n = 1,5 \text{ mm}$, $S = 4,5\%$)

The same comportment of the device is observed for other free surfaces or nozzle diameters as shown in Fig. 7 and 8. In all cases two regions are outlined and the increase in the extraction efficiency begins always with the formation of the band of non-coalesced drops. This phenomena can be used to improve throughput while maintaining high efficiency. As can be seen when using a dispersion plate with 8% free surface is used, extraction rate of 100% can be obtained even at $25,68 \text{ m}^3/\text{m}^2\text{h}$ ($F = 0,051 \text{ m}^3/\text{h}$), while maintaining the same separation efficiency of 99,9%.

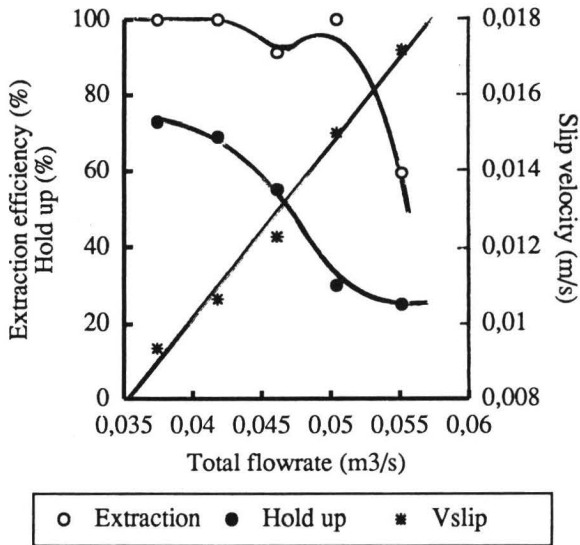


Fig. 8 Influence of the total flowrate upon the extraction efficiency, hold-up and the relative velocity ($D_n = 2 \text{ mm}$, $S = 8 \%$)

CONCLUSION

The results obtained show the advantages of the new type of mixer-settler over ordinary units. It allows one to obtain high efficiency rates in equipment of smaller dimensions. In all cases the unit shows effective separation for throughputs in the range over which coalescing devices show reasonable efficiency. It should be added that if droplets with a mean diameter of $150 \mu\text{m}$ have to be removed and the difference in the density of both phases is about 100 kg/m^3 , the throughput in a drum separator has to be below $4.3 \text{ m}^3/\text{m}^2\text{h}$. In the same conditions a Lurgi Multi-Tray Settler can handle approximately $22 \text{ m}^3/\text{m}^2\text{h}$, the Segmental Circular Settler of Davy Power Gas - approximately $10 \text{ m}^3/\text{m}^2\text{h}$ and the new device - $20\text{-}25 \text{ m}^3/\text{m}^2\text{h}$. It is necessary however to mention that the throughputs can be limited by the rate of coalescence of residual drops on the interface.

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1.8

**INFLUENCE OF THE PACKING GEOMETRY ON THE
FLUID DYNAMICS OF SOLVENT EXTRACTION COLUMNS
WITH STRUCTURED PACKINGS**

J.T. LEU and A. VOGELPOHL

Institut für Thermische Verfahrenstechnik
Technische Universität Clausthal
Leibnizstr. 15, 3392 Clausthal-Zellerfeld, Germany

ABSTRACT

An extensive research programme has been carried out on the fluid dynamics of a pulsed and nonpulsed extraction column with structured packings on a pilot scale. Special emphasis was placed on the fluid dynamic behaviour of the column and its dependence on the packing geometry. The investigations encompassed measurements of the drop size distribution, the hold-up and the flooding throughput. The objective was to establish selection criteria for structured packings as column internals and to improve the basis for the design of this type of extraction column.

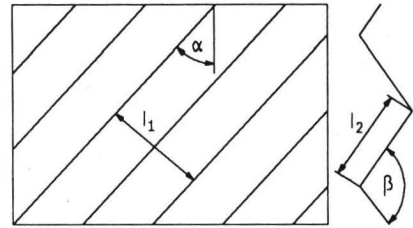
INTRODUCTION

One of the main objectives of the design of multistage extraction columns is to determine the minimum column dimensions to fulfill a specified separation. This has led to an increasing use of structured packings in pulsed and nonpulsed extraction columns as these show several advantages, e.g. a low friction loss and a good separation efficiency due to reduced backmixing. However, since there is only little information about structured packings and their suitability as column internals, the design of this type of column still requires extensive and, therefore, expensive pilot tests. The aim of the work presented here has been to establish selection criteria by exploring the characteristic parameters of the packing geometry and the arrangement of the packing elements within the column. Therefore, extensive measurements of the drop size distribution, the hold-up and the maximum throughput were carried out on a pilot scale as a function of throughput and pulsation intensity.

PACKING GEOMETRIES AND EXPERIMENTAL SET-UP

The geometrical parameters of the packings under investigation differ with respect to the lamella configuration (slantwise corrugated sheet metal or sheet metal grid arranged in

layers), specific surface, various angles and linear dimensions of the lamellae, the element height and punching. Experimental studies were carried out with the standard test system toluene(dispersed)/water, recommended by Misek et al. (1985), with a total of eight combinations of the geometrical parameters as outlined above. This paper is restricted to the presentation of the studies on seven combinations of corrugated sheet metal packings as shown in Fig. 1 and Table 1.



slantwise corrugated sheet metal
arranged in layers

Fig. 1 Lamella configuration

TABLE 1

Geometrical parameters of the corrugated sheet metal packings under investigation

Packing type	Specific surface, m^2/m^3	Lamella angle	Element height, mm	Punching, Hole diameter, mm	Manufacturer
M-S350/A45/H100	350	45°	95	no	Montz
S-S350/A30/H100	350	30°	105	no	Sulzer
M-S250/A45/H100	250	45°	95	no	Montz
M-S500/A45/H100	500	45°	95	no	Montz
S-S350/A45/H200	350	45°	210	no	Sulzer
S-S350/A45/H100/P4	350	45°	105	yes, 4	Sulzer
M-S350/A45/H200/P4	350	45°	190	yes, 4	Montz

In two liquid pulsed pilot columns with a nominal diameter of 150 mm and an active column length of 1 and 3 m, drop size distributions were determined at 6 and 4 positions respectively along the active part. The experimental set-up of the column with an active length of 1 m and the positions of the measuring devices are shown schematically in Fig. 2. The drop size distribution was measured with a photoelectric suction probe (DSD). The integral hold-up was determined over the active length of the column by means of the displacement method. Additionally, an average hold-up was measured over a column section with the differential pressure method (DP) as proposed by Jenkins (1984) and Lorenz (1990). The flooding point was determined by a stepwise increase of the throughput. Flooding, which is characterized by a nonsteady-state behaviour of the column, was recognized by visual observation as well as control of the differential pressure of the individual column sections. At a phase ratio of one, the cumulative load amounted approximately to 40 to 80% of the maximum throughput and the pulsation intensity was varied from 0.0 to 2.5 Hz at a constant pulsation amplitude A_p of 4 mm.

active column length: 1 m

position of measuring devices:

DSD	drop size distribution (photoelectric suction probe)
DP	differential pressure (wet/wet transmitter)
T	temperature (thermocouples)

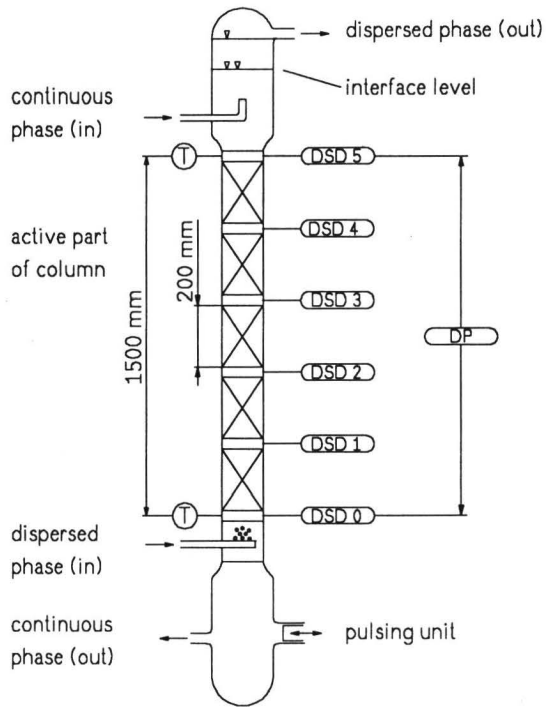


Fig. 2 Experimental set-up

RESULTS AND DISCUSSION

Drop size distribution

As is the case for all extractors, the drop size distribution in each cross section of the column results from the interaction between drop breakage and coalescence. For the system under consideration, coalescence is only of minor importance. Nevertheless, the great obstruction to the drop movement within the packing elements promotes the tendency of the dispersion to coalesce. Therefore, the measured drop size profiles in the nonpulsed column, illustrated in Fig. 3, show more or less constant mean drop diameters over the column length caused by alternate dominance of dispersing and coalescence effects. No significant difference between the seven geometries under investigation can be recognized. Only a slight predominance of drop breakage may be observed for the packing type S-S350/A30/H100. This type is characterized by steeper packing channels and, therefore, by only minor obstruction to the drop movement. The dispersing effect of the packings under investigation is intensified by liquid-pulsation. As the measured drop size profiles in Fig. 3 show, the decrease in the average drop diameter occurs essentially during the passage through the first packing

elements immediately above the distributor. Thereafter, a stable drop size distribution is approached which depends on the dispersing effect of the packing geometry. At a constant pulsation intensity of 15 mm/s, the stable drop size diameter is attained sooner with a higher specific surface of the packing and a smaller element height. With augmented specific surface of the packing, the number of lamellae in the cross section, where drop break-up may occur, increases. This leads to a better dispersing effect of the active part of the column and, therefore, to a smaller mean drop diameter. As shown by motion pictures and single-drop experiments in parallel, breakage mainly occurs during the entry into the packing elements. In consequence, an increase of the element height reduces the dispersing effect of the column and, hence, produces a larger mean drop diameter leaving the active part of the column. Break-up within the packing structure does occur, but is only of minor importance for the stable drop size, unless, as one can observe for the punched packing types, the drops are forced through the holes in the flanks of the packing channels.

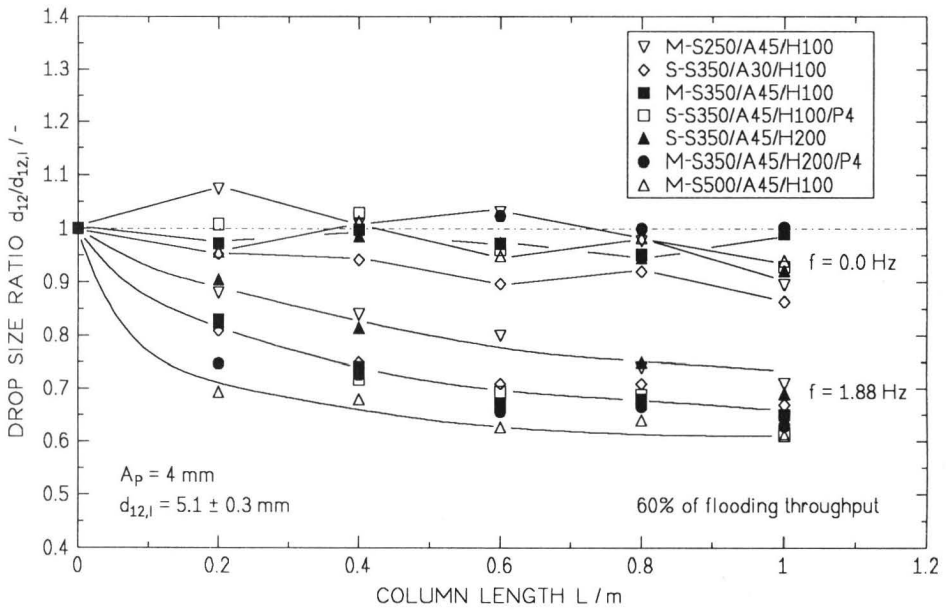


Fig. 3 Sauter mean diameter ratio as a function of column length

The dependence of the drop size established after one meter active column length on the pulsation intensity and the packing geometry is illustrated in the upper part of Fig. 4 (DSD5 position of measuring). Because of the increasing energy input and the associated increase of the forces which destabilize the drops, the Sauter mean diameter decreases with increasing pulsation intensity.

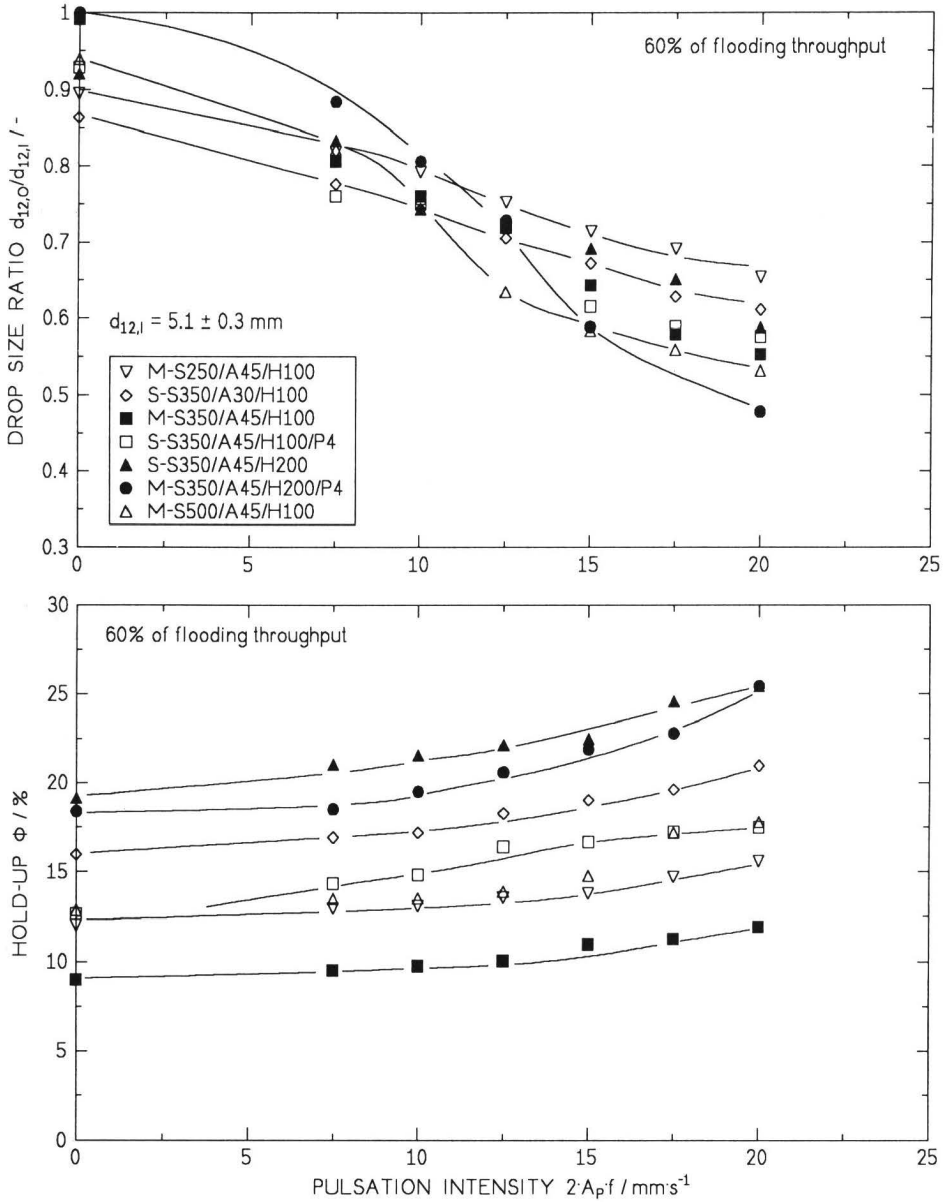


Fig. 4 Sauter mean diameter ratio and integral hold-up as a function of pulsation intensity

Coalescence within the elements has an opposite influence on the drop size. Under nonpulsed condition, as mentioned above, and for small values of the pulsation intensity the drop size is decisively determined by coalescence effects. Since a good dispersing performance is

associated with a high obstruction to the drop movement, the drop size in packings with a high specific surface shows a major dependence on the pulsation intensity. The packing type with an angle of 30° is characterized by a comparatively flat curve due to a smaller tendency of the dispersion to coalesce coupled with a considerable dispersing performance.

Hold-up

The hold-up is directly influenced by the throughput of both phases and by the relative velocity of the drop swarm which depends on the drop size distribution and the retarding effects on the drop motion associated with the pulsation and, decisively, the packing geometry. Under all operating conditions, the local hold-up is more or less constant along the column, although the drop size decreases continuously in the flow direction of the dispersed phase. The larger obstruction to drop movement for bigger drops causes similar relative velocities of drop swarms with different mean drop sizes. The dependence of the total hold-up on the pulsation intensity and the packing geometry is illustrated in the lower part of Fig. 4 for a throughput of about 60% of the flooding load. The curves exhibit an increase of the hold-up associated with a decrease in drop size illustrated in the upper part of Fig. 4. For pulsation intensities below 7.5 mm/s, the hold-up is almost constant for all of the packing types due to the delayed movement of the drops within the packing elements. The considerable differences in the established hold-up of the packing types is mainly caused by the big differences in the actual throughput.

Flooding

The flooding point curves for the packing types measured as a function of pulsation intensity are presented in Fig. 5. For lower values of the pulsation intensity as well as under nonpulsed conditions all of the packings under investigation exhibit a high maximum load. Despite the high obstruction to the drop movement and, therefore, high tendency of drops to coalesce in this operating range, the continual re-dispersing keeps up the flow of the dispersed phase until the countercurrent flow is finally disrupted. It has been found that packing types which provide a good dispersing performance, as those with a high specific surface, yield only a small maximum throughput. In contrast, packings with a small lamella angle, as the one examined with an angle of 30° , provide a high flooding throughput due to a high relative velocity. A very important result of the investigation is illustrated in Fig. 6. Keeping the number of packing elements in the column constant, the maximum cumulative load may be shifted to higher values by providing sufficient space between the individual packing elements. Similar to the influence of plate spacing in sieve-plate columns, the increase of element spacing results in an increase of the average velocity of drop ascent and consequently in a higher flooding point. As shown by the curves in Fig. 6, this phenomenon is far more pronounced for nonpulsed conditions. Beyond a maximum element spacing of about 120 mm no further shift may be observed.

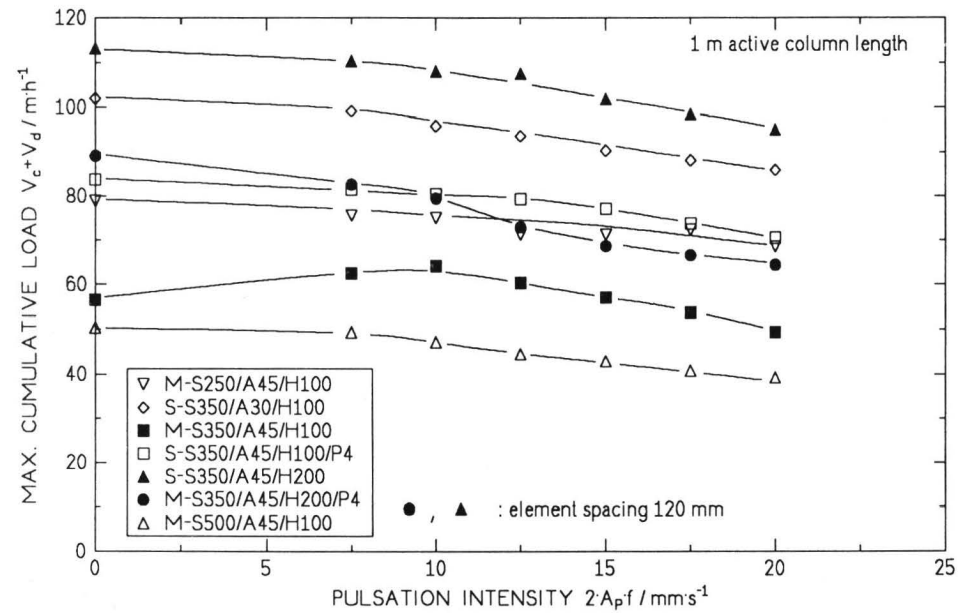


Fig. 5 Flooding throughput as a function of pulsation intensity

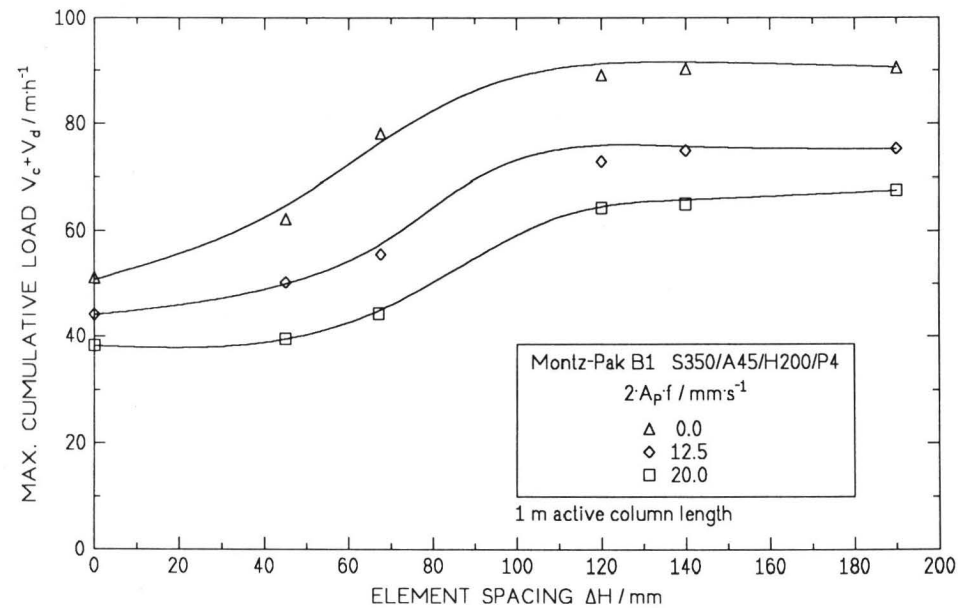


Fig. 6 Shift of flooding throughput and dependence on element spacing

MODELLING

In order to develop a sound scale-up strategy, a model concept has been developed to predict the fluid dynamic behaviour of regularly packed columns on the basis of experimental data from single drop experiments on a laboratory scale. Therefore, single drop experiments have been carried out over a wide range of drop size and pulsation intensity with two different experimental set-ups. On the one hand, the drop break-up rate and the daughter drop distribution have been measured, on the other hand the drop rise velocity has been determined as a function of design of the internals. As a result, drop size distribution profiles in packed columns may be predicted by modelling the repeated break-up within the packing elements. Furthermore, the hold-up of the dispersed phase may be calculated on the basis of the drop swarm velocity derived from the single drop velocity. The computed results are confirmed by experimental data from pilot column studies. The model concept is presented in detail by Haverland (1988), Lorenz (1990), Hoting and Vogelpohl (1993).

CONCLUSIONS

The determination of suitable structured packings in extraction columns is always a matter of optimization because of the partly contradicting influence of the dispersing effect and the obstruction to drop movement. By providing sufficient space between the packing elements, the maximum load may be shifted to higher values which is important for the overall performance of packings with a good dispersing performance.

ACKNOWLEDGEMENTS

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NON-STANDARD NOMENCLATURE

A	abbreviation of ascent angle
d_{12}	Sauter mean diameter (m)
H	height of the packing element (m)
ΔH	element spacing (m)
P	abbreviation of punched lamellae
S	abbreviation of specific surface
α	ascent angle of the packing channel towards the vertical
β	folding angle of the lamellae

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1.9

EXTRACTION DEMONSTRATION TEST OF ANNULAR PULSED COLUMN: II. SYSTEM TEST

T.TSUYUKI, C.TANAKA*, H.SHIMAUCHI*, I.OKADA*, A.IDEGAMI*,
K.KITAMURA*, M.TOMITAKA*, H.KITADE*, F.DRAIN**

Japan Nuclear Fuel Limited.(JNFL)
1-2-10, Hirakawa-cho, Chiyoda-ku, Tokyo, 102 Japan
*Sumitomo Metal Mining Co.,Ltd.(SMM)
2-7-17, Ikenohata, Taitoh-ku, Tokyo, 110 Japan
**Societe Generale Pour Les Techniques Nouvelles(SGN)
1, rue des Herons, Montigny-le-Bretonneux, 78182
Saint-Quentin-en-Yvelines, Cedex, France

ABSTRACT

Performance tests of an extraction system composed of three annular pulsed columns has been carried out in the Extraction Demonstration Test Facility (EDTF) which is the large-scale uranium extraction test facility. The contents of the test are as follows.

- (1)Normal operation test (confirmation of sequential start-up,shutdown and capacity change)
- (2)Disturbed operation test (such as feed flowrate increase, solvent flowrate decrease, acidity decrease of FP scrubbing solution, pulsation and all feeds stopped)

In these tests,operating procedures were established and controllability of the system was confirmed to be satisfactory. These test results will contribute to enhancement of reliability of the reprocessing plant and fixation of the introduced technology in Japan.

INTRODUCTION

Establishment of operating procedures and control methods of the extraction system is important to achieve high availability and enhance reliability of a reprocessing plant. For this purpose, the system test was carried out in EDTF using a simulated Purex HNO_3 -U-30%TBP diluted with n-dodecane system, following the performance test of each annular pulsed column (Tsuyuki,T., 1993, this conference).

The system test consists of normal operation test and disturbed operation test. The former was performed to confirm the operating procedures concerning start-up, shutdown and capacity change. The latter was performed to evaluate the effect of significant disturbances on the process and to examine an early detection method of them and corrective procedures for returning to the normal operation.

This paper briefly describes these test results.

EXPERIMENTAL PROCEDURES

In the system test, three annular pulsed columns (extraction, FP scrubbing, and diluent washing) and their ancillary equipment (vacuum type metering feeding equipment named "gedeon", air lifts so on) were operated together.

In addition, cylindrical pulsed columns and mixer settlers were also operated to recycle test solutions. Fig.1 shows a chemical flowsheet for the system test. Operation of the system was controlled by a distributed control system (DCS).

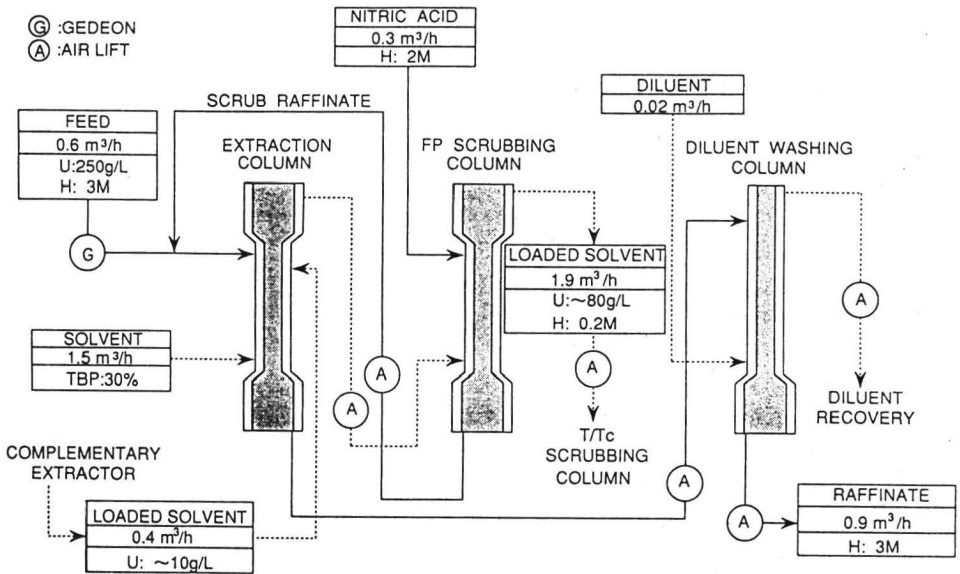


Fig 1 Chemical flowsheet in the system test

NORMAL OPERATION TEST

Start-up and shutdown of the system was carried out according to the sequence programmed in DCS in advance. Main steps of start-up are as follows : pulsation start-up, organic (solvent and diluent) feed to extraction and diluent washing columns and start-up of corresponding air-lifts, scrub solution feed to FP scrubbing column and its withdrawal, main feed (uranyl nitrate) start to extraction column and raffinate withdrawal. The time required to reach steady state was followed by density monitors installed in each column.

Two capacity change procedures (stepwise change and gradual one) were tested within the capacity range from 3.2 to 4.8t/d. In these tests, the set value of each flowrate was changed simultaneously. To determine the capacity range of the system, a low capacity test under 2t/d condition was also conducted.

DISTURBED OPERATION TEST

The following significant disturbances were put into the system at steady state under the normal operating condition.

- Feed flowrate increase by 10%
- Solvent flowrate decrease by 10%
- Feed increase and solvent decrease by 10% each simultaneously
- Acidity decrease of scrubbing solution from 2 to 0.5M

Magnitude of disturbances was decided based on the maximum deviation in flowrate or concentration control. Duration of these disturbances was extended up to another steady state, as long as uranium leakage in the raffinate did not occurred. Transient behavior was followed by the density monitors and sampling.

- Pulsation and all feeds stopped

This last disturbance is important to choose adequate procedures after incidental shutdown of the system. After stopping all actuators, the system was left for 4 hours and restarted by two different methods (with or without prior solvent feed). Variation of uranium concentration profile in the extraction column after shutdown and uranium content in the raffinate during the restart procedure were mainly investigated.

RESULTS AND DISCUSSION

NORMAL OPERATION TEST

The start-up and shutdown sequence proceeded smoothly. Liquid transfer means were operated satisfactorily and interface levels of pulsed columns did not deviate by more than 10% from the set values. Judging from the variation of liquid densities and uranium concentration of each part of columns, the time required to reach steady state is about 16 hours.

Comparison of two capacity change procedures gave the conclusion that the gradual one with suitable duration of "variation ramp" is preferable from the flowrate control point of view, because each flowrate changed smoothly followed to the set value (Fig.2) and no overshooting phenomena were observed in this procedure. Interface levels of pulsed columns were kept stable and the uranium concentration profile in the extraction column was scarcely affected. Operation experience under low capacity (2t/d) and the maximum capacity (4.8t/d) verified that the codecontamination system has a wide stable capacity range.

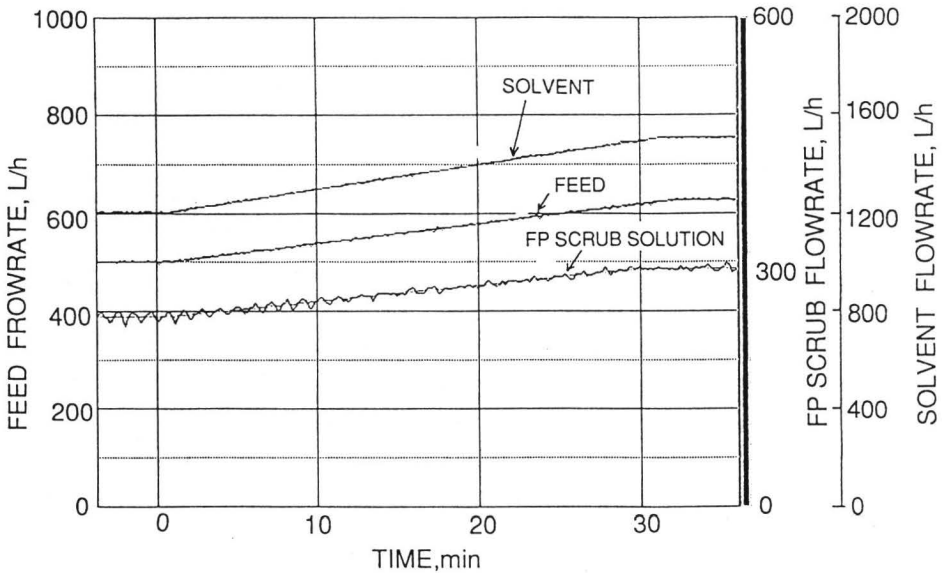


Fig.2 Flowrates of feed,solvent and FPscrub solution during capacity change from 3.2t/d to 4t/d with the duration of "variation ramp"of 30 minutes

DISTURBED OPERATION TEST

Feed flowrate increase

Fig.3 shows the variation of uranium concentration profiles in the extraction column. No uranium leakage occurred and uranium content in the raffinate was kept less than detection limit (1mg/L). The uranium concentration profile descended about 65cm and stabilized there. This variation was easily detected by "extraction front monitor", which indicates the difference between two densities monitored in the upper part of the column, shown in Fig.4. A density monitor installed in the top settler of the extraction column is also sensitive to this disturbance (Fig.5).

Solvent flowrate decrease

A similar result to that of feed flowrate increase was obtained. The extraction front descended about 76cm. Consequently, the extraction column has a margin to absorb the disturbance of feed flowrate increase or solvent flowrate decrease up to 10%.

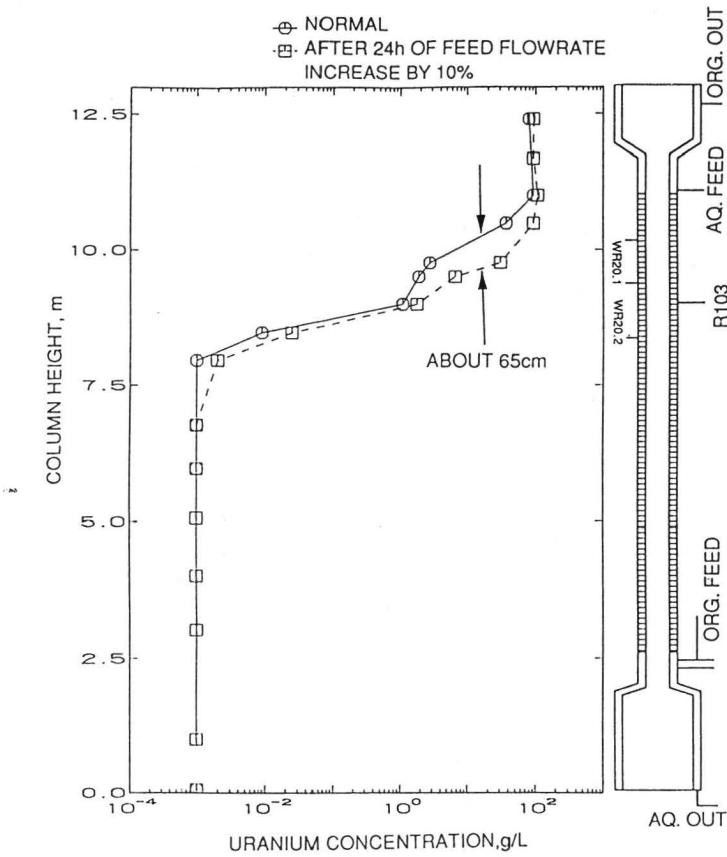


Fig.3 Uranium concentration profiles in the extraction column in the case of feed flowrate increase by 10%

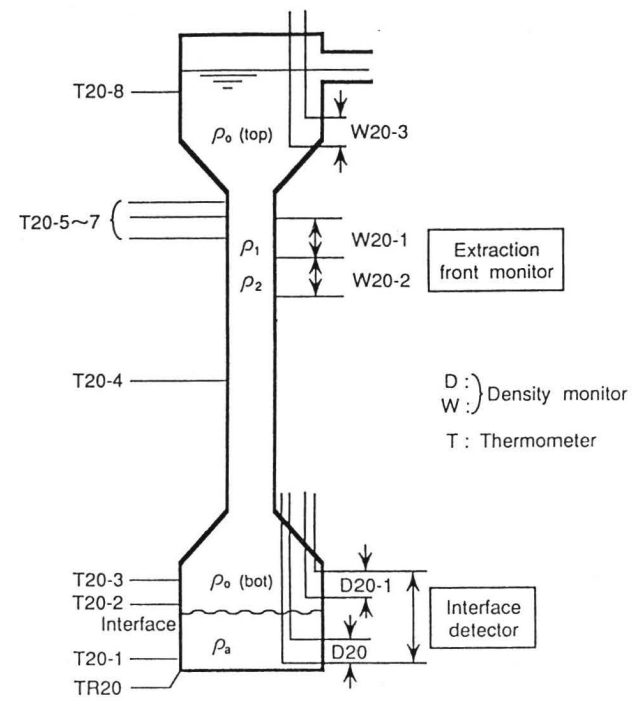


Fig 4 Schematic diagram of monitors installed in pulsed column (Extraction column)

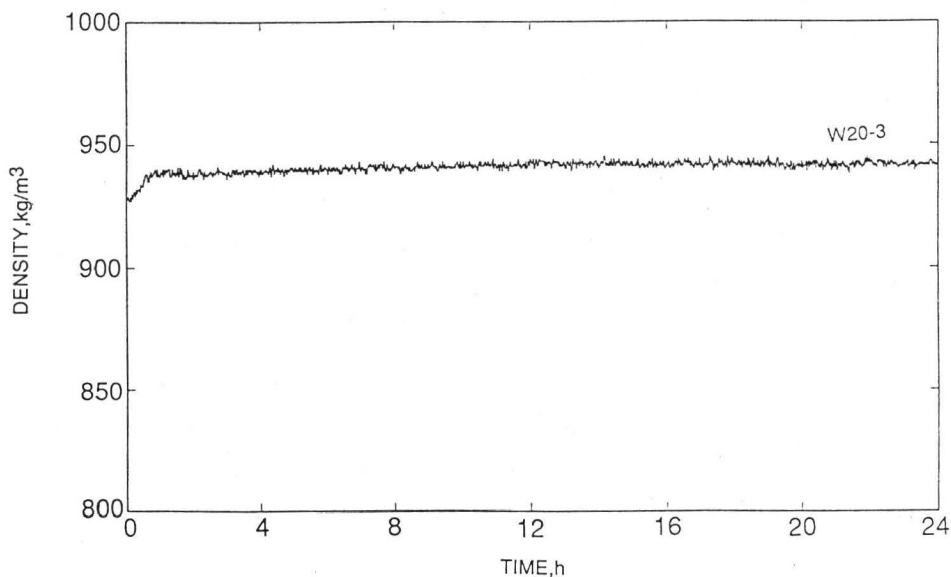


Fig.5 Indicated value of density monitor installed in the top settler of extraction column after feed flowrate increase by 10%.

Simultaneous feed flowrate increase and solvent flowrate decrease

The density of scrubbing raffinate solution showed a linear increase (Fig.6) and the temperature pattern in the extraction column varied drastically (Fig.7) with evolution of disturbance. A corrective procedure was applied and uranium concentration in the raffinate recovered to 10mg/L two hours after and below 1mg/L four hours after.

It should be noted that monitoring of scrubbing raffinate density and temperature pattern in the extraction column is effective in detecting a severe disturbance.

Acidity decrease of scrubbing solution

Uranium concentration and acidity in the scrubbing raffinate solution varied from 12 to 22g/L and from 3.2 to 2.2M respectively 48 hours after. There was no remarkable change in the uranium concentration profile in the extraction column.

Pulsation and all feeds stopped

Uranium concentration distribution became almost uniform in the extraction column three hours after stopping. Uranium concentration in aqueous raffinate in the bottom settler of the extraction column was about 50mg/L four hours after.

Restart procedure was carried out successfully in manual operating mode. The peak of uranium concentration in the raffinate was about 300mg/L after restart and total amount of uranium in the

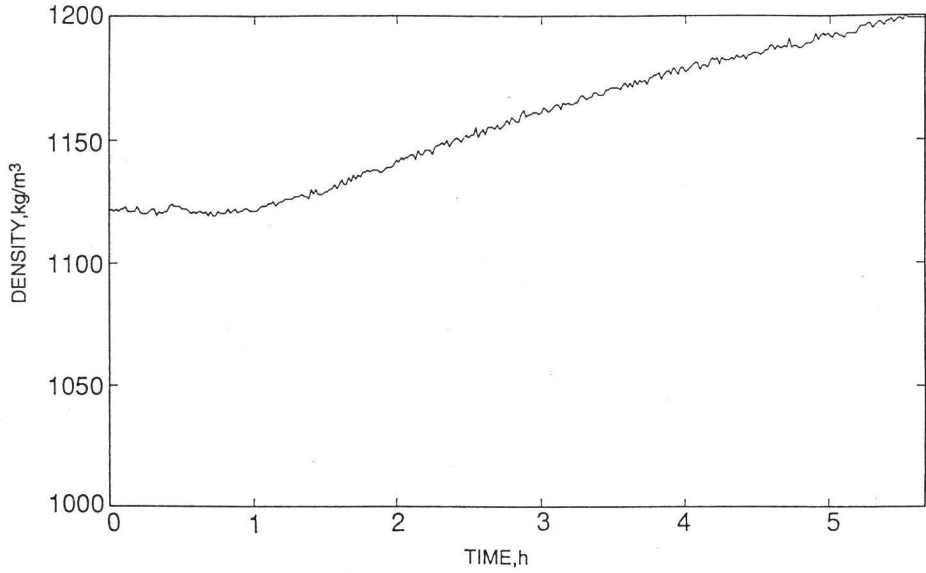


Fig.6 Indicated value of density monitor for scrubbing raffinate solution after simultaneous feed increase and solvent decrease by 10% each

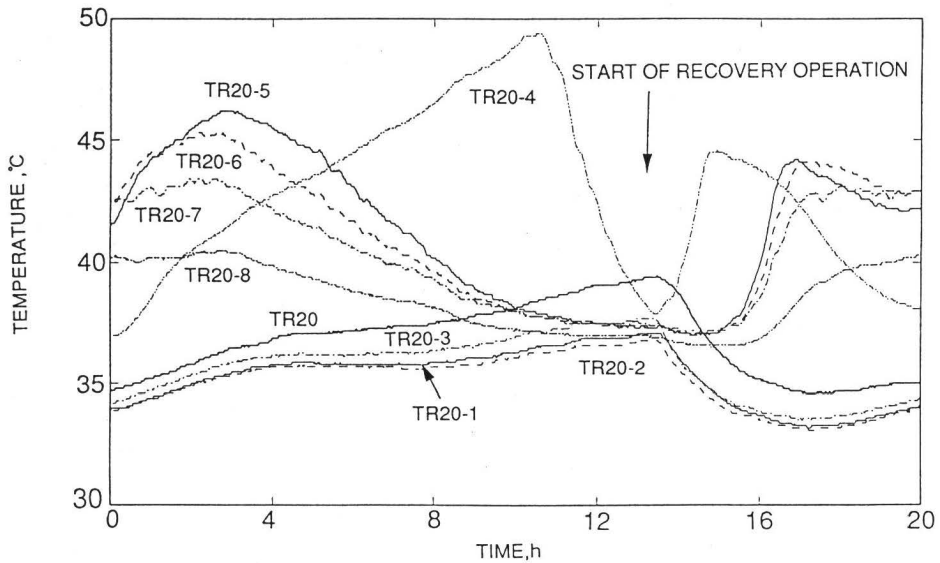


Fig.7 Temperature change pattern in the extraction column after simultaneous feed increase and solvent decrease by 10% each

raffinate was only 240g in the case without prior solvent feed. A similar result was obtained in the case with prior solvent feed.

CONCLUSIONS

The system test was carried out in the large-scale uranium extraction test facility (EDTF) and operating procedures and controllability of the system were confirmed to be satisfactory. Major conclusions are as follows.

- (1) Start-up and shutdown sequence was confirmed to be satisfactory and a suitable capacity change procedure was established.
- (2) The system has a wide stable capacity range from 2 to 4.8 t/d.
- (3) Density monitors installed in the upper part of the extraction column and scrubbing raffinate solution line and temperature pattern in the extraction column were verified to be useful for early detection of disturbances such as feed flowrate increase and solvent flowrate decrease.
- (4) Restart procedure was successfully carried out.

These results will be reflected in the operation of the extraction process in the JNFL Rokkasho plant and contribute to enhancement of reliability of it.

ACKNOWLEDGEMENT

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1.10

**EXTRACTION OF VANILLIN IN ACID SOLUTION
CONTAINING STICKY SOLIDS****F. G. ZHU AND S. JIN**

Far East Chemical Engineering Research Centre of Fragrance & Flavor
1893 Zhong Shan Nan Road, Shanghai 200011, China

Y. J. SI

East China University of Chemical Technology
130 Meilong Road, Shanghai 200237, China

ABSTRACT

A special reciprocating plate extraction contactor using vibration of high frequency and low amplitude, and the materials which are oil-attractive, water-repellent and corrosion-resisting, as well as the method of reverse phase extraction have been studied for extracting vanillin from acidified solution containing sticky particles. The experimental results show that it has considerable advantages, i.e., better extraction efficiency, higher throughput, less time of phase separation, more effective prevention of solids accumulating in the column, and longer service life in corrosion. The extraction of liquid-liquid and liquid-solid can be performed continuously in the same column when the vanillin transfers from drops phase including particles adsorbed vanillin to continuous phase. Extraction efficiency of 95% and crude vanillin of 88.6% can be obtained, with a total yield of the purification processes from 66.5% up to 86.5%.

INTRODUCTION

In a new process of manufacturing vanillin, it is required to extract vanillin contained in the acidic feed stream, in which there are particles of resin, gum and lignin etc. Some particles separate out when the mass-transfer proceeds. The particles adsorb solute vanillin to reduce the extraction efficiency, and accumulate on the plates to clog the passageway of two fluids, so that the operation has to be stopped and the limit of extraction efficiency was less than 90%.

Up to now, the extractions of liquid-liquid and liquid-solid are usually performed in different contactors, such as RDC (Reman, 1955; Kusters, 1983; Zhu, 1984), RPC (Baird, 1973; Karr, 1976 and 1980), and others for the former, in which only a modicum of solids are allowed, and several kinds of leaches (

Karnofsky, 1950; Cofield, 1951; Stein, 1976) for the latter. Because the solids are sticky, the liquid-solid extraction will become even more complicated. Recent researches (U.S.Patent, 1981 and 1982; China Patent, 1985) described modified contactors which could be used for feed containing some solids but not for sticky solids yet.

Moreover, the conditions of temperature 60°C, H_2SO_4 10% or HCl 5% in extraction, and temperature 60°C, NaOH 10% in cleaning are selected, therefore the materials will withstand corrosion of both acid and alkali solution (Hojo, 1979, 1982 and 1986).

EXPERIMENTAL

Apparatus structure

The special reciprocating plate contactor as shown in Figure 1 was constructed from extraction section of 50mm diameter, 870 mm height, two settling sections of 90 mm diameter at top and bottom, and total 1600mm height, in which 35 plates with 60% opening were fixed on the shaft, with frequency and amplitude of vibration varied according to the experimental requirement. Epoxy resin, teflon, and stainless steel were used as vibrating plates for different tests. An interface meter was set at the bottom settling section instead of the top for reverse phase extraction. There were three outlets for extract overflow, raffinate and resinous solids which were heated to about 105°C by steam passing through a conical jacket, and two inlets for solvent and feed. The structure of this column is different from conventional RPC.

Experimental flow chart

The setup is illustrated in Figure 2. A measuring pump drew acid liquid from a feed tank, in which a stirrer was used for dispersing solids, and transported them into the tower passing a heater at 60°C. Solvent toluene was pumped to the column by another measuring pump flowing through a heater at 60°C also. The vibration frequency of the shaft could be regulated by controlling the input voltage of a direct current motor. The interface position was adjusted by using an electromagnetic valve which could control the outflow of the raffinate. The resin, in which the temperature reached 105°C, was drained away intermittently twice a day.

When operating, the column was first filled up with solvent toluene, then the solvent and feed were set according to the flow rate desired. After replacing the column volume three times, it could be considered to have attained a steady state, and samples of inlet and outlet solutions were collected for analysis.

RESULTS AND DISCUSSIONS

Effect of mass-transfer directions

Accumulation

The accumulation of solids in different mass-transfer directions was plotted against time in Figure 3. When the feed containing vanillin and solids acted as dispersed phase, and the solvent as continuous phase in RPC, i. e., the vanillin transferred from d to c direction, the precipitate of solids on the plates was less than 50% of that from c to d at any time after eight hours. If using RDC, the accumulation quantity was much more, even as high as 5 – 6 times larger. Because in mass-transfer direction from d to c the solids were included within the dispersed drops and did not contact with plates, only a small amount of precipitate accumulated on them. In RDC, the stator rings and rotating disks were placed horizontally, so the settling solids accumulated more and more. The precipitate quantity in our special RPC can be expressed by our own experimental model:

$$Q_p = 1.16C_s \exp(-t) [\Delta\rho / (\bar{\mu}\sigma)]^{0.5} (\mu_d / \mu_c)^{0.1} A^{-0.08} f^{-0.9} \quad (1)$$

Throughput

From d to c mass-transfer direction, the increase of total throughput was over 30% (Fig. 4) and the time of phase separation was cut by about 20% in comparison with the opposite direction. This phenomenon can be explained by Marangoni effect (Laddha, 1976). When the solute vanillin transfers from dispersed phase to continuous phase , the coalescence between drops occurs spontaneously because the liquid films break easily, in which the vanillin concentration is higher, but for the opposite case, the films are more stable, and the drops tend to separate from each other.

The total throughput can be compared with the correlations given by Baird (1971):

$$1.5U_d + U_c = 0.0224 [\sigma^3 / (\Psi_R^2 \bar{\rho})]^{1/5} [g^2 \Delta\rho^2 / (\rho_c \mu_c)]^{1/3} \quad (2)$$

$$\Psi_R = (2\pi^2 / 3) \bar{\rho} [(1 - A_0^2) / (\eta A_0)^2] [(2A_0)^3 / H_s] \quad (3)$$

The calculated values of Baird's equation are lower than our experimental values due to solids in the dispersed phase and larger average diameter of drops in this mass-transfer direction (Fig. 5).

The average diameter of drops d_{32} in this column can still be calculated by modified Hefez's formula (1979):

$$d_{32} = 0.44 [\sigma^3 / (\Psi_R^2 \bar{\rho})]^{1/5} \quad (4)$$

Efficiency

When mass transfers in d to c direction and the $\partial \sigma / \partial c$ is less than zero as for the toluene–vanillin–water system, drops coalescing can enhance the mass-transfer rate, and vibration frequency may be raised about 30%. Figure 6 shows the extrac-

tion stages in different vanillin transfer directions. Due to the joint action of stronger coalescence and higher vibration frequency for dispersing, the tower efficiency can reach 0.9 extraction stages per meter, and increases 50% in comparison with c to d direction in which it is only 0.6 stages / m.

Effect of vibration frequency and amplitude

Generally, the extraction efficiency increases with frequency (Fig. 7). In order to disperse solids within drops, increase vanillin yield and reduce solids accumulation, a higher vibration frequency is necessary. At amplitude 2.5 mm, frequency over 300 rpm, the extraction efficiency increases. When $A = 7.5\text{mm}$, the frequency 150 rpm, the extraction efficiency increases slowly, and at this amplitude, above 300 rpm, the extraction efficiency falls because the mass-transfer coefficient goes down as the drops become rigid.

Simultaneously, the throughput will decrease significantly. The best conditions are amplitude 5 mm, frequency 250 rpm. Thus, the extraction efficiency is over 95%, the throughput is more than $6.62 \text{ m}^3 / \text{m}^2\text{h}$, the purity of vanillin in extract removed solvent reaches 88.6% as the phase ratio reduces to 0.8, and it makes a total yield of purification processes from 66.5% up to 86.5%.

The results of measuring input power P of vibration are close to the equation (Hafez, 1978):

$$P = 2\pi A f n \Delta N_{\max} \pi D^2 / (4\xi) \quad (5)$$

$$\Delta N_{\max} = 9.7 \times 10^3 A f + 1.8 \times 10^6 A^2 f^2 \quad (6)$$

Effect of material characteristic

Figure 8 represents the repellent action between water and three kinds of materials which are teflon (photo A), epoxy resin (photo B) and stainless steel (photo C). The less the wetting of a plate, the more difficult the precipitation of sticky solids on the plate. The comparison of materials corrosion in alkali or acid solution is shown in Table 1, in which it can be seen that teflon is the best, but in rigidity and economy, epoxy resin is excellent. Stainless steel can not be used because it attracts water strongly.

Table 1 Comparison of material characteristics

Materials	Corrosion (5% HCl or 10% H ₂ SO ₄)	Corrosion (10% NaOH)	Capacity of H ₂ O-attract	Rigidity	cost
Teflon	best	best	weakest	weak	expensive
Epoxy resin	good	good	weaker	stronger	cheap
Stainless steel	corrosion	good	strong	strongest	middle

The rate equation (7), (8) of resin corrosion in NaOH, H₂SO₄ solution have been offered by Hojo and Tsuda (1991):

$$w = k_1(t - t_0)^{1/2} \quad (7)$$

$$y = k_2(t - t_0)^{1/2} \quad (8)$$

The service life of epoxy resin is more than five years according to the calculation and our own experiment.

CONCLUSIONS

This investigation has shown that the special RPC can be used for liquid-liquid and liquid-solid extraction processes in which there are sticky particles suspending in the feed, and optimum process conditions have been obtained. Reverse phase extraction, vibration of high frequency and low amplitude, and the oil-attractive and water-repellent materials are three important factors which prevent sticky solids accumulating in the column. For industrial design and calculation, mathematical models have been selected and some have been found by experiment. Epoxy resin and teflon are best materials for reverse phase extraction, resisting both acid and alkali corrosion.

ACKNOWLEDGMENTS

The authors are very grateful to Professor Ken Tsuda and Junjiro Kawasaki of Tokyo Institute of Technology where they gave the guidance and offered useful materials and data. Thanks are due to Ms. Hai-Yan Fei, Zhen-Ping Ye and Mr. Zhen-Xun Gong for the experimental work.

NOMENCLATURE

A_0	fractional open area, mm^2
A	amplitude of vibration, mm
C_s	solids concentration, g/l
d_{32}	average drop diameter, mm
D	column diameter, mm
f	frequency of vibration, rpm
g	gravity acceleration, cm/s^2
H_s	distance between plates, cm
k_1, k_2	coefficient
n	plate number
P	input power, w
Q_p	precipitate quantity, g/m^2
t_0, t	incubation period, time, h
U_d, U_c	flow velocity of dispersed and continuous phases, m/s
w	amount of dissolution, mg/m^2
y	penetration depth of solution, μm
η	orifice coefficient
σ	interfacial tension, dynes/cm
ζ	mechanical efficiency of vibration
$\bar{\rho}, \rho_c, \Delta\rho$	average & continuous phase density, density difference, g/cm^3
$\bar{\mu}, \mu_c, \mu_d$	average, continuous and dispersed phase viscosity, cp

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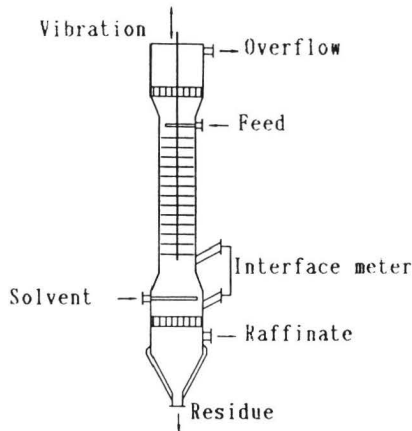


Fig.1 Structure of extractor

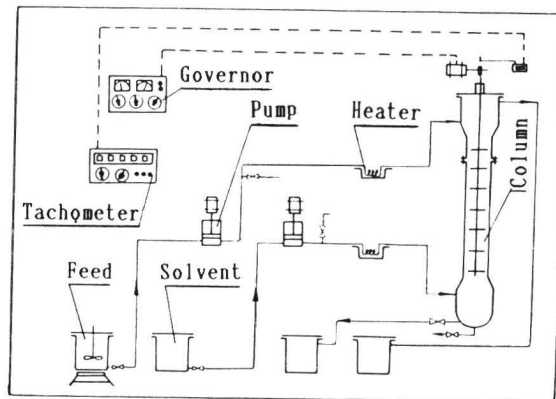


Fig.2 Experiment setup

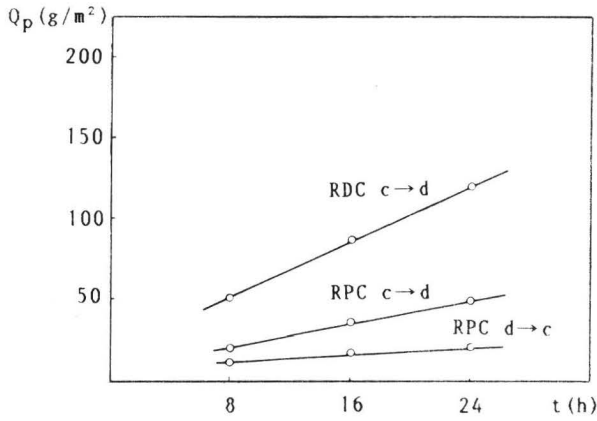


Fig.3 The accumulation in different transfer directions

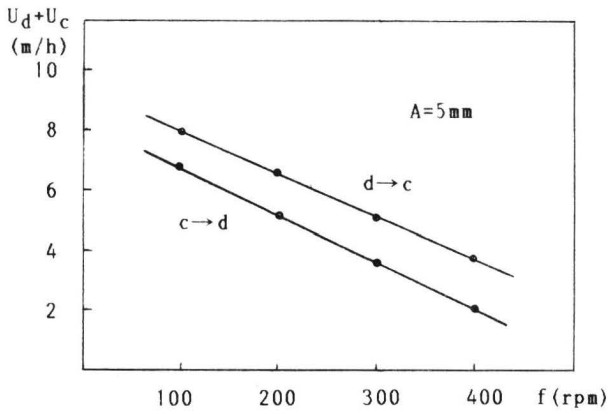


Fig.4 Throughput in different transfer directions

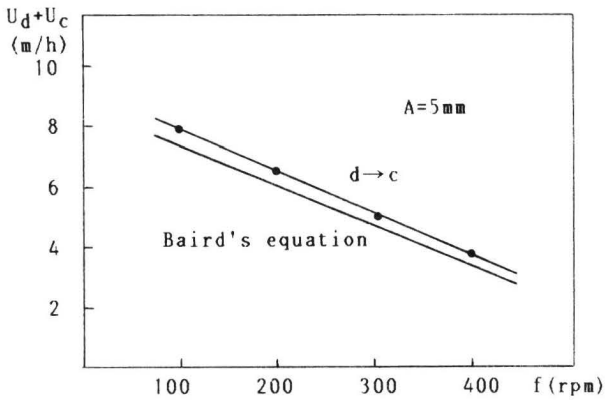


Fig.5 Comparison of throughput

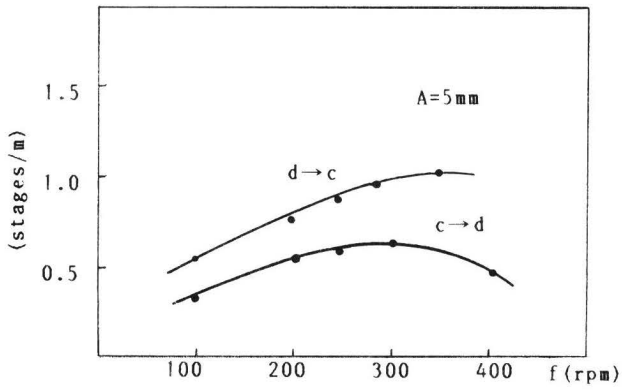


Fig.6 Column efficiency

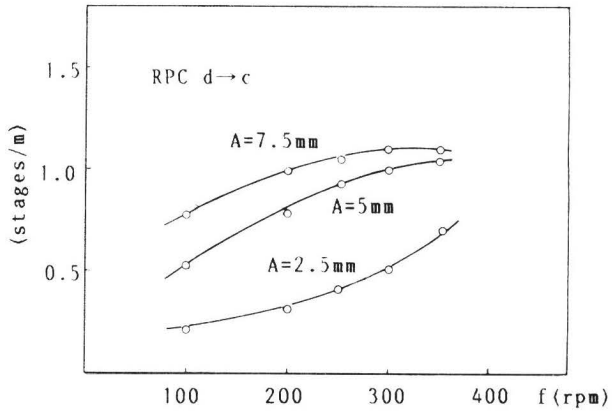


Fig.7 Extraction efficiency in different vibration conditions

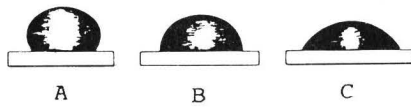


Fig.8 Effect of different materials

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DEVELOPMENT OF A REFLUX-TYPE CENTRIFUGAL CONTACTOR

Y.UEDA, R.SHIMIZU, S.NEMOTO, Y.TANAKA, and T.KAWATA

Reprocessing Technology Development Division

Tokai Works, Power Reactor and Nuclear Fuel Development Corporation

Tokai-mura, Ibaraki-ken, Japan

ABSTRACT

An advanced centrifugal contactor with a feature which allows either the aqueous or organic output flow to be refluxed without external piping and pumps has been developed. The reflux function can be achieved by either installing an obstacle plate with a slit over the collector space or by installing a skirt with orifices over the rotor. This contactor introduces certain advantages when used in the solvent and diluent washing processes in nuclear fuel reprocessing. Advantages of this reflux-type contactor include reducing the amount of waste, improving the scrub efficiency, and improving the control of the interface position. Hydraulic tests were performed and the reflux function was demonstrated. In a preliminary study, the relationship between the structure and the reflux function was investigated. A diluent washing test using the reflux-type contactor was also performed. The test results have verified the advantages of using reflux-type contactors in the nuclear fuel reprocessing process. This paper presents the structure of the reflux-type contactor along with the test results.

INTRODUCTION

The centrifugal contactor has excellent phase separation and a smaller hold up volume than that of conventional contactors such as mixer-settlers and pulse columns. These features are particularly beneficial to the reprocessing of spent FBR nuclear fuel.

Recirculating the flow containing the washing reagent in solvent and diluent washing processes offers certain advantages such as reducing the amount of waste, improving the scrub efficiency, and improving the control of the interface position. To achieve these advantages, mixer-settlers with recirculating lines are used in some LWR fuel reprocessing plant PNC(1987). When applying a centrifugal contactor in such a manner that its output is recirculated by using external piping and pumps, the advantage of its compactness is lost. However, a centrifugal contactor with a feature allowing the output flow to be recirculated without external piping and pumps will have all of the above advantages and will retain its original compactness.

An advanced centrifugal contactor based on this concept and offering such a feature has been designed and fabricated at PNC. Hydraulic performance and diluent washing tests were done on the contactors. This paper presents structural concepts of reflux type contactors along with the test results.

LIQUID FLOW IN A REFLUX-TYPE CONTACTOR

Figure 1 shows the basic structure of a normal contactor. This is an annular type centrifugal contactor which was developed at Argonne National Laboratory, Leonard et al. (1980). Feed solutions enter the mixing zone between the spinning rotor and its housing through the feed ports. The liquid-liquid dispersion formed in the mixing zone enters the rotor and separates into two phases. The rotor discharges the separated phases into the organic and aqueous collector spaces.

Figure 2 shows a comparison of liquid flow through a reflux-type contactor with that through a normal contactor. In a reflux-type contactor, part of the flow of one phase (either aqueous or organic) out of the rotor is diverted back into the mixing zone before reaching the collector space. The remainder of this phase flows into the collector space. In this paper, the diverted flow rate to the mixing zone is expressed as $F(r)$ and the flow rate of the liquid that goes into the collector space is expressed as $F(out)$.

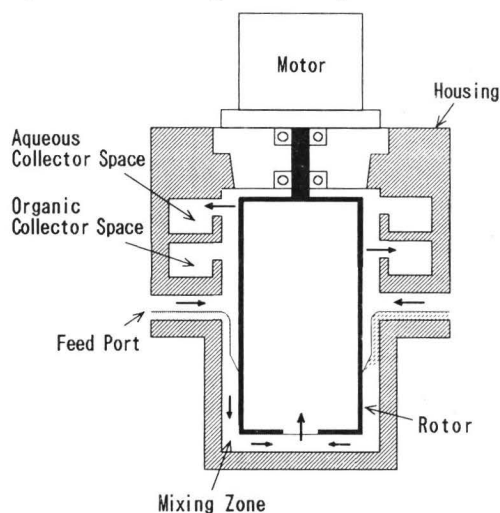


Fig.1 View of the Centrifugal Contactor

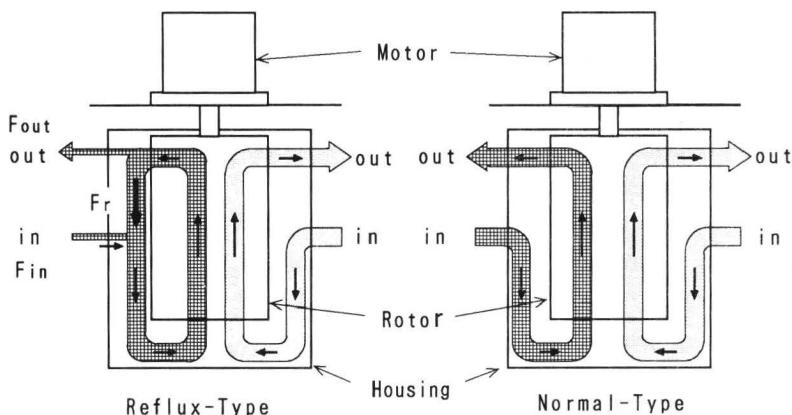


Fig.2 Liquid Flow through the Contactor

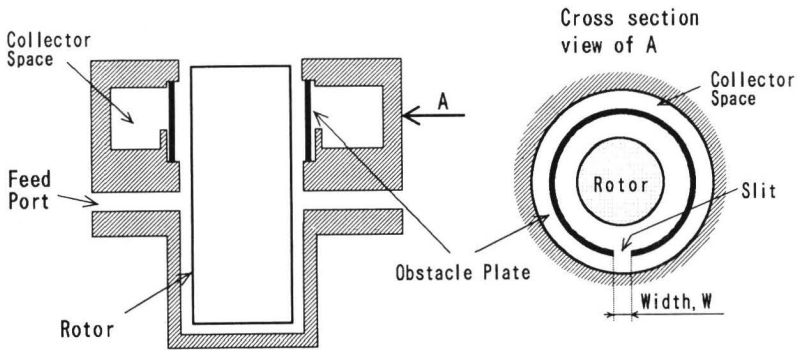


Fig.3 Housing-Reflux Type Contactor

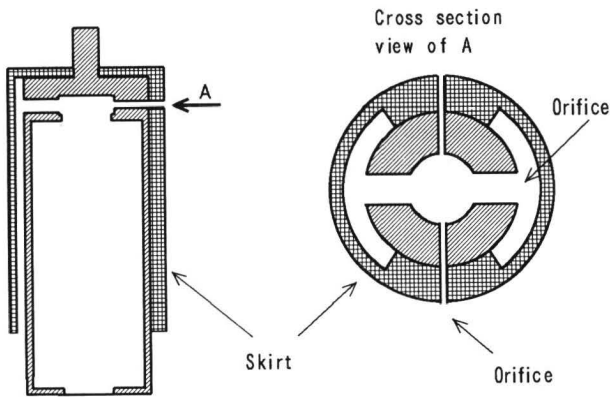


Fig.4 Rotor-Reflux Type Contactor

STRUCTURE OF A REFLUX-TYPE CONTACTOR

Figures 3 and 4 are conceptual diagrams of two typical types of reflux contactors. The diagrams focus only on the refluxed phase.

Figure 3 shows a housing-type reflux contactor. In this type, an obstacle plate with a slit is installed over the collector space. The rotor is the same as in a normal contactor. The obstacle plate diverts part of the discharged flow from the rotor back into the mixing zone between the rotor and its housing. The remainder, $F(\text{out})$, flows through the slit into the collector space.

Figure 4 shows a rotor-type reflux contactor. In this type, a skirt with orifices is placed over the rotor. The housing remains the same as in a normal contactor. The skirt has been machined such that a partial gap exists between the outer surface of the rotor and the inner surface of the skirt. The skirt diverts the discharged flow from the orifices into the gap and back to the mixing zone. The liquid which is discharged from the orifices through the skirt, $F(\text{out})$, flows into the collector space.

It is expected that the ratio of the refluxed flow rate, $F(r)$, to the collector space flow rate, $F(out)$, can be changed by changing the size of the diverting device, i.e., it will increase as the size of the slit or orifices through the skirt decreases. This ratio is expressed as the reflux ratio(R), $F(r)/F(out)$, in this paper.

HYDRAULIC PERFORMANCE TESTS

The relationship between the reflux ratio and the size of the slit or orifices was studied in both types of reflux contactors (housing-type and rotor-type). Both types of contactors were fabricated with various slit and orifice sizes, and the reflux ratio was measured under various feed flow rates.

Figure 5 shows the results of the housing-type reflux contactor tests. The X-axis is the width of the slit (ref. Figure 3) and the Y-axis is the reflux ratio (R). $F(rotor)$ is the flow rate of the refluxed phase discharged from the rotor. The refluxed phase in this test was organic. $F(out)$ is expected to be nearly proportional to the ratio of the width of the slit to the inner circumference of the obstacle plate as shown in equation 1. The width of the slit is (W) and the inner diameter of the obstacle plate is (Dp). The coefficient showing the ratio of $F(out)$ to the flow that reaches the slit is (k). (When (k)=1, all the flow that reaches the slit goes through the slit into the collector space). In the steady state when continuous flow is established, $F(rotor)$ can be written as in equation 2. From equation 1 and 2, the reflux ratio (R) can be written as in equation 3.

$$F(out) \doteq k \cdot [W/(\pi \cdot Dp)] \cdot F(rotor) \quad (1)$$

$$F(rotor) = F(in) + F(r) = F(out) + F(r) \quad (2)$$

$$R \doteq \pi \cdot Dp / (k \cdot W) - 1 \quad (3)$$

The correlation of equation 3 when (k) = 1 is shown in Figure 5 for comparison with the actual test results. Figure 5 shows that R increases as the width of the slit decreases as expected. However, R depends on $F(rotor)$ and increases as $F(rotor)$ increases. In all cases, R is smaller than expected from equation 3 when (k) = 1.

Figure 6 shows the results of the rotor-type reflux contactor tests. The X-axis is the diameter of the orifices through the skirt and the Y-axis is the reflux ratio (R). The refluxed phase in this test was organic. Figure 6 shows that R increases as the diameter of the orifices decreases as expected. However, the effect of $F(rotor)$ on R is different from that in the housing-type reflux contactor. In the rotor-type reflux contactor, an increase in $F(rotor)$ causes a drastic increase in R , especially in the case of smaller orifice diameters. In this type of contactor, it is not easy to expect a relationship between R and the orifice size because hydraulic behavior through an orifice is more complex than that through a slit as in the case of a housing type contactor.

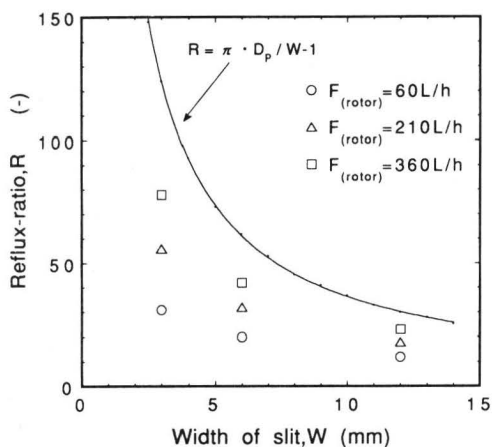


Fig.5 Result of Hydraulic Tests (Housing-Reflux Type)

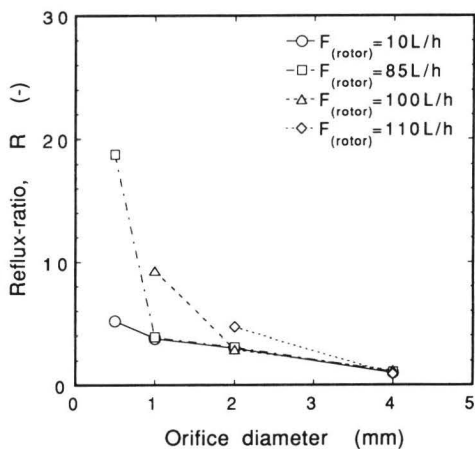


Fig.6 Result of Hydraulic Tests (Rotor-Reflux Type)

DILUENT WASHING TEST

A diluent washing test was performed to study the effect of reflux ratio on scrub efficiency. Figure 7 is a schematic diagram showing the test set up and flow conditions. TBP in the aqueous phase was washed by n-dodecane under various reflux ratios. The test results are shown in Figure 8. In this figure, the X-axis is the ratio of organic to aqueous flow from the mixing zone into the rotor, and the Y-axis is scrub efficiency (the ratio of the amount of TBP washed from aqueous phase to that in original aqueous phase). Note in the chart in Figure 8 that measurements were made at reflux ratios of 0, 2, and 13 and the ratio of organic to aqueous

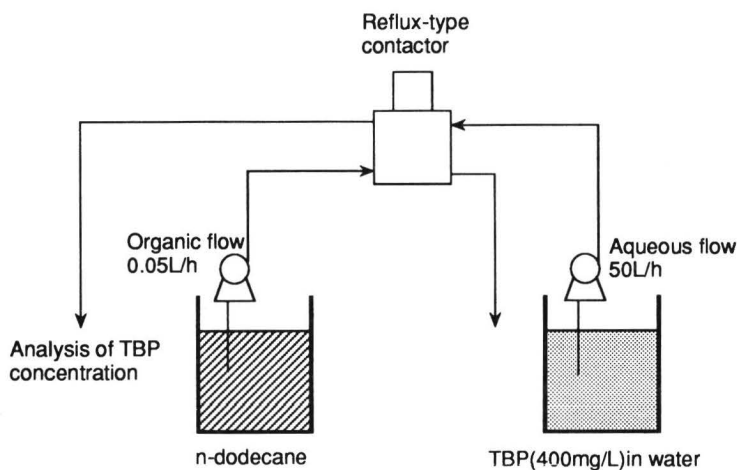


Fig.7 Diluent Washing Test System and Conditions

flow from the mixing zone into the rotor was incremented by the reflux function. (The external flow rates of organic and aqueous to the contactor were not changed but remained constant as shown in Figure 7.) Figure 8 indicates that the scrub efficiency was increased according to the reflux ratio.

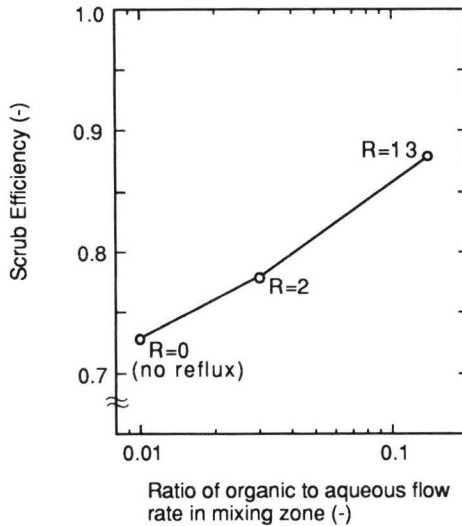


Fig.8 Effect of Reflux-Ratio on Scrub Efficiency

CONCLUSION

The concept of the reflux-type contactor was developed and demonstrated through the fabrication and hydraulic performance tests. The key factor of the contactor, reflux ratio, can be changed by changing the size of the slit or orifices as expected. Reflux ratio was also affected by the flow rate from the rotor. These characteristics and relationships were investigated in a preliminary study. Reflux ratio increased as the size of the slit or the orifices decreased. It also increased as flow rate from the rotor increased. A diluent washing test was performed using reflux-type contactors. The washing test results support the concept that higher reflux ratio improves the scrub efficiency in the diluent washing process. This series of hydraulic and diluent washing tests suggests the applicability and advantages of reflux-type contactors in the nuclear fuel process.

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1.12

**DEVELOPMENT OF HIGH EFFICIENCY AIR PULSED EJECTOR
MIXER SETTLER**

S.B.KOGANTI, C.V.RAJAGOPALAN, K.PERIASAMY, V. SREEDHARAN and
G.R.BALASUBRAMANIAN

Reprocessing Programme, Indira Gandhi Centre for Atomic Research,
Kalpakkam-603 102, Tamilnadu, INDIA

ABSTRACT

A novel air pulsed mixer settler, employing a simple ejector device utilizing part of the pulsed air energy to pump aqueous and organic phases from the respective settlers to the mixer of interest and the rest of the energy to create dispersion for effective mass transfer has been devised and the preliminary performance studies with nitric acid - 30%TBP/n-dodecane system are presented. The salient features of this unit are; high mass transfer stage efficiency of near 100%, even at pulsing frequencies as low as 0.66 s^{-1} and most important - complete elimination of interstage pumping devices while still retaining individual stage configuration (hydraulic independence from other stages of the multistage bank).

INTRODUCTION

Mixer settlers are simple devices for effective mass transfer in liquid-liquid extraction which are easy to fabricate and are very reliable though their contactor effectiveness may not match differential contactors e.g. pulsed sieve plate columns, and far less effective compared to centrifugal units. Air pulsed mixer settlers are widely used in nuclear fuel reprocessing applications due to the absence of moving parts in the radioactive environment, thereby reducing the maintenance problems. A detailed technical review of liquid-liquid extraction equipment used in nuclear fuel reprocessing industry was presented by Vassallo(1981). An air pulsed mixer settler was first described by Thornton(1956) who used a liquid pulse through an ejector to effect the phase dispersion in the KAPL type of mixer settler(Davidson, 1949). The ejector basically serves the same purpose as the impeller in the KAPL unit. The heavy phase is drawn through the induction pipe and pumped through the distribution nozzle mounted on the top of the ejector to disperse the heavy phase into the light phase. McHenry et al.,(1964, 1967) developed a laboratory air pulsed mixer settler with a hold-up volume of 300 cm^3 per stage. Pulsing is accomplished through two pulse tubes located near the top and bottom of the mixing chamber and extending up to the manifolds. Another version of air pulsed mixer settler

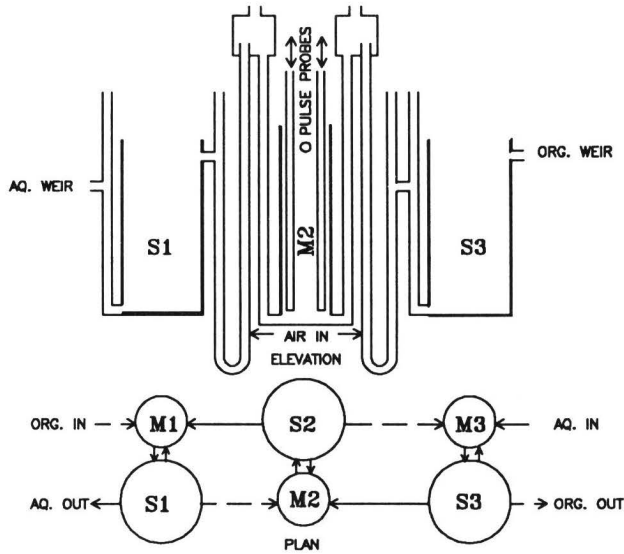


Fig.1 Schematic of the BARC mixer settler

developed at Bhabha Atomic Research Centre (BARC), India by Srinivasan et. al.,(1973) uses two perforated probes, connected to alternate pressure and vacuum, controlled by a timer. The probes are placed inside the mixer and the alternate jets issuing out of the perforations all along the length of the probes inside the mixer volume create enough turbulence to disperse one of the phases. The clear separated phases from the settlers are allowed to flow over the respective weirs and are airlifted to the mixer to effect phase movement across the multistage bank. The schematic of the unit is described in Figure 1. Johannisbauer et al.,(1974) considered the scale-up of air pulsed mixer settlers for reprocessing of nuclear fuels.

PRINCIPLE OF CONSTRUCTION

The present air pulsed mixer settler devised by Koganti et al.,(1992) is essentially the same as shown in Figure 1 except that both air lift pumps and the perforated pulse probes are replaced by an ejector fitted at the bottom of the mixer as shown in Figure 2. The

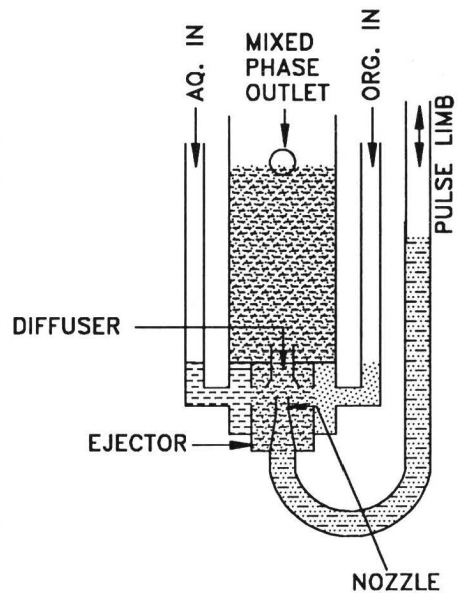


Fig.2 Mixer with single nozzle ejector

experimental mixer settler unit consists of a 35 mm diameter cylindrical mixer with an effective liquid height of 210 mm and a cylindrical settler of 102 mm diameter with an effective settling height of 200 mm. The feed inlet lines are connected to the induction chamber and it is essential that the induction chamber should be isolated from the rest of the mixer volume except through the ejector. The motive end of the ejector is connected to a common manifold through a pulse tube with a U-bend to prevent the air blowing into the mixer. The manifold is connected to a pressure and vacuum source through a two-way three-port solenoid valve operated by an electronic timer unit. The timer can be set to different frequencies and the pulse amplitude is controlled by varying the pressure and vacuum. The motive force for the ejector is derived from the oscillating liquid in the pulse tube creating enough negative pressure in the induction chamber of the mixer. This in turn brings down the operating liquid level in the feed lines close to the induction chamber thereby enabling the gravity flow of both phases into the mixer. The liquid dispersion created in the diffuser section of the ejector travels up the mixer exiting at the top and overflows to the middle of the settler section. The light phase overflows through the organic weir at the top of the settler and the heavy phase flows through a pneumatic interface control device by means of which the interface level in the settler can be varied to accommodate liquid pairs of different densities. The discharge level of the mixer is about 10 mm higher, compared to the surface level of the organic phase in the settler, to prevent the liquid flowing back to the mixer from the settler during the suction stroke of the pulsing. Any number of stages can be coupled to form a counter-current extraction bank. A six stage unit was constructed for testing the performance in a multistage bank.

MAIN CHARACTERISTICS

The important characteristics of the unit are as follows:

- Part of the energy of pulsed air is utilized for the transfer of both phases across the stages, thereby eliminating the need for interstage pumping devices, and the rest is for creating dispersion within a stage. Counter-current flow of the phases between the stages is independent of density difference.
- High mass transfer efficiency of near 100% within each stage, even at pulsing frequencies as low as 0.66 s^{-1} compared to the BARC type of mixer settler which gives transfer efficiency of above 95% at pulsing frequencies of $1.66 - 2 \text{ s}^{-1}$ with two pulse probes.
- The mixer settler bank is strictly a stage-wise unit and each stage is completely separated from others. Therefore no backmixing occurs between the stages. Concentration profiles in the stages are not affected, unlike differential contactors, in the event of stoppage of the unit.

- Either of the phases can be made to disperse within a certain range of flow ratio beyond which phase inversion occurs, depending on the system used and the material of construction. Phase inversion in no way makes the performance deteriorate and using pneumatic interface control devices, the position of the coalescence front in each settler can be separately adjusted to obtain the maximum separation capacity of the settler.
- Mixing zone volumes can be designed to vary residence time, to accommodate systems with slow mass transfer kinetics. For example it is known that uranium kinetics with 30% TBP are slow during stripping operation compared to extraction operation.
- For radioactive process applications the problem of entrained air activity is considerably reduced as no air is bubbled through the liquid.

EXPERIMENTAL WORK AND RESULTS

Since a mixer with the ejector fitted at the bottom forms the main component of the unit, performance study was restricted to a single mixer initially, with a primary objective of observing free liquid level in the feed lines and the mass transfer performance of the mixer as a function of phase flow ratio, total throughput, amplitude and frequency of pulsing. Two types of ejectors were studied. The double nozzle ejector is similar to the one used in fluidic pumping devices and the single nozzle ejector is the same as the conventional one with straight bore nozzle. Metering pumps each with a maximum capacity of $8.33 \text{ cm}^3/\text{s}$ were used to feed the phases to the vented inlet lines. The system studied was HNO_3 - used 30%TBP/n-dodecane. Since mass transfer kinetics for uranium, plutonium and nitric acid are relatively fast and are comparable, the performance with nitric acid should simulate the behaviour of the unit with uranium and plutonium as well.

Hydraulic performance

Hydraulic performance data with a single mixer is presented in Table 1. From the results, it is seen that the objective of keeping the liquid levels low in the feed limbs, is achieved with both types of nozzles up to a combined throughput of $16.66 \text{ cm}^3/\text{s}$. The ejector with a single nozzle performed better than the one with a double nozzle.

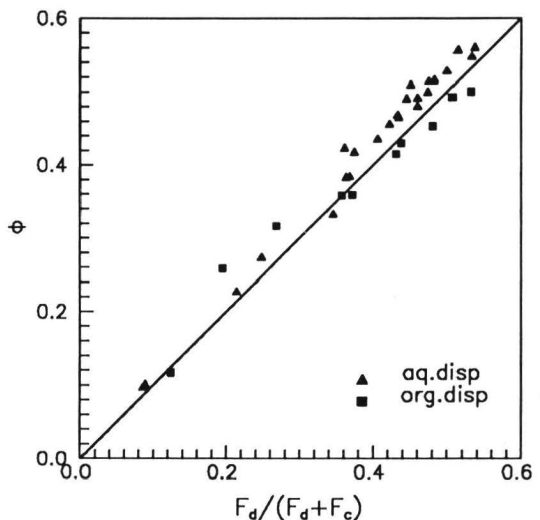


Fig.3 Dispersed phase hold-up with volumetric fraction

Single nozzle diameter was varied from 2 to 4.5 mm during the preliminary scouting runs and, based on the manifold pressure and vacuum requirements, 4 mm diameter was chosen for all the experimental runs. In order to determine the extent of mixing, separate runs were conducted to measure the dispersed phase hold-up in the dispersion, using 0.5 M HNO_3 - 30% TBP/n-dodecane pre-equilibrated system. About 15 cm^3 of dispersion was drawn from the middle of the mixer section and centrifuged to obtain the dispersed phase hold-up values.

TABLE 1
Hydraulic and Mass Transfer Data with Single and Double Nozzle Ejectors.

Run No	F_a/F_o	$F_a + F_o$ (cm^3/s)	A_p (cm)	f (1/s)	η_o %	η_a %	Feed limb Level (cm)		Ejector type
							Org.	Aq.	
1	0.27	5.5	29	1.0	101.0	103.0	4-9	0-4	Double Nozzle
2	0.5	5.5	29	1.0	99.6	98.4	"	"	
3	1	5.68	29	1.0	99.4	99.0	"	"	
4	2.09	5.62	30	1.0	95.5	98.4	"	"	
5	1.0	8.4	31	1.0	98.8	97.2	"	"	Single Nozzle
6	0.985	11.35	33	1.0	99.4	99.5	"	"	
7	0.879	15.75	35	1.0	99.7	100.8	6-12	1-6	
8	0.5	5.4	29	1.0	99.8	101.3	0-2	0-1.5	
9	1.05	8.46	30	1.0	100.8	101.9	0-3	0-2	Single Nozzle
10	0.81	16.0	34	1.0	99.2	103.3	1-4	0-2.5	
11	0.535	5.8	34	0.833	99.1	100.6	"	"	
12	0.949	8.21	35	0.833	98.3	96.4	2-4	0-2.5	
13	0.825	16.3	38	0.833	99.9	96.8	9-12	2-4	Single Nozzle
14	0.493	5.6	42.5	0.666	100.0	98.2	0-3	0-1	
15	0.962	8.66	45	0.666	99.46	102.0	1-4	0-2	
16	0.825	16.58	50	0.666	99.45	101.0	6-10	1-4	

From Figure 3, it is seen that the dispersed phase hold-up is approximately the same as its volumetric fraction in the feed, indicating a homogeneous mixture. From Figure 3, it is evident that hold-up values for aqueous dispersion lie above the diagonal line and below for organic dispersion for all runs excepting three which could be attributed to experimental errors. Considering the two-phase theory for co-current upflow, this trend is expected and the experimental results also indicate that the average drop diameter in the dispersion is very small conforming to the visual observations of lower than 1 mm. If the

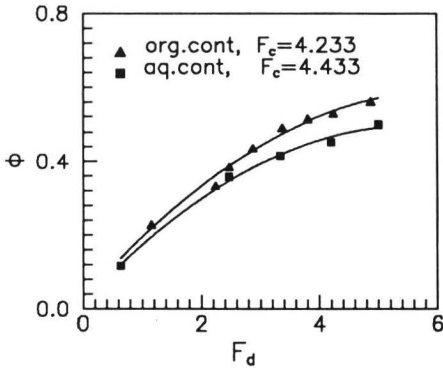


Fig.4 Variation of hold-up with dispersed phase flow rate

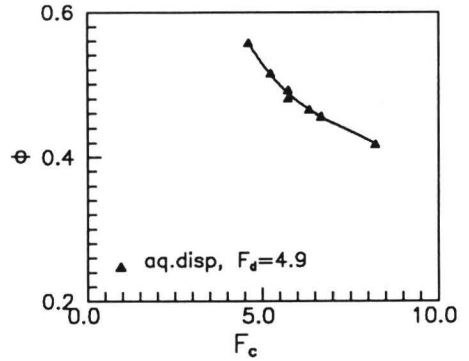


Fig.5 Variation of hold-up with continuous phase flow rate

drop diameter were to be bigger, the deviation from the diagonal line would be more pronounced due to increased terminal settling velocity of the dispersed phase drops. The extent of deviation will also depend on the diameter of the mixer, volumetric flow rates of individual phases and wetting characteristics of the phases. Variation of dispersed phase hold-up with the flow rates of dispersed and continuous phases is shown in Figure 4 and 5. The decrease in dispersed phase hold-up with increase in continuous phase flow rate as shown in Figure 5 is obvious from co-current upflow, unlike the behaviour in counter-current differential contactors where hold-up increases with increase in continuous phase flow rate. The hydraulic behaviour of the six stage bank is excellent and did not pose any unforeseen problems. Using 10 mm stainless steel Raschig ring packing in the middle 100 mm portion of the settler, the entrainment levels in continuous phase were brought down from 0.5% to lower than 0.2%. Interface position was varied all the way from the top of the settler to bottom by applying the calculated air pressure to the interface control device.

Mass transfer performance

Mass transfer data for a single mixer are presented in Table 1 which indicate stage efficiencies of near 100% in all cases. For aqueous continuous operation with BARC type of mixer settlers, it is possible that some of the larger organic drops may rise quickly through the mixer leading to lower mass transfer stage efficiency. This problem should be more pronounced with increased organic flow. In the present design both phases necessarily have to pass through the small diffuser cross section at velocities of the order of 4 m. s^{-1} ensuring proper dispersion leading to higher efficiency. In the present study mass transfer was always from aqueous to organic phase. Mass transfer efficiency is calculated from the analytical results of both feed samples and the centrifuged samples obtained from the mixer overflow before and after re-equilibration. Efficiencies based on aqueous and organic phases are calculated as shown below.

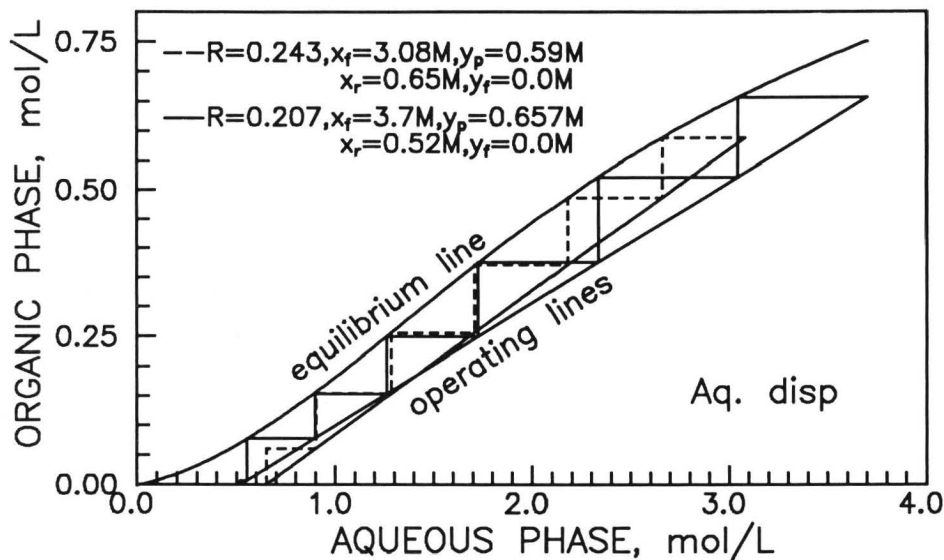


Fig.6 Mass transfer performance of mixer settler bank

$$\eta_a = (C_{af} - C_a) / (C_{af} - C_a^*) \quad (1)$$

$$\eta_o = (C_o - C_{of}) / (C_o^* - C_{of}) \quad (2)$$

Mass transfer performance of the six stage bank is shown in Figure 6 on a McCabe-Thiele diagram. It is known that TBP undergoes acid hydrolysis and percentage of TBP varies with time due to evaporation of diluent. Since old TBP is employed in all the experimental runs, the equilibrium curve for the system was generated prior to the mass transfer runs. Aqueous to organic feed ratio of about 0.2 is chosen so that the operating line is approximately parallel to the equilibrium line, to avoid the problem of pinching where small analytical errors lead to large deviations in estimating the number of theoretical stages. Both runs show six stage equivalent performance proving the excellent mass transfer behaviour.

CONCLUSIONS

The experimental runs confirm the favourable characteristics of the new ejector mixer settler bank. The most important characteristics are; elimination of the complete interstage pumping devices and high mass transfer efficiency at reduced energy input compared to the conventional air pulsed mixer settler. A single stage version of the same with mixer located inside the settler to reduce the floor space has also been tested. In the present study no attempt has been made to optimize the size of the mixer or the scale-up of the unit. This unit is most suitable for nuclear fuel reprocessing applications.

NOMENCLATURE

A_p	amplitude of pulse, referred to the pulse limb of 12 mm diameter (cm)
η_a	single stage mass transfer efficiency based on aqueous phase (%)
η_o	single stage mass transfer efficiency based on organic phase (%)
f	frequency of pulsing (s^{-1})
F	volumetric flow rate ($cm^3 \cdot s^{-1}$)
R	volumetric flow rate ratio, dispersed / continuous

Subscripts

a	aqueous
c	continuous phase
d	dispersed phase
f	feed
o	organic phase
p	product
r	raffinate

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A NEW LIQUID-LIQUID MIXER SETTLER EXTRACTOR

ZHONG Chenghua

Jiangxi Research Institute of Rare Earth
Shuanggang, Nanchang 330013, P.R. CHINA**ABSTRACT**

This paper reports a new mixer settler extractor. It consists of four parts, the upper and the lower parts of which are respectively an "upper settling section" and a "lower settling section"; the middle two parts of which are a "mixing chamber" and a "sideward settling section" side by side. The upper and the lower settling sections can respectively keep a layer of aqueous phase and a layer of organic phase. The aqueous and the organic clarified phases respectively from the upper and the lower settling section flow into the sideward settling section, but not into the mixing chamber. The extractor can be applied to solvent extraction systems with fast or slow mass transfer rate and disengagement rate. However high, low or normal is the process flow rate (O/A), the extractor shows considerably improved performance.

INTRODUCTION

Mixer settler extractors are widely used in the metallurgical industry. Although many variations on the mixer settler have been proposed, there are shortcomings including large area of equipment and hold-up capacity, and low throughput capacity per unit volume of mixer-settler. The development of the CMS (Combined Mixer Settler) by Davy McKee (Hardwick, 1980) is an important advance in the improvement of mixer-settlers, the design of which reduces considerably the area of the extractor and satisfies mixer O/A ratio requirements without external recycle of the minority phase. The CMS extractor, however, is only applied to solvent extraction systems with rapid mass transfer rate and disengagement rate. Only when the aqueous to organic phase feed flow ratio is high or low, does it have large throughput capacity per unit volume. In the case of slow mass transfer rate and disengagement rate, its advantages are not remarkable, due mainly to the cross section of the separation zone being the same as that of the dispersion zone in the CMS extractor and the exits of the mixed phase equalling the cross sectional area of this extractor. Moreover, the upper separation zone only clarifies organic phase, the lower separation zone only clarifies aqueous phase. This means that the clarifying aqueous phase and the clarifying organic phase, which ought to be clarified from the

upper and the lower separation zones respectively, flow back to the mixing zone. Therefore, these affect the performance of the CMS extractor and reduce the throughput capacity per unit volume.

A new mixer settler extractor has been designed and studied by the author. Its structure is different from existing mixer settlers. The design and study purpose of this extractor was to increase the throughput capacity per unit volume, to decrease the hold-up capacity and the area of the extractor, and to control more stably the two phases flowing between stages.

PRINCIPLES AND STRUCTURE DESCRIPTION

This new extractor is a box-type mixer-settler, which is shown schematically in Figure 1. It consists of four parts co-existing in a box. The upper and the lower parts are respectively an "upper settling section" and a "lower settling section", in the middle of the box, the two parts, a mixing chamber and a "sideward settling section", are side by side. Three settling sections, the upper, the lower and the sideward, serve as the settling chambers of this extractor. There are three settling-interfaces between the organic and aqueous phase including the upper, the lower and the sideward settling sections in this extractor, thus it is advantageous for clarification.

Mixing chamber

The inlets of the organic and the aqueous phases entering the mixing chamber supported by level baffle plates are fixed in the middle of the mixing chamber. The pumping duty and agitation in the mixing chamber are provided by the agitator of two level agitating vanes whose shape is a large trapezium. The upper and the lower vanes of the agitator are respectively above and under the inlet. Because the diameters near the inlets of the upper and the lower vanes are larger, in the centre between the upper and the lower vanes there is a large negative pressure to meet amply the pumping of the organic and aqueous phases into the mixing chamber, hence the optimum parameters of the agitator design were determined by the mass transfer requirement. The liquid flowing into the mixing chamber from the inlets is rapidly disperses into small droplets by intense mixing in the middle of the mixing chamber. Since the agitating vanes have large diameters and area, the slower rotation speed, in the mixing chamber there is a large range of turbulence, and overmixing around the agitating vanes can be avoided (Shen, 1982, 1983). The mixed phases which flow from the upper exit at the top of the mixing chamber and from the lower exit at the bottom of the mixing chamber enter respectively into the upper and the lower settling sections. Since the upper and the lower turbulence levels in the mixing chamber are less than in the middle, thus mixed phase separation could be beneficial. the ratio of the height to the side of the mixing chamber is large, whose purpose is to reduce the bottom area per unit volume, decrease the short cut of the liquids in the mixing chamber and increase the stage efficiency.

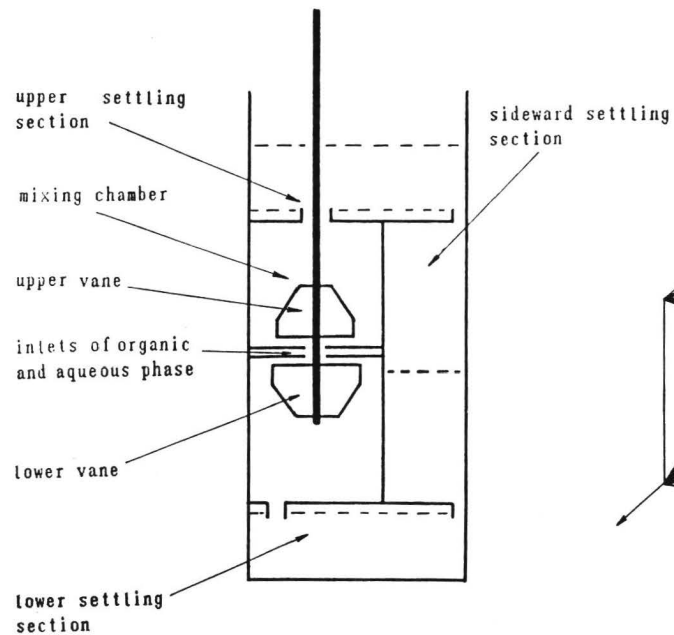


Figure 1

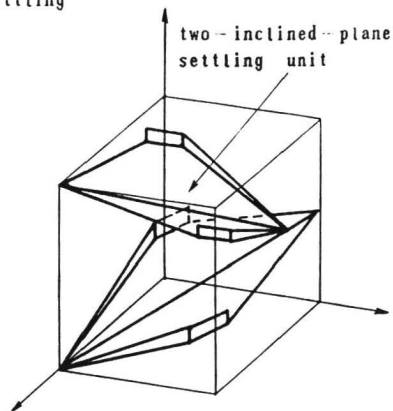


Figure 2

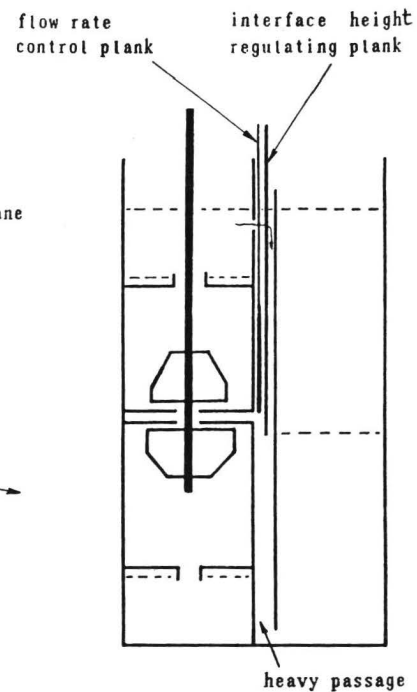


Figure 3

Settling Chamber

The bottom of the mixing chamber, in which there is a lower exit having a coffer-dam, was extended to the sideward settling section, in which there was an overflow-weir of organic phase to keep a layer of the organic phase under the bottom. On the top of the mixing chamber there was an upper plate, which can be movable or fixed, and it had an overflow port at its side and an upper exit of mixed phase having a coffer-dam inside the plate. The agitator shaft passed through this exit. Therefore the upper plate was filled with and retained aqueous phase. A number of two-inclined-plane settling units, a new assisted settling device by the author, were put into the sideward settling section, as shown in Figure 2. The phenomenon of dispersing in the course of the aqueous phase streaming down from the upper plate and the organic phase streaming up from the lower settling section is avoided. This settling device assisted the mixed phase from the upper and the lower settling sections to clarify. If this settling unit is made of assisted settling material, it could be even more effective. In the settling chamber of this extractor there are many layers of disengagement interface, thus total settling interfacial area is large, and also the vertical direction of the sideward settling section has assisted settling action. The mixed phase from the mixing chamber flowed very slowly in the settling chamber, which is favourable to the agglomeration of droplets, hence assisting the disengagement of mixed phase. Therefore, the settling chamber design of this extractor has considerably reduced the bottom-area and the volume of the settling chamber.

Phase Flow Stability

The organic and aqueous phase flow stability between stages influences the stage efficiency and stabilization of the product quality separated by the extractor. The height fluctuation of the settled interface within the unit and its settled interfacial area are the principal factors affecting the two phase flow stability, and the change of the mixing ratio within the mixing chamber is also a factor. The range of the height fluctuation of the interface within the extractor is determined mainly by the control of the heavy passage. Conventional heavy phase passage controlling interfacial height is that there is no organic phase in the passage and within the passage the aqueous phase weir is moved. This method has some problems as follows: (1) The organic phase entrained in the aqueous phase appears gradually within the aqueous phase passage, thus the larger pumping draft demanded by the agitator can pump out organic phase from the heavy phase passage, otherwise it can affect the phase flow stability; (2) Since the density of the organic phase is smaller than the aqueous, the change of the aqueous height in the passage is smaller than the settled interface between two phases, thus reducing the controllable sensitivity of the heavy phase passage to the settled interface in the extractor. The heavy phase passage in the new extractor is shown in Figure 3. The top of it communicates with the top of

an adjacent stage into which the heavy phase flows, the organic phase in the adjacent stage can flow into the heavy phase passage. There is a regulating plate for the interface height and a control plate for the flow rate in the heavy phase passage. The settled interface height in the heavy phase passage is equal to that in the sideward settled section of this stage. When the settled interface height is higher than the bottom of the interface regulating plate, the aqueous phase flows into the mixing chamber of the next stage through this passage. When the settled interface height is lower than the bottom of the regulating plate, the organic phase in the passage flows into the mixing chamber, and the organic phase in the next stage flows back into its mixing chamber through the passage. This condition appears only if the aqueous phase feed flow stops. The pumping flow rate of the mixing chamber can be made to approach the aqueous phase flow rate by adjusting the flow-control plate. The settled interface height can be chosen by adjusting the interface regulating plate. This method reduces the pumping draft demanded and the power consumption, decreases the fluctuation range of the settled interface height, and can make two phases to flow more stably, thus the agitator design and its parameters may be mainly determined by the mass transfer demand. In large-scale industrial equipment, the flow-control plate within the passage may be controlled by a simple device to achieve self-regulation. In addition, because the cross-sectional area of the sideward settling section in this new extractor is much smaller than the conventional mixer-settler, the organic and the aqueous phase flows of this new extractor between stages are stable, thus being beneficial to the improvement of the stage efficiency and the stability of the product quality separated by the extractor.

EXPERIMENTAL

This paper reports the real solution experiments with single stage and multistage with this new extractor.

Single Stage Experimental

In order that mixing, disengagement and flow could be visually studied, this new extractor was built in Perspex. The single-stage extractor has a level-cross-sectional area of 0.025 m^2 and a height of 0.52 m . The ratio of the height to the level-cross-sectional area of this extractor is $H:S = 1:0.05 \text{ m/m}^2$. The ratio of the height to the level-cross-sectional area of the CMS contactor is respectively as follows: $1:0.2$, $1:0.4$, $1:0.09$, $1:0.72 \text{ m/m}^2$ (Bonney, 1981; Hardwick, 1980). It can be seen that the bottom area per unit volume of the new extractor is smaller than the CMS contactor. The aqueous phase for the experiment was acid rare earth chlorides liquors, the organic phase was HEH (EHP) kerosene. The rotation speed of the agitator was about 300 r/s .

The single stage experimental results have shown that this new extractor has the following

advantages:

(1) This new extractor has high stage-efficiency. Even when the increased total (organic plus aqueous) flow is such that the mixer retention time in the mixing chamber approaches the extraction equilibrium time in a separatory funnel, it has stage efficiency above 95%, as shown in Table 1.

TABLE 1
Single-stage experiment on the stage efficiency

Total solution flow cm ³ /min	Mixer retention time min	Throughput capacity m ³ /hm ³	Stage efficiency %
637	7	3.07	99.5
744	6	3.50	98.9
894	5	4.29	98.0
1116	4	5.37	96.6
1247	3.5	6.00	95.7

*Extraction equilibrium time in separatory funnel was 3 to 4 minutes.

(2) In the case of the stage-efficiency above 95%, the throughput capacity per unit volume of this new extractor is twice to three times as large as that of the conventional mixer-settler.

(3) In the case of the normal feed flow ratio, the throughput capacity per unit bottom-area of this new extractor is approximately seven times as large as that of a conventional mixer-settler.

(4) This new extractor can be applied to the higher or lower feed flow ratio, it can also satisfy the conflicting process demands of feed flow and mixing chamber phase ratio without external recycle of the minority phase. The operational O/A ratio required may be chosen by adjusting the height of the two-phase interface in the sideward settling section, and by regulating the high position of the overflow port of the organic and aqueous phase respectively in the lower and the upper settling sections, so that it achieves the optimum operating state. Elimination of the recycle of the minority phase means that the volume and bottom-area of this new extractor may be reduced. The larger the difference between the organic and aqueous phase feed flow rates, the larger the increase of the throughput capacity per unit bottom-area of this new extractor as compared with the comparable conventional mixer-settler unit. Under high feed flow ratio, this is over tenfold.

(5) The design of the settling chamber of this new extractor has a satisfactory disengagement effect. The organic phase entrained in the aqueous phase and the aqueous phase entrained in the organic phase are all below 100 mL/m³. The value of organic phase entrained in the aqueous phase and the value of aqueous entrained in the organic phase may be converted to

each other by adjusting the height of the overflow ports in the upper and the lower settling section, and regulating the size of the upper exit and the lower exit of the mixed phase, as well as adjusting the height of two-phase interface within the sideward settling section.

(6) The hold-up volume of the organic and aqueous phases in the new extractor has been decreased approximately 60 per cent as compared with the conventional mixer settler unit.

Multistage Experimental

In order to study the flow property of the multistage extractor, a six-stage experiment was made using real solution, aqueous phase was the acid rare earth chlorides liquors, and organic phase was HEH(EHP)-kerosene. The unit was built in Perspex, each has a level cross-sectional area of 0.023 m^2 and a height of 0.5 m. The ratio of the height to the level cross-sectional area of one stage of the unit is $H:S = 1:0.045 \text{ m/m}^2$.

The multistage experimental results have shown:

(1) The two-phase interface in each of the stages was stable. The height of the two-phase interface could be chosen accurately by adjusting the interface-regulating-plate in the heavy phase passage. The organic and aqueous phases flowing between stages were stable.

(2) The clarifying property of this new extractor was noticeable. Under the normal feed flow ratio, its settling flow capacity of per unit volume of the settling chamber was about $11.9 \text{ m}^2/\text{hm}^2$, which is approximately four times as large as that of the comparable conventional mixer settler unit.

(3) The organic and the aqueous phase entrained respectively in the aqueous and the organic phase are all below 100 mL/m^3 .

(4) The separation performance of the counter-current extraction has shown that the stage-efficiency of each of the stages was over 95%.

The multistage experiment for counter-current extraction demonstrates the advantages mentioned in the single stage. Furthermore, its throughput capacity per unit volume and the throughput capacity of per unit bottom area are larger than those of the single-stage, and the hold-up capacity of organic and aqueous phases has been decreased approximately 70 per cent as compared with the conventional mixer-settler unit.

CONCLUSIONS

The new extractor design which possesses noticeable advantages achieves the expected purpose. This new extractor can be not only be applied to solvent extraction systems with rapid mass transfer rate and disengagement rate, but also to slow mass transfer rate and disengagement rate. The new extractor may suit both high or low feed flow ratio and a normal feed flow ratio.

However, the structure of this new extractor is complex and is more difficult to build than the

CMS contactor. But in the case of the slow mass transfer rate, the slow disengagement rate, or the normal feed flow ratio, the increased advantages of the new extractor outweigh the increased complexity of the design and difficulty of the manufacture.

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DEVELOPMENT OF THE JAMESON CELL FOR SOLVENT EXTRACTION : ENTRAINED ORGANIC PHASE RECOVERY

D.J.READETT

Hydrometallurgical Research
Mount Isa Mines Ltd
Mount Isa, Qld 4825, Australia

AND

MARK STEEMSON

Hydrometallurgical Research Laboratories
Mount Isa Mines Holdings Ltd
Albion, Qld 4001, Australia

INTRODUCTION

In a recent paper by Miller and Readett (1992) the background to Mount Isa Mines Copper Leach Solvent Extraction - Electrowinning Plant was discussed. One subject touched on was the use of a Jameson cell to recover entrained organic from electrolyte. This paper follows the development of the Jameson cell from the original laboratory test work through to the early operational history at Mount Isa Mines Copper Leach SX-EW Plant.

JAMESON CELL - GENERAL PRINCIPLES

The principles of operation of the cell can be explained with reference to Figure 1, which shows a Jameson column in diagrammatic form.

The feed solution (electrolyte with entrained organic) and the operating air are brought into contact in the *downcomer*. The feed is delivered under pressure to the top of the downcomer, where it first enters a calming zone, before passing through an *orifice plate* or nozzle. The solution is forced through the orifice creating a high speed jet which is directed vertically downward along the axis of the downcomer. Air is drawn into the top of the downcomer, above the lowest extremity of the feed nozzle assembly, and is entrained into the plunging jet, in the form of fine air bubbles. The downcomer fills with a dense foam, in which the bubbles are separated by a thin liquid film containing the organic to be floated. Since the organic does not have to travel far to reach the surface of a bubble, a favourable environment is provided for the rapid capture of the organic by the bubbles.

The dense foam discharges from the bottom of the downcomer into the cell or vessel which acts as a disengagement chamber. The bubbles carrying organic rise to form a froth layer which moves upward and over the tip into a recovery system. The clean electrolyte flows downward toward the discharge point.

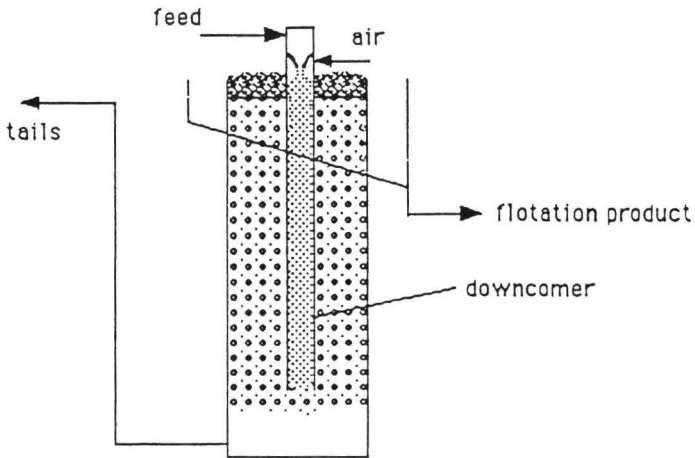


Fig. 1 Diagrammatic Sketch of of the Jameson Column

LABORATORY TRIALS

During 1989 two series of laboratory trials were conducted at Mount Isa Mines, Mount Isa and University of Newcastle. The test work was designed to assess the performance of a Jameson cell using both electrolyte and raffinate with various levels of entrained organic.

Procedure

All tests conducted were on artificially prepared oil-enriched electrolyte. Solvent extraction organic was entrained in electrolyte solutions using a 5L Denver flotation cell operating at $1200\text{r}/\text{min}^{-1}$. An oil entrainment level of $70 - 120\text{mL}/\text{m}^3$ could be consistently achieved using this procedure.

Oil entrainment levels were measured using 50mL entrainment measurement tubes spun at $3500\text{r}/\text{min}^{-1}$ in a high speed centrifuge.

In a typical continuous trial organic oil enriched electrolyte was prepared and the entrainment level measured. Feed to the Jameson cell was then introduced via a mono or peristaltic pump. The feed rate was adjusted to maintain a constant column pressure drop (either 100 or 200kPa). After removal of air from the orifice, air at the desired flowrate was either induced (natural induction) or pumped (using compressed air) into the column. Several tailings solution samples were then taken for oil entrainment measurement.

In most trials, multiple column passes were tested. Cleaned product from the column was recycled as feed for second or third column passes, depending on product oil levels. For each recycled pass, a similar procedure to the initial feed was followed.

INITIAL BATCH TESTING

A series of initial batch tests with total recycle of product were conducted on artificial feed to determine retention time requirements for the riser. The column was operated at 90kPa with air and solution flowrate of 4L/min and 5.5L/min respectively. Feed solutions were enriched to an oil level of 65 - 75mL/m³.

Table 1 summarises extraction results after 5 minute of batch testing for a range of feed materials. In all cases, total oil removal was achieved. In one test (using 10% M5640/90% Shellsol 2046 organic entrained in artificial raffinate) the batch kinetics were monitored over the 5 minute period. Table 2 presents these results. After 30 seconds, 60 - 65% oil removal occurred; after 1 minute, 70 - 75%.

TABLE 1
Jameson Column Batch Trail Results
(90kPa pressure, air/soln = 0.73, 5 minute batch trials)

Test Solution Organic (10% v/v in Shellsol 2046)	Initial Oil Level (mL/m ³)	Final Oil Level (mL/m ³)
M5640 in raffinate	75	0
M5640 in electrolyte	73	0
P5100 in raffinate	75	0
P5100 in electrolyte	64	0

TABLE 2
Batch Kinetic Results for 10% M5640/90% Shellsol 2046 (75mL/m³)
Entrained in Artificial Raffinate

Time (s)	Oil Concentration (mL/m ³)
0	75
30	28
60	20
90	20
120	20
300	0

CONTINUOUS TESTING

Continuous Jameson cell tests on solvent extraction pilot plant electrolyte dosed with pilot plant organic (10% LIX 984 in Shellsol 2046) were conducted using both 3L (0.5 - 0.6 minute solution retention times) and 12L (1.6 - 2.2 minute solution retention times) risers. Tests with the larger riser were preformed at two column pressure drops, 100 and 200kPa. Several column passes were used in each trial, depending on product electrolyte organic levels. The initial feed was typically 70 - 120mL/m³ entrained organic phase. The following results were noted from the tests:

- . Extractions of oil were higher using the larger 200kPa column pressure drop. Typical first and second pass extractions were 70 - 75% and 80 - 90% compared to 40 - 50% and 60 - 70% at the lower (100kPa) pressure.
- . Higher extractions generally occurred at higher oil entrainment feed levels. With a "slug" of feed during Run 1, high oil extractions resulted even at low pressure drop levels. This implies that the column will act as an emergency scavenger in case of severe oil spills.
- . Some evidence exists that shorter riser retention times resulted in better cell performance. This is possibly due to a large "froth" loading inhibiting air-electrolyte separation when longer riser retention times were tested. Indeed, stage extractions were significantly higher in test 2 (riser retention time of 0.6 mins), than tests 3, 7 or 10 (riser retention time was 2.2 mins). With the higher column pressure drop, first pass extractions were greater, even with the larger 12L riser.

The continuous test cell results presented indicate that the Jameson cell was an effective tool for oil removal from electrolyte streams.

DESIGN

On the basis of the results, an average of 75% recovery of entrained organic phase, it was decided to design a Jameson cell suitable for the Mount Isa Copper SX-EW Pilot Plant. The cell would replace a more conventional sand filter resulting in a significant reduction in both capital expenditure and operating costs.

The cell was similar to others already built, except in one respect - it was to be deeper. The most important dimensions are (mm):

Height of basic column	3000
Overall height of downcomer	3600
Launder width	300
Downcomer diameter	200
Orifice diameter	26

The cell is more than twice as deep as other Jameson cells, as used for mineral flotation. The larger relative volume has been provided to increase the residence time of the liquor in the cell. Laboratory work had suggested that it would be advisable to allow a residence time of

around 5 minutes, so that the liquid would be exposed to bubbles in addition to those with which it travelled down the downcomer.

The cell was constructed from 316L stainless steel, to withstand the acid contents. The downcomer is of high-density polyethylene and the nozzle is made from a fluorocarbon ester. To minimise any possible acid mist problems the cell and launder were fitted with hinged lids.

SX-EW PILOT PLANT OPERATIONS

Rich electrolyte exits from the strip mixer settler underflow weir and reports to a 5m³ sump. From the sump the electrolyte is pumped at an average flow of 27m³/hr to the Jameson cell. The entrained organic phase is recovered as a froth and is periodically purged (every 2 - 4 hours) and recovered in a settling tank. Discharge rich electrolyte flows into a 5m³ sump from where it is pumped to the electrowinning circulating tank.

During the commissioning period of the Copper SX-EW Pilot Plant only low flow rates through the SX plant were achievable. Visual inspection of the Jameson cell operation indicated that it was functioning well. This was backed up by the fact that only minimal transfer of organic was detected in the circulating electrolyte tank.

Since commissioning the flow rates through the SX plant have gradually increased and by January 1991 the plant was operating at its design flow rates. It was therefore decided that this was an opportune time to conduct an investigation of the performance of the Jameson cell in the recovery of entrained organic phase from the rich electrolyte which exits the strip mixer settler.

TEST WORK

Two different methods were utilised to determine the Jameson cell performance. These methods are detailed below.

1. On a shift basis the plant operators collected all of the organic phase recovered from the Jameson cell. The volume of organic phase was then recorded. At the same time any organic phase bypassing the cell was collected from the electrowinning tanks using "petrosorb" adsorbent material. The volume of organic phase recovered in this fashion was also recorded. A summary of the results was obtained over a sixty day period.

2. On a daily basis entrainment measurements were conducted on the inlet and outlet electrolyte streams of the Jameson cell. Samples were collected and introduced into 50mL entrainment bottles designed to measure organic entrainment in an aqueous phase. The bottles were then spun in a centrifuge after which the entrainment values could be determined.

DISCUSSION

From the information gained on the volume of organic phase recovered (Figure 2) it can be seen that during the initial test period the Jameson cell recoveries decreased dramatically. This was due to errors in the measurement of recovered organic phase and an increase in crud in the SX plant. The entrainment bottle measurements showed an average recovery of 70% initially. This indicated that the cell was not working as efficiently as the initial laboratory studies had indicated.

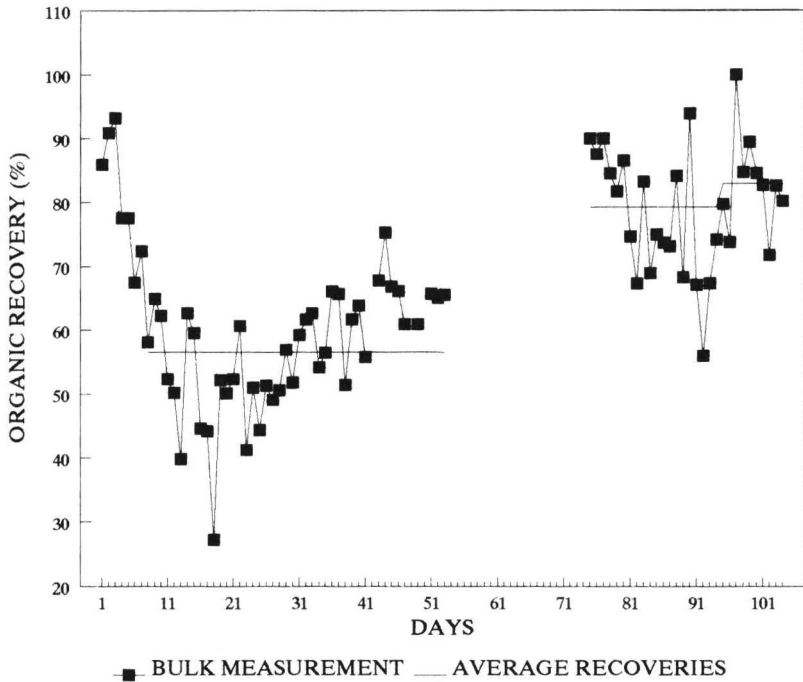


Fig. 2 Jameson Cell Entrained Organic Recovery

The entrainment values recorded during the next test period were relatively high averaging $100\text{mL}/\text{m}^3$ from the strip settler. These high values in part can be attributed to the very high crud loading experienced for the duration of the tests. This also resulted in much of the organic phase recovered from the Jameson cell being in the form of crud. It had been anticipated that the discharge from the Jameson cell could be redirected directly back into the SX circuit. The crud associated with this discharge has meant this was not possible during this period. Jameson cell recoveries averaged only 50 % during this period according to the bulk measurements and 60% according to the entrainment measurements.

As the crud problem was resolved the recoveries for the Jameson cell improved to 60 - 70%. The recovered organic phase was also clean enough to return directly to the SX circuit.

On the basis of an average electrolyte flow rate into the Jameson cell it was discovered that the orifice plate being used was oversized. This had resulted in the cell not operating under ideal conditions with a jet velocity of only 11 m/s and operating pressure of only 60 kPa. A smaller diameter orifice plate was installed and the test work was continued to determine whether ideal conditions were achievable and the effect this had on the recovery of the entrained organic. The smaller orifice was designed to give an average jet velocity of 19 m/s and a column pressure drop of 170 kPa.

The continued test work showed that there was an initial increase in the organic phase recovery from 65% to 80%. However significant organic entrainment in electrolyte from S-1 was still apparent. This high entrainment continued for 2 weeks and was found to be a result of the S-1 mixers being run aqueous phase continuous. Once the S-1 mixers were changed

back to running organic phase continuous (day 73) the overall entrainment decreased by 75%. At the same time a further improvement in the Jameson cell recovery up to an average of 83% was noted. These results are highlighted in Figure 2.

The Jameson cell is now operating more efficiently than was predicted from the initial pilot scale trials conducted in 1989. Results from these trials indicated that recoveries of 40 to 75% were attainable depending on the column pressure drop.

CONCLUSION

The use of a Jameson cell for organic phase recovery from electrolyte has been successfully implemented from laboratory trials into an operating SX circuit. The low capital and operating costs are combined with a >80% recovery of organic phase to give an economically viable alternative to the more conventional sand filter systems.

On the basis of these results a predicted recovery of organic entrainment in excess of 95% could be obtainable with two Jameson cells in series.

ACKNOWLEDGEMENTS

The authors wish to thank Mount Isa Mines for allowing them to publish this paper. The advice and assistance of Prof. Jameson, Nick Riches, Bob Clayton, Bob Greenalsh and Richard Jackson was greatly appreciated. A special thanks also to the SX-EW Plant Operators for their assistance and diligence during the period of plant trials.

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1.15

EMULSION BREAKING BY COMBINED ELECTROSTATIC AND CENTRIFUGAL FIELDS

P.J.BAILES and M.WATSON
Department of Chemical Engineering
University of Bradford
Bradford, W.Yorks., BD7 1DP, UK

ABSTRACT

A novel, spinning, electrostatic coalescer, which utilizes pulsating high voltage DC and low-G centrifugal fields simultaneously has been developed. The device is suitable for resolving a water-in-oil liquid membrane emulsion into its constituent phases. In this work the chosen formulation for the feed emulsion was a mixture containing 1% Span 80 surfactant and equal parts by volume of distilled water, Isopar M kerosene, and light liquid paraffin BPC. The design of a small scale spinning coalescer is described and its performance is reported for a range of applied voltage, pulsation frequency, and rotation speed. The test unit had a nominal volume of 750 mL and was capable of reducing the water content of the feed emulsion from 33% to less than 1%, at an emulsion throughput of 1.25 mL/s. The results show that when both fields are applied simultaneously emulsion resolution is significantly better than that obtained when either field is applied on its own.

INTRODUCTION

Traditional solvent extraction processes require eventual disengagement of the liquid phases but this is seldom a serious obstacle to the implementation of the process as a whole. In contrast, extractions by means of liquid membrane emulsions include in the flowsheet of an economically viable process a requirement for liquid phase separation that does represent a technical barrier to progress. Specifically, the problem occurs with the emulsion after it has been used for extraction. At this point it is necessary to break the emulsion in order to recover the internal phase and to recycle the membrane phase for the purpose of making fresh emulsion. The need to re-use the membrane phase mitigates against the use of chemical demulsifiers as an aid to phase separation and consequently efforts have been directed towards employing physical methods for breaking emulsions. However, a robust emulsion that will stand up to the rigours of the extraction process is by definition extremely stable and represents a significant challenge for existing physical liquid phase separation technology.

Many of the extractions for which liquid membrane emulsions have been proposed require water-in-oil emulsions and in such cases emulsion resolution can be greatly facilitated by the use of applied electric fields to promote coalescence between the water drops (Davies (1981), Draxler and Marr (1986), and Goto, Irie, Kondo and Nakashio (1989)). Nevertheless, overall rates of demulsification are often inhibited by the formation of a "sponge" layer at the bulk interface (Hsu and Li (1985) and Yamaguchi, Kobayashi, Ohbori and Katayama (1985)). The present study was undertaken to see whether a centrifugal field could be superimposed on the electrical field in order to enhance the rate of coalescence of the drops with the interface.

SPINNING ELECTROSTATIC COALESCER

Factors underlying the design

In a conventional electrical demulsifier the water drops which have grown in size due to the electric field, fall to the bulk interface under the influence of gravity but do not coalesce with it immediately. This is because the rate at which drops coalesce with the bulk interface is governed by the rate at which the film between the drop and the interface drains and this in turn is reduced by the presence of surfactant or a highly viscous continuous phase. The reduction in interfacial area as drop coalescence proceeds ensures that surfactant concentration in the vicinity of the bulk interface is higher than elsewhere. The result is that the rate at which the enlarged drops coalesce with the bulk interface is less than the rate at which the drops arrive at the interface. This leads to a build up of drops at the interface which is seen as a "sponge" layer. Once established it is probable that the "sponge" layer with its very high water content will effectively mask the potential at the interface and thereby further diminish the rate of coalescence at the bulk interface. The object was therefore to apply simultaneously both an electric field and a centrifugal force in such a way as to set up a bulk interface at right angles to the direction of the aligned electric field and centrifugal force, the bulk interface being located within the electric field. It was anticipated that a low-G centrifugal field would be sufficient to cause the drops to coalesce with the bulk interface because of the growth in drop size due to electrostatic coalescence. With this in mind a hydrocyclone was initially considered as a way of generating the desired centrifugal force, however, a mechanical centrifuge was chosen instead in order to gain the flexibility of being able to increase the centrifugal force without having to increase the flow through it, or change the inlet condition of the emulsion.

Construction of the coalescer

The final design for the continuous combined field coalescer was the result of a development programme that involved preliminary trials with a simple batch version, tests with different electrode assemblies, and several design studies to determine a satisfactory simple arrangement

for introducing the emulsion and removing the separated phases. Operation with emulsions containing a high proportion of water meant that short circuiting between the electrodes was a significant problem and in view of this the high voltage electrode was covered in a layer of insulation and energized by means of pulsed DC. The outcome of all these preparatory investigations was the continuous spinning electrostatic coalescer (CSEC) shown diagrammatically in Figures 1 and 2 (Bailes and Watson (1990)).

The CSEC comprises three main elements: the electrode and inlet assembly, the coalescer body, and the seal housings. The coalescer body rotates, the other elements are stationary. Except for the electrodes, the prototype was fabricated from Tufnol, a fabric based laminate capable of being machined to the tolerances required. This material is non-conducting, chemically inert to the liquids used, and relatively lightweight. Its use eliminated several difficulties that complicate the design if metallic materials are employed instead.

The electrode and inlet assembly consisted of two pipes arranged concentrically, and joined together at one end by a support plate and at the other end by an end cap. The annular gap between these two pipes contained an electrolyte which was in contact with the high voltage supply via a wire so that the electrolyte formed the high voltage electrode. The inner of the two pipes was an emulsion inlet tube which terminated within the vessel in a distributor cap that had radially directed apertures. The concentric pipe electrode was fabricated entirely from ABS plastic and therefore served as an insulation coated high voltage electrode. The electrode insulation coating thickness was 1.75 mm.

The coalescer body was a cylindrical vessel which was sealed by an end-plate at the bottom and partially closed at the top by two weir plates. The bottom end-plate also provided a means of mechanical connection to the drive motor via a steel shaft. The weir plates permitted the organic and aqueous phases to be removed by the separate routes indicated in Figure 2. The aqueous weir plate had 12 radial channels cut in the underside to allow water to flow from the inner wall of the coalescer body towards the central axis and out through the annulus between the two weir plates. The organic phase was able to leave the coalescer body by means of the annular duct created between the electrode insulation and the organic weir plate where it emerged in the upper seal housing and finally passed through the outlet port. An aluminium liner fitted to the curved inner surface of the coalescer body served as the other electrode of the apparatus. This was connected to earth through the wall of the coalescer body and then by means of a lightning conductor- type structure that extended to the earthed support bearing on the coalescer drive shaft. The aluminium liner and the insulation coated high voltage electrode formed a concentric arrangement such that the electrode separation was 24.9 mm.

The seal housings were fixed in position and enclosed the three seals that allowed the coalescer body to rotate beneath them while permitting removal of the separated phases

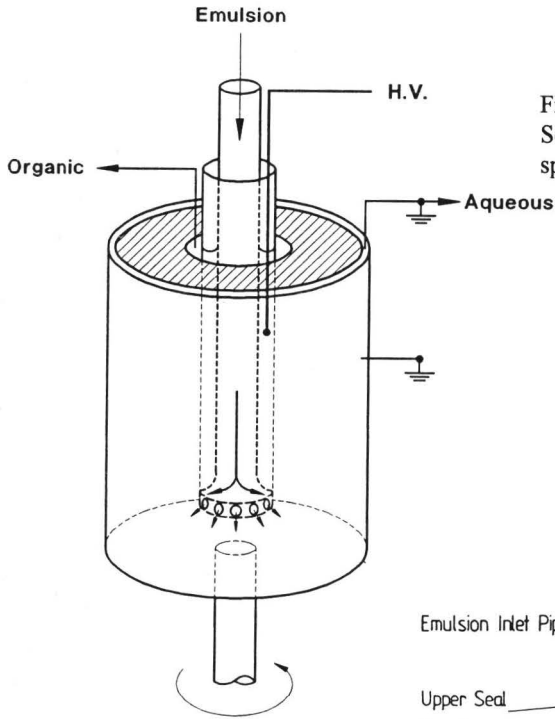
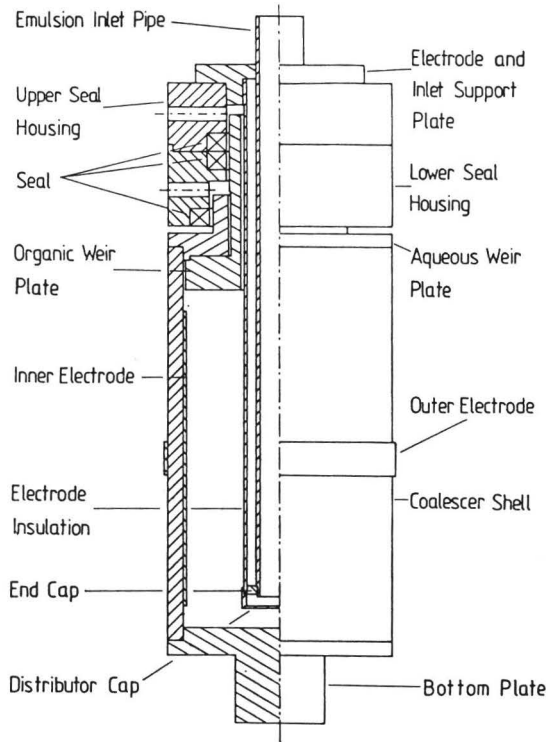


Fig. 1
Schematic diagram of the continuous spinning electrostatic coalescer

Fig. 2
Diagram showing internal details of CSEC



through the two exit ports. It may be seen from Figure 2 that the bottom two seals and the lower seal housing isolated the aqueous phase while the uppermost single seal and the electrode and inlet support plate isolated the organic phase. The rotary shaft seals were of the lip type made of nitrile rubber. Further details of the design are given by Watson (1990).

EXPERIMENTAL

Ancillary equipment

A DC shunt wound motor was used to drive the coalescer at speeds up to a maximum of 1750 min^{-1} . The speed setting was made by means of an AC controller and was fully variable over the range 200-1750 min^{-1} . The electrical equipment required to produce the pulsating high voltage was same as that described by Bailes and Larkai (1981). The remaining parts of the experimental rig were mainly concerned with the generation of a continuous flow of feed emulsion. The organic and aqueous components of the emulsion were pumped from separate reservoirs and metered by rotameters at 0.833 and 0.417 mL/s respectively, into a 1.0 L (94 mm i.d) fully baffled cylindrical glass mixing vessel. Agitation was by means of a 30 mm diameter Rushton turbine impeller rotated at 900 min^{-1} . The mixer provided a steady flow of the prescribed emulsion at a temperature of approximately 23 C.

System

The organic phase comprised two oils, one of high viscosity (light liquid paraffin BPC) the other of low viscosity (Isopar M kerosene), and a surfactant (Span 80). The aqueous phase was distilled water. The formulation of the water-in-oil emulsion used for the tests was, by volume, 33% water, 33% Isopar M, 33% paraffin, and 1% Span 80. Physical and electrical properties of the system are given by Watson (1990).

Procedure

A continuous flow of freshly made emulsion was passed into the coalescer body which was spinning and which had pulsed DC applied between the inner high voltage electrode and the aluminium earthed electrode. As a consequence, the water drops in the emulsion were made to coalesce and move outward through the less dense organic phase and an aqueous layer was formed on the inner periphery of the vessel. The ultimate depth of this layer was controlled by needle valves in the exit lines from the coalescer and once adjusted the settings for these remained unchanged throughout the experimental programme. The valve settings were chosen to give a reject ratio that would minimise the contamination of the effluent organic phase with the aqueous; the quality of the aqueous stream suffered accordingly but for present purposes this aspect was not part of the performance evaluation. The separated aqueous and organic components were drawn off through their respective ports. Organic entrainment in the aqueous stream was not routinely measured, but, the water was turbid in appearance for the reason given above. Samples of the effluent organic phase were taken after a run time that

corresponded to six residence times and the aqueous content of these was determined by Karl Fischer analysis.

RESULTS AND DISCUSSION

The performance of the CSEC was measured in terms of an aqueous resolution R_a , defined as: $R_a = (A_i - A_o)/A_i$ where A_i is the volume percentage of water in the emulsion entering the coalescer and A_o is the volume percentage of water in the organic stream leaving the coalescer. Results are presented to show the effect of rotational speed, applied voltage, and pulsation frequency upon aqueous resolution. In each experiment the emulsion flow rate was maintained at 1.25 mL/s. The stability of the standard emulsion used for the tests may be judged from the fact that in the absence of both applied fields with gravity separation only, it took 24 hours for the aqueous resolution to reach 0.95.

Two additional experiments were carried out to provide a further context in which to view the performance of the CSEC. The first of these revealed that with the use of the centrifugal field alone, that is, with no voltage applied, the inlet emulsion was unchanged on exit even at the maximum available rotational speed. The second experiment was to determine R_a when the emulsion was subject to the electric field in the absence of the centrifugal field. This measurement was made by replacing the coalescer body of the CSEC with a geometrically identical fixed body manufactured from acrylic tubing and fitted with exit pipes for aqueous and organic phases. Under these circumstances the aqueous resolution was found to be 0.74 for an applied voltage of 15 kV pulsed at 25 Hz, and 0.92 when 20 kV was applied at 25 Hz. The benefit of operating the coalescer with both fields in action simultaneously is clear from Figure 3. This shows the effect of applied voltage upon aqueous resolution with the coalescer spinning at a speed of 1500 min^{-1} . It is apparent that the fractional reduction in aqueous content of the inlet emulsion increases rapidly with electric field up to a nominal voltage of about 12 kV, thereafter further increases in the applied voltage result in a more gradual increase in the aqueous resolution. The existence of two regimes may possibly be attributable to a critical field intensity for coalescence as discussed by Brown and Hanson (1965). It is also evident from Figure 3 that the choice of pulsation frequency influences the outcome and for a given voltage the results at 25 Hz are better than those at 2 Hz and 50 Hz.

Confirmation of the importance of pulsation frequency may be found in Figure 4. An optimum frequency is clearly apparent at approximately 25 Hz irrespective of the speed of rotation. Also noticeable from Figure 4 is the fact that beyond a rotation speed 1500 min^{-1} higher speeds are not rewarded with a proportional increase in aqueous resolution, whereas below 1500 min^{-1} the effect on aqueous resolution of increasing rotational speed is much more marked. For the CSEC operating at 1500 min^{-1} the settling force experienced by the drops is approximately one hundred times that in a normal gravitational field. This force effectively

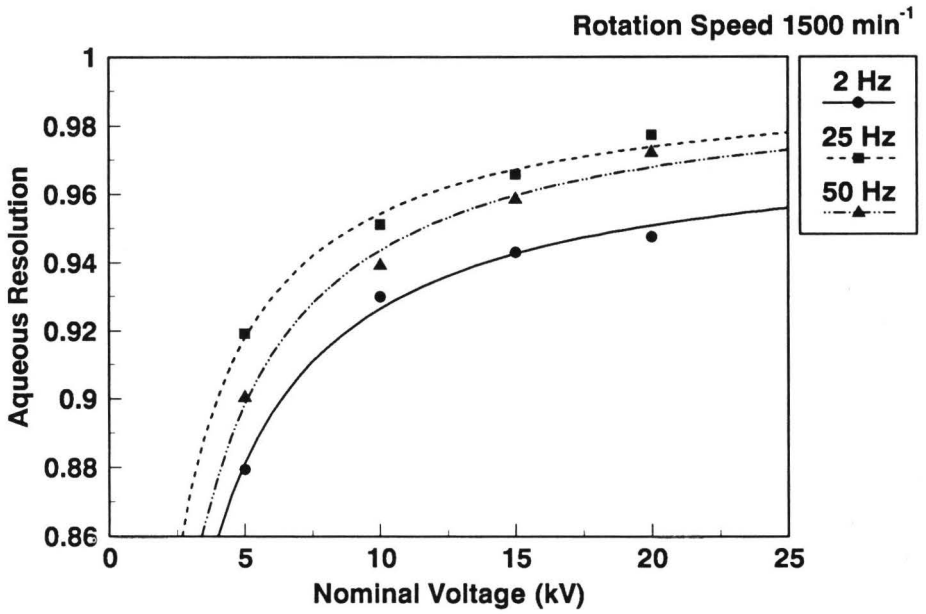


Fig. 3 Change in aqueous resolution as a function of the nominally applied voltage

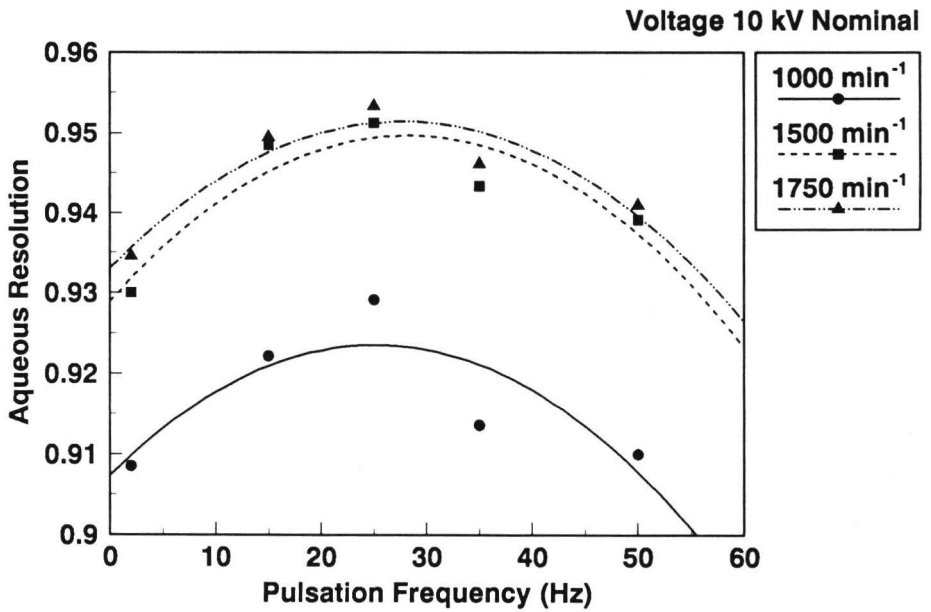


Fig. 4 Influence of the speed of rotation on the optimum pulsation frequency

defines a minimum drop size that can be removed from the emulsion within the available residence time. It is probable that at speeds higher than 1500 min^{-1} the drops that remain belong to the smallest size classes of the original drop size distribution. Electrically augmented coalescence will have shifted the distribution towards the larger size classes but a proportion of the aqueous phase will still be present as extremely fine drops. The closer the approach to complete resolution the greater the likelihood that the remaining drops are very small and spaced far apart. Eventually, increments in voltage and rotation speed are of diminishing efficacy as the emulsion becomes progressively dehydrated.

CONCLUSIONS

A small scale spinning coalescer has been constructed and tested and it has been shown that the electrostatic coalescence of water-in-oil liquid membrane emulsions is enhanced by the addition of a centrifugal field.

ACKNOWLEDGEMENTS

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1.16

**DROPLET COALESCENCE OF TOLUENE-IN-WATER DISPERSIONS
BY FLOW THROUGH FIBRE BEDS**

R. MAGIERA and E. BLASS

Lehrstuhl A für Verfahrenstechnik
Technische Universität München
Arcisstr. 21, D-8000 München 2, Germany**ABSTRACT**

The separation of toluene droplets ($< 100\ \mu\text{m}$) in toluene-in-water dispersions of 0.1% by volume of the organic phase was studied by using fibre bed coalescers. Glass fibres and stainless steel fibres were used as packing media. For the experiments we varied the drop size, the volumetric flow rate of the dispersion, the thickness of the fibres and the depth of the fibre beds. During the tests the hold-up of the dispersed phase remaining in the continuous phase behind the packed bed was measured. The results are discussed and compared with previous work.

INTRODUCTION

In chemical engineering practice, especially in the field of environmental protection techniques, there is often the problem of separating fine insoluble droplets from industrial effluents and municipal sewage. Such oil-in-water dispersions result from unintentional oil spillages, bilge water in ships, from cleaning processes at car washes etc.. They are also produced in form of cooling and cutting agents by metal-processing industry. To separate these dispersions the droplets have to coalesce into a coherent phase. Dispersions of drop sizes of more than $100\ \mu\text{m}$ can easily be separated by settling the drops with gravity force. With smaller drops the sedimentation is too slow, so that other methods are employed, e.g. centrifuges, electric fields, chemical and thermal processes or flow through fibrous porous materials.

Fibre beds as coalescence aids are successfully used to improve separation performance especially for secondary dispersions. Further preferences are a simple set-up, low costs and a continuous operation, if the dispersion has no solid particles obstructing the fibre material. However, the safe selection and design of a fibre bed is not yet possible. Therefore these studies intend to reduce the lack of fundamental knowledge on fibre bed separation by investigating systematically the influence of significant parameters.

EXPERIMENTAL

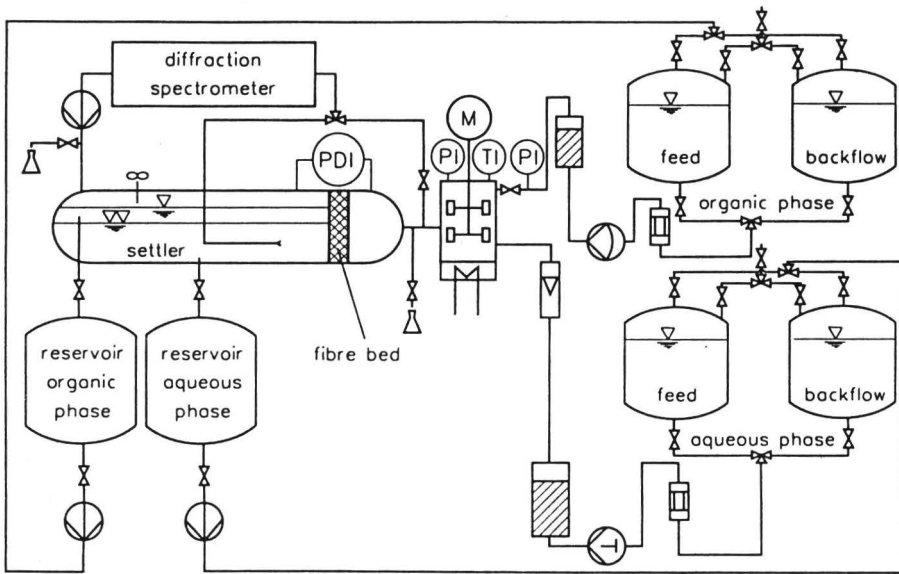


Fig.1 Diagram of the pilot plant

Fig.1 shows the experimental set-up used for continuous separation experiments. A piston pump and a diaphragm pump respectively are used to deliver the aqueous and organic phase from the storage tanks through activated carbon beds and then into the stirred tank, where the dispersion is produced and held at a temperature of 20 degrees Celsius. The physical properties of both liquids are given in Table 1. At the outlet of the agitated vessel the secondary dispersion flows into the coalescer. It consists of a fibre bed and a gravity settler. The coarse dispersion leaving the fibre packing is separated in the settler within a few seconds. At the exits of the settler the separated phases are drawn off, collected in the reservoirs and taken back to the storage tanks. During the experiments the drop size distribution in the secondary dispersion is analysed by a diffraction spectrometer. For the determination of the drop hold-up by infrared photometry samples are drawn from the entrance of the fine dispersion and after the fibre bed. The wetting abilities of the used fibre material are quantified by contact angle measurements.

RESULTS AND DISCUSSION

The tasks of the fibre material are to catch the droplets in the dispersion and to release them only after they have coalesced into large drops. The relatively large drops leaving the fibre bed have a higher velocity of ascent or descent compared to the original drops and, therefore, are easier to separate in a simple gravity settler.

At the entrance of the fibre bed the hold-up of the dispersed organic phase remained approximately constant at 0.1 % by volume. Ideally, this hold-up is totally separated and only the dissolved part of the organic phase in the aqueous phase remains. This fraction can only be removed by chemical or thermal separation processes.

In Figures 2 and 3 the influence of the superficial velocity on the unseparated drop hold-up is demonstrated. The drop size obtains the characteristic diameter of the present RRSB-distribution (cumulative distribution function determined empirically by Rosin, Rammler, Sperling and Bennet). L indicates the depth of the fibre bed, ϵ_v is used for the voidage fraction of the packing. Porous beds of glass fibres and stainless steel fibres with different diameter d_f are chosen as coalescence aid. The following observations can be made:

The separation performance depends on the wetting behaviour of the fibre material. Glass is about equally well wetted by both the organic and aqueous phases. Stainless steel shows clearer differences in the wettability of the solid surface by the two liquids. Compared with the stainless steel fibres under equal conditions the glass fibres work better. The separation performance decreases at increasing superficial velocity for all fibre materials, the degree of the dependence is lower for thinner fibres. With increasing fibre thickness the unseparated drop hold-up increases (Fig.2). A minimum depth L is necessary for the uniform flow through the fibre bed and sufficient to reach the best possible stimulation of coalescence. A deterioration of the separation performance with increasing superficial velocity can be observed, particularly for the fibre bed depth of 5 mm (Fig.3).

Figures 4 and 5 show the dependence of the unseparated drop hold-up on the drop size at a constant superficial velocity. The separation performance declines for smaller drops for both fibre materials, distinctly for the thicker fibres. The lowest dependence appears at the 2 μm glass fibre, which works best (Fig.4). The separation performance decreases for decreasing drop size, extremely so for the fibre bed depth of 5 mm. Both deeper packings separate very well with hardly any difference. The increase of the unseparated drop hold-up appears only for much smaller drops (Fig.5).

In comparing the present results with the data of Rebelein (1989) who also has carried out experiments with the same pilot plant with identical fibre materials, but different liquid systems, the same dependences can be observed. The only exception is the influence of the fibre bed depth on the unseparated drop hold-up. Contrary to the results shown in Fig.5 there is no dependence of the separation performance on different packing depth at varying drop size.

A new calculation model is to be developed for an improved design of fibre bed coalescers which is based on the physical processes occurring in the packed bed.

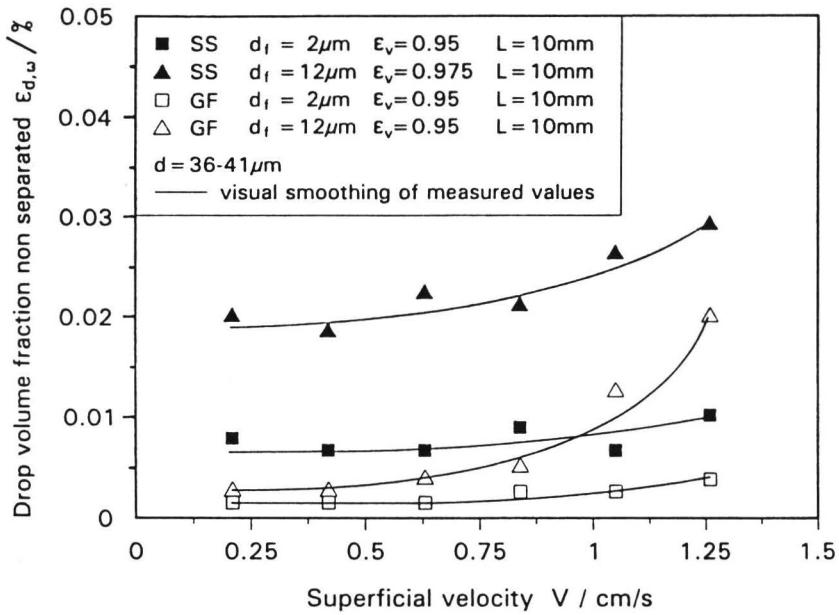


Fig.2 Unseparated drop hold-up for different fibre material and fibre thickness when superficial velocity varies

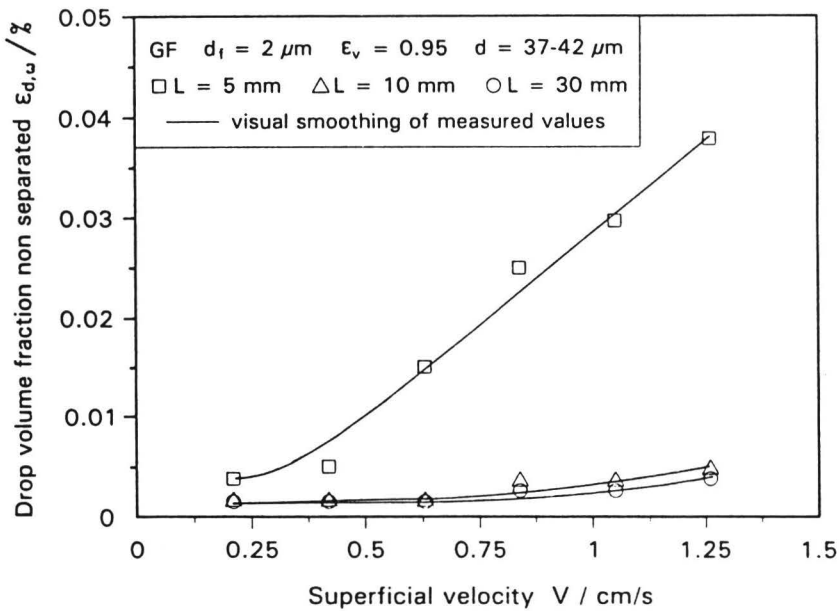


Fig.3 Unseparated drop hold-up for different fibre bed depth when superficial velocity varies

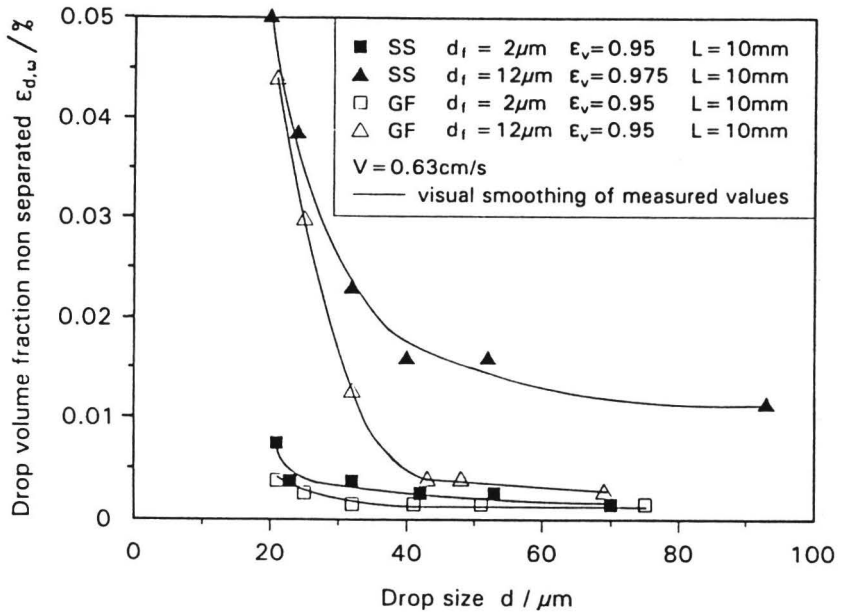


Fig.4 Unseparated drop hold-up for different fibre material and fibre thickness when drop size varies

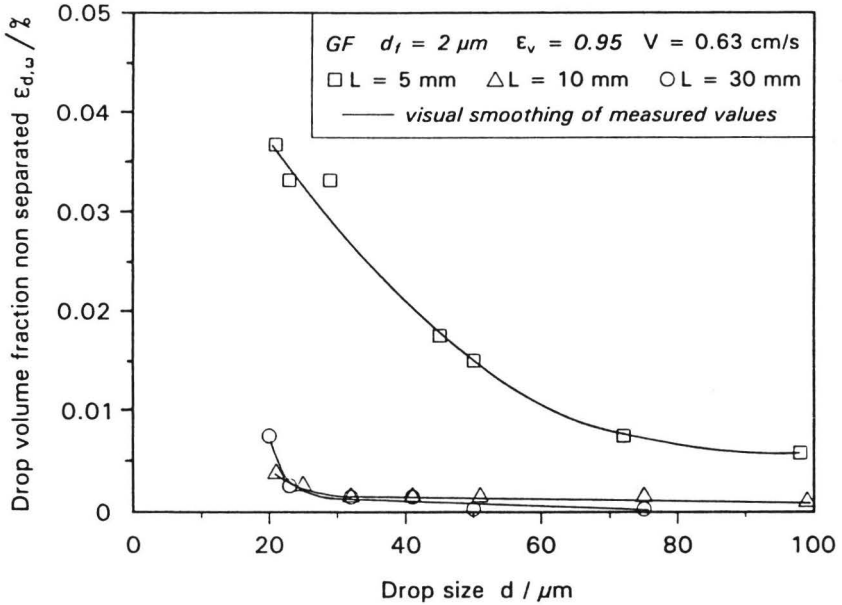


Fig.5 Unseparated drop hold-up for different fibre bed depth when drop size varies

TABLE 1

Physical properties of the test system (20 degrees Celsius)

	toluene	water
density, kg/m^3	868,2	997,5
viscosity, mPas	0,684	1,067
interfacial tension, mN/m	31,0	
solubility of toluene in water, % by volume	0,055	

NOMENCLATURE

The nomenclature used coincides with the standard nomenclature with the following exceptions:

Non-Standard nomenclature:

d_f	fibre diameter (μm)
L	fibre bed depth (mm)
$\epsilon_{d,\omega}$	drop volume fraction non separated (%)
ϵ_v	voidage fraction (-)

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1.17

APPLICATION OF THE DAVY COMBINED MIXER ELECTROSTATICALLY ASSISTED SETTLER (CMAS) TO COPPER STRIPPING FROM ORGANIC SX SOLUTIONS

M DILLEY, M T ERRINGTON, D NADEN

Davy McKee Stockton Limited, Ashmore House, Richardson Road,
Stockton-on-Tees, Cleveland, TS18 3RE, England

ABSTRACT

A series of on-site pilot plant runs were carried out to determine the performance of the Davy McKee CMAS unit operated under organic continuous conditions for copper stripping from loaded organic phase. The unit was operated in parallel to the commercial mixer settler (MS) plant using plant loaded organic feed and spent electrolyte. The unit performed similarly to the commercial MS plant at 5 to 8 times the volumetric throughput. It is considered that optimisation of the CMAS design will lead to further performance advantages. Sufficient data have been generated in the pilot plant programmes to design a demonstration or small commercial plant.

BACKGROUND

Commercial combined mixer settler (CMS) plants are successfully operating in South Africa for the recovery of uranium from dilute acid leach solutions and these are described elsewhere (Rowden et al, 1981; Bonney and Rowden 1981). Laboratory testwork indicated that the basic CMS design could be applied to copper stripping to yield greatly increased volumetric throughput (20-30 m³/m²h) over conventional mixer settler operation (3.5 m³/m²h) with much smaller equipment and plot areas. The laboratory programme was followed by a pilot plant activity at an operating copper solvent extraction (SX) plant in which the pilot plant was used to evaluate the application of the CMS to the SX strip section. Operating with real plant solutions it was found that although high efficiencies were obtained at similar volumetric throughputs to those achieved in the laboratory, unacceptably high aqueous entrainment values were observed in the organic phase. A further programme of testwork was planned operating under organic continuous conditions using electrostatic coalescence techniques to reduce the aqueous entrainment. This paper presents a summary of the information obtained in the second phase programme and discusses the application of CMAS to the copper strip system.

AIMS OF THE PROGRAMME

The test programme was designed to evaluate and obtain design data on the use of electrostatic assisted coalescence techniques in the CMS unit for the reduction of aqueous in organic phase entrainment whilst maintaining equivalent stage efficiencies and significantly higher volumetric throughput than in conventional solvent extraction plants. Commercial scale SX₃ strip plants are typically operated with a volumetric throughput of 3.5 m³/m²h to 5.0 m³/m²h and a strip efficiency of greater

than 95%. Operating conditions at this plant with organic phase continuous operation resulted in an aqueous in organic phase entrainment of up to 3000 ml/m³ and for aqueous phase continuous operation up to 500 ml/m³. Organic in aqueous phase entrainment for organic phase continuous operation was 30 ml/m³ and for aqueous phase continuous it was greater than 100 ml/m³.

The effect of the major operating variables, impeller type and tip speed and electric field strength on strip efficiency, dispersion bed depth and entrainment at equilibrium operating conditions were measured in a series of runs. The results of these tests were then used to select the preferred operating conditions for a longer continuous run in order to compare operation with that of the commercial scale plant. The strip efficiency is defined as:-

$$\frac{Cu_{OF} - Cu_{OD}}{Cu_{OF} - Cu_{ODE}} \times 100$$

Where Cu_{OF} , Copper content of the organic feed (gpl) to stage simulated.
 Cu_{OD} , Copper content of the organic discharge (gpl) from stage simulated.

Cu_{ODE} , Copper content of the organic discharge (gpl) at equilibrium.

PILOT PLANT DESCRIPTION

The CMAS pilot plant was operated in parallel with the first strip mixer-settler of the commercial plant. Loaded organic phase from the organic weir of the last extraction stage with an aqueous entrainment of up to 500 (ml/m³) was pumped through a manual control valve and flowmeter into the draught tube of the CMAS unit. The electrolyte taken from the electrolyte weir of the second strip mixer-settler with an organic phase entrainment of over 100 (ml/m³) was pumped through a manual control valve and flowmeter into the draught tube of the CMAS unit. Both pumps were provided with a recycle line to allow control at low flows. The CMAS unit and dimensions are shown in Figure 1. The unit contained a standard Davy McKee type pump-mix impeller which drew the aqueous (A) and organic (O) phases through a concentric draught tube into the mixing zone. Two types of impeller were used, CC4 and CC8, and these are shown in Figure 2. "Egg box" baffles were positioned above and below the mixing zone to prevent mass rotation and turbulence. The solutions were mixed to form a dispersion of the required phase continuity and O/A ratio. Dispersion passed into the upper and lower separation zones where settling occurred. An earthed stainless steel meshed grid was positioned on top of the upper egg box baffle with the insulated electrodes positioned approximately 1 metre above this. The organic phase overflowed a fixed weir at the top of the unit and gravitated to the organic weir of the strip settler. Aqueous phase underflowed into the aqueous weir section and then overflowed an adjustable weir and gravitated to the electrolyte weir. During operation it was found that the pilot plant construction, feed quality, as well as the considerable interactions which occur between the various variables studied imposed some constraints on the data which could be obtained. The general conclusions obtained are discussed in the following sections.

TEST PROGRAMME RESULTS

Two Davy impeller types CC4 and CC8 (CC8 having higher spoiler blades) were operated over a range of tip speeds with a constant field strength in the upper settler of 10 kV. The results illustrated by Figures 3 to 6 clearly

follow the expected trend of increased tip speed increasing the dispersion bed depth, entrainment values and strip efficiency. Strip efficiencies in excess of 90% were achieved at volumetric throughputs up to $25 \text{ m}^3/\text{m}^2\text{h}$ using both impeller types at tip speeds of 1.8 to 2.3 m/s and in the case of the CC8 impeller operated at a tip speed of 2.9 m/s, at up to $30 \text{ m}^3/\text{m}^2\text{h}$ (Figure 3). Aqueous in organic phase entrainment levels were higher than expected. The expected beneficial effect on both aqueous in organic entrainment and efficiency of an increase in dispersion bed depth when operating with the CC8 was not evident (Figures 4 and 5). This was due to the upper dispersion expanding beyond the earth grid position and coming close to the electrodes causing an increased rate of coalescence of the bulk. Such an increased coalescence rate results in smaller aqueous droplets and these are swept from the CMAS as aqueous in organic phase entrainment. Comparison of the results not influenced by bulk coalescence with laboratory data indicates that modification to the unit to enable dispersion bed depths to be increased would result in significantly reduced aqueous in organic phase entrainment. Organic in aqueous phase entrainment of 30 to $65 \text{ ml}/\text{m}^3$ obtained over a wide range of operating conditions (Figure 6) compared well with the commercial plant average of $30 \text{ ml}/\text{m}^3$ obtained during the same operating period, particularly when considering that the organic feed contained approximately $100 \text{ ml}/\text{m}^3$ entrainment and passed through a centrifugal pump prior to entry to the CMS.

The benefits of operating with an electrostatic field on aqueous in organic phase entrainment over a range of volumetric throughputs is illustrated by Figure 7. A reduction in entrainment by an order of magnitude when operating with an electrostatic field of 10 kV is observed. Tests were also carried out at a field strength of 15 kV. In this programme most of these tests were affected by the ingress of crud which had a significant effect upon the dispersion bed depth. Those results obtained at similar throughputs to the 10 kV testwork are illustrated by Figure 8. In addition, tests were carried out by disconnecting the earth grid and using the bulk electrolyte in the lower section of the CMAS as the earth. These tests confirmed the benefits of operating with a deep dispersion bed on aqueous in organic phase entrainment levels.

EXTENDED CMAS RUN COMPARISON WITH THE COMMERCIAL MS PLANT

Following the short run tests discussed above, an extended run in the CMAS pilot plant was carried out over a period of 50 hours. A CC8 impeller was used with an operating tip speed of 2.9 m/s and a volumetric throughput of $20 \text{ m}^3/\text{m}^2\text{h}$. The performance of the unit during the extended run was stable and the results were similar to those obtained in the shorter test runs. The mean strip efficiency was 93.7% (sd 2.4%). Organic loss to electrolyte was $81 \text{ ml}/\text{m}^3$ (sd $19 \text{ ml}/\text{m}^3$) which was significantly less than the incoming electrolyte feed of $227 \text{ ml}/\text{m}^3$ (sd $49 \text{ ml}/\text{m}^3$). The mean aqueous in organic entrainment was $12,289$ (sd $455 \text{ ml}/\text{m}^3$) using a feed with an entrainment of up to $3000 \text{ ml}/\text{m}^3$. The results of the CMAS extended run are summarised in Table 1 and a comparison with the first strip stage of the operating SX plant over the same period is given in Table 2. A slightly lower strip efficiency was observed as well as slightly higher entrainments. However both were due to the effect of crud ingress in the CMAS. It is considered that both would be improved by modifying the design to achieve deeper dispersion bands which would not extend above the earth grid of the upper settler.

CONCLUSIONS

The CMAS performed similarly to the commercial MS plant at 5 to 8 times the volumetric throughput and the benefits of operating with electrostatic coalescence have been demonstrated. Information generated in the programme leads to the conclusion that improvement in the CMAS unit operation and hence higher volumetric throughput with lower entrainment will be achieved by modification to the unit design to prevent excessive bulk coalescence. Overall, sufficient information has been generated in the pilot plant programme to design a demonstration or small commercial plant and opportunities are currently being sought.

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Bonney C F, Dilley M, Gillet G A and Rowden G A, 1981. Society of Chemical Industry Symposium. Hydrometallurgy 1981 Manchester. Bonney C F and Rowden G A. February 1981, American Institute of Mining Engineers.

TABLE 1

Extended Run at $24 \text{ m}^3/\text{m}^2\text{h}$ using the CC8 Impeller with a Tip Speed of 2.9 m/s and a Field Strength of 10 kV

Elapsed Time Hours	Volumetric Throughput $\text{m}^3/\text{m}^2\text{h}$	Entrainment ml/m^3		Efficiency %
		Aq in Org	Org in Aq	
6	24.4	12750	94	92
10	23.8	11850	-	91
15	23.1	12200	107	92
20	22.0	12600	46	91
30	23.9	12250	-	96
35	23.9	12050	75	93
40	25.1	11450	83	93
45	24.6	13050	-	97
50	24.0	12400	83	97

TABLE 2

Comparison of CMAS Pilot Plant Performance with the Commercial MS Plant

	CMAS (Extended Run)	Main Plant 1st Strip
Volumetric throughput, $\text{m}^3/\text{m}^2\text{h}$	22.0 - 25.0	2.50
Strip efficiency, %	91% - 97%	>95.0%
Aqueous in organic entrainment (operating organic continuous)	12,200 ml/m^3	3,000 ml/m^3
Organic in aqueous entrainment	45 - 110 ml/m^3 (1)	30 ml/m^3

(1) Influenced by incoming entrainment of 180 to $270 \text{ ml}/\text{m}^3$.
The CMAS was affected by crud during the extended run.

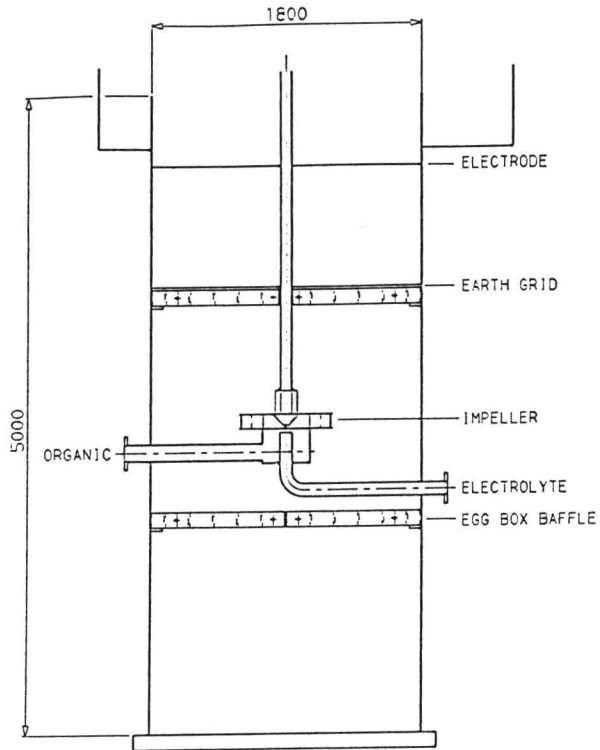
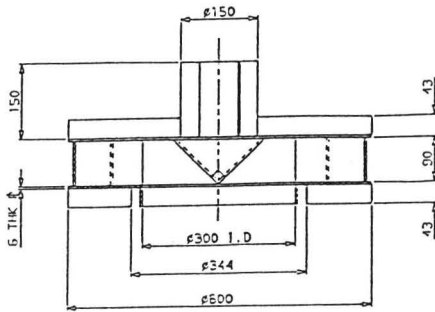
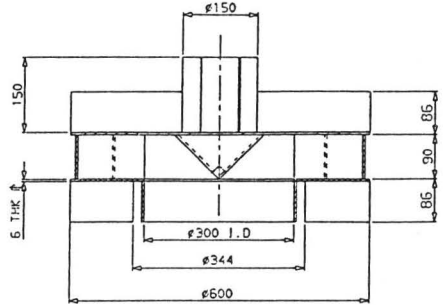


Figure 1



CC4 Impeller



CC8 Impeller

Figure 2

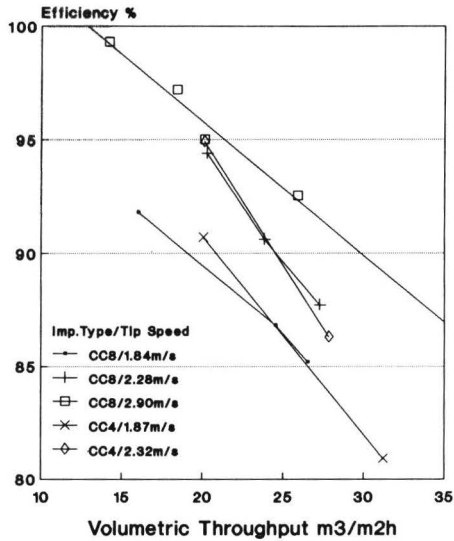


Figure 3
Effect of Impeller Type/
Tip Speed on Efficiency

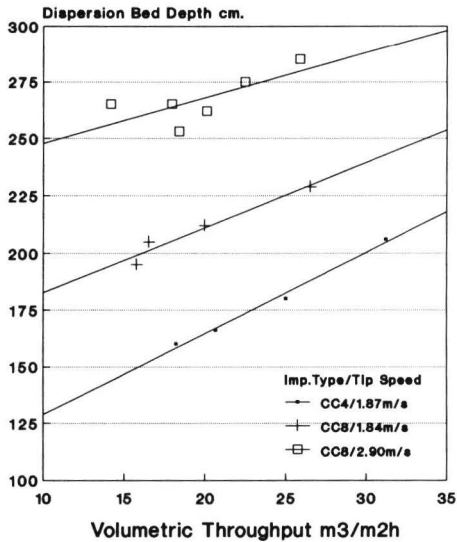


Figure 4
Effect of Impeller Type/
Tip Speed on Dispersion
Bed Depth

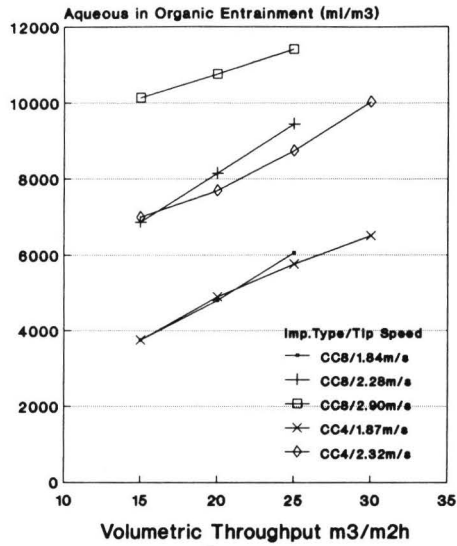


Figure 5
Effect of Impeller Type/
Tip Speed on Aqueous in
Organic Phase Entrainment

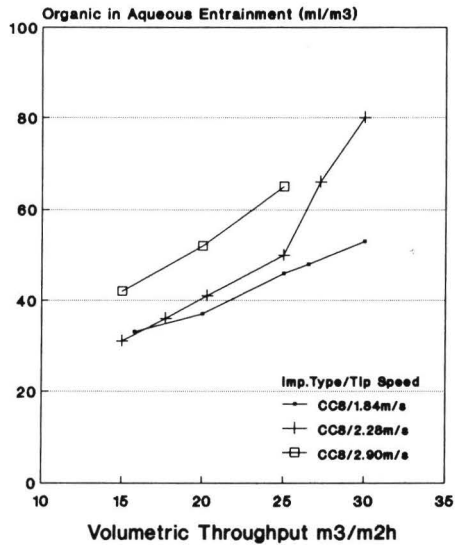


Figure 6
Effect of Impeller Type/
Tip Speed on Organic in
Aqueous Phase Entrainment

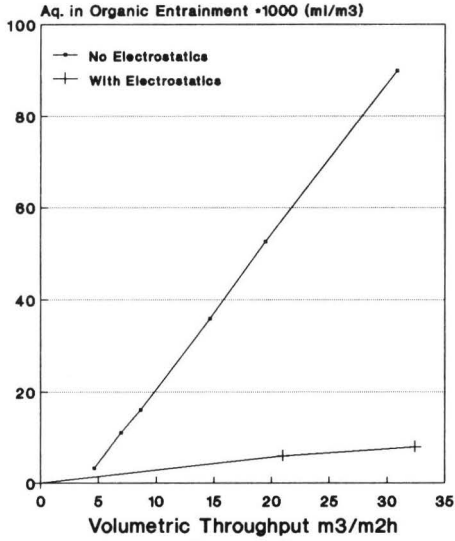
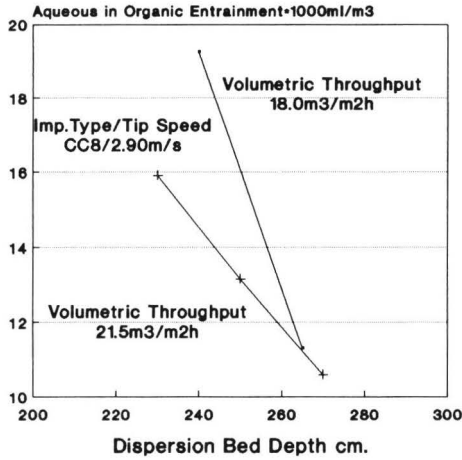


Figure 7
Effect of Operation With and
Without Electrostatics on
Aq. in Org. Phase Entrainment



Field Strength
— 10kV — 15kV
Figure 8
Effect of Dispersion Bed Depth
and Field Strength on Aqueous
in Organic Phase Entrainment

HYDRAULIC AND MASS TRANSFER CHARACTERISTICS OF A RADIALY PULSED EXTRACTION COLUMN

**S. B. KOGANTI, K. PERIASAMY, C.V. RAJAGOPALAN, V. SREEDHARAN and
G.R. BALASUBRAMANIAN**

Reprocessing Programme, Indira Gandhi Centre for Atomic Research,
Kalpakkam 603102, INDIA.

S. SUBBA RAO and Y.B.G. VARMA.

Department of Chemical Engineering, Indian Institute of Technology,
Madras 600036, INDIA.

ABSTRACT

Flooding throughput and dispersed phase hold-up of a radially pulsed extraction column, a slightly modified version of the unit originally proposed by Koganti et al.(1984), are well correlated with commonly used slip velocity equations for the system nitric acid - 30% TBP/n-dodecane with either phase dispersed. Mass transfer characteristics are compared with a liquid pulsed sieve plate column. Under the operating condition of frequency and amplitude of pulsing, dispersed phase hold-up values are high and HTU values are less compared to a liquid pulsed sieve plate column of the same diameter and height.

INTRODUCTION

Liquid pulsed sieve plate columns are widely used in nuclear industry in general and nuclear fuel reprocessing in particular, due to many advantages of non-moving parts, the possibility of pulsing the liquid contents with air and higher contactor effectiveness and lesser floor area compared to mixer-settlers. It is known that pulsing in the liquid flow direction gives rise to axial mixing which reduces mass transfer efficiency. Imparting liquid jets radially at many locations along the column creates intense mixing giving rise to higher values of dispersed phase hold-up, which in turn reduces height of transfer unit (Koganti et al.1984). In the earlier study the authors did not attempt to correlate the flooding throughput and dispersed phase hold-up.

Vassallo (1982) reported an extensive set of hold-up measurements for the system 30 vol% TBP/OK dispersed in 2 M nitric acid in a 72 mm i.d. pulsed perforated plate column (hole size 3.2 mm, triangular pitch, 23% free area) with an effective dispersion height of 3.2m. These data and the data reported by Batey et al.(1983) for the system 20 vol% TBP/OK dispersed in 3 M nitric acid are well correlated by Batey et al. (1986) using the droplet

characteristic velocity concept originally proposed by Pratt and subsequently used by Thornton (1957) for correlating the flooding capacities of liquid pulsed sieve plate columns. Fei and Slater (1983) and Godfrey and Slater (1991) discussed various hold-up equations used in different contactors below flooding point.

DETAILS OF COLUMN CONSTRUCTION

A stainless steel column of 52.4 mm i.d. and 1100 mm dispersion length is fabricated with 11 mixing sections of height 50 mm each spaced alternately with 50 mm high calming sections. Perforated plates of 52 mm diameter with 4 mm holes on a triangular pitch of 5.75 mm having a free area of 40%, are placed all along the column which separate all 11 mixing and 10 calming sections. In the mixing sections 1 mm holes are drilled on the column wall whose thickness is reduced by machining the o.d. to 56 mm. Two semi annular enclosures are built around each mixing section as shown in Figure 1.

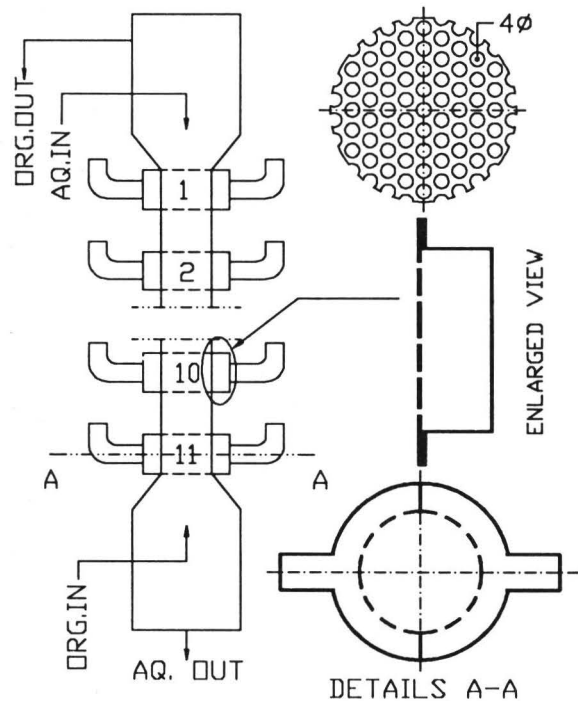


Fig.1 Schematic of the radially pulsed column

discharges liquid into the column through 1 mm holes, the other limb draws the same volume from the column. Liquid movement through the 1 mm holes and the interaction of the radial jets with the liquid, creates enough turbulence to disperse one of the counter moving phases.

EXPERIMENTAL

Experimental data for flooding throughput and dispersed phase hold-up for either phase dispersed are obtained using pre-equilibrated 0.5M HNO_3 - 30 vol% TBP/n-dodecane

system, as a function of pulsing frequency and phase flow ratio. Amplitude of pulsing is referred to the average displacement of liquid column in all the 12 mm i.d. transparent tubes. For a given pressure and vacuum settings, the amplitude in the pulse limbs was found to vary along the length of the column and an average value of around 21 cm is maintained for most of the experimental runs during this study. Flooding capacities are measured by increasing the dispersed phase flow rate gradually for a given continuous phase flow rate, keeping all other variables constant during the run. Flooding throughputs are very low for frequencies above 1.16 s^{-1} and mixing was poor (bigger aqueous drops were seen falling to the interface) for frequencies below 0.65 s^{-1} .

Hold-up values are measured at 4 different locations of the column by draining about 15 mL of the dispersion into a graduated tube and noting the volumes of dispersed and continuous phases after centrifuging the dispersion. The average of these four values is taken as the mean value for the column. Mean hold-up values are also obtained by measuring the hydrostatic pressure difference across the dispersion height. Both methods agree very well for aqueous dispersion and agreement is rather poor for organic dispersion. Mass transfer measurements are obtained with the HNO_3 - 30% TBP/ n-dodecane system with aqueous feed acidity of 3-4 M and organic feed of $\sim 0.0 \text{ M}$. Preliminary mass transfer runs are conducted with a view to optimize the relative height of mixing section to calming section and it was found that pulsing the alternate mixing sections gives the best mass transfer performance. Further hydraulic and mass transfer experiments are conducted only with alternate mixing sections operating.

RESULTS AND DISCUSSION

Flooding Throughput

Flooding curves for both aqueous and organic as dispersed phase are shown in Figures 2 and 3. The mean velocity of the dispersed phase relative to that of continuous phase for counter current differential contactors is given by Pratt(1953) as;

$$V_{\text{slip}} = V_d / \phi + V_c / (1 - \phi) = V_0 (1 - \phi) \quad (1)$$

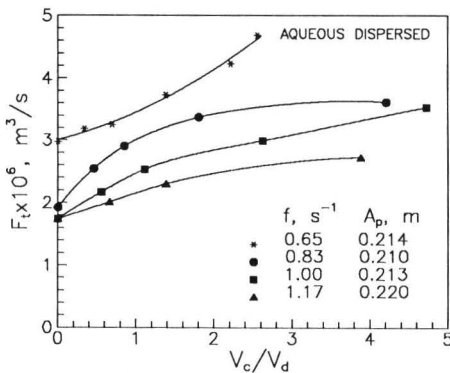


Fig.2 Flooding throughput for aqueous as dispersed phase

Since Equation 1 was found to be applicable at and near flooding for most of the mechanically agitated contactors, the same was tested for determining the flood point. From Fig.4 it can be seen that Eqn.1 correlates the aqueous dispersion data well and the same was observed with organic dispersion as well. The V_0 values obtained are listed in Fig.4. The dependency of V_0 on (f, A_p) is shown in Fig.5 and the

resulting flooding correlations are:

1) For aqueous dispersion,

$$V_{df}/\phi_f + V_{cf}/(1-\phi_f) = 9.932 \times 10^{-3} \cdot \exp[-4.3607(f \cdot A_p)] \cdot (1-\phi_f) \quad (2)$$

and 2) for organic dispersion

$$V_{df}/\phi_f + V_{cf}/(1-\phi_f) = 13.06 \times 10^{-3} \cdot \exp[-3.654(f \cdot A_p)] \cdot (1-\phi_f) \quad (3)$$

Flood point hold-up, ϕ_f is difficult to measure experimentally and can be calculated from Eqn. 1 as;

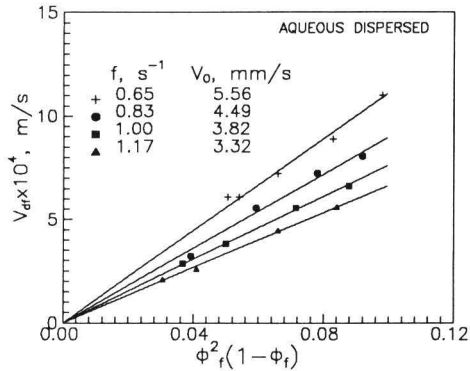
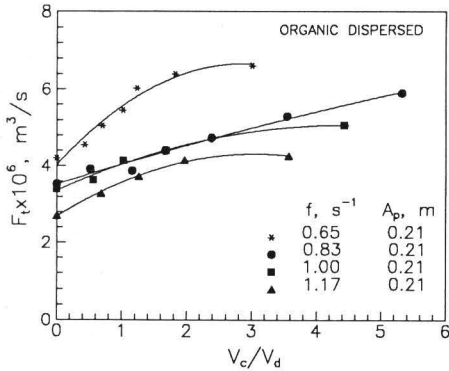


Fig.3 Flooding throughput for organic as dispersed phase

Fig.4 Test of Equation 1 for flood point determination

$$\phi_f = [(R^2 + 8 \cdot R)^{0.5} - 3 \cdot R] / [4(1-R)] \quad (4)$$

From Fig.5 it can be seen that the V_0 values for organic dispersion are about 1.5 times those of aqueous dispersion for the same energy input. The variation in V_0 is as expected in that the dispersed phase drops in the more viscous continuous phase tend to move slower compared to less viscous continuous phase. Though exact drop size measurements were not attempted, it is seen from the photographs that the drops are of the order of 0.2 mm, for either phase dispersed.

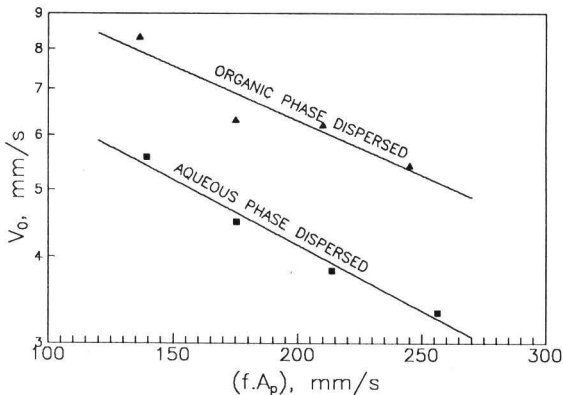


Fig.5 Correlation of flooding throughputs

Dispersed Phase hold-up

Typical dispersed phase hold-up values for aqueous dispersion are shown in Figures 6 and 7 as a function of V_d for frequencies of 0.65 and 1.17 s⁻¹. These values along with the hold-up results for f equal to 0.83 and 1.0 s⁻¹ are replotted in Fig.8 in accordance with the modified form of Eqn. 1. This plot

clearly shows that the data are not linear unlike the behaviour with liquid pulsed sieve plate columns (Batey et al, 1986). The curvature is more pronounced with increase in f values. It is possible to obtain V_0 by considering slip velocity as a function of $(1 - \phi)^m$ as shown by

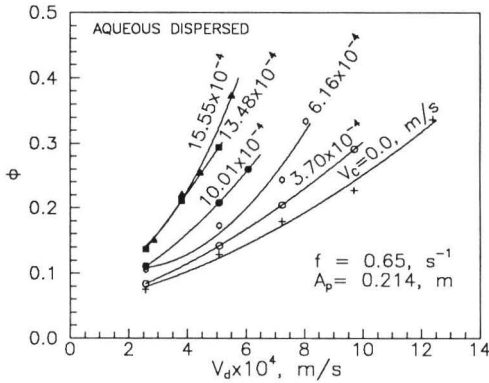


Fig.6 Variation of hold-up with V_d for aqueous dispersion

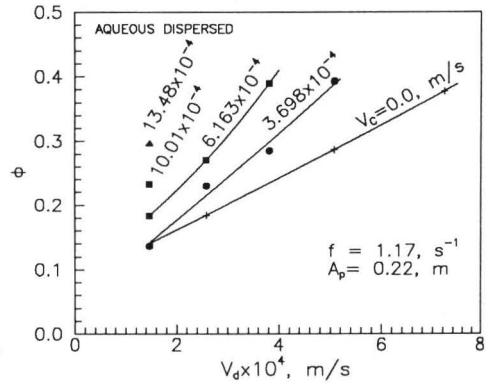


Fig.7 Variation of hold-up with V_d for aqueous dispersion

Fei and Slater (1983) and Godfrey and Slater (1991).

$$V_d / \phi + V_c / (1 - \phi) = V_0 (1 - \phi)^m \quad (5)$$

The results of least square analysis, obtained for V_0 and m for the experimental hold-up data at different frequencies are shown in Table 1, for both aqueous and organic as dispersed phase. Considering the overall data for either phase dispersed, the following correlations (Eqn. 6-9) based on Eqn.5 are obtained.

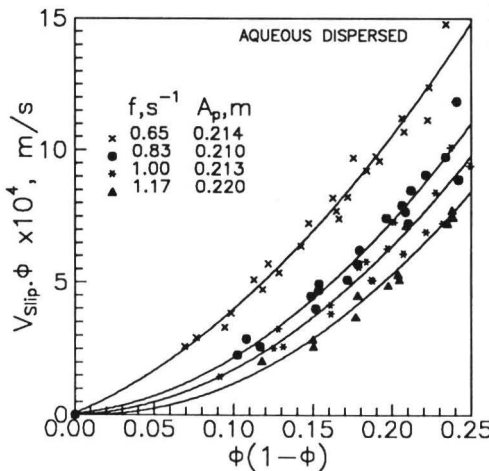


Fig.8 Plot of modified form of Equation 1

TABLE 1

V_0 and m values for Equation 5

f (s^{-1})	Aq. dispersion		Org. dispersion	
	V_0 (mm/s)	m	V_0 (mm/s)	m
0.65	3.54	-0.18	7.36	0.60
0.83	2.10	-0.53	4.22	0.00
1.00	1.75	-0.60	2.76	-0.95
1.17	1.36	-0.85	3.19	-0.05

1) For aqueous dispersion

$$V_d / \phi + V_c / (1 - \phi) = 2.54 \times 10^{-4} (f \cdot A_p)^{-1.28} (1 - \phi)^{-0.46} \quad (6)$$

and in terms of experimental variables

$$\phi = 6.27 \times 10^2 (f \cdot A_p)^{1.257} V_d^{0.686} V_c^{0.038} \quad (7)$$

2) For organic dispersion

$$V_d / \phi + V_c / (1 - \phi) = 5.133 \times 10^{-4} (f \cdot A_p)^{-1.245} (1 - \phi)^{-0.076} \quad (8)$$

and

$$\phi = 2.625 \times 10^2 (f \cdot A_p)^{1.328} V_d^{0.626} V_c^{0.0264} \quad (9)$$

The exponent on $(f \cdot A_p)$ in Eqn. 6 and 8 is of interest as it is known that the drop diameter, $d_{vs} \propto 1/\Psi^{0.4}$ (Shinner and Church, 1960) and $\Psi \propto (f \cdot A_p)^3$ which will result in $d_{vs} \propto (f \cdot A_p)^{-1.2}$.

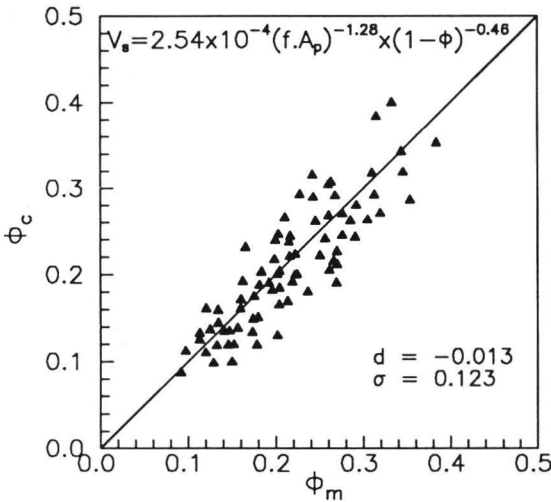


Fig.9 Hold-up correlation for aqueous dispersion data

The hold-up dependency on V_d is observed to be similar to that of pulsed sieve plate columns. The perforation size and free area may not influence the column hydraulic performance as the drop size is very small in all the experiments. The calculated values of ϕ using Eqn.6 are shown in Fig.9 for aqueous dispersion data.

Mass Transfer Performance

During the mass transfer runs steady state is achieved after about 3 hours. Preliminary mass transfer data presented in Table 2 show that mixing in the alternate sections gives better mass transfer performance compared to mixing in all the 11

sections. Having perforated plates in all the sections improves the mass transfer performance probably by way of reducing the axial mixing. Comparative performance with a liquid pulsed sieve plate column (3.2 mm perforations, 23% free area, 1100 mm effective dispersion height) for similar experimental conditions is shown in Figure 10. Aqueous to organic flow rate ratio (R) of 0.25 is chosen for the above runs so that the operating lines are almost parallel to the equilibrium line. These conditions clearly show the equilibrium

stages on a McCabe -Thiele diagram and avoid approaching pinching, where small analytical errors will lead to large deviations in estimating the NTU values. From Fig.10 it can be seen that the HTU value for the present column is about half that of liquid pulsed sieve plate column. Additional mass transfer data as a function of R and f are presented in Table 3.

TABLE 2

Preliminary mass transfer data (System : HNO_3 - 30% TBP/n-dodecane)

Run No	$F_a \times 10^6$ (m^3/s)	$F_o \times 10^6$ (m^3/s)	R	f (s^{-1})	A_p (m)	NTU _{org}	NTU _{aq}	Remarks
1	1.00	2.87	0.348	0.78	0.175	3.2	1.75	(a)
2	1.07	3.00	0.355	0.78	0.170	3.44	1.98	(b)
3	1.20	2.67	0.450	0.83	0.170	4.04	1.62	(c)
4	0.44	1.75	0.252	1.00	0.150	2.89	2.53	(a)
5	0.53	2.08	0.252	1.00	0.210	5.20	4.34	(b)
6	1.05	2.87	0.366	1.17	0.150	3.74	2.02	(b)
7	1.0	2.93	0.341	1.17	0.100	3.62	2.02	(a)
8	0.35	2.08	0.168	1.00	0.21	2.45	3.30	(d)
9	0.5	2.08	0.24	1.00	0.21	3.02	3.17	(e)
10	0.53	2.22	0.240	1.00	0.21	2.56	2.57	(f)

(a) pulsing in all stages, (b) pulsing in 1,3,5,7,9,11 stages, (c) pulsing in 1,3,5,7,9,11 with simultaneous pressure and vacuum in both pulse limbs, (d) pulsing in 1,6,11 stages, (e) pulsing in 1,4,7,10 stages, (f) pulsing in 1,3,5,7,9,11 stages with perforated plates only in pulsing stages.

TABLE 3

Additional mass transfer data (System : HNO_3 -30%TBP/n-dodecane)

Run No	$F_a \times 10^6$ (m^3/s)	$F_o \times 10^6$ (m^3/s)	R	f (s^{-1})	A_p (m)	NTU _{org}	NTU _{aq}
1	0.775	2.183	0.355	1.0	0.21	5.11	2.61
2	"	"	"	1.17	0.21	4.25	2.48
3	1.0	2.00	0.5	0.83	0.21	5.01	1.6
4	"	"	"	1.0	0.21	5.27	1.9
5	"	"	"	1.17	0.21	5.10	1.99
6	1.25	1.25	1.0	0.83	0.21	4.34	0.75
7	"	"	"	1.0	0.21	6.55	0.94
8	"	"	"	1.17	0.21	8.03	2.63
9	0.6	2.4	0.25	0.5	0.21	1.0	1.05
10	"	"	"	0.67	0.21	3.13	3.11
11	"	"	"	0.83	0.21	4.19	3.96
12	"	"	"	0.83	0.27	4.76	4.64
13	"	"	"	1.00	0.15	4.0	3.88
14	"	"	"	1.00	0.21	4.30	4.49
15	"	"	"	1.17	0.21	4.06	4.31
Liquid pulsed sieve plate column							
16	"	"	"	1.0	0.026	1.03	0.94
17	"	"	"	1.0	0.053	1.90	1.82
18	"	"	"	1.17	0.026	1.23	1.22
19	"	"	"	1.17	0.053	1.89	1.85

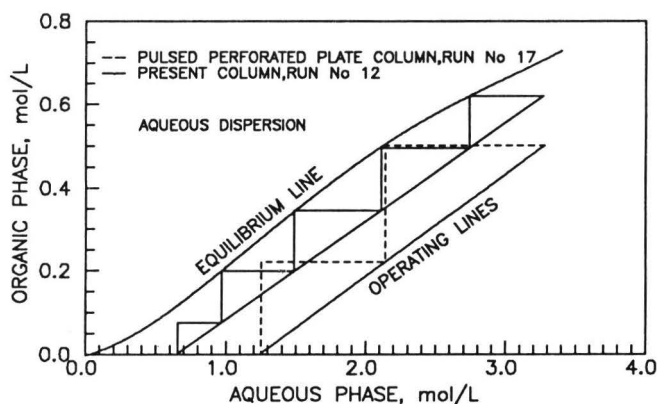


Fig.10 Comparison of mass transfer performance

CONCLUSIONS

Radial pulsing at many locations reduces HTU values compared to the conventional liquid pulsed sieve plate columns. Flooding capacities of this unit are much lower, due to increased hold-up obtained for the given V_c and V_d values, than for liquid pulsed sieve plate columns. Flooding throughputs and dispersed phase hold-up are correlated with commonly used slip velocity equations. Flooding throughput for organic dispersion are about 1.5 times higher compared to the aqueous dispersion. This unit can find application for final purification of plutonium in nuclear fuel reprocessing industry.

NOMENCLATURE

A_p	amplitude of pulse, referred to the displacement in the pulse limb (m)
Ψ	power input per unit volume in the mixing section (W/m^3)
f	frequency of pulsing (s^{-1})
V	velocity (m/s), (mm/s)

Subscripts

a	aqueous
c	continuous phase, calculated
cf	continuous phase at flooding
df	dispersed phase at flooding
m	measured
o	organic
slip, s	slip between the phases
vs	volume to surface area
0	characteristic velocity

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SESSION 2

PROCESSES

2.1

**SEPARATION AND RECOVERY OF NICKEL AND COBALT IN
AMMONIACAL SYSTEMS - PROCESS DEVELOPMENT**

M.J. PRICE and J.G. REID
Queensland Nickel Pty. Ltd.
P.M.B. 5, Mail Centre,
Townsville, Queensland, 4818, Australia

ABSTRACT

In 1989 Queensland Nickel, Townsville, Australia, commissioned a solvent extraction plant capable of separating nickel from cobalt, both present as ammines in Caron type ammoniacal leach liquors. The solvent extraction plant is unique in that it operates with ammoniacal liquors in both the extraction and stripping stages. The plant was designed on the basis of results derived during 2½ years of research and testwork at both laboratory and pilot plant levels.

The extraction of nickel from ammoniacal solvents using both oxime and β -diketone reagents was studied, as was the performance of the nickel loaded organic reagents when stripped with high strength ammoniacal ammonium carbonate solutions ($\approx 280 \text{ gL}^{-1} \text{ NH}_3$).

Nickel transfer kinetics, organic reagent stability, organic reagent poisoning, cobalt nickel separation, and pregnant liquor pretreatment aspects were all thoroughly researched to provide adequate data for economic evaluation and scale up purposes. A reagent mixture based on Henkel reagent LIX 84 (modified) and Escaid 110 aliphatic solvent was selected for plant operation. During an extended continuous shift operation with the pilot plant processing a side stream of actual plant pregnant liquor, the nickel/cobalt ratio of the loaded strip averaged 8000/1 while the nickel content of the raffinate averaged 10 mg/dm^3 .

Continuous pilot plant operation highlighted the need to have in place, before plant start up, means of reversing both reagent poisoning by cobalt complexation and reagent degradation.

INTRODUCTION

Prior to the introduction of the ammoniacal solvent extraction (ASX) circuit at Queensland Nickel (QNPL) cobalt together with some nickel was removed from the ammoniacal product liquor stream by sulphiding. Early in 1985 when it became known

that the market for the mixed nickel-cobalt sulphide would cease, a research project was initiated to replace the QNPL sulphiding circuit with an alternative system to separate nickel from cobalt with the long term aim of producing higher purity nickel and cobalt products. The system developed had to be compatible with existing pre- and post- sulphiding circuits and obviously it had to be totally reliable and economically viable.

The constraints on the project, particularly those associated with the existing circuits of the QNPL plant, really created the concept of a totally ammoniacal solvent extraction system. There was no place in the QNPL flow sheet for acidic reagents. To convert the concept to a reality it was necessary to identify an organic reagent capable of extracting either nickel or cobalt (not both) from ammoniacal liquors and then releasing the loaded element when stripped with strong ammoniacal liquors. A literature search failed to uncover any systems that could be adapted to the QNPL situation.

MATERIALS AND PROCEDURES

Reagents

The organic reagents tested in this investigation were used as received from commercial suppliers, no purification was attempted or considered desirable. Included in the reagents tested were Henkel LIX 54 (an aryl alkyl β -diketone, $MW \approx 344$), LIX 64N (a mixture of 2-hydroxy-5-nonyl benzophenoneoxime $MW \approx 399$ and 5,8-diethyl-7-hydroxy dodecan-6-oxime $MW \approx 257$) LIX84 (2-hydroxy-5-t-nonyl acetophenoneoxime $MW \approx 263$) and Acorga PT5050 (2-hydroxy-5-nonyl salicylaldoxime $MW \approx 263$ modified with tridecanol). The diluents used with the organic reagents varied from aliphatic, Escaid 110, to aromatic, Pegasol R150 and intermediate types such as Shellsol 2046.

Feed Solutions

The product liquor subjected to both laboratory and pilot plant extraction studies was obtained directly from the operating plant, no laboratory prepared nickel/cobalt solutions were used in the study. Plant derived product liquor typically consisted of Ni 10 gL^{-1} , Co 0.5 gL^{-1} , NH_3 95 gL^{-1} , CO_2 60 gL^{-1} and a number of minor components.

Strip Liquors

Plant produced ammoniacal liquors were available but were limited to approximately $180 \text{ gL}^{-1} \text{NH}_3$, consequently higher ammonia content liquors had to be prepared in the laboratory from aqueous and anhydrous ammonia mixtures and gaseous carbon dioxide.

During the operation of the Pilot Plant, modifications to the operating plant enabled the production of high strength liquors ($>280 \text{ gL}^{-1}\text{NH}_3$) for stripping purposes.

Experimental Procedures

Solvent extraction tests were conducted at room temperature in separating funnels, continuous solvent extraction and stripping test work using a Bell Mini Rig was conducted at temperatures up to 55°C . The separated phases after suitable treatment were analysed for Ni, Co and such other elements as were required using the technique of atomic absorption spectroscopy.

Cobalt (II) and Cobalt (III) ammines were identified by high pressure liquid chromatography separation on Dowex 50W x 8 ion exchange resin. Cobalt (II) was determined quantitatively by selective extraction of the aqueous phase under nitrogen.

TESTING THE CONCEPT

All available organic reagents were tested for their ability to extract nickel from product liquor and their ability to release nickel when stripped with strong ammoniacal ammonium carbonate liquor.

Nickel Extraction with LIX 64N

When initial tests with LIX 64N, 25% V/V in Shellsol 2046 and product liquor failed to extract all the available nickel the product liquor was carefully distilled to lower the ammonia content in stages from 95 gL^{-1} to 25 gL^{-1} . Further testwork with the reagent showed increasing extraction efficiency with decreasing NH_3 concentration, Figure 1.

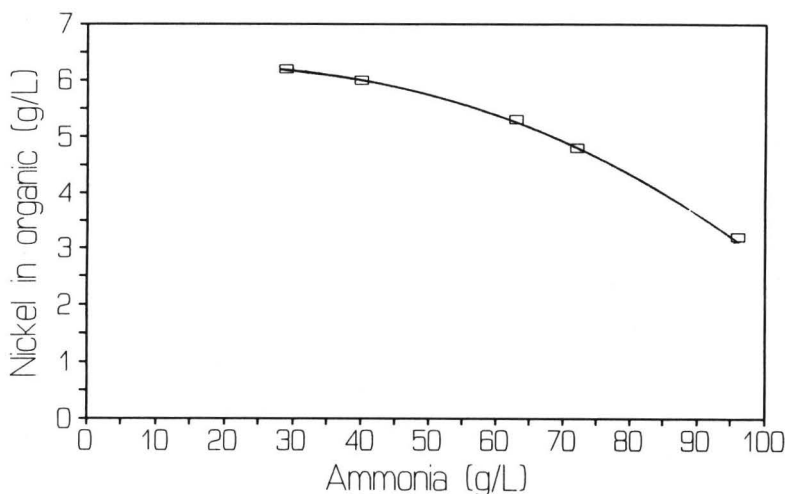
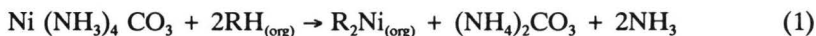


Fig.1 NH_3 concentration and nickel extraction

From this it was inferred that the relationship:-



was reversible and therefore high $\text{NH}_3/\text{NH}_4^+$ concentration solutions should be effective stripping agents. In practice this proved to be the case and the extraction and stripping isotherms, Figure 2 and Figure 3, were typical of those developed for other reagents tested. The nickel loading of approximately 6.5 gL^{-1} for LIX 64N is the maximum possible for this reagent at a concentration of 25% v/v in Shellsol 2046.

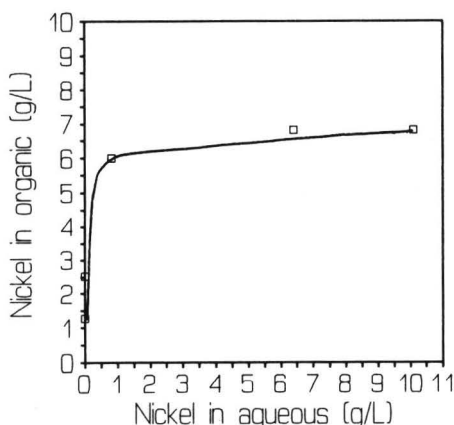


Fig. 2 Nickel extraction isotherm

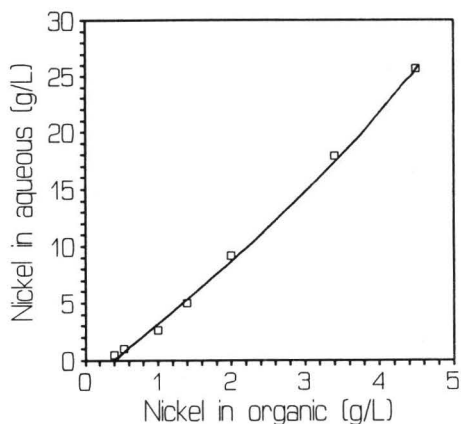


Fig. 3 Nickel stripping isotherm

The composition of the aqueous feed liquor was Ni 13, Co 0.49, NH_3 39 and CO_2 27 all gL^{-1} . The composition of the aqueous strip liquor was NH_3 210 and CO_2 200 gL^{-1} .

Special Product Liquor

Product liquor, when distilled to lower the NH_3 concentration to approximately 30 gL^{-1} , was called special product liquor or SPL. This distillation step had a beneficial effect in that impurities, such as arsenic, iron and manganese, were precipitated while magnesium and silica were partially removed.

Strip Liquor Composition

Strip liquor composition could be varied in two ways, first by changing the total NH_3 concentration and second by changing the free ammonia concentration. It was necessary to examine the effect of NH_3 concentration changes on the efficiency of nickel stripping from the loaded organic reagent.

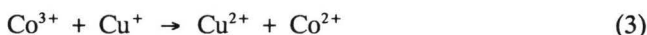
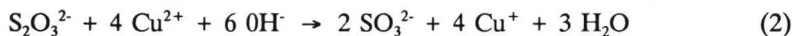
A nickel loaded organic reagent was contacted in separating funnels with strip liquors at O/A ratios of 1/2.5 at room temperature. In the case of modified LIX 84 the following data were recorded.

TABLE 1
Effect of total NH_3 on stripping

$\text{NH}_3 \text{ gL}^{-1}$ (Total)	Ni gL^{-1} Stripped Organic
200	4
230	3.2
270	1.2
300	0.56

Cobalt Extraction

Cobalt is not co-extracted with nickel from ammoniacal media provided it is present as Co(III). All the organic reagents tested showed excellent selectivity for Ni(II) over Co(III) amines. It is not possible however to produce a plant product liquor free of Co(II) amines, due mainly to the presence of reduced sulphur anions which, in the presence of copper, are able to reduce Co(III) to Co(II).



Unfortunately when cobalt is extracted by the organic reagent it is not stripped by the ammoniacal liquor and a procedure to reverse this cobalt bonding was developed and tested in the Pilot Plant.

Kinetics

It should be noted that there was no prior knowledge available to QNPL regarding the concept of ammoniacal stripping of nickel despite close working relationships with major producers of solvent extraction reagents. It was necessary to determine the extraction and stripping kinetics for nickel and compare these data with available information for copper in order to assess the potential of ammoniacal stripping. Information such as that in Table 2 coupled with an intensive evaluation period using a Bell Corporation Mini Rig continuous mixer settler eliminated the need to Pilot Plant test a number of reagents. Acorga PT5050 was eliminated from further testing because it did not strip adequately with ammonium carbonate liquors. Henkel LIX 54 reagent suffered from the disadvantage that it degraded in ammoniacal strip liquor

while Henkel 64N reagent did not load sufficient nickel at operable reagent concentrations.

TABLE 2
% approach to equilibrium

Reagent 25% v/v	Extraction		Stripping	
	15 s	30 s	15 s	30 s
Contact time	15 s	30 s	15 s	30 s
LIX 54	91	97	99	99
PT5050	98	100	70	90

Bell Mini Rig Data

The circuit consisted of 3 extraction, 3 stripping and one loaded organic scrub cell. The feed liquor composition was Ni 9 gL⁻¹, Co 0.34 gL⁻¹, NH₃ 25 gL⁻¹, CO₂ 14 gL⁻¹, while the organic reagent was a 42.5% V/V solution of LIX 54 in high aromatic solvent Mobil Pegasol R150.

Typical flow rates were 100 ml/min for both SPL and organic reagent and 13 ml/min for the ammoniacal strip liquor. The circuit was operated in aqueous continuous mode in both extraction and stripping circuits, the ratio of the organic to aqueous phases in the mixer boxes was maintained at 1:1 or thereabouts by the use of aqueous recycle from the settler back to the mixer in the strip circuit cells.

The system was operated continuously for 96 h at 40°C with the stripped organic recycled from the stripping to the extraction cells via a small intermediate vessel. The results are given in Table 3.

TABLE 3
Operating data LIX 54 reagent
24 h averages

	Co	Ni
Raffinate (gL ⁻¹)	0.34	0.005
Loaded strip (gL ⁻¹)	0.013	68.6
Stripped organic (gL ⁻¹)	0.006	0.01
O/A ratios	1:1 extraction, 7.5:1 stripping	

PILOT SCALE WORK ON THE CONCEPT

The laboratory studies with the Mini Rig allowed a design for the Pilot Plant to be developed and its assembly commenced. The Pilot Plant was operated 24 hours a day on a continuous shift basis 7 days a week while a reagent was being evaluated. Figure 4 shows details of the most important units of the plant.

Pilot Plant Cells

The cells were of two types, the major difference being the configuration of the mixer boxes. In Figure 4 only single mixer boxes are shown but in practice some cells were operated with dual boxes. This was found to be necessary due to the somewhat slower stripping kinetics of nickel compared with copper kinetics from known operating plants.

Cell dimensions	1.55 x 0.6 x 0.9 (surface area = 0.93 m ²)
Mixer Box	0.575 m Diameter
Impeller	Various Configurations
Phase Flow (total)	60 - 70 L/min (SPL + Organic Reagent)
Operating Temperature	45°C

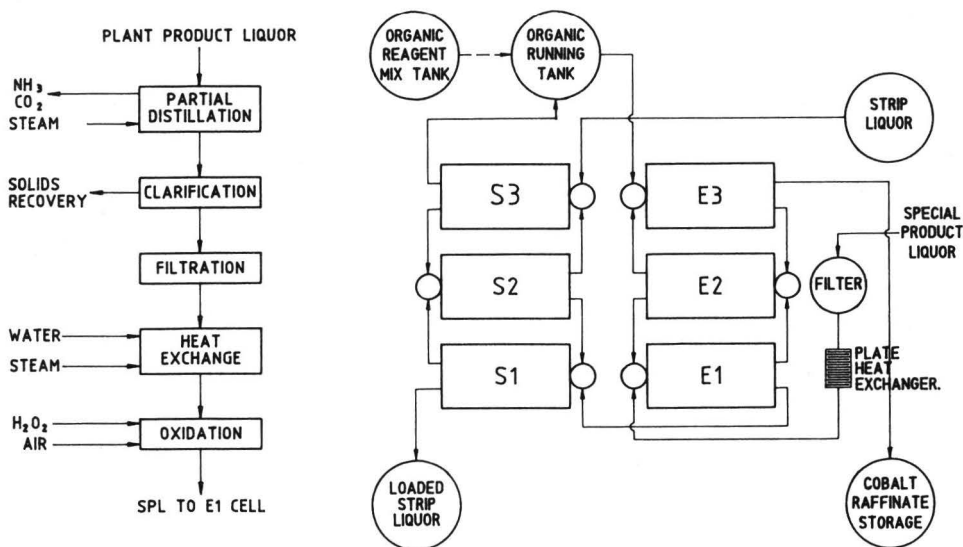


Fig. 4 SPL production and ASX configuration

The Pilot Plant stage ran for approximately 12 months providing data that were invaluable for full scale plant design purposes. During the operation of the Pilot Plant parallel studies on existing plant equipment were conducted; of particular importance

was the modification of the existing gas cooler condensers to allow production of high strength, $280 \text{ gL}^{-1}\text{NH}_3$, ammoniacal strip liquor.

SIGNIFICANT DATA FROM THE PILOT PLANT

The best all round reagent mixture was a 30% V/V solution of LIX 84, modified by Henkel in an aliphatic kerosene Escaid 110. This mixture had a nickel loading capacity of 13 gL^{-1} . Sharp phase separations were achieved with low reagent degradation, good kinetics and nickel transfer efficiency. Because of the preliminary distillation step, crud was almost non-existent in the mixer-settlers. It was determined that 700 L/min of $280 \text{ gL}^{-1} \text{NH}_3$ would be adequate for a full scale plant. Depending on the free NH_3 content of this liquor the stripped organic reagent would have a residual nickel concentration of approximately 1.5 gL^{-1} . The circuit produced on average a cobalt raffinate of approximately 10 mg/dm^3 nickel and a loaded strip liquor of $78 \text{ gL}^{-1} \text{Ni}$. A combination of air sparging, retention time and peroxide addition was used to control the Co^{2+} level in the SPL feed to the first extraction cell at 1 to 2 mg/dm^3 . The main degradation product of the reagent remained in the organic phase indicating that oxime regeneration was possible. Based on the Pilot Plant work and studies with after settler designs anticipated organic losses in raffinate of $15 - 20 \text{ cm}^3/\text{m}^3$, were expected in a full scale plant. The basic nickel carbonate recovered from the nickel loaded strip liquor was of high purity and sulphur free. This had important potential benefits in the downstream recovery of nickel metal. There were of course many other items of information obtained which together with those listed above showed that the concept was viable and could be incorporated into the existing plant flow sheet and would have a major impact on both nickel quality and production costs. Approval was given for the construction of the full scale plant and this commenced operation in 1989.

ACKNOWLEDGEMENTS

The authors thank QNI management for permission to publish this paper. Thanks are also due to the Henkel Corporation and ICI Acorga staff for reagent formulation and helpful discussions.

2.2

**EXTRACTION TECHNOLOGY FOR RHENIUM RECOVERY
FROM CHLORIDE-SULFATE ZINC-CADMIUM SOLUTIONS**

A.N.ZAGORODNYAYA, E.I.PONOMAREVA, Z.S.ABISHEVA

Institute of Metallurgy and Ore Beneficiation of the Academy
of Sciences of Republic of Kazakhstan
29/33 Shevchenko Street, Alma-Ata 480100, Kazakhstan

ABSTRACT

On the basis of studies carried out on the extraction of rhenium with trialkyl amine (TAA) from industrial chloride-sulfate zinc-cadmium solutions and on the re-extraction of it with aqueous ammonia solutions, optimal parameters to develop the process have been defined. The process suggested has been introduced at one of the non-ferrous metallurgy enterprises in Republic of Kazakhstan and has been successfully employed since 1984.

INTRODUCTION

The problems of rhenium extraction from solutions resulting from the processing of conventional rhenium-containing copper and molybdenum raw materials have been described in the literature in detail (Vinogradova, 1976; Stepanov, 1979; Zelikman, 1967; Hadler, 1987; Vasiljev, 1977; Lakeewod, 1971).

Intermediate products of the lead industry, in particular dust generated by sinter oxidizing roasting of charge, have been used for rhenium production by the scientific workers of our Institute for the first time in worldwide metal production (Ponomareva, 1973). Treatment of this dust by sulfatizing roasting method (Getskin, 1958) and leaching of roasted pellets with sulfuric acid solutions result in the production of the solutions which differ in quantitative and qualitative composition from the solutions formed during decomposition of copper and molybdenum concentrates and lead-zinc sublimates produced by shaft furnace smelting of cupreous shales.

Existing extraction technologies for rhenium recovery from lead dust processing solutions have therefore not given positive results.

The paper deals with the development of the process for rhenium recovery from solutions resulting from decomposition of rhenium-containing dust produced by the lead industry.

EXPERIMENTAL

Industrial solutions containing, g/dm³: 20 H₂SO₄, 100 Zn, 35 Cl, 35 Cd, 5 As, 3 Fe, 0.02 Cu, 0.18 Re, 0.127 In, and commercial TAA, kerosene, higher alcohols were used as starting materials. Extractant constituents were prepared for the work according to the conventional methods. Rhenium and cadmium contents in the organic phase were determined using both the difference between initial and equilibrium concentration in the aqueous phase and the analysis of the organic phase. Quantitative analysis of rhenium was accomplished by using calorimeter and weight methods (Borisova, 1974) and atomic absorption analysis was used for cadmium (Britske, 1992).

RESULTS AND DISCUSSION

Basic parameters peculiar to the extraction and the re-extraction (the concentration and composition of the extractant and the re-extractant, the organic phase and aqueous phase ratio, the number of steps, the contact time between phases) have been studied. It has been determined that regardless of the extraction conditions, cadmium is partially co-extracted with the rhenium. Under the most favourable conditions of the process and when rhenium extraction is almost complete, cadmium recovery is not high and can make up 1-4 % of its content in the solution. Separation coefficients and separation factors and the extent of metals extraction show that rhenium extraction is preferred (Fig. 1,2).

However, cadmium content in the extract is 2-5 times higher than rhenium concentration. Cadmium extraction proceeds due to the presence of its halide complexes in the solution. During re-extraction with aqueous ammonia solutions, rhenium and cadmium are almost completely recovered and distributed between aqueous and solid phases. At high ratio of the orga-

nic phase to aqueous phase, the basic amount of metals precipitates. Solid products having various chemical composition are produced depending on rhenium and cadmium contents in the extract and on re-extraction conditions (Table 1).

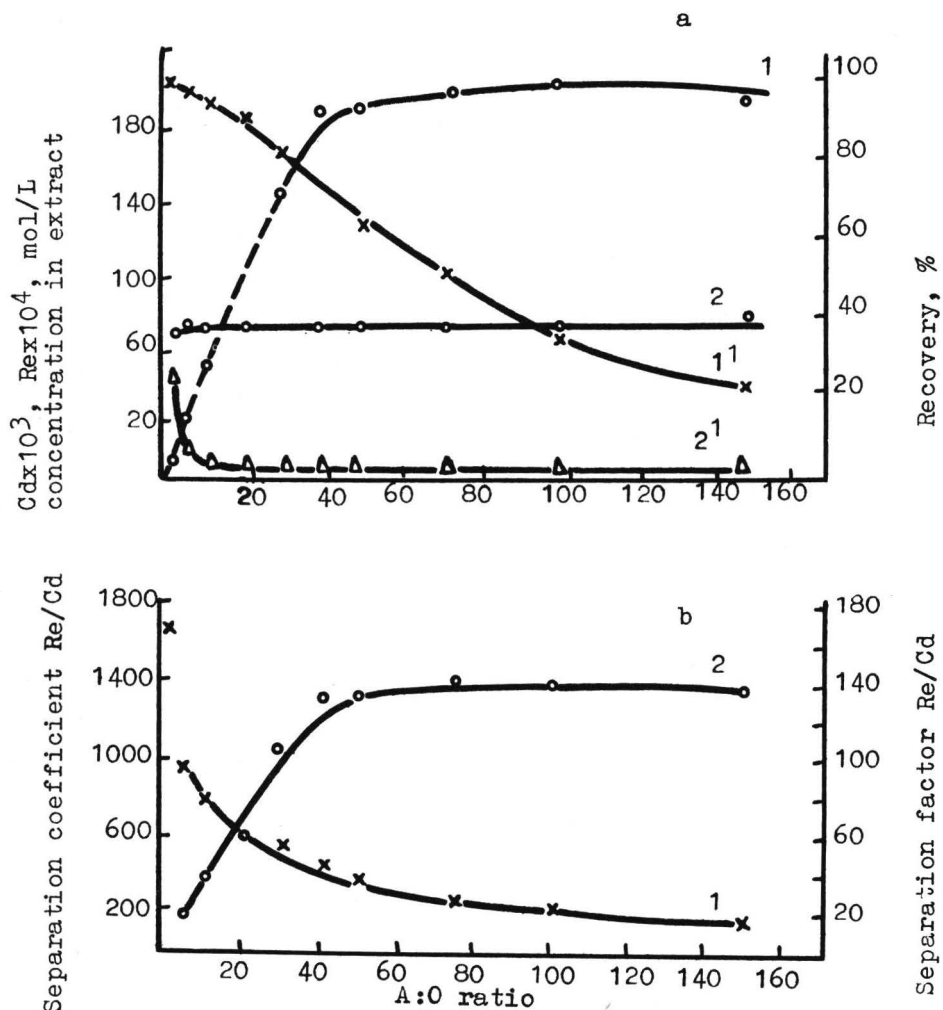


Fig. 1. Effect of the organic phase and aqueous phase ratio on the recovery (1', 2') and the concentration (1, 2) in the extract (a), separation coefficients (1) and separation factor (2) (b) of rhenium and cadmium. 1 and 1' are rhenium; 2 and 2' are cadmium.

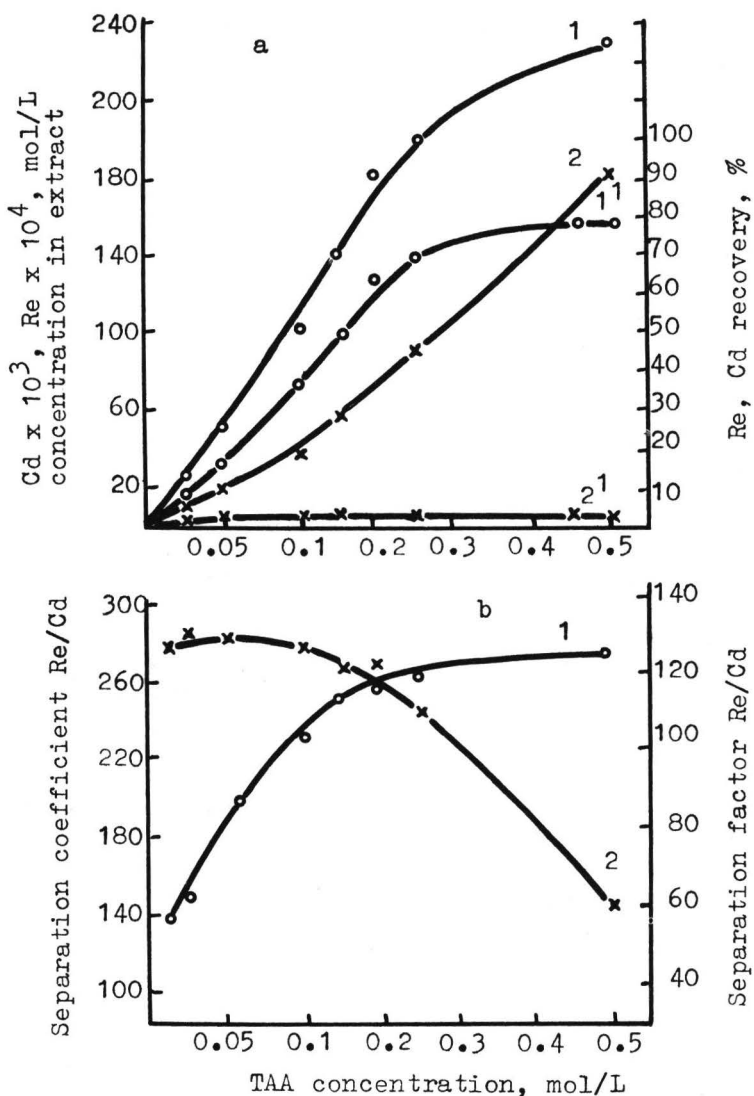


Fig. 2. Effect of TAA concentration in the solvent on the recovery (1¹, 2¹) and the concentration (1, 2) in the extract (a), separation coefficient (1) and separation factor (2) (b) of rhenium and cadmium. 1 and 1¹ are rhenium; 2 and 2¹ are cadmium.

X-ray diffraction, petrographic, and infrared spectroscopic analyses have been used to identify four compounds:

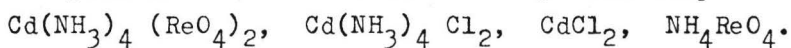


TABLE 1
Composition of rhenium-containing solid products

Products	Content, mass %								
	Re	Cd	Zn	Fe	Sb	Tl	Cl	2-SO ₄	+NH ₄
1	4.6	53.8	0.260	0.07	0.042	0.01	7.66	0.21	14.00
2	32.0	30.7	0.100	0.03	0.039	0.01	7.37	0.43	11.98
3	45.0	14.9	0.084	0.05	0.010	0.01	0.14	0.34	9.00
4	48.0	1.1	0.016	0.05	0.026	0.01	0.20	0.20	9.00
5	39.1	14.9	0.061	0.04	0.030	0.03	0.01	0.58	11.00

Recovery of ammonium perrhenate from these products by conventional recrystallization has failed.

Therefore a study on the separation between rhenium and cadmium has been carried out. The work was conducted using both the extract and the product of re-extraction. Based on the data obtained, the conditions allowing ammonium perrhenate production have been chosen. For this purpose, the extract is prewashed with water prior to re-extraction at O:A = 1:3-5 that allows cadmium extraction of 60-80 % of its content in the extract. This method provides a decrease in the ratio of cadmium to rhenium in re-extraction products. To produce ammonium perrhenate, these products are decomposed using water or inorganic acid solutions under the proper conditions. On the basis of the investigations conducted, a flowsheet for rhenium recovery from chloride-sulfate zinc-cadmium solutions is suggested (Fig. 3).

The main procedures of the flowsheet are as follows: rhenium extraction, cadmium re-extraction, solid-phase re-extraction of Re and Cd, solid product processing, crystallization of crude ammonium perrhenate and production of high-grade rhenium salt from it.

Extraction is conducted in mixer-settler type extractors in 5 steps. TAA solution of 10-15 % dissolved in kerosene with addition of 20 % higher alcohols is used as the solvent. Depending on the rhenium content in the initial solution, the process is accomplished at O:A = 1:30 to 1:50. In this process, extracts containing 1-2 g/L rhenium and 7-12 g/L cadmium are produced. Raffinate containing 5 mg/L rhenium is directed to the basic process for recovering indium, cadmium, thallium, and zinc.

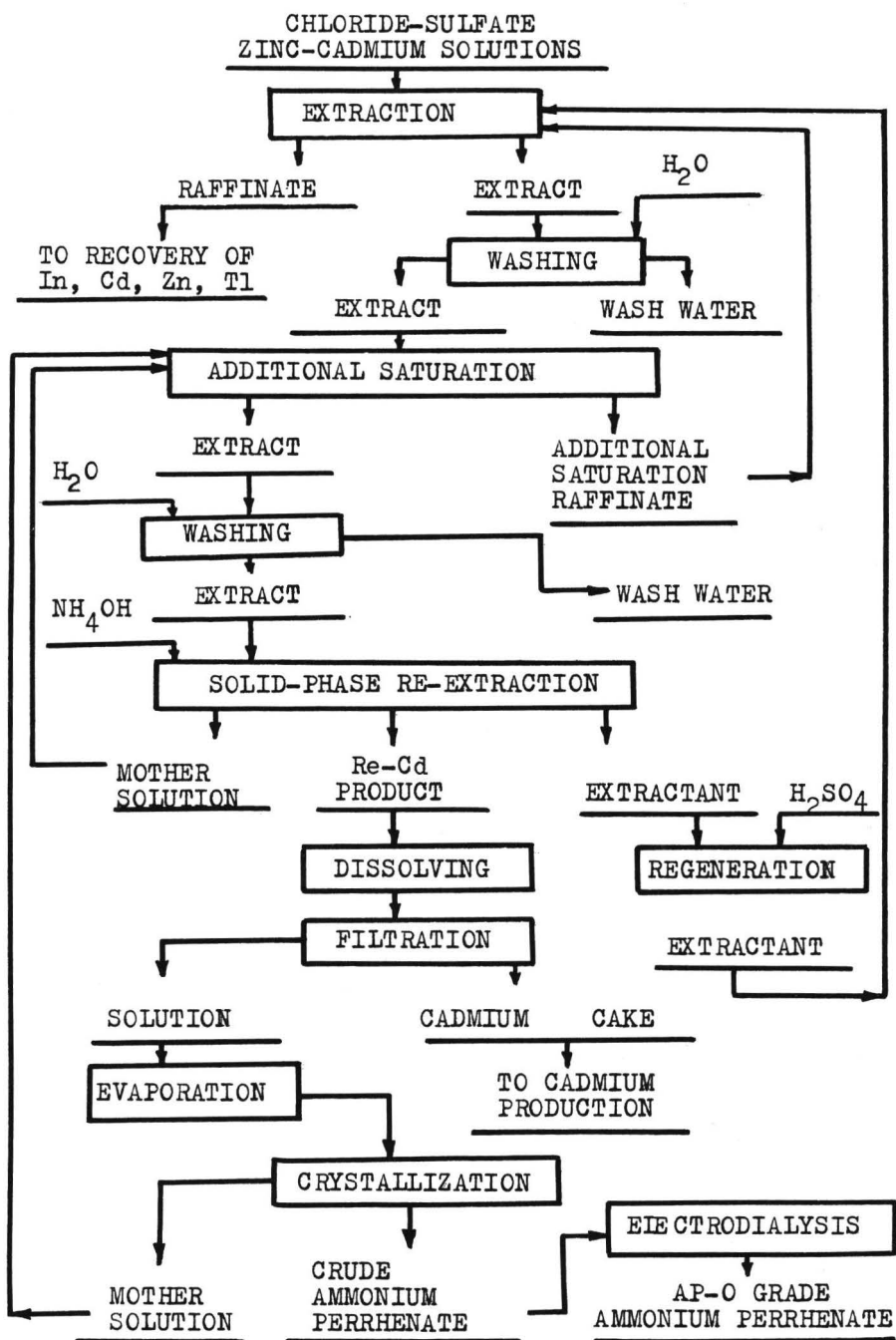


Fig. 3. Flowsheet for recovering rhenium from chloride-sulfate zinc-cadmium solution

The extract is used for cadmium recovery. The process is conducted in one step at O:A = 1:3 to 1:5 using circulating water. In this case, cadmium recovery from the extract reaches 60 to 80 %; almost all rhenium is left in the extract. Re-extraction of rhenium and remaining cadmium is accomplished with 6-8 M aqueous ammonia solution at O:A = 10:1 to 15:1. Re-extraction product containing complex salts of rhenium and cadmium dissolves in water, cadmium precipitates in the form of $\text{Cd}(\text{OH})\text{Cl}$, and rhenium passes into solution as NH_4ReO_4 . Solution is evaporated and crude ammonium perrhenate is recovered by crystallization, then it is subjected to treatment using electrodialysis. The variant of re-extraction product treatment by decomposition with water is shown in Fig. 3. During decomposition of re-extraction products with inorganic acid solutions under the proper conditions, rhenium precipitates in the form of crude ammonium perrhenate and cadmium passes into solution. Ammonium perrhenate after filtration is subjected to electrodialysis to produce rhenium acid or ammonium perrhenate. The use of acid decomposition of re-extraction products eliminates the need for a number of steps: extract washing with water, rhenium-containing solutions evaporation.

The percentage extraction of rhenium from solution reaches 97 % at the extraction stage, 99 % at the re-extraction stage, and 86.7 % in the marketable ammonium perrhenate. 3 % of rhenium is irrevocably lost with raffinates.

This extraction technology is used by one of the enterprises in the Republic of Kazakhstan.

CONCLUSION

Extraction technology has been developed for rhenium recovery from complex chloride-sulfate zinc-cadmium solutions generated during decomposition of metallurgical dust of the lead industry by using sulfatizing roasting and leaching of pellets with sulfuric acid. Rhenium is produced in the form of rhenium acid and high-purity ammonium perrhenate.

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2.3

**THE PURIFICATION OF NICKEL SULPHATE USING
DI-(2-ETHYLHEXYL) PHOSPHORIC ACID**

P.D.A. CLARK, P.M. COLE and M.H. FOX
Hydrometallurgy Division, Mintek
Private Bag X3015, Randburg 2125, South Africa.

ABSTRACT

A solvent extraction process has been developed to purify nickel sulphate solution with respect to calcium and magnesium by extraction with a 20 % ν solution of di-(2-ethylhexyl) phosphoric acid in Shellsol AB.

The process uses six extraction stages to purify solutions containing 100 g/L nickel. The co-extracted nickel is stripped from the organic phase in four stages using sulphuric acid, and calcium and magnesium are stripped using hydrochloric acid in one stage. The stripped organic phase is pre-loaded with nickel in four stages before it is introduced into the extraction circuit. The purified raffinate is passed over an activated carbon bed to remove dissolved solvent before the crystallization of nickel sulphate.

The development of this process, via batch tests and bench-scale counter current test work, is described. A plant capable of producing six tons of nickel sulphate heptahydrate crystals per day was designed and constructed, and the operation of this plant is described.

INTRODUCTION

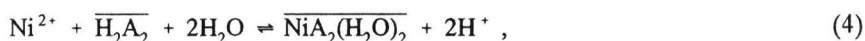
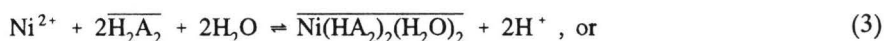
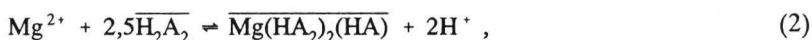
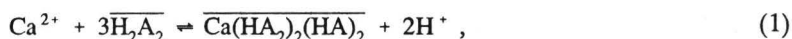
A nickel sulphate solution that is produced in an existing process must be purified so that high-purity nickel sulphate heptahydrate can be crystallized from it. The iron and aluminium impurities are precipitated by neutralization with limestone, which introduces additional calcium and magnesium into the solution. This solution typically has a nickel concentration of 90 to 100 g/L, 600 mg/L calcium, between 250 and 2500 mg/L magnesium, and a pH of between 4.5 and 5. Crystals produced from this solution are not sufficiently pure with respect to the alkaline earth metals for use in electrodeless plating. Owing to the expensive and inefficient nature of selective nickel-removal processes, such as recrystallization, precipitation, and ion exchange, a process to remove

the maximum amounts of calcium and magnesium, while minimizing the nickel loss, was sought. Solvent extraction of the impurities from a high-tenor nickel solution would result in low nickel losses, and was therefore considered for this purification step. Bench-scale continuous counter current tests by the authors have shown that the process described can also be applied to cobalt sulphate solutions.

EXPERIMENTAL

Choice of extractant

Similarly charged cations with larger ionic radii are more readily solvated than those with smaller ionic radii. For this reason the organophosphorous acids extract calcium (ionic radius 0.99 Å) and magnesium (ionic radius 0.65 Å) at pH values lower than their extraction pH values for nickel (ionic radius 0.62 Å). This means that they are ideally suited for the purification of nickel sulphate by extraction of the calcium and magnesium impurities. The following commercially available organophosphorous extractants were identified for this purpose : D2EHPA (a phosphoric acid), Ionquest 801 (a phosphonic acid), and Cyanex 272 (a phosphinic acid). Preston and du Preez (1988) established that the following reactions occur during the extraction of calcium, magnesium, and nickel by organophosphorous acids.



where

HA represents the organophosphorous acid,

H_2A_2 represents the dimer of the organic acid in the diluent,

HA_2 represents the conjugate base of the dimer,

A represents the conjugate base of the organophosphorous acid, and

a bar denotes species in the organic phase.

Owing to the stoichiometric requirements, a high extractant concentration is necessary to ensure reasonable phase ratios on a continuous plant. An extractant concentration

of 20 % ν in Shellsol AB was therefore chosen for each organophosphorous acid.

So that the correct reagent could be chosen (for the specific plant solutions), the extraction of nickel, calcium, and magnesium was determined at various pH values for each extractant. These tests were carried out at an O:A ratio of 4:1. A synthetic sulphate solution containing 99.7 g/L nickel, 1620 mg/L magnesium, and 532 mg/L calcium was used for these batch tests. The results are shown in Figures 1 to 3.

A suitable extractant will extract calcium and magnesium effectively, while minimizing the co-extraction of nickel. This is especially relevant with the high ratio of nickel to alkaline earth metals in the solution. For an extraction circuit to function efficiently, the operating pH value must be at a point where a high percentage of the metal is extracted.

A comparison of the nickel co-extraction at the pH values for high magnesium and calcium extraction, for each of the solvent systems, is given in Table 1. It can be seen from this comparison that D2EHPA exhibits the lowest co-extraction of nickel at the pH value where calcium and magnesium are extracted. D2EHPA, which is also the cheapest of the three reagents, was therefore chosen for the purification operation.

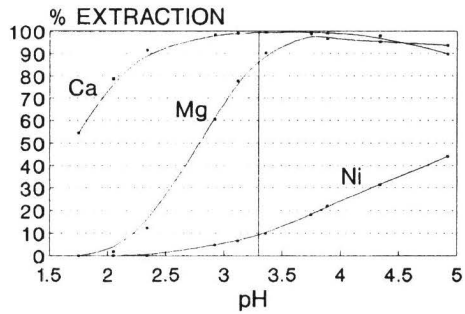


Fig.1 pH vs fractional extraction
Organic phase : 20% ν D2EHPA in Shellsol AB

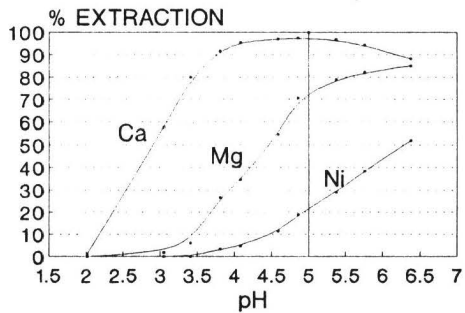


Fig.2 pH vs fractional extraction
Organic phase : 20% ν Ionquest 801 in Shellsol AB

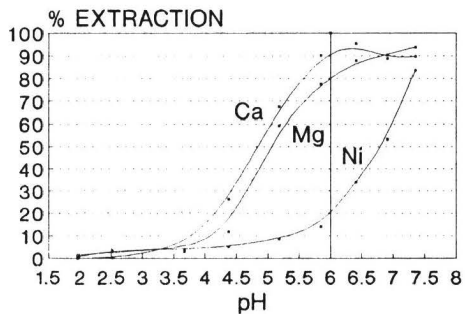


Fig.3 pH vs fractional extraction
Organic phase : 20% ν Cyanex 272 in Shellsol AB

TABLE 1

Comparison of solvent systems

Extractant system (20 % v/v in Shellsol AB)	Extraction pH	Nickel co-extraction (%)
D2EHPA	3.3	< 10
Ionquest 801	5.0	> 20
Cyanex 272	6.0	≈ 20

Extraction

Extraction isotherms were determined in order to establish the phase ratio and number of stages required in a counter current extraction system to reduce magnesium to less than 200 mg/L and calcium to less than 10 mg/L. Figures 4 and 5 show the isotherms at pH 3.3 for calcium and magnesium respectively. Only magnesium need be considered for the operating line because calcium (saturated at 600 mg/L) will be quantitatively extracted in one stage, even for an operating line above the magnesium isotherm. From a McCabe-Thiele analysis, shown in Figure 5, it was estimated that five stages operating at an O:A ratio of 8:1 would be required to purify a solution containing 2500 mg/L magnesium to the raffinate specification of 200 mg/L.

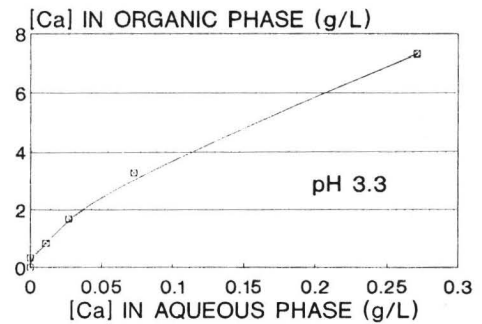


Fig.4 Calcium extraction isotherm
Aqueous phase : 102 g/L Ni, 1620 mg/L Mg, 532 mg/L Ca
Organic phase : 20% v/v D2EHPA in Shellsol AB

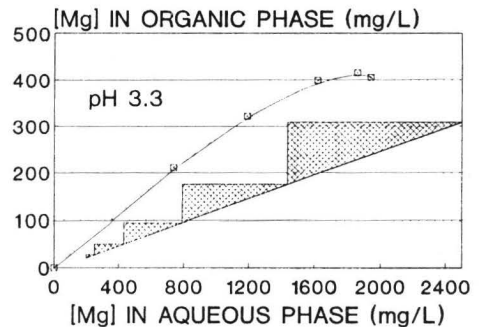


Fig.5 Magnesium extraction isotherm
Aqueous phase : 102 g/L Ni, 1620 mg/L Mg, 532 mg/L Ca
Organic phase : 20% v/v D2EHPA in Shellsol AB

Nickel stripping

Although the nickel co-extraction is less than 10 per cent, the loaded organic phase will contain significant amounts of nickel due to the high nickel concentration in the feed.

Most of this nickel can be recovered by selective stripping from the organic phase with sulphuric acid before the impurities are stripped. To ensure that the impurities remain loaded in the organic phase, the pH value in this circuit must be maintained at the same level as the extraction circuit. At this pH value, the distribution ratio of nickel will be the same as that in the extraction circuit. By ensuring a nickel concentration in the aqueous phase of 20 g/L, at least 80 per cent of the co-extracted nickel can be stripped. A sulphuric acid concentration of 40 g/L will provide a solution containing 20 g/L nickel.

Calcium and magnesium stripping

Calcium and magnesium are stripped off the organic phase with hydrochloric acid to prevent the formation of gypsum in the mixer-settlers. A high concentration of acid (6M) will result in a small volume of concentrated effluent. In order to achieve calcium and magnesium stripping, the effluent stream must leave the plant at a pH of less than 1. Under these conditions, some co-extracted iron will also be stripped from the organic phase.

Organic pre-loading

The control of a constant pH profile across an extraction bank can be simplified by converting the organic acid to a salt. To avoid the introduction of foreign cations into the raffinate the organic phase must be pre-loaded with nickel. The nickel sulphate stream from the sulphuric acid stripping circuit, with sodium hydroxide as a neutralizing agent, can be employed for this purpose.

CONTINUOUS COUNTER CURRENT TESTWORK

Thirteen mixer-settler units, each having a mixer volume of 100 mL and a settler volume of 400 mL, were used to test the process on a continuous basis. The staging was optimized during the continuous bench-scale testwork from an initial plant layout consisting of five extraction stages, three for nickel stripping, two for calcium and magnesium stripping, and two organic pre-loading stages. In order to allow for a retention time (τ) in the mixers of approximately 3 minutes, an organic flowrate of 32 mL/min was chosen.

Feed solution containing the highest expected magnesium concentration (2500 mg/L) was processed at an O:A ratio of 8:1 and at a pH of 3.3. During this operation it was necessary to add a sixth extraction stage to reduce the magnesium level

in the raffinate to a new specification of 100 mg/L. Calcium was extracted to a level of less than 5 mg/L in the first stage.

The stripping of nickel from the organic phase in three stages was 94 per cent efficient, but excessive magnesium stripping (72 per cent) occurred. With the introduction of a fourth stripping stage, the nickel stripping efficiency was maintained and magnesium stripping was limited to 20 per cent. No calcium was stripped in these stages. The stripping of the calcium and magnesium with 6M hydrochloric acid was efficient, and only one stage was required. An internal recycle of the aqueous phase was employed to ensure efficient mass transfer in the mixer.

Pre-loading of the stripped organic with nickel in two stages resulted in 2 g/L sodium loading, despite the introduction of sodium hydroxide into the first stage and control of this stage to a pH value of less than 5. Two additional pre-loading stages that countercurrently contacted the organic phase with 100 g/L nickel solution, successfully reduced the level of co-extracted sodium to 120 mg/L.

FULL SCALE PLANT OPERATION

A 15-stage solvent extraction plant, with the configuration shown in Figure 6, was commissioned at Mintek's premises in Randburg, South Africa.

Equipment

The fibreglass mixer-settlers consist of 100L mixers (0,52m×0,52m×0,37m) and 400L settlers (2,08m×0,52m×0,37m), with Perspex impellers directly driven by 560 W air motors. Steady-head tanks are used for all solutions that are fed to the plant. This allows the use of inexpensive, magnetically driven centrifugal pumps, while maintaining constant flowrates. An activated carbon adsorption train removes dissolved solvent from the raffinate. Paddle-wheel flowmeters are used to monitor the flowrates of the feed and solvent streams, and turbine flowmeters monitor the reagent lines. The pH values of the aqueous phases in selected stages are measured with combined glass electrodes. Capacitive switches are used to signal high and low levels on all the holding and make-up tanks.

Operation

The operating conditions of the various sections of the plant for a feed solution containing 250 mg/L magnesium and 600 mg/L calcium are shown in Table 2.

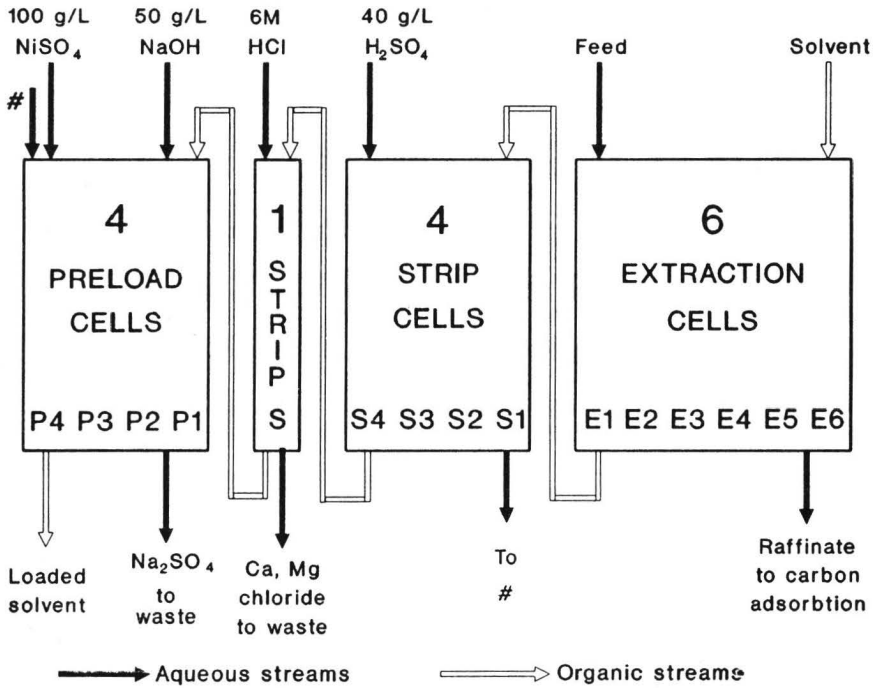


Fig.6 Full scale plant configuration

TABLE 2

Full scale plant operating conditions

Plant section	O:A ratio	Aq. flowrate (L/min)	τ (min)	pH
Extraction	3.0	8	3.1	3.3
Nickel stripping	5.5	4.1	3.6	3.5
Calcium and magnesium stripping	80	0.3	4.1	< 1
Organic pre-loading (P1)	3.4	7.0	3.2	4-5
Organic pre-loading (P2,P3,P4)	5.6	4.3	3.5	4-5

Internal recycling of the aqueous phase is employed in stages where the O:A ratios are greater than 5. The concentrations of various elements in the aqueous and organic solutions from each stage of the full-scale plant are shown in Figures 7 and 8 respectively.

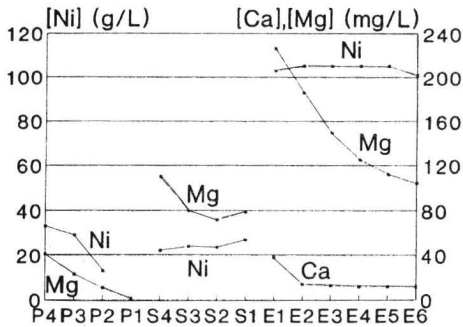


Fig. 7 Aqueous solution analyses

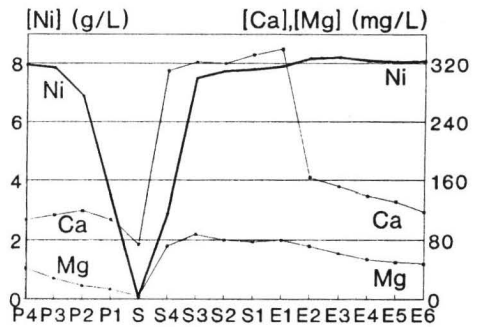


Fig. 8 Organic solution analyses

Magnesium is reduced to the desired 100 mg/L across the extraction circuit, and calcium is extracted in the first stage (E1). Minimal stripping of calcium and magnesium occurs during the efficient stripping of nickel with sulphuric acid. Magnesium that is stripped in S4 is re-extracted in S3. The pre-loaded organic contains less than 20 mg/L sodium, due to the scrubbing effect of the high nickel concentrations in stages P2 to P4. No solvent is detected in the raffinate after carbon adsorption.

CONCLUSIONS

A solvent extraction process was developed to purify nickel sulphate solution with respect to calcium and magnesium. The staging of the solvent extraction plant was optimized during a continuous counter current bench-scale test, which proved that six extraction stages are required to purify the nickel sulphate solution. The co-extracted nickel is stripped off the organic in four stages using sulphuric acid. The calcium and magnesium are stripped using hydrochloric acid in one stage. The stripped organic is pre-loaded with nickel in four stages prior to its introduction into the extraction circuit. The raffinate from the production plant contains less than 100 mg/L magnesium and less than 5 mg/L calcium.

ACKNOWLEDGEMENT

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2.4

DEVELOPMENT OF COPPER EXTRACTION TECHNOLOGY IN CHINA

YANG JIAOYONG

Beijing General Research Institute of Mining and Metallurgy (BGRIMM)
1 Wenxing St., Xizhimenwai Beijing, 100044, China

ABSTRACT

This paper summarizes the character of Chinese copper resources. It introduces the development of copper extraction technology in China, including the state of semi-industrial test work, and some small extraction factory production. Finally it discusses the prospect of the Chinese copper extracting industry development in the next few years.

INTRODUCTION

The development of the copper solvent extraction technique has changed the constitution of world copper production. The leaching-solvent extraction-electrowinning (L-SX-EW) process, dominated by solvent extraction, can be employed to treat copper ores of much lower grade and other copper-containing materials at the lowest production cost and less pollution of the environment. After steady development and improvement for more than twenty years the L-SX-EW technology has become a new approach which can be competitive with conventional pyrometallurgical processes. According to statistics (Merigold, 1992) about 800,000 tonnes of cathode copper was produced by L-SX-EW process in 1991, accounting for 11% of the Non-socialist world copper mine production of that year.

China is short of copper but is not deficient in copper resources. With regard to the prospective reserves of copper it ranks one of the first of several countries. Taking a general view of China's copper resource distribution, it is found that single and easily mined deposits account for only 15% of the total proved copper reserves. Most of the copper deposits are low-grade and / or complicated ores. A considerable portion of the deposits are in areas where the climate is harsh and hard to reach. Since conventional mining, mineral processing and metallurgical processes were employed over the years China's copper industry has not made marked progress.

People expect that the L-SX-EW techniques will bring new prospects to China's copper industry. Much work has been done on the synthesis of solvent extraction reagents, the application of copper solvent extraction techniques and the development of commercial solvent extraction equipment since early 1970's. A number of semi-industrial plants were built during this period. However, only from 1990 has China's copper solvent extraction industry has made great progress. During the last two years with the help of Henkel Co. MID (Minerals Industry Division) LIX reagents were introduced and several SX circuits

were established. Though these SX circuits are very small in size they indicate that copper solvent extraction techniques have reached a new stage in China.

THE DEVELOPMENT OF REAGENTS

Almost at the same time that the first copper solvent extraction circuit in the world was established, a ketoxime type reagent, N-510(Chen, 1981) (2-hydroxy-5-(1-methylheptyl) benzophenone oxime), was synthesized in China. It was put into production in small quantity in 1974. Its properties are similar to those of LIX 65N and it is suitable for extracting copper from low copper and low acid solutions. It was this reagent that supported the semi-industrial tests of copper solvent extraction in some mines in China in the 1970's. N-510 was employed in Hainan Nongken Copper Plant, the only plant that keeps continuous operation, until last year.

Being similar to LIX 64, an extractant, 03045 (2-hydroxy-5-dodecylbenzophenone oxime) (GRINFM, 1974) has also been subjected to semi-industrial tests, But its loading capacity and kinetics are not as good as those of N-510.

Another reagent, N-530 (2-hydroxy-4-(1-methylheptyloxy) benzophenone oxime) (Chen, 1984) was synthesized in the mid 1970's. It was suitable for extracting copper from high acid and high copper (20- 30g/L Cu) solution.

7804 (Tian 1989) a reagent similar to SME 529, was synthesized in the mid 1980's. This reagent, made from China's own raw materials, used is superior to N-510 in loading capacity and kinetics. But since the raw material for synthesizing this reagent is a mixture, the reagent usually contains some impurities. These impurities will result in difficulties in phase disengagement. Therefore, after being employed in a mine for extraction of copper from mine waste water for a period of time in 1989 this reagent had to be replaced finally by LIX 984.

A kind of aldoxime reagent, N-590 (2-hydroxy-5-(1-methyl heptyl) benzal oxime) (Chen 1991) was developed using China's own raw materials. Loading capacity, extraction rate and Cu/Fe separation of this reagent was excellent. But, like other aldoxime reagent, such as P50 and LIX 860, the loaded N-590 is difficult to strip, hence the copper content in the regenerated organic phase is high. Therefore this reagent has not been used in semi-industrial tests yet.

In general, China is now able to synthesize any kind of solvent extraction reagent. But the production of reagents is nearly zero except for a small quantity of N-510. One reason is the lack of pure organic raw materials, and the other is that the producers can not obtain a reasonable profit due to the scarcity of users. Therefore China can not develop its copper solvent extraction industry by depending on its own solvent reagents in the near future.

APPLICATIONS OF SOLVENT EXTRACTION TECHNOLOGY

Several solvent extraction circuits of semi-industrial scale were built at some mines in the 1970's. Attempts were made to produce high quality cathode copper from refractory oxide ores, sulphide ores, tailings as well as water at mines using the solvent extraction process. These plants are listed in Table 1.

Table 1
Semi-industry copper SX plants

Plants	Type of ore and leaching methods	Composition of Solution		Reagent	Number of stages		Date of start up
		g/l Cu	pH		Extr	trip.	
Enping Copper Plant (1978)	Chalcocite Bacter leaching	1.5	1.8	N-510	4	3	1976
Wushan Coper Plant (1977)	waste water at mine	0.8-1.5	2.2	N-510	4	3	1976
Tongshan Copper Mine (1982)	oxide ores heap leaching	0.6	2.2	N-510	4	3	1980
Tonglulshan Copper Mine (1979)	tailings agitation leaching	2.3	2.0	03045	4	3	1978
Dongxiang Copper Mine (1980)	Copper concentrate FeCl ₃ leaching	50g/L Cu 70g/L Fe	1.5	N-530	5	9	1979
Kafang Copper Mine (1976)	Oxide ores Vat leaching	2.5	2.0	N-510	4	3	1976

*Two times washing altogether 10 stages

It can be seen from Table 1 that solvent extraction can be employed in China's copper mines to produce high quality copper. Unfortunately these plants were shut down one after another in the early 1980's. Since then China's copper solvent extraction has gone into low ebb. As all these plants were shut down during that time, a new SX circuit was established in Hainan Nongken Copper Plant (Wei, 1985) in 1983 with help from Beijing General Research Institute of Mining and Metallurgy(BGRIMM). A new type of extraction device

with a shallow mixer settler developed by BGRIMM was first employed by the plant. Though very small in size this plant is the first commercial copper solvent extraction plant in China. It has been operating up to now. The plant also gave the subsequently established plants the opportunity to practise.

Oxide copper ores associated with iron minerals are treated in this plant. The copper minerals are mainly malachite, chrysocolla and a small amount of chrysocolla. Copper content of the ore is about 1-2%. The coarse portion of the ore is subjected to vat leaching, where as the fine portion is subject to agitating leaching. Leach solution containing 1.5-4 g/L Cu is sent to the SX circuit together with wash water. N-510 is chosen as reagent with a concentration of 15 Vol. %. Since the loading capacity and extraction rate are low, 4 stages of extraction and 3 stages of stripping are needed. The stripped pregnant solution containing 45 g/L Cu and 135 g/L H_2SO_4 is sent to the electrowinning circuit to produce high quality cathode copper. The extracting device has some advantage such as uniform mixing, high stage efficiency, high phase disengagement rate and low organic entrainment. In particular, due to the hydraulically independent properties of each stage, the established equilibrium in the circuit will not be disturbed in case of start up and shut down. This type of extraction device has been improved greatly in recent designs for new plants.

As mentioned before, China's copper solvent extraction industry has obviously developed since 1990. This is because copper SX techniques are accepted by more and more people. On the other hand it is attributed to the help given by Henkel MID, including the provision of technical data and information and supply of LIX reagents. The seven copper solvent extraction plants built in the period 1990-1992 in China are summarized in Table 2. Those plants which were put into production are operating normally with satisfactory profit. Their success attracts other mines and more SX circuits will be established.

Table 2
Copper solvent extraction plants in China (BGRIMM, 1992a)

Plant	Time of Commissioning	type of ores and leaching method	Solution		reagent	Number of stages	
			Cu g/L	pH		extr.	stri.
Hainan Nongken Copper Plant	1983.8	oxide ores(1-2% Cu) Vat and agitation leaching	1.5-4	2	N510* LIX 84	4	3
Wu shan Copper Plant	1990.3	oxide ores(2.5% Cu) waste water at mine	0.8-1.5	2	7804 LIX 984	2	1

(Table 2 cont'd)

Hongda Copper Plant	1991.8	oxide ores(1%Cu) agitating leaching	2.0	2	LIX 84	2	1
Eryuan Non- ferrous Metals Plant	1991. 10	oxide ores (3%Cu)	4.0	2	LIX 84	2	1
Jijie Copper Plant	1992.5	oxide ores (2%Cu) Vat and agitating leaching	3-4	2	LIX 984	2	1
Guang Tong Copper Plant	1992. 12	oxide ores (2%Cu) heap leaching	3.5	2	LIX 84	2	1
Malage Copper Plant	under con- struc- tion	oxide ores (2.5%Cu) Vat and agitation	2.0	2	LIX 984	2	1
Damei- qiao Copper Plant	under con- struc- tion	oxide ores (0.7% Cu) heap leaching	2.0	2	LIX 984	2	1

*N-510 was replaced by LIX 84 in 1992.

FUTURE

At long last China's copper solvent extraction industry has made the first encouraging step. Greater progress will follow. In the years to come China's copper SX industry will be developed along the following lines:

* Small sized copper SX plants will be built one after another in most provinces. This is because that China's easily leached oxide ore deposits are highly scattered and each deposit has only limited reserve. The SX technique is particularly suitable for the local township enterprises to produce cathode copper at small scale. This is the main developing trend of the copper SX in the next two years in China.

* Extraction of copper from ammoniacal solution will be important. Oxide ores from Tangdan Copper Mine, China's largest oxide copper deposit, contain more basic gangues (CaO+MgO>40%) and less copper(0.5 %). They are not suited to acid leaching. A

satisfactory treating process has not been found though research work has long been conducted. Combined continuous extended (or pilot) test on ammoniacal leaching, solvent extraction with LIX 54 and electrowinning were accomplished by BGRIMM together with Tangdan Mine in 1990 (BGRIMM, 1992b), and good results were obtained. It is expected that a large sized SX plant will be built if the industrial tests succeed.

Another case of copper solvent extraction from ammoniacal solution will be in the plants where copper-zinc or copper-zinc-lead complex ores are treated. There are many such multi-metallic complex ores in China. But effective processes for recovering copper from these ores has not been found so far. Test results show that the ammoniacal leaching-solvent extraction process is a promising process.

* Extraction of copper from acidic solutions with a Fe/Cu ratio > 10 is another feature of China's copper SX plants. The open-pit mining at Dexing copper Mine, China's largest of its kind, discards a large quantity of submarginal ores (sulphide copper ores containing 0.12% Cu). Bacterial heap leaching of this kind of ore has been conducted (Wang, 1989). The leach solution contains 1 g/L Cu, and also 12 g/L Fe. Many oxide copper minerals in China are associated with iron. Sometimes the copper minerals are disseminated in iron ores. Iron is inevitably dissolved during the leaching of copper, and its concentration is usually more than 10 g/L. Therefore, solvent reagents with high selectivity of copper over iron will be attractive.

* Recovery of copper from leach solutions of metallurgical slags and copper scraps and pcb etchant by SX process (BGRIMM, 1992c) is an aspect not to be ignored.

To sum up, the copper SX technique has a broad prospect in China. It will play an important role in China's copper industry together with conventional copper metallurgical technology.

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2.5

THE DEVELOPMENT OF A PROCESS FOR THE TREATMENT OF BATTERY SLUDGE FOR THE RECOVERY OF CADMIUM AND NICKEL PRODUCTS**GORDON M. RITCEY**

Gordon M. Ritcey & Associates
258 Grandview Road, Nepean, Ontario
Canada K2H 8A9

ABSTRACT

Nickel and cadmium salts are used in the preparation of nickel-cadmium rechargeable batteries, and the acidic waste effluent from the process contains dissolved nickel and cadmium. These metals are normally removed from the effluent by lime precipitation to produce a disposable liquid, while the solids are sent to hazardous landfill disposal.

Over the last few years there has been increasing concern about such hazardous waste disposal, due to the problems of seepage, the increasingly high cost of landfill sites, the high cost of conversion to non-hazardous wastes, and the liability for remediation. Thus, there are valid reasons for developing technology for reclaiming the metal values from the wastes for recycle, and therefore providing an improved disposal situation with reduced environmental impact.

Over a period of about two years, UNC Reclamation in Florida have investigated the possibility of taking such sludges from the battery manufacturers and treating the sludges to produce separate products of cadmium and nickel. The typical sludge contains about 2% Ni, 0.5% Cd, 0.1% Co plus other impurities.

The process involves dissolution in nitric acid plus hydrofluoric acid, followed by filtration. After pH adjustment, the cadmium is extracted, the solvent scrubbed, and the cadmium recovered as cadmium nitrate by crystallization from the strip liquor.

The raffinate from cadmium extraction is adjusted in pH for the recovery of nickel by solvent extraction. Again, scrubbing is necessary prior to stripping in order to produce a specification product. The product is $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

A description of the development of this proprietary process is presented, together with the final circuit design for the plant.

INTRODUCTION

Throughout the world there is an ever-increasing enforcement of environmental legislation limiting the discharge of metals and other wastes. Thus the metallurgical process originally designed and put into operation for specific purposes of metals recovery or downstream fabrication is probably not capable of treating the wastes generated. These wastes become a

liability in today's environmental climate. The combination of increasingly lower waste discharge limits and the growing scarcity of landfill space are causing waste treatment and disposal costs to escalate.

UNC Reclamation, located in Mulberry, Florida, had a processing plant originally used for recovering uranium from phosphoric acid which was closed in 1980 due to failing uranium markets. In 1987, with increasing requirements of environmental control becoming evident, the company was re-started with the objective of providing a metal recovery service for a) elimination of hazardous waste (by receiving the waste from a company); and b) recovery of the metal values in the waste for recycling. The background of UNC in solvent extraction technology and refining techniques proved valuable in the development of treatment technologies for processing wastes for recovery of high purity products for recycle. Among the wastes to be considered for treatment were sludges resulting from the manufacture of Ni-Cd batteries, and fly ash carrying vanadium and other metals.

Nickel and cadmium salts are used in the preparation of nickel-cadmium rechargeable batteries. Acidic wastewater effluent from the manufacturing process contains dissolved nickel and cadmium. These metals are usually removed by treatment with lime or caustic to precipitate the metal hydroxides. Solid-liquid separation produces wastewater suitable for discharge, with solids going to hazardous landfill. In recent years there has been an interest in recovering the cadmium and nickel, due to the high cost of conversion of the waste to non-hazardous wastes and the liability for remediation.

This paper first briefly describes the overall process of treating such sludges, and then details the solvent extraction separation processes. The process of separation of cadmium from nickel, and the purification of the products that was initiated by UNC was based on the work of Ritcey and Ashbrook who described in their patent (Ritcey & Ashbrook, 1965) the use of scrubbing and pH control during extraction with DEHPA by pre-equilibration of the organic phase. Other publications related to the process are: Ritcey, Ashbrook & Lucas, 1975; Ritcey & Ashbrook, 1979, 1982. At the time the author became associated with the project the decision had already been made to use, if possible, DEHPA in both the Cd and Ni circuits. Considerable process optimization was necessary to eventually produce the desired high quality products.

OVERALL PROCESS DESCRIPTION

Leaching

Leaching of the sludge is accomplished using a mixture of nitric and hydrofluorosilicic acids. Following filtration, some sludge is added to the filtrate to a pH of about 5.5, precipitating the calcium, magnesium and lead as fluorides, and iron and silicon as hydrous oxides. The typical analyses of the leach feed solution to solvent extraction, in g/L, are as follows: 8.45 Cd, 22.8 Ni, 0.93 Co, 0.082 Fe, 0.008 Ca, 0.007 Mg.

Cadmium Circuit

Feed solution to the cadmium circuit is adjusted to pH 3.0 prior to extraction with ammonia-pre-equilibrated DEHPA. Following scrubbing with cadmium nitrate solution to remove co-extracted impurities of Co, Ni, and ammonia, the scrubbed solvent is contacted with nitric acid to recover cadmium nitrate. The cadmium nitrate strip solution is evaporated at 260°F (127°C). The solution is then chilled to approximately 60°F (15°C), at which point approximately 50% of the cadmium nitrate crystallizes. The crystals are removed by centrifugation, and the mother liquor returned to the crystallizer.

Nickel Circuit

The raffinate from cadmium extraction is adjusted to about pH 5.5, and contacted with ammonia-pre-equilibrated DEHPA to extract the nickel. Purification is achieved again by scrubbing (this time with nickel nitrate) to remove ammonia. Controlled pH-stripping of the nickel is accomplished at pH 1.0-1.7. Finally the solvent is stripped with 10% acid to remove any cadmium together with residual nickel. That solution is returned to the cadmium extraction circuit. As in the cadmium circuit, the nickel is recovered by evaporation at a temperature of 270°F (133°C), crystallized by cooling to 70°F (20°C), and then centrifuged.

BENCH TESTS

Cadmium Circuit

The initial bench tests (Ritcey, 1990) were to determine the relative extraction of the several metals in solution, at varying pH values. A synthetic solution having the following composition was used (concentrations in g/L): 0.73 Cd, 0.40 Ni, 0.40 Co, 0.28 Fe, 0.34 Ca, 0.24 Mg. The solvent was 10% DEHPA + 2.5% TBP in Shell Varsol 140 diluent. The contact time was 5 minutes at A/O ratio 2/1. Analyses of the nitric acid strip (1M HNO₃) solution are given in Table 1, indicating that the extraction should be at about pH 2.5 for the best discrimination over impurities.

Next, the rate of extraction on discrimination was investigated. The data suggested that a 2-minute contact time was optimum for maximum rejection of impurities.

Equilibrium data and the McCabe-Thiele diagram on an actual leach solution indicated that 4-stages of extraction would be required, and that an equilibrium pH of 2.5 was preferred.

The tests on the effect of phase continuity on extraction, phase separation, and metals discrimination indicate: a) all phase separations are fast at 15-30 seconds; b) for extraction of Cd, 1-3 minutes is adequate; and c) organic phase continuity appears to have only a slight advantage over aqueous phase continuity regarding discrimination over Co and Ni.

Of interest was the possibility of improving the phase separation time by using a modifier other than TBP. With the addition of Versatic 10, the phase separation was improved in both extraction and stripping, and the discrimination over other metals was improved. The Cd

loading at 2 minutes was lower, but could be improved with a longer contact time.

Solutions of $\text{Cd}(\text{NO}_3)_2$, at 50 g/L Cd, were investigated at pH 2.0 and pH 2.5 for scrubbing. The loaded solvent was scrubbed 4 times with the solution, A/O 1/1. The strip solution results in Table 2 indicate that there is a good discrimination of Cd over Co and Ni, and that pH 2.0 is preferred, but at the expense of a slightly lower Cd saturation level.

TABLE 1
Equilibrium pH and Metals Discrimination

Ext'n Equil pH	Cd/Ca	Cd/Mg	Cd/Co	Cd/Ni
2.0	0.67	98.0	51.6	163.3
2.5	1.44	15.7	23.0	76.1
3.0	1.93	4.7	4.6	15.7
3.5	2.06	3.2	1.9	2.7
4.0	1.98	3.0	1.3	1.6
4.5	1.40	1.6	1.1	1.0

Nickel Circuit

The extraction tests were performed at an equilibrium pH of about 5.5, based on previous and current work. Although the plant had started with 1.2 M DEHPA, this was subsequently reduced in concentration to 0.8 M. Basic extraction data on Ni were obtained with the McCabe-Thiele diagram indicating about 4 stages for extraction.

An examination of phase continuity indicated that lower raffinate Ni values were obtained in the aqueous continuous operation, but clearer organic phases resulted when run organic continuous. The phase continuity appeared to have no effect on extraction of Co or Cd. A contact time of 1 minute was sufficient for Ni extraction.

TABLE 2
Scrubbing with $\text{Cd}(\text{NO}_3)_2$ Solution
at pH 2.0 and pH 2.5

Scrub pH	Cd/Co	Cd/Ni
none	266	31
2.0	11,500	23,000
2.5	10,571	12,333

Scrubbing tests indicated again that a concentrated $\text{Ni}(\text{NO}_3)_2$ solution effectively removed impurities, with the exception of all the co-extracted ammonia and cadmium. The tests indicated that Ni could be selectively stripped ahead of the Cd, followed by a stronger acid strip to remove the Cd.

With the NH_3 problem, this was more difficult to solve on the bench as it was soon evident that with the several scrub stages and bleed streams, much depended upon good control and flow ratios and pH. Weak acid scrubbing appeared effective and was verified on a small mini-circuit.

Stripping was found to be effective using pH 2.8 nitric acid in about 4 stages, or using pH 1.5 in fewer stages. However at the lower pH, co-extracted Cd was also stripped with the Ni.

Crystallization

Concurrent with the bench tests on the development of the leaching and solvent extraction circuits, research was also being conducted to optimize the production of the final Cd and Ni nitrate crystals which would meet the respective specifications for the products. Therefore the method of scrubbing, the acidity used in stripping, bleeds to recycle, etc all were found to have a bearing on the type and quality of product achieved. Thus, even though considerable information was achieved on the bench, it was not until the pilot plant studies were in progress that optimization of crystallization was attained, at the same time that the integrated circuit optimization was achieved.

CONTINUOUS TESTING

Mini-Circuit

Following the attainment of sufficient bench data, and once a flowsheet appeared to be taking shape, small-scale continuous tests were run. These were on a small Bell 10-stage mixer settler unit. Sufficient tests were performed to confirm bench data, or to find an unexpected problem requiring more research and improvements either in the leaching-purification process, the solvent extraction, or in the crystallization recovery process. It became an iterative research process of bench and small-scale continuous testing. After several months, the overall process was scaled-up to a small pilot plant.

Pilot Plant for Cd and Ni Recovery

Feed liquor from leaching, at 185-195°F (85-90°C), contains cadmium, nickel, cobalt (500 mg/L), and zinc (40 mg/L). Prior to extraction of Cd the pH was adjusted to pH 3.0. Extraction was in 5 stages of mixer settlers, in contact with 0.5 M DEHPA, at O/A 2.2. The equilibrium pH was maintained at 3.0-3.5. Lower pH resulted in lower Cd loading, and higher pH resulted in increased Co and Ni extraction. Control of pH was by pre-equilibration of the organic phase with ammonia. Organic continuous was maintained in extraction. A bleed of the solvent, before pre-equilibration, was treated with H_3PO_4 to remove iron that accumulated.

The loaded solvent, at 6 g/L Cd, was scrubbed in 2-stages, O/A 12.5 with a diluted bleed stream of $Cd(NO_3)_2$ (25 g/L Cd) from the strip circuit. The pH was 2.5-3.0. A bleed of the scrub recycle was returned to extraction as the Co and Ni built-up in concentration. The continuous phase was aqueous.

Cadmium was recovered from the scrubbed solvent by stripping with 8.5 M HNO_3 at O/A up to 25/1. The aqueous was the continuous phase. In 2 stages, 97% Cd was stripped. Depending upon the phase ratio used, 80-120 g/L Cd was obtained in the strip liquor. A bleed of the strip was sent to the scrub circuit.

The Cd circuit raffinate was adjusted to pH 5.5 with ammonia, and entered a 4-stage solvent extraction circuit for Ni recovery. The feed flow was 1514 mL/min in contact with ammonia-pre-equilibrated 0.8 M DEHPA (containing 3.5% TBP diluted in Amsco 460 kerosene) at a

flow of 1893 mL/min. The extraction temperature was about 90°F (32°C), and solvent loading about 16 g/L Ni. Organic continuous phase was maintained. Loaded solvent was scrubbed in 4-stages, O/A 5/1, with 25-50 g/L $\text{Ni}(\text{NO}_3)_2$, at pH 5.0-5.5 to remove the majority of the ammonia.

Following that scrub section, a 2-stage scrub using a weak acid (water adjusted to a pH of 1.0) removed any residual ammonia. The O/A ratio was 10/1, and the flows were controlled such that the equilibrium pH 5.3-5.7 was maintained. About 4% of the Ni was also removed. The nickel was recovered in 2-3 stages using pH 1.0-1.7 HNO_3 , A/O 10/1, providing a product strip containing about 115 g/L Ni.

Any Cd that remained in the raffinate from the Cd circuit (feed to Ni extraction) was also co-extracted with the Ni. However it was not stripped with the Ni. Consequently it was removed with 100 g/L HNO_3 . Any residual Ni on the solvent was also stripped. This solution was returned to the Cd extraction circuit.

FINAL PRODUCTS

Cadmium

Although the cadmium product was the nitrate form, the grade was not optimized to meet certain specifications. One reason was the possibility of producing the product in another form. However, on the basis of cadmium nitrate specifications, ammonia and calcium were shown to exceed the specification. Following changes in the leaching process, the Ca was subsequently reduced, and based on the ammonia reduction in the Ni circuit, it should also be reduced similarly in the Cd circuit.

Nickel

The product analyses and the specifications on the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are given in Table 3.

TABLE 3
Typical $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Product Analysis

Element	Product	Specifications	Element	Product	Specifications
Ni	18.0%	14-17%	Cd	16.2 mg/L	<20
Co	3890	<7000	Ca	<1.0	<5
Mg	8.1	<10	Fe	26.1	<10
Na	<1.0	<500	K	<1.0	<50
Cu	1.6	<5	NH_3	147.0	<300
SO_4	<10.0	<40	Cl	<10.0	<40

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FLOWSHEET

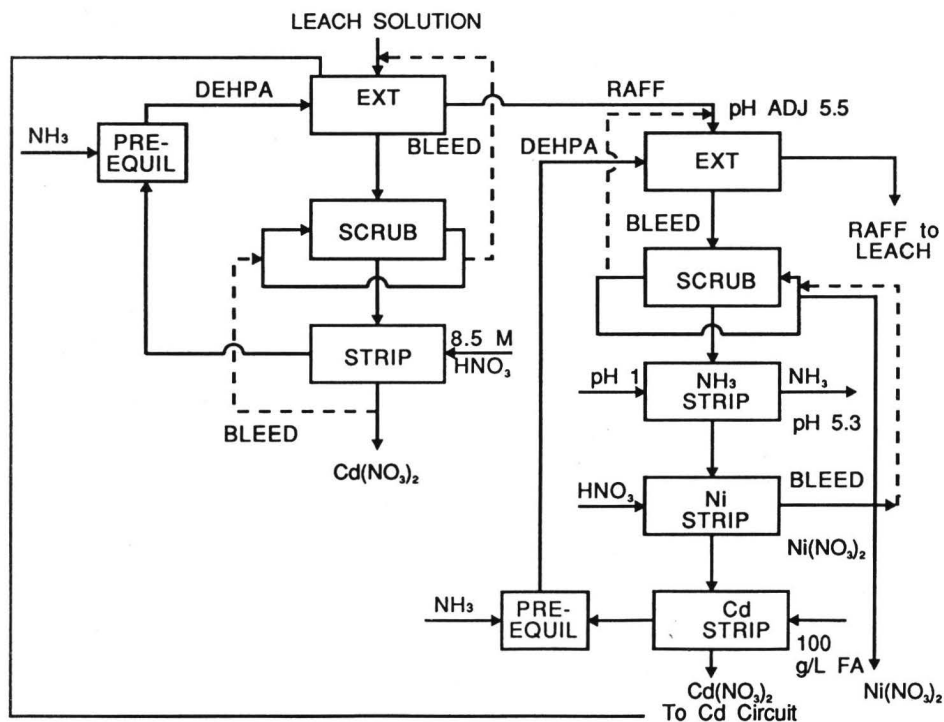


Figure 1: Simplified Flowsheet for Separation and Recovery of Cd and Ni

2.6

**SEMI-INDUSTRIAL TEST ON CO-EXTRACTION SEPARATION OF Pt
AND Pd BY PETROLEUM SULFOXIDES (Ⅳ)**

**Gu Guobang, Cheng Fei, Zhang Zhenmin,
Zeng Fangrong, Long Tiwu
Department of Applied Chemistry
South China University of Technology
Guangzhou, 510641, P. R. China**

ABSTRACT

A new technology of co-extraction separation of Pt and Pd by petroleum sulfoxides (Ⅳ) has been studied. The semi-industrial test shows that the percent extractions and strippings of Pt and Pd are higher than 99%. The total recoveries of Pt and Pd are higher than 98%. The metal Pt and Pd products have come up to the standard of 99.99%.

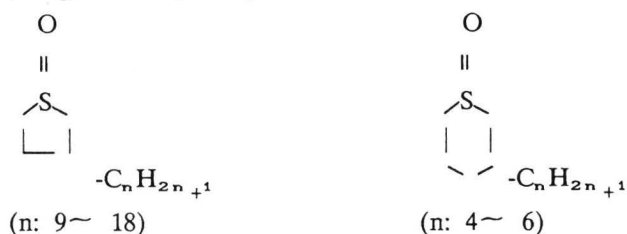
INTRODUCTION

So far, conventional chemical precipitation methods are still the main process for refining of Pt and Pd in China. Because of its long production period, low yield and high cost, scientists are endeavouring to study the solvent extraction separation technology of precious metals. In general, Pt and Pd are extracted and separated by two different extractants. Pt and Pd are co-extracted by an amino-acid derivative at Lonrho Refining Plant in South Africa, but they are co-stripped subsequently (Yang, 1988). In this paper, we have studied a new technology with which Pt and Pd are co-extracted by petroleum sulfoxides (Ⅳ) and stripped with two different stripping reagents. Compared with the previous process, this process has the main advantages of simplifying the working process, convenient operation and low production cost. Rh and Ir are mainly kept in the co-extraction raffinate with a small expansion of the volume and can be separated easily by further solvent extraction.

EXPERIMENT

Reagents

Petroleum Sulfoxides(Ⅳ)[PSO(Ⅳ)]: are made in South China University of Technology. It is a complicated mixture in which there are about 20% non-sulfoxide components, i.e., organic sulfide, esters, sulfones and saturated hydrocarbons, etc. It has been found that there are such structure sulfoxides in the sulfoxide components as(Long and Gu, 1990):



The main physical characters of the PSO(Ⅳ) are shown in Table 1:

TABLE 1

Main physical characters of PSO(Ⅳ)

average molecular weight	250
appearance	clear brown liquid
sulfinyl sulfur	6.4%
density	0.95
viscosity at 28°C	14.4mPa.S
boiling point	300°C (disruption)
solubility in water at 20°C	0.17g/100g H ₂ O

Sulfonated Kerosene: industrial grade. Other chemical reagents are analytical grade.

Precious metals feed

The Precious metals feed is a distillation residue solution from which Os and Ru has been distilled. After the extraction of Au by dibutylcarbitol (DBC), the main components of the feed are shown in Table 2.

TABLE 2

Main Components of the test feed /g.L⁻¹

Test number	Au	Pd	Pt	Rh	Ir	Cu	Fe	Ni
1	0.100	3.25	7.66	0.548	0.548	21.44	2.60	6.52
2	0.067	2.21	4.95	0.216	0.193	12.92	1.88	6.48
3	0.045	4.84	6.75	0.356	0.413	9.00	1.42	6.62
4	0.042	1.38	9.02	1.80	0.268	5.36	2.52	1.64

Equipment

The semi-industrial test of Pt Pd co-extraction was carried out in a mixing-clarification box system. The efficient volume of the extraction box is 5L in which the mixing chamber is 1L. The efficient volume of stripping box is 15L in which the mixing chamber is 4L.

Separation process

The co-extraction separation process of Pd and Pd is shown schematically in Figure 1.

RESULTS AND DISCUSSIONS

After the continuous running of 4 batches of feed, the results of the semi-industrial test are shown in Table 3 and Table 4.

The Tables 3 and 4 show that for Pt and Pd, extraction yields $\geq 99.5\%$, stripping yields $\geq 99\%$. The total recoveries of Pt and Pd are higher than 98%.

The Pt-stripping liquor and Pd-stripping liquor were refined twice, then reduced to metals. The metal Pt and Pd products all have come up to standard of 99.99%.

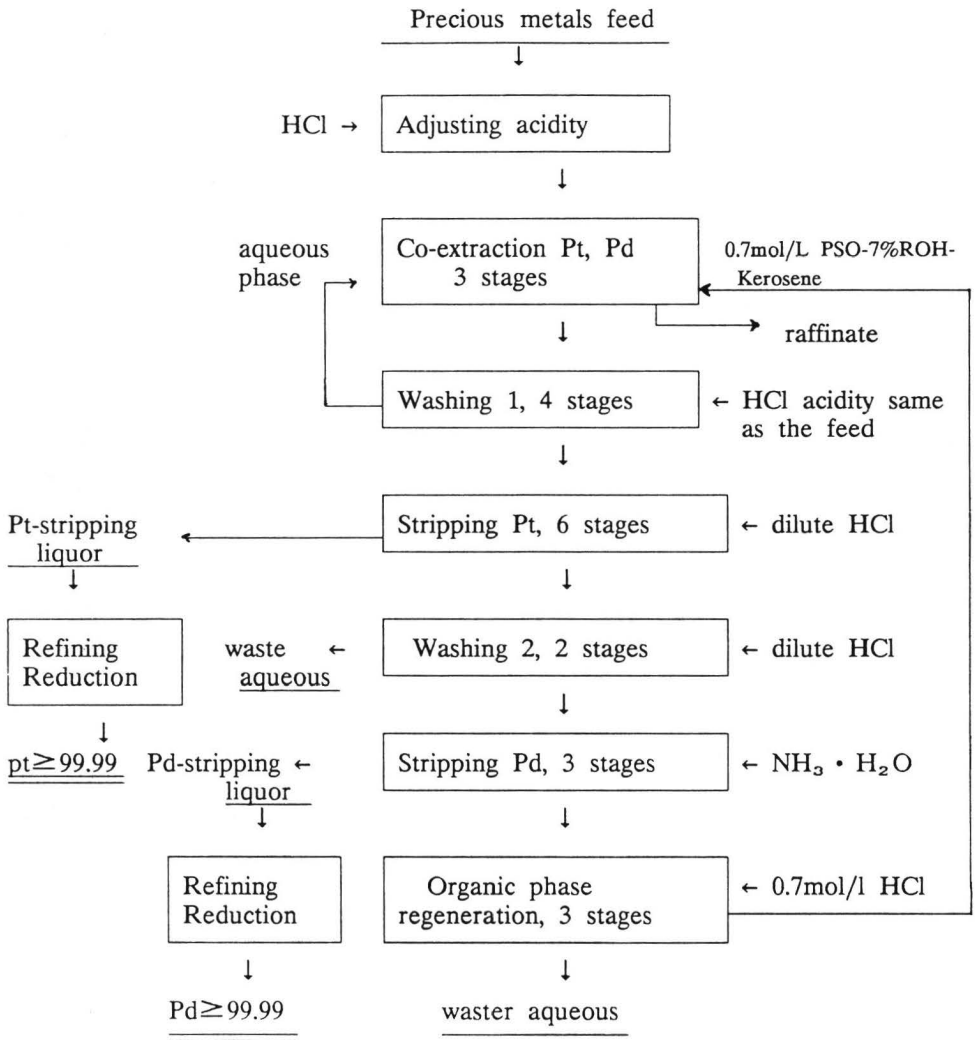


Figure 1. Flowsheet for co-extraction process of Pt and Pd

TABLE 3

Distribution of Pt and Pd in the various aqueous phases

Test number	Name	Feed	Raffinate	Pt Stripping	washing 2	Pd stripping	Organic phase regeneration
1	V/L	140	328	150	250	130	144
	Pd/g	455	1.0	0.5	0.9	422	1.9
	Pt/g	1072	4.3	1027	19.3	0.1	2.9
2	V/L	140	335	140	150	130	140
	Pd/g	309	0.3	0.4	0.2	312	0.6
	Pt/g	693	0.7	700	11.1	0.3	0.8
3	V/L	76	214	130	162	125	130
	Pd/g	368	0.1	0.8	0.1	348	0.8
	Pt/g	513	1.3	541	7.0	0.2	2.0
4	V/L	128	310	130	258	200	120
	Pd/g	1766	6.2	2.0	0.9	1788	2.0
	Pt/g	1178	0.2	1192	10.3	0.2	2.6
Total	V/L	484	1187	550	820	585	534
	Pd/g	2898	7.6	3.7	2.1	2870	5.3
	Pt/g	3501	8.7	3460	43.8	0.8	10.3

TABLE 4
Metal balances of Pt and Pd

	Feed/g	Total product/g	Total recovery/%
Pd	2898	2923	100.8
Pt	3501	3431	98.0

The distribution of Rh and Ir in the process are shown in Table 5. It can be seen that Rh and Ir are mainly kept in the co-extraction raffinate, which provides a good condition for the further solvent extraction and separation of Rh and Ir.

TABLE 5

Distribution of Rh and Ir in the process

	Feed/g	Distribution /%				Total Recovery	
		Raffinate	Waste Liquor	Filter Paper ash		/g	/%
Rh	364.4	314.9	12.3	7.8		335.0	91.9
Ir	169.4	174.3	1.2	1.2		176.7	116

CONCLUSION

1. The technology of co-extraction and separation of Pt and Pd by PSO(IV) from the precious metals feed in which Au has been extracted by DBC is feasible. The percent extractions and strippings of Pt and Pd are $\geq 99\%$. Total recoveries of Pt and Pd are $\geq 98\%$. The metal Pt and Pd products have come up to the standard of 99.99%.
2. Rh and Ir are mainly kept in the raffinate, which provides a good condition for the further separation of Rh and Ir.
3. The process is simple, reasonable and easily operated. Petroleum sulfoxides are non-toxic, non-stinking, non-corrosive and low cost. It is expected that the new technology will bring obvious economic benefit.

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2.7

CONTINUOUS HYDROLYTIC STRIPPING OF IRON FROM VERSATIC ACID USING FORMIC ACID SOLUTIONS

A.J. MONHEMIUS, X. YU and S.B. DOUGILL

Department of Mineral Resources Engineering,
Royal School of Mines, Imperial College,
London SW7 2BP, UK

ABSTRACT

The design of a continuous autoclave of 2L reaction capacity is described. Continuous hydrolytic stripping experiments were carried out in this system which showed that the reaction kinetics for the precipitation of iron oxide from iron-loaded Versatic acid and the physical characteristics of the hematite product were reproducible. The use of formic acid as the hydrolising agent instead of water had a significant effect on the kinetics of the precipitation reaction and the characteristics of the oxide produced. A preliminary economic evaluation of a process flowsheet which integrates hydrolytic stripping for iron removal with a chloride leaching process revealed that the loading of iron into the organic phase by oxidative extraction accounted for 40% of the plant capital cost.

INTRODUCTION

Hydrolytic stripping is a novel process which offers the possibility of removing iron from aqueous leach liquors as a stable oxide product in an uncontaminated form, thus avoiding the residue disposal difficulties of the Jarosite process and Goethite processes. The overall chemistry of the process is represented by Equation (1), which shows iron, dissolved in an organic phase as a carboxylate salt, being reacted with water at elevated temperatures to produce iron oxide by hydrolysis, with re-formation of the carboxylic acid in the organic phase.



Over the last few years, the reaction kinetics and other aspects of the hydrolytic stripping process have been investigated in the Hydrometallurgy Research Group at the Royal School of Mines, Imperial College. It was found that, although detailed study could be made of the kinetics of the reaction, reproducibility of the morphology of the iron oxide products and the solid-liquid filtration characteristics was very difficult to attain with the batch experimental systems used. This was thought to result mainly from variability in the homogeneous nucleation of iron oxide crystallites.

The results of experiments carried out in a purpose-built, continuous pressurised reaction system are described in this paper, which show that the reaction kinetics and particle size distributions of samples are to a great extent reproducible, indicating that steady state conditions prevail in the continuous reaction system. Thus the problems of poor reproducibility with the batch reaction systems can be overcome by the use of the continuous miniplant reaction system.

An investigation of the market potential for hematite powders has shown that it is desirable to use the precipitated hematite as a pigment, taking into consideration market sizes and economic value, together with the physical and chemical properties of the iron oxides produced by hydrolytic stripping, such as particle size, colour and purity. The responses from pigment manufacturers following assessment of the initial hematite solids produced by the hydrolytic stripping reaction with water, however, suggested that the colour shade of the solids needed to be modified to achieve higher economic value. Modifications to the chemistry of the hydrolytic stripping system to achieve this are described.

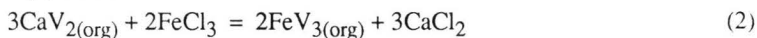
CONTINUOUS AUTOCLAVE SYSTEM

A continuous autoclave miniplant system, which is illustrated schematically in Figure 1, was constructed to carry out the hydrolytic stripping reaction. The autoclave (capacity 2L) was divided vertically into four compartments, each with its own stirrer. The mixture of organic and aqueous phases was pumped under pressure into the top of the autoclave and the slurry of liquid and precipitated solids was collected via a pipe near the bottom of the vessel and passed under pressure into a second holding autoclave, which could be connected to an on-line pressure filter or to a collecting vessel through a three-way valve. Two timer-controlled valves on the discharge line made it possible to maintain a stable flow from the pressure vessel according to the residence time required.

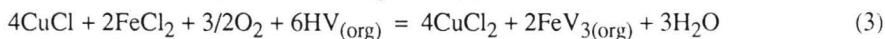
Organic Phase Loading

A 100L reaction unit, complete with heating and stirring facilities, was used for preparation of large quantities of Fe-Versatic solutions, which were used to feed the continuous autoclave system. Solutions of Versatic 10, a tertiary carboxylic acid (HV), in a diluent, Escaid 110, (33% HV by volume) were used throughout this work.

For ease of operation, large volumes of iron-loaded Versatic acid were generally made by the Ca/Fe exchange method, described previously (Monhemius and Thorsen, 1980) and illustrated in Equation (2) below.



In order to simulate a method by which iron can be extracted from cuprous-ferrous solutions, similar in composition to those produced by chloride leaching of complex sulphide ores, e.g. Demarthe (1978), oxidative extraction of iron from cuprous/ferrous chloride solutions into Versatic acid was carried out, as shown in Equation (3)



Loadings of up to 30g/L of iron in the organic solution could be achieved in two and half hours reaction time by this method.

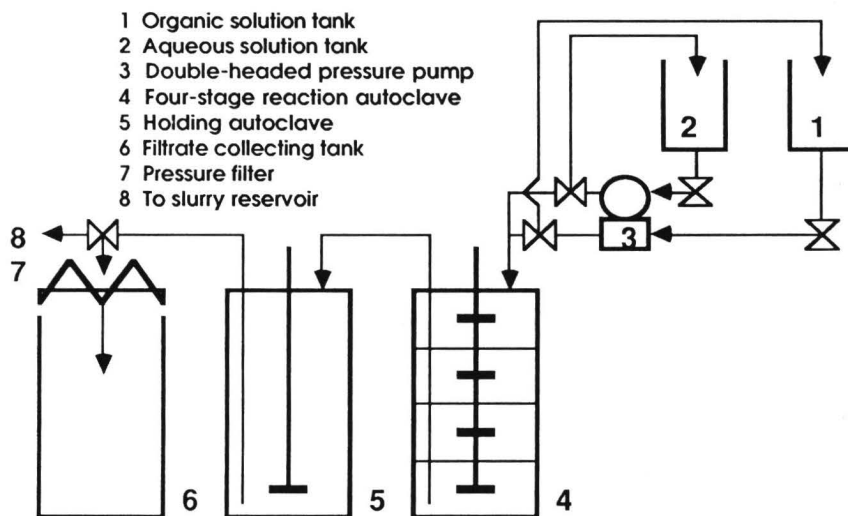


Fig.1 Flowsheet of the continuous autoclave miniplant system

HYDROLYTIC STRIPPING WITH WATER

A series of seven experiments was conducted with the continuous system described above under similar experimental conditions to verify the reproducibility of the reaction kinetics and the particle characteristics of the solids produced. The experimental conditions chosen were: aqueous to organic volume ratio, 1/12; temperature, 180°C; and stirring rate, 950 min⁻¹. The organic and aqueous phases were pumped into the autoclave at a flow rate which gave an average residence time of 27 minutes. The initial concentrations of iron in the loaded organic phases in the replica experiments were in the range 17 to 20g Fe/L. The residual concentrations of iron in the organic phase discharged from the reaction autoclave was 1.2 ± 0.7 g Fe/L in each case. The solids precipitated in these runs had a mean maximum size of 21.4 ± 4.1 μ m, with 5.8 ± 2.7 wt% less than 1.2 μ m. It was concluded that both the reaction kinetics and the particle size characteristics of the iron oxide solids were largely reproducible, indicating that the reaction proceeded under steady-state conditions in the continuous reaction system.

A series of factorially-designed experiments were used to investigate the effects of process variables on the product characteristics. The conditions and results of these tests are presented in Table 1. The effects of reaction temperature (T), reaction time (t) and V_{aq}/V_{org} ratio (R) on the maximum sizes and percentages of solids less than 1.2 μ m were estimated from the factorial design results and are given in Table 2. It was concluded that:

- (a) An increase in temperature reduces the maximum size of the product and increases the percentage of particles of less than 1.2 μ m.

TABLE 1
Factorial design experiments

RUN	CONDITIONS			RESULTS	
	T °C	t min	R v_{aq}/v_{org}	Max.size μm	<1.2 μm %
1	180	18	1/20	13.6	9.8
2	200	18	1/20	10.5	9.8
3	180	27	1/20	17.7	5.0
4	200	27	1/20	13.6	8.9
5	180	18	1/13	23.7	4.2
6	200	18	1/11	13.6	11.0
7	180	27	1/12	23.7	4.8
8	200	27	1/13	10.5	9.7

TABLE 2
Estimated effects

VARIABLE	EFFECT	
	Max. size (μm)	<1.2 μm (wt%)
Temperature (T)	-7.6	+4.5
Time (t)	+1.0	-2.2
v_{aq}/v_{org} (R)	+4.0	-1.5

- (b) Increased reaction time does not significantly affect the maximum particle of the product, but does cause a decrease in the percentage of the particles of less than 1.2 μm .
- (c) An increase of v_{aq}/v_{org} causes slight increase in the maximum sizes of the solids but has little or no effect on the percentage of particles of less than 1.2 μm .

The rate of reaction as a function of temperature in the continuous system is illustrated in Figure 2. The colour of the hematite powders produced in the continuous system was deep brown. Assessment of this material by a pigment manufacturer indicated that modification to a lighter, reddish shade was required to achieve a higher economic value. This led to the investigation of alternative stripping solutions for hydrolysis and morphology modification.

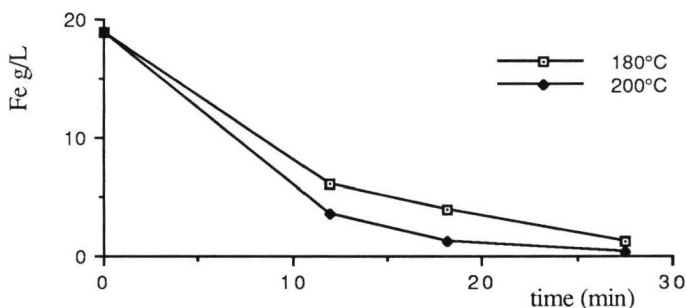


Fig.2 Kinetics of continuous hydrolytic stripping with water

HYDROLYTIC STRIPPING WITH FORMIC ACID

Acids can be used as an alternative to water as hydrolysing agents for hydrolytic stripping. Batch and continuous reaction using sulphuric acid has previously been shown to produce goethite contaminated with sulphate (Doyle-Garner and Monhemius, 1985); furthermore, the presence of sulphate in the aqueous phase adds another variable to the system, making control very complex.

Aqueous soluble organic acids (formic, acetic, oxalic and citric), whose anions do not participate in the precipitation of iron were investigated. Preliminary experiments indicated that formic acid was the most promising, based on the product characteristics and reaction rates. The optimum conditions for hydrolytic stripping with formic acid at atmospheric pressure, using iron Versatic preloaded with calcium, for a batch reaction were: 0.4M formic acid at 100°C for 60 minutes with an aqueous/organic ratio of 1/3 and a stirring rate of 600 min⁻¹. The rate of hydrolytic stripping under these conditions is shown in Figure 3, where an initial rate of reaction of 0.53g/L.min was achieved. In the continuous mode, using a four-stage cascade, the optimum conditions at 100°C were: 0.7M formic acid, 140 minutes total residence time, with an aqueous/organic ratio of 1/2 and a stirring rate of 800 min⁻¹. Hematite of submicron size was produced, of reddish orange colour. However it was decided that, at atmospheric pressure, the process kinetics were too slow and the aqueous/organic ratio required was too high. Attention was then turned to the use of formic acid at elevated temperatures.

Initially, batch hydrolytic stripping tests with formic acid solutions at elevated temperatures were conducted using organic solutions loaded via the Ca/Fe exchange extraction. The tests were carried out in a 300 mL laboratory autoclave, using 0.4 M formic acid, a v_{aq}/v_{org} ratio of 1/10 and temperatures of 105, 120, 130 and 145°C. The results are presented in Figure 3. It may be seen that to strip the iron from the organic solution at 105°C took 30 minutes, while it took only 2 minutes at 145°C. The activation energy for the stripping process was estimated as 90kJ/mol, from the Arrhenius plot shown in Figure 5.

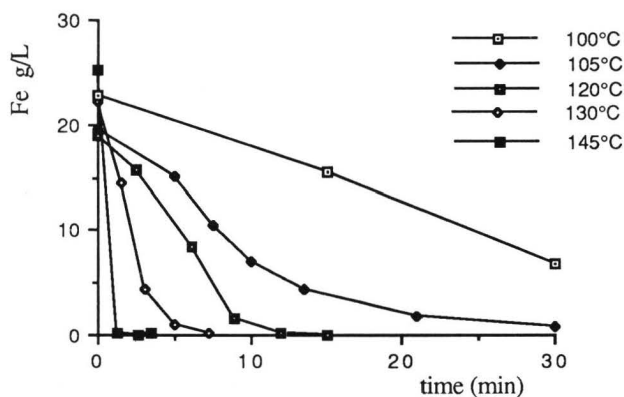


Fig. 3 Kinetics of batch hydrolytic stripping with formic acid (calcium preloading)

Oxidative solvent extraction

The oxidative solvent extraction process for extracting iron from artificial leach liquors containing Cu and Fe was investigated, as described by Equation 3. These liquors were of similar composition to those produced in the MINEMET process, one of the processes developed for the recovery of copper and zinc from complex sulphide ores (Demarthe, J.M. & Georgeaux, 1978).

Batch hydrolytic stripping experiments with formic acid using iron-loaded Versatic obtained from cuprous-ferrous chloride solutions were firstly studied at 100°C at atmospheric pressure. The optimum conditions were determined to be: 1M formic acid at 3/1 organic to aqueous ratio. Clusters of hematite and goethite were produced about 0.5 μm in size. Although the initial rate of reaction was 0.68g/L.min, the reaction required 1 hour to completion; the data are shown in Figure 4.

The kinetics of the hydrolytic stripping with formic acid of organic solutions loaded via Cu/Fe oxidative extraction was then studied at elevated temperatures under pressure. A laboratory-scale autoclave of 300 ml internal volume, fitted with a gas dispersion shaft/impeller assembly, was used for these experiments. The reaction was carried out using 0.8M HCOOH and a $v_{\text{aq}}/v_{\text{org}}$ of 1/10. The kinetic data are shown in Figure 4. An activation energy of 156 kJ/mol was estimated from the Arrhenius plot, shown in Figure 5, which indicates a considerable temperature effect on the reaction rate.

Hydrolytic stripping of the oxidatively loaded organic phase at 185°C produced well-formed, submicron crystals of hematite, of uniform spherical shape and bright red in colour, very suitable for pigment manufacturing. Lower temperatures led to less ordered crystal structures of various sizes and shapes, which resulted in darker, purplish colours. The solids were largely hydrophilic in nature, which should allow a two-stage liquid-solid separation on an industrial scale, involving settling followed by filtration.

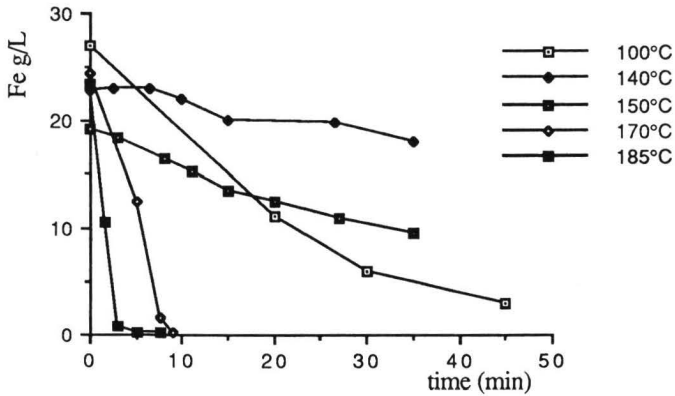


Fig. 4 Kinetics of hydrolytic stripping with formic acid (loaded from Cu/Fe solutions).

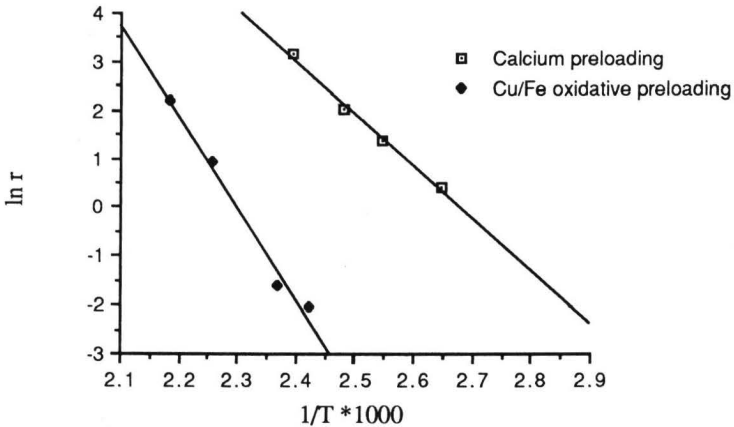


Fig. 5 Arrhenius plot for the kinetic data shown in Figs 3 and 4.
(r = initial reaction rate g/L min T = temperature K)

Hydrolytic stripping in the continuous autoclave system, using formic acid, with organic solutions loaded via Cu/Fe oxidative extraction resulted in lower iron stripping efficiencies than when using water as the hydrolysing agent. This was due to the design of the multistage system within the pressure vessel, which did not allow for the recirculation and dispersion of the gas phase, found to be essential in order to ensure that the reaction occurs in the chemical reaction controlled range. For this reason also, the reaction carried out in the 2L autoclave was less efficient than in the 300mL autoclave and the hematite produced was of larger sizes and deeper colour.

PRELIMINARY ECONOMIC EVALUATION

A conceptual flowsheet for the solvent extraction/hydrolytic stripping process was developed with the objective of integrating it with a chloride leaching process for copper extraction from complex ores, such as the MINEMET process. A preliminary economic evaluation of this process, based on a plant producing 15,000 ton/annum iron oxide, which would result from a production of 12,000 ton/annum copper, assuming a chalcopryrite feed, indicated a capital cost for the solvent extraction-hydrolytic stripping plant of about £9.7 million, of which the solvent extraction section accounted for 40%. The operating cost was estimated to be £3.53 million per annum, which is equivalent to £235/ton of iron oxide produced. This cost estimation can only be taken as "order of magnitude" in its precision; however, it reveals that the solvent extraction of iron into the organic solution from the leach liquor accounts for a major part of the total capital and operating costs, because of long loading times resulting from the slow rates of oxidative extraction. Significant increases in extraction rates would lead to major savings in the costs of iron oxide production by hydrolytic stripping.

CONCLUSIONS

It is possible to produce hematite powders of different colour shades and particle sizes by the hydrolytic stripping process, suitable for sale into the pigment market. The colour shade and particle size of the hematite depends on the preparation method of the iron-loaded organic solution and the rate of precipitation. Higher rates favour precipitation of fine powders of brighter red shades, while lower rates tend to produce coarser powders of deeper brown appearance.

The rate of precipitation of hematite during hydrolytic stripping can be controlled by varying the reaction temperature, and by using formic acid solutions instead of water as the hydrolysing agent. It is essential to have good gas dispersal in the reactor when using formic acid in order to achieve fast, chemically-controlled rates of precipitation.

The estimated production cost for hematite pigment by hydrolytic stripping is high compared with current prices for synthetic iron oxides pigments. However, the cost of waste disposal for the iron residues produced by the current iron removal processes could offset the higher operating cost of this novel process.

ACKNOWLEDGEMENTS

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ACID-EXTRACTION TECHNOLOGY OF RARE METALS RECOVERY FROM PHOSPHORUS FURNACE FLUE DUST

Z.S.ABISHEVA, A.S.KASYMOVA, E.I.PONOMAREVA, I.A.BLAIDA

Institute of Metallurgy and Ore Beneficiation of the Academy
of Sciences of Republic of Kazakhstan

29/33 Shevchenko Street, Alma-Ata 480100, Kazakhstan

ABSTRACT

An acid-extraction complex process has been developed for treatment of phosphorus furnace flue dust (so-called Cottrell dust) involving dust stripping with sulfuric acid by hydro- and pyrometallurgical methods, sorption of rubidium, conversion of phosphorus macrocomponent to target (phosphorus-containing) and microcomponent to intermediate (gallium-containing) products using ammonia, and extraction of gallium from hydrochloric acid solutions. The mechanism of reciprocal influence of gallium microamounts extraction in the presence of macroelements has been studied. Temperature effect on the extraction of gallium and iron has been examined. Kinetic mechanisms of gallium extraction with tributyl phosphate and re-extraction with water have been studied.

INTRODUCTION

Meeting ever-widening applications of employing gallium and rubidium compounds demands use of such rich raw material source as wastes of phosphorus industry in their production (Reznik, 1985; Sittig, 1980).

Extraction as the most efficient method for recovery of gallium from hydrochloric acid solutions (Reznik, 1985) generated during treatment of phosphorus production Cottrell dust using tributyl phosphate is the basis of the technology proposed.

The results of both the fundamental research on gallium extraction and commercial scale operations of the process are presented in the paper.

EXPERIMENTAL

Cottrell dust from phosphorus plants in Kazakhstan was used to conduct the work. All reagents used were of very high purity, 100 % tri-n-butyl phosphate (TBP) was used as the extractant. Recovery of rubidium was accomplished using synthetic inorganic sorbent $\Phi C-1$ nickel ferrocyanide-base (Kozlova, 1979). Element and phase composition of the dust was analyzed using various physicochemical methods. Concentration of gallium in both solid products and solutions was determined using "Hitachi" Atomic Absorption Spectrophotometer and rubidium content - using flame photometer " $\Psi C \Pi -1$ ". A Lewis cell was used for the investigation of the kinetic mechanisms of extraction processes. Extraction of gallium under laboratory conditions was developed in a separating funnel mounted on a mechanical vibrating apparatus. Recovery of gallium from process solutions was accomplished in mixer-settler type extractors.

RESULTS AND DISCUSSION

Chemical composition of Cottrell dust, mass %: 20-45 P_2O_5 , 20-40 SiO_2 , 8-16 CaO , 1-5 MgO , 7-12 K_2O , 1-2 Na_2O , 0.5-2.0 Fe_2O_3 , 2-8 F, $2 \cdot 10^{-2} Ga$, $4 \cdot 10^{-2} Rb$, $1 \cdot 10^{-4} Te$, $8 \cdot 10^{-3} Cd$, $1 \cdot 10^{-4} In$ is similar to the composition of initial charge (Ershov, 1979) but at the same time it should be considered as the concentrate of both phosphorus compounds and rare metals (Reznik, 1985).

Hydro- and pyrometallurgical treatment of Cottrell dust results in the production of solutions containing microamounts of gallium and rubidium compared with macroamounts of phosphorus, potassium, and other elements. Partial recovery of rubidium from sulfuric acid solutions and concentration of it in eluants to $1-2 \text{ g/dm}^3$ can be obtained by using inorganic sorbent $\Phi C-1$.

For separation of gallium and phosphorus compounds, the method of step neutralization allowing the production of gallium and phosphorus-containing products at pH of 3 and pH of 7-8, respectively, has been used. The latter (40-45 mass % P_2O_5) having good agrochemical characteristics is recommended for use as phosphorus nitrogen fertilizer.

Hydrated gallium-containing product dissolves in hydrochloric acid for subsequent extraction of gallium. The solutions generated in this process have complex salt composition. In connection with this, the mechanisms of reciprocal influence of gallium microamounts extraction in the presence of Fe^{3+} , Al^{3+} , Na^+ , K^+ , PO_4^{3-} , SO_4^{2-} , F^- macroelements have been investigated. Fig 1 and 2 show the results of this study.

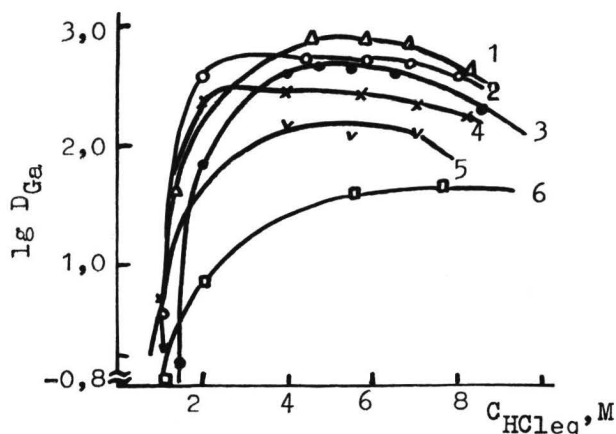


Fig. 1. Extraction of Ga (initial $C_{\text{Ga}} = 1.61 \cdot 10^{-3} \text{ mol/dm}^3$) with TBP from hydrochloric acid solutions in the presence of macroelements (0.5 mol/dm^3): 1 - Al^{3+} , 2 - Na^+ , 4 - K^+ , 5 - PO_4^{3-} , 6 - Fe^{3+} , 3 - without macroelements (temperature = 22°C).

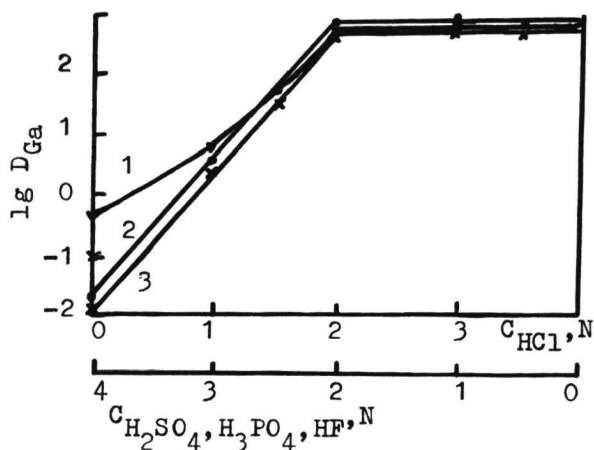


Fig. 2. Dependence of gallium distribution coefficients on the ratio of acid concentrations at $\sum \text{H}^+ = 4 \text{ N}$: 1 - $\text{HCl} + \text{HF}$, 2 - $\text{HCl} + \text{H}_2\text{SO}_4$, 3 - $\text{HCl} + \text{H}_3\text{PO}_4$.

In the system under investigation, the factor of reciprocal influence - the suppression of gallium extraction - has been estimated according to the ratio of gallium distribution coefficient (D_1/D_2 is the degree of suppression) without (D_1) and with macroelements (D_2). According to estimated values of the degree of gallium extraction suppression, macroelements are arranged in the following order: $\text{Al}^{3+}(D_1/D_2=0.7) < \text{SO}_4^{2-}(0.8) < \text{Na}^+(0.98) < \text{F}^-(1.0) < \text{K}^+(1.6) < \text{PO}_4^{3-}(4.0) < \text{Fe}^{3+}(14)$. The highest degree of suppression of extracting gallium in the presence of Fe^{3+} is caused by the "total ion" effect (Zolotov, 1973) which is characterized by decreasing distribution coefficient of micro- (gallium) and macroelements (iron) with increasing latter concentration in the organic phase (at $C_{\text{Fe}}=0.084 \text{ mol/dm}^3$ $D_{\text{Ga}}=200$, $D_{\text{Fe}}=6.36 \cdot 10^3$; at $C_{\text{Fe}}=3.15 \text{ mol/dm}^3$ $D_{\text{Ga}}=2.5$, $D_{\text{Fe}}=0.62$). In the presence of phosphate-ions, the suppression of gallium extraction is much weaker (at $C_{\text{PO}_4^{3-}}=0.1 \text{ mol/dm}^3$ $D_{\text{Ga}}=220$, $D_{\text{PO}_4}=0.84$; at $C_{\text{PO}_4^{3-}}=0.95 \text{ mol/dm}^3$ $D_{\text{Ga}}=114$, $D_{\text{PO}_4}=0.73$) due to the formation of non-extractable complexes of gallium and the competing extraction of phosphoric acid.

The results obtained conform to the well-known reciprocal influence theory saying that the phenomenon of extraction suppression is stronger under other equal conditions for that element which forms complex acid dissociating stronger in the organic phase (Zolotov, 1973).

Al^{3+} , SO_4^{2-} , Na^+ have salting out effects due to the change in activity coefficient of chloride ions on the one hand and the effect of similar ions on the other hand (Reznik, 1985). Gallium is practically not extracted from H_2SO_4 , H_3PO_4 , and HF solutions and if only chloride ions are introduced into system, gallium distribution coefficient grows by several orders of magnitude (Fig. 1,2).

The temperature effect on the extraction of gallium and iron (III), the latter being a foreign matter which is most difficult to strip, has been studied (Fig. 3).

The character of temperature dependence of gallium distribution coefficients varies with the change in metal concentration which indicates the dissimilar extraction mechanisms of

gallium micro- and macroamounts. The extraction of gallium microamounts is an exothermic reaction ($\Delta H_{Ga} = -20.85$ kJ/mol) and the extraction of gallium ($\Delta H_{Ga} = 19.64$) and iron ($\Delta H_{Fe} = 8.4$) macroamounts is an endothermic reaction. This difference in the extraction of gallium microamounts and iron macroamounts can be used for increasing coefficients of separation between gallium and iron during extraction from process solutions (for example, $\beta_{Ga/Fe} = 15$ at 25°C , $\beta_{Ga/Fe} = 104$ at 15°C).

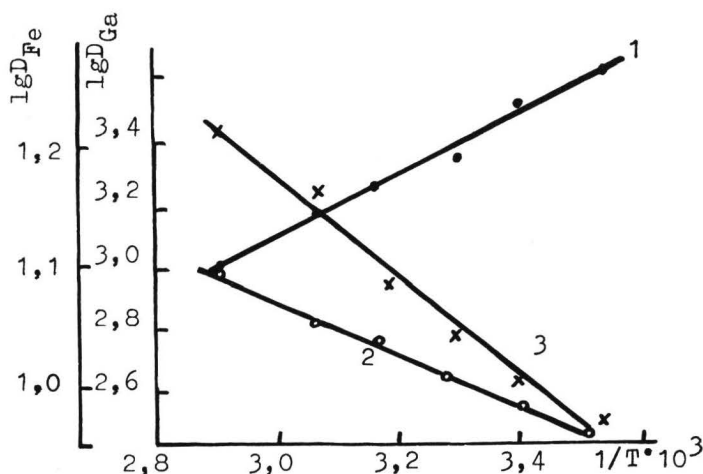


Fig. 3. Dependence of distribution coefficients of gallium and iron on temperature, concentration, mol/dm³: 1 - 10^{-2} Ga, 2 - 1.0 Ga, 3 - 0.8 Fe.

The kinetic mechanisms of the process which occur in the systems of TBP-HCl-Ga and TBP, pregnant Ga-H₂O solution have been studied.

The values of apparent activation energy calculated from the logarithmic dependence of the constant of extraction and re-extraction rate on temperature indicate the chemical nature of the limiting stage of the processes (extraction: at $C_{Ga} = 1.506 \cdot 10^{-3}$ – $16.49 \cdot 10^{-3}$ mol/dm³ $E_A = 30.6$ kJ/mol, at $C_{Ga} = 0.57$ mol/dm³ $E_A = 34.8$ kJ/mol; re-extraction: at $C_{Ga} = 14.34 \cdot 10^{-3}$ mol/dm³ $E_A = 22.3$ kJ/mol; at $C_{Ga} = 0.57$ mol/dm³ $E_A = 46.0$ kJ/mol). The effect of reacting components (gallium, tributyl phosphate, hydrochloric acid) concentration on the rate of extraction has been studied to determine the stoichiometry of che-

mical reaction. First orders for metal and hydrochloric acid and third order for extractant have been determined. The constancy of slopes of straight lines $\lg(C_0 - C_p)/(C_\tau - C_p) - f(\tau)$ (Fig. 4). over the wide range of initial concentration of gallium ($1.506 \cdot 10^{-3} - 0.3 \text{ mol/dm}^3$) confirms the first order of proceeding reaction via metal and the presence of no more than one limiting stage of extraction. A decrease in the value of effective constant of surface reaction rate from $K_s = (25 \pm 1.9) \mu\text{m/s}$ to $K_s = (18.6 \pm 0.8) \mu\text{m/s}$ and in corresponding slope of straight line $\lg(C_0 - C_p)/(C_\tau - C_p) - f(\tau)$ (Fig. 4) as well as an increase in E_A values indicate a drop in adsorption of gallium complexes at the interface.

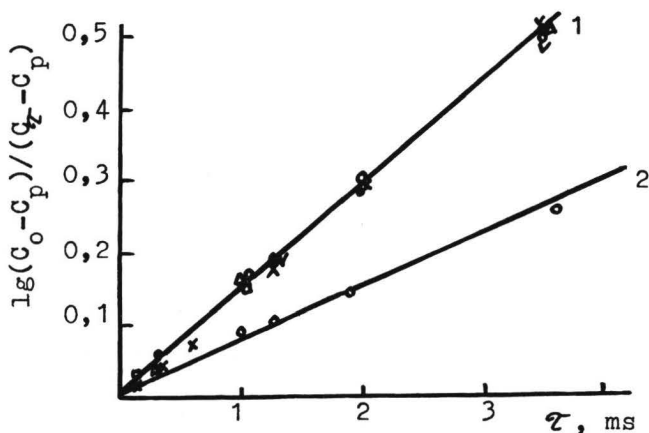


Fig. 4. Dependence of $\lg(C_0 - C_p)/(C_\tau - C_p)$ parameter on phases contact time at $C_{Ga} \cdot 10^3 \text{ mol/dm}^3$: 1 - from 1.506 to 298.8, 2 - 573.9 (C_0 , C_p , C_τ are initial, equilibrium, and at instant concentration of Ga, respectively).

For re-extraction, it has been determined that the rate-controlling stage is the interface destruction reaction of organic complex which has first order for gallium.

Based on the fundamental research conducted to solve technical problems, the following recommendations are suggested: to accomplish processes at the greatest developed interface, to maintain the temperature and HCl concentration during extraction not higher than 20°C and in the range of 2 to 4 mol/dm^3 , respectively.

When extraction was accomplished from process solutions having the concentration of $\text{HCl} < 4 \text{ mol/dm}^3$ at $\text{O:A} = 1:10$ in three steps, recoveries in organic phase were as high as 99 % for gallium and 70 % for iron, other impurities being completely stripped. The change in acid concentration up to 2.1 mol/dm^3 HCl at $1:25$ volume ratio of organic phase to aqueous phase according to counterflow diagram in 7 steps limited extraction of iron to 20 %, the percentage extraction of gallium still being high (about 99 %).

Water and alkali solution having a pH of 12.5 to 13 are recommended to use as re-extractants, the choice of which in every particular case should be tempered with the knowledge of iron content in organic phase. When the process was accomplished in counterflow at $\text{O:A} = 3:1$ with 9 steps, more than 99 % of gallium was extracted in aqueous phase from which metallic gallium was recovered after pretreatment with alkali using the method of cementation on aluminum gallate.

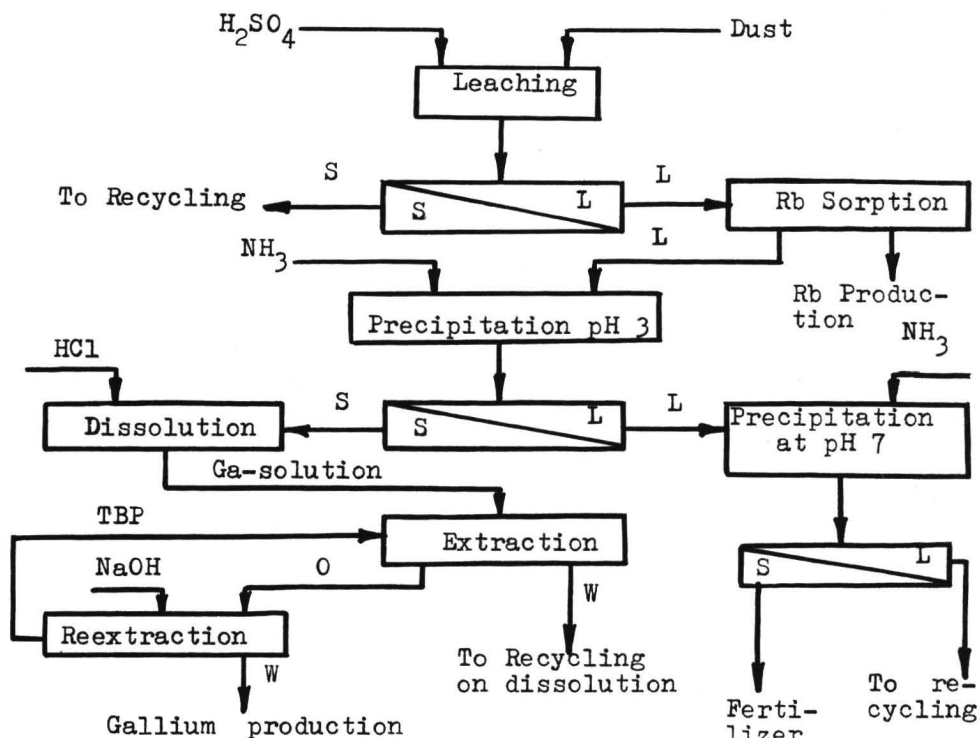


Fig. 5. Flowsheet for processing of Cottrell dust.

Gallium recovered by using this technology is characterized by very-high purity and can be successfully used for semi-conducting materials production.

Thus, on the basis of the fundamental research conducted and the results of pilot trials obtained, the low waste flowsheet (Fig. 5) for processing of phosphorus production dust, allowing the complex recovery of metal values has been developed.

CONCLUSIONS

The conditions of separation and preconcentration of rubidium and gallium microelements from phosphorus macrocomponent by a step neutralization method have been developed.

The process of interaction between microamounts of gallium during extraction in the presence of macroelements - foreign matters has been studied. The factor of gallium extraction suppression has been determined.

The effect of temperature on the extraction of gallium and iron has been investigated. Endothermic extraction of iron macroamounts in contrast to exothermic reaction for gallium microamounts allows the solution of the problem of partial separation between these elements.

The procedures for extraction and re-extraction have been defined based on the study of the kinetic mechanisms and methods for their intensification have been recommended.

Extraction processes of recovering gallium under plant conditions have been developed.

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2.9

RHENIUM PROCESSING WITH CENTRIFUGAL EXTRACTORS

LANIN V.P., CHIBRIKINA E.I., PUSHKOV A.A.,
Mendeleev Institute of Chemical Technology,
125190 Moscow, Miusskaya pl., 9 Russia.
KUZNETSOV G.I., NIKOLAEV YU.M., SAVIN A.V.,
NPO NIKIMT, Moscow, Russia.
ZHALIMBETOV A.K., TULEKBAEVA A.K.,
Chimkent lead smelter, Kazakhstan.

ABSTRACT

The paper is devoted to Re extraction from sulphuric acid solutions after leaching Pb-Zn dusts and purification from cadmium with centrifugal extractors CENTREK. Results obtained did not differ from those obtained in mixer-settlers. However, stable emulsions formed in the process led to disturbance in the hydrodynamics and continuous process in mixer-settlers. The use of centrifugal extractors allows considerable increase in plant capacity.

INTRODUCTION

When lead ores and scrap are worked up at agglomerating and smelting shops of the Chimkent lead smelter, lead-zinc dusts are formed, which are the main source of Re. The solutions after leaching of these dusts differ in qualitative and quantitative composition from solutions received from traditional rhenium-containing raw materials: copper and molybdenum concentrates. The solutions from dusts contain in g/L: H_2SO_4 - 20, Zn - 100, Cd - 25, Cl^- - 10-35, As - 5, Fe - 3, Cu - 0.02, Re - 0.02-0.18. The technology of Re extraction from these solutions was developed and introduced in practice by Institute of metallurgy and beneficiation of Kazakhstan AS and the Chimkent lead smelter (Zagorodnyaya et al, 1991b). The solvent used is 10-15% (vol) TAA in kerosene with 20% (vol) of highmolecular weight alcohols (HMA). The process comprises the following operations: extraction (4-5 stages), extract scrubbing (1 stage), Re stripping by ammonia solution (1 stage).

The extraction process is carried out in mixer-settlers with counter current flow; scrubbing and stripping is done periodically in tanks with a mixer. However, the formation of stable emulsions and interphase crud has very often occurred which does not allow in some cases to carry out the process without stopping and mechanical cleaning of equipment.

It has been shown (Kuznetsov et al, 1975; Lanin et al, 1985) that centrifugal extractors can be used for extraction of a number of metals with TBP, D2EHPH and TOA, stage efficiency being about 0.95 using short phase contact time. At present considerable experience is accumulated in centrifugal extractor operation in extraction and purification of a large number of rare metals (Kuznetsov et al, 1992). That is why the study of the possibility of centrifugal extractor utilization in rhenium processing from lead-zinc dusts has been done.

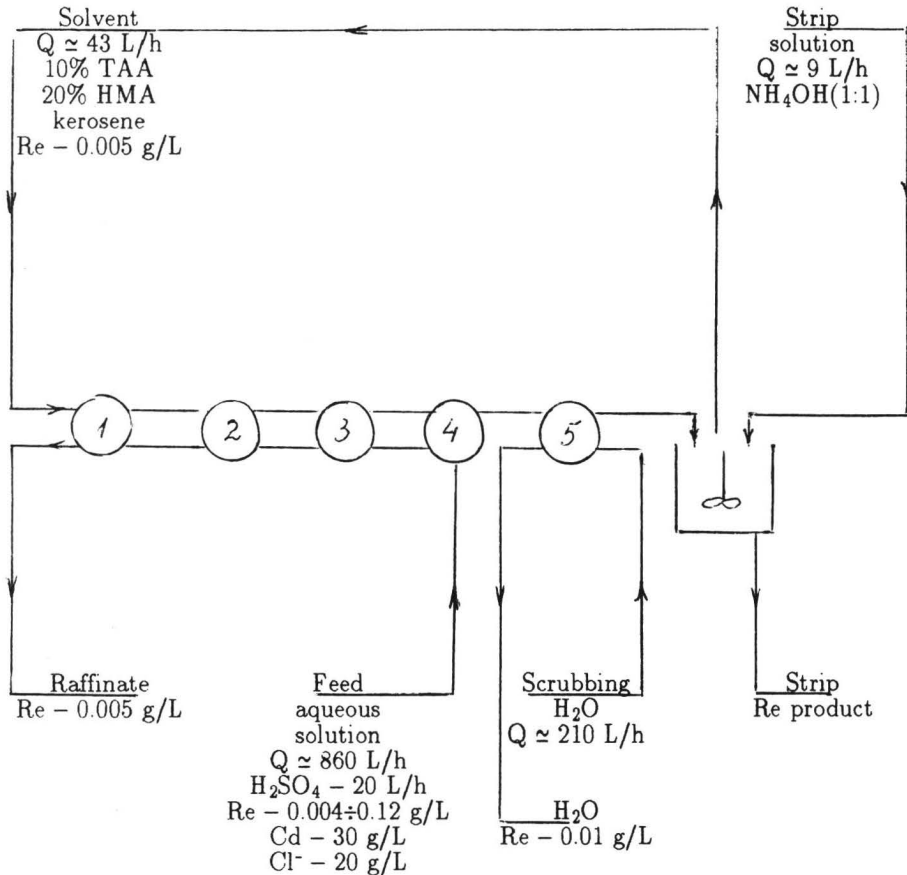


Fig.1 Re extraction process with centrifugal extractors EC-125.

EXPERIMENTAL WORK

Kinetics of rhenium extraction from sulphuric acid solutions with 10% TAA in kerosene and 20% HMA were determined with use of a diffusion cell having a mixer (Kasimov et al, 1985) and centrifugal extractor, EC-33, with a rotor of cylindrical form diameter of which is 33 mm (Kuznetsov et al, 1986).

First the Re extraction from plant solution was carried out with the installation of four extractors EC-33, then semi-production testing of the technology (Zagorodnyaya et al, 1991b) – was done with installation of five extractors EC-125. (Fig.1), four of them were for extraction and one for scrubbing. Analysis: Re – by extraction photometry, Cd – atomic – absorption, H_2SO_4 – alkalimetric and Cl^- – argentometric methods.

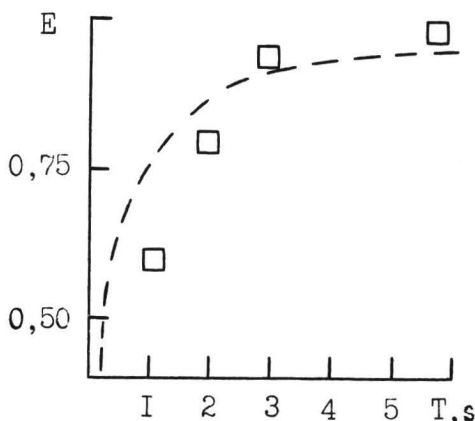


Fig.2. Dependence of Re mass transfer efficiency (E) on phase contact time (T) in centrifugal extractor.

System: 10% TAA – H_2SO_4 20g/L, Re 0.16 g/L. T – 293K.
(dotted line – calculated data).

The diagram of extractors is shown in the paper "Processing of enriched uranium in centrifugal extractors", ISEC'93.

RESULTS AND DISCUSSION

Fig.2 shows experimental and calculated dependence of extraction efficiency on phase contact time obtained with use of the value of mass transfer coefficient $K_y = 0.95 \cdot 10^{-6} \text{ m.s}^{-1}$ (this value was obtained in the diffusion cell with mixer) and model of full mixing in both phases (Kuznetsov et al, 1991). One can see that the Re extraction process is sufficiently fast and the interval of about 4 s is already enough to reach efficiency 0.95. On the basis of these results the process of Re extraction was tested in a bank of EC-33-4. The results are shown in Tables 1 and 2.

TABLE 1

Rhenium extraction from sulphuric acid
solutions of Pb-Zn dusts.

Solvent - 10% TAA, EC-33-4, T - 298K.

Capacity on sum of phases - 20 L/h.

NN	A/O	Concentration, g/L			DF	NN	A/O	Concentration, g/L			DF
		Re ₀	Cd ₀	Re _a				Re ₀	Cd ₀	Re _a	
Dusts of agglomerating shop.						Dusts of smelting shop.					
Feed aqueous solution (g/L):						Feed aqueous solution (g/L):					
H ₂ SO ₄ - 20, Re - 0.04,						H ₂ SO ₄ - 19, Re - 0.075,					
Cd - 16.6, Cl ⁻ - 19.8.						Cd - 21.4, Cl ⁻ - 18.4.					
1	0.04	0.95	5.1	0.014	77	1	0.03	1.10	-	0.005	-
2	0.04	1.10	5.8	0.010	79	2	0.03	1.00	-	0.005	-
3	0.05	0.95	4.2	0.010	94	3	0.03	1.30	-	0.005	-
4	0.07	0.70	5.0	0.005	60	4	0.04	1.20	-	0.008	-
5	0.04	1.00	5.4	0.010	112	5	0.04	1.80	-	0.008	-
6	0.04	0.80	5.1	0.010	95	6	0.06	2.00	-	0.005	-
7	0.04	1.00	5.3	0.010	114	7	0.06	1.20	-	0.005	-

Dusts mixture of agglomerating and smelting shops after sulphatization. Feed aqueous solution (g/L): H₂SO₄ - 20, Re - 0.065, Cd - 31.6, Cl⁻ - 17.7.

1	0.05	0.45	5.7	0.008	39	3	0.07	0.40	6.0	0.008	39
2	0.06	0.40	6.1	0.004	32	4	0.12	0.30	6.1	0.006	24

TABLE 2

Rhenium extract scrubbing with water.

EC-33-4; Capacity on sum of phases - 20 L/h; T - 298 K

NN	O/A	Concentration, g/L			DF	NN	O/A	Concentration,g/L			DF
		Re ₀	Cd ₀	Re _a				Re ₀	Cd ₀	Re _a	
Extract: Re – 0.90 g/L Cd – 5.0 g/L						Extract: Re – 1.5g/L Cd – 4.65 g/L					
1	10	0.90	4.3	0.005	1.2	5	1.0	1.50	0.82	0.010	5.7
2	9	0.90	3.7	0.006	1.4	6	1.0	1.45	0.95	0.010	4.7
3	1.8	0.85	2.3	0.010	2.1	7	1.0	1.49	0.77	0.010	5.8
4	1.7	0.88	2.2	0.010	2.2						

The data in Table 1 and 2 show that the utilization of centrifugal extractors allows quantitative extraction of Re from sulphuric acid solutions with TAA. Re concentration in raffinate (0.005–0.01 g/L) corresponds to that of existing technology (Zagorodnyaya et al, 1991b). The decontamination factor (DF) of rhenium from cadmium for solutions of dusts of the agglomerating shop is about 100, while for solutions after dusts sulphatization it does not exceed 40.

The best results of scrubbing of rhenium from cadmium ($DF=5$) are achieved with flow ratio O/A about 1, when this ratio is higher, K_0 is decreased to 2 ($O/A=1.8$) and 1.2–1.4 ($O/A=10$).

It should be noted that in all cases of Re extraction from plant solutions and scrubbing of extracts the normal hydrodynamic regime of centrifugal extractors operation is not disturbed.

Rhenium stripping was carried out with aqueous ammonia solution (1:1) in two stages in counter current flow. Re content in extract was 0.6 g/L, in TAA 0.01–0.02 g/L ($O/A=9-10$). As the concentration of Re in strip product solution is high, the accumulation of ammonium perrhenate precipitates occurred in the separating chamber of centrifugal extractors. To avoid this, temperature should be 333–334 K (Zagorodnyaya et al, 1991a).

The following testing of technology was carried out with the installation of EC-125-5. Taking into account the possible accumulation of ammonium perrhenate precipitates in the separating chamber the stripping operation proceeded in a tank with a mixing device.

The effect of solvent loading by rhenium on its content in raffinate and effect of flow ratio (O/A) in the scrubbing operation on the decontamination of rhenium from cadmium were investigated. The results are given in Table 3.

One can see that increasing rhenium content in the extract leads to increasing its concentration in raffinate. Satisfactory results (0.005 g/L) are achieved when flow ratio O/A 1:15, i.e. concentration of rhenium in extract is about 1,5 g/L.

Concentration of rhenium in raffinate depends on its concentration in feed solvent. Decontamination factor of rhenium from cadmium in extraction process described is 8×10^3 to 10×10^3 .

Additional decontamination of rhenium from cadmium can be obtained by scrubbing extracts with water (test. N 5 to 9, Table 3). A satisfactory value DF (5–8) is obtained only at $O/A = 1$ to 5–8. Re content in water after washing does not exceed 0.01 g/L. Re concentration in solvent for a normal process is approximately 0.005 g/L. Mass transfer efficiency in centrifugal extractors is about 0.9.

TABLE 3
 Rhenium extraction from sulphuric acid solution
 after leaching of Pb-Zn dusts with TAA
 in centrifugal extractors EC-125.

Flows: Q_1 - solvent; Q_2 - feed aqueous;

Q_3 - scrub; Q_4 - strip;

A: 1 - feed aqueous solution; 2 - process solvent;

3 - raffinate; 4 - extract from stage 4;

5 - extract from stage 5;

NN	Flows $Q_1:Q_2:Q_3:Q_4$	A	Concentration, g/L				DF
			Re	Cd	Cl^-	H_2SO_4	
1	1:40:5:0.2	1	0.100	32.0	19.1	40	-
		2	0.200	-	-	-	-
		3	0.070	-	-	-	-
		4	3.5	0.08	-	-	14000
2	1:30:5:0.2	1	0.110	33.2	19.1	38	-
		2	0.350	-	-	-	-
		3	0.030	-	-	-	-
		4	3.5	0.091	-	-	11600
3	1:20:5:0.2	1	0.150	30.3	17.7	32	-
		2	0.005	-	-	-	-
		3	0.014	-	-	-	-
		4	3.25	0.098	-	-	6700
4	1:15:5:0.2	1	0.140	30.7	24.8	35	-
		2	0.005	-	-	-	-
		3	0.006	-	-	-	-
		4	1.5	0.18	-	-	1800
5	1:15:8:0.3	4	2.5	0.11	3.33	-	-
		5	2.5	0.008	1.3	-	14
6	1:15:8:0.1	4	2.0	0.09	3.3	-	-
		5	2.0	0.012	2.3	-	7.5
7	1:15:8:0.2	4	1.87	0.094	3.3	-	-
		5	1.87	0.002	2.3	-	4.7
8	1:15:5:0.2	4	2.0	0.095	3.33	-	-
		5	2.0	0.02	3.2	-	4.7
9	1:15:5:0.1	4	1.87	0.11	3.4	-	-
		5	1.87	0.024	3.3	-	4.6

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2.10

**AMMONIACAL SOLVENT EXTRACTION AT QUEENSLAND NICKEL
PROCESS INSTALLATION AND OPERATION**

J.G. REID and M.J. PRICE

Queensland Nickel Pty. Ltd.
P.M.B. 5, Mail Centre
Townsville, Queensland, 4818, Australia

ABSTRACT

In 1986 the decision was made to initiate research work into a superior method of separating nickel and cobalt in the Caron type hydrometallurgical process operated by Queensland Nickel. This was with the knowledge that by moving to treat imported ores, cobalt would become relatively more important to the project.

The success of the research and development work led to the decision in 1988 to design and construct a solvent extraction plant that would operate with ammoniacal liquors in both the extraction and stripping stages. The new ammoniacal solvent extraction plant (ASX) was commissioned in 1989. All design and construction work was undertaken in-house utilizing Queensland Nickel personnel.

This paper gives a brief outline of the original process operation, followed by the overall process changes and new products brought about by the introduction of the ASX circuit.

In 1991 the Queensland Nickel plant produced 25,000 t of nickel and 1,000 t of cobalt.

INTRODUCTION

The nickel refinery near Townsville commenced processing Greenvale lateritic nickel ore in 1974. Since 1988 increasing quantities of imported laterite ores have been replacing the depleted Greenvale ore. Substitution will be complete in 1993.

The project developers and original joint owners were Freeport Minerals of the U.S. and Metals Exploration Ltd, an Australian Company. Freeport provided the technology for the plant construction from their experience with the Nicaro plant in Cuba during the 1940's.

The installed process was basically that developed by Professor Caron at Delft University during the 1920's. The reduction roast, ammonia, ammonium carbonate leach Caron process has an advantage over the more commonly used smelting plants for nickel laterite ore processing in that it is possible to recover significant quantities of cobalt from the ore.

The Caron process can be used to treat either the upper horizon limonite or lower horizon saprolite of a typical laterite ore profile but works best with the higher cobalt content limonite ore. The ore from the Greenvale Mine was a mixture of both the limonite and saprolite horizons and hence contained relatively low cobalt grades compared with straight limonite ore. With the exhaustion of the Greenvale mine, the ore now being imported from New Caledonia and Indonesia is predominantly from the upper limonitic horizon and hence contains higher cobalt grades.

It was with the knowledge that the plant would be moving towards the treatment of a higher percentage of limonitic ore that research work into a more efficient method of separating nickel and cobalt was initiated in 1986.

The motivation to develop a new means of separation was driven by the following factors.

- (1) The existing plant which thickened, dried, compacted and drummed the nickel-cobalt sulphide then being produced (28% Ni, 14% Co, 35% S) was operating at near capacity and would have required expansion to handle the anticipated increased cobalt production.
- (2) Some of the imported ores contain significantly higher manganese contents than Greenvale ore and without capital expenditure on new plant, would have resulted in an out-of-specification manganese content of the nickel product.
- (3) Energy costs were high to spray dry the existing product because of the high nickel content.
- (4) Shipping costs between Townsville and Kokkola in Finland (where the cobalt product is refined) were high because of the distance involved and the high nickel content of the product.

Further benefits which arose after the process was installed were:

- (a) A higher nickel final product purity resulted from all anionic contaminants being eliminated in the nickel transfer from aqueous to organic phase.
- (b) Process steam savings.
- (c) Increased overall nickel recovery.
- (d) Increased overall cobalt recovery.
- (e) Opportunity for further cobalt processing.

ORIGINAL PROCESS FLOWSHEET

Ore Drying and Grinding

As the hydrometallurgical processing is preceded by ore reduction roasting it is necessary to first dry and grind the ore. The drying is undertaken in three rotary dryers all of which were originally oil fired. In 1981 two of the dryers were converted to coal. The dryers supply an average of 6200 tonnes of dry ore daily for grinding. Dry

grinding is undertaken in two ball mills to produce a product of approximately 60%, - 45 micron sizing.

Ore Reduction

The ground ore is transported pneumatically to the top of 10 Herreshoff multi hearth reduction roasters, each with a nominal hourly capacity of 26 tonnes of ore. In the roasters the nickel and cobalt contained in the ore as oxides and silicates is reduced to the elemental form. It is necessary to roast the ore as only nickel and cobalt in the elemental form will dissolve in an aerated ammonia-ammonium carbonate leach solution.

Reduced Ore Leaching and Washing

In the leaching section consisting of three banks of four atmospheric pressure aeration leach tanks, a slurry of ore and ammonia-ammonium carbonate liquor is agitated, allowing dissolution of the nickel and cobalt.

The leached ore is separated from the nickel and cobalt containing pregnant liquor in seven counter current washing thickeners. The pregnant liquor flow is approximately 83 L/s and contains nominally 10 g/L nickel and 0.5 g/L cobalt in solution.

Precipitation of Nickel-Cobalt Sulphide

Prior to the 1989 installation of the ASX circuit the treatment plant produced a nickel-cobalt sulphide precipitate by the injection of hydrogen sulphide into the pregnant leach liquor. It was not possible to precipitate the cobalt without also precipitating nickel.

The result was a mixed sulphide product which contained nickel and cobalt in a ratio of about 2:1 (28% Ni and 14% Co). Consequently the product mass was three times that of pure cobalt sulphide. The mixed sulphide slurry was thickened, spray dried, compacted and drummed for export.

Precipitation of Nickel Carbonate

After the cobalt removal stage, the nickel ammine liquor was passed to four nickel precipitation stills, where steam injection boiled off the ammonia and carbon dioxide, allowing the nickel to precipitate as basic nickel carbonate.

Nickel Carbonate Calcination and Reduction

The nickel carbonate was thickened and filtered before being fed to an oil fired rotary calcining kiln. In the kiln the nickel carbonate was converted to nickel oxide (77% Ni) which passed through hydrogen reduction furnaces for upgrading to 85-90% Ni. The nickel oxide was compacted into cylindrical rondelles (30 mm high by 30 mm in diameter) and packed in 250 kg drums for shipment.

This section of the plant has not changed significantly since the installation of the ASX process.

NEW PROCESS FLOWSHEET - INCORPORATING AMMONIACAL SOLVENT EXTRACTION

ASX Development

The laboratory research and pilot plant testing of the ASX process was undertaken between 1986 and 1988. This work established that a reagent based on LIX84, modified by Henkel, was the most suitable of available alternatives for the proposed circuit. Details of this research are reported in an accompanying ISEC 93 paper.

After a survey of a number of existing copper and uranium solvent extraction plants it was decided that the design and construction of the ASX plant would best be undertaken in-house. The logic of this decision was reinforced by the situation whereby no similar plant existed anywhere in the world.

Laboratory and pilot testing had confirmed that optimum results were obtained in a configuration of three extraction and three strip stages, six mixer settler cells in all. No scrubbing stages were found to be necessary. Extensive hydrodynamic testing confirmed that two stage mixers were the optimum design with the first mixer fitted with a 6 vane pump-mix turbine impeller and the second mixer fitted with an axial flow impeller. The mixer-settler cells were constructed entirely from 316 Stainless Steel. A photograph of the ASX plant is shown in Fig. 1.

As well as the construction of the ASX plant, extensive modifications were required for liquor distribution through heat exchangers, clarifiers, filters, condensers, etc.

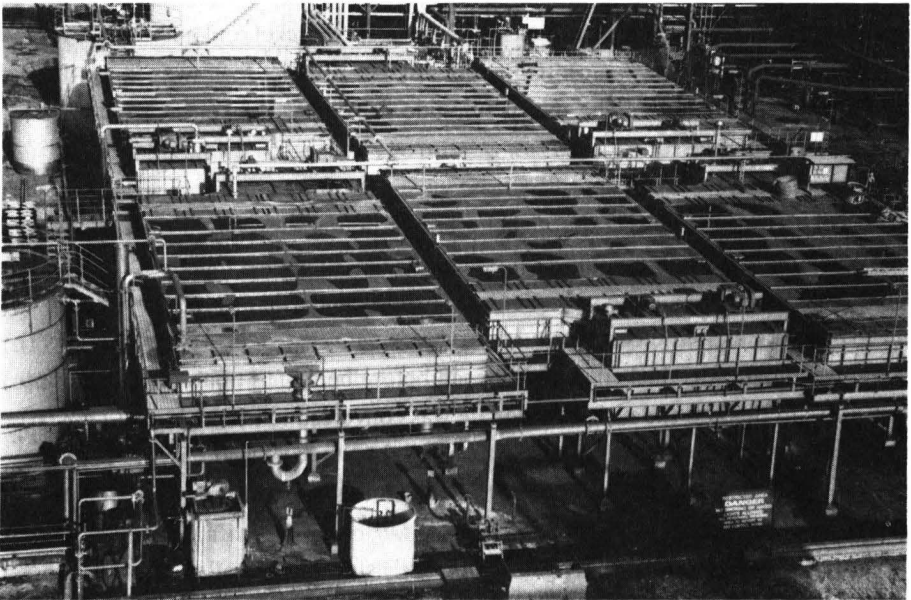


Fig. 1 ASX Plant

Most of these modifications primarily involved piping changes to existing equipment. The ASX circuit installation and plant modifications, including reagent inventory, cost approximately A\$8,000,000.

Pregnant Liquor Preboil

Before being fed to the ASX plant the pregnant leach liquor is pre-boiled in a still (converted from previous nickel carbonate precipitation service) which lowers the ammonia content from 80 g/L to 40 g/L, and allows optimum organic nickel loading efficiency. This step has the secondary benefit of precipitating most of the small amounts of manganese, iron, and arsenic present in the leach liquor, thus enhancing the purity of the final nickel product.

Following the preboil step the liquor is aerated to ensure that the cobalt ions are present as Co^{3+} rather than Co^{2+} thus preventing cobalt loading onto the oxime extractant along with the nickel.

Strip Liquor Production

Although low strength ammonia-ammonium carbonate liquor had always been produced at the plant, the high strength ammonia liquor required to strip the nickel from the nickel loaded organic had not previously been produced. By altering the operation of the existing ammonia and carbon dioxide gas condensation vessels, the desired ammonia strength ($> 270 \text{ g/L NH}_3$) was achieved.

ASX Circuit Operation

After the preboil step, the purified pregnant liquor is passed through the three extraction stages of the ASX circuit where the nickel is transferred to the organic phase and the cobalt remains with the aqueous phase.

After the nickel is removed, the aqueous phase passes out of the extraction side of the ASX circuit as raffinate, which contains more than 99% of the cobalt and less than 0.1% of the nickel that entered in the pregnant liquor. Residual organic phase is scavenged from the raffinate in a coalescing vessel. The flow rates of the pregnant liquor and organic are approximately the same, so that the 10 g/L nickel in the pregnant liquor loads to 10 g/L nickel in the organic phase.

The nickel loaded organic phase is then passed through the three strip stages where the nickel is transferred into the ammoniacal strip liquor. The strip liquor flow is nominally 12% of the organic flow so that the nickel loading in the strip liquor is 8 times higher than that in the organic liquor. Recycle lines on each mixer settler allows the desired organic to aqueous ratio to be maintained in the mixers.

The loaded strip liquor normally contains 80 g/L Ni and $< 20 \text{ mg/dm}^3$ Co. It passes out of the ASX circuit through a coalescing vessel for removal of entrained organic phase and is pumped to two nickel carbonate precipitation stills.

The raffinate stream, nominally containing 0.5 g/L cobalt and 10 mg/dm^3 nickel, is

injected with hydrogen sulphide, with which both the cobalt and nickel react and precipitate as sulphides. Because so little nickel is present the product contains approximately 42% Co, 1% Ni, 35% S, the remainder being oxygen and bound moisture.

The precipitate is thickened, spray dried, compacted and drummed, in the same equipment used for the pre-ASX mixed nickel-cobalt sulphide. As the original sulphide contained only 14% Co the plant now has the capacity to handle three times as much cobalt as previously.

Since the installation of the ASX circuit the overall cobalt recovery is considerably higher than was achieved in the original circuit, as is the overall nickel recovery.

A flowsheet of the plant incorporating the ASX circuit is shown in Fig 2.

Precipitation of Nickel Carbonate from ASX Loaded Strip Liquor

Electric power and steam are produced in a coal fired steam boiler and turbo generators on site. The low pressure turbine discharge steam is used for nickel precipitation and ammonia recovery from tailings.

One major advantage of the ASX circuit has been that the high ammonia strength strip liquor allows a nickel strip liquor loading of over 80 g/L nickel. This in turn means that the liquor volume treated in the basic nickel carbonate precipitation stills is only about one eighth the original, with an associated saving in steam. The nickel carbonate slurry (16% solids) generated in the stills is pumped to a thickener to produce a 40% solids underflow and recyclable clean liquor overflow.

Both soluble and insoluble nickel losses in the nickel carbonate thickener overflow liquor were significantly reduced from pre-ASX levels.

Because the cobalt content of the loaded strip liquor is normally approximately 20 mg/dm³, the cobalt content of the final nickel product is approximately 0.03%.

Finally, another significant difference between the pre and post ASX nickel carbonate precipitate is that the sulphur levels are much lower. This has a significant downstream benefit.

Nickel Carbonate Calcination and Reduction

Before the ASX installation, sulphur removal from the nickel carbonate required that calcination be undertaken under oxidizing conditions at 1400° C, to ensure that the nickel oxide (77% Ni) discharge from the calciner met the stringent sulphur limits required by customers.

Since the ASX installation, the low sulphur content of the nickel carbonate allows the calciner to be operated at lower temperatures. The calciner can also be operated under a reduction atmosphere and a new product containing >97% nickel has been introduced to the Queensland Nickel product range.

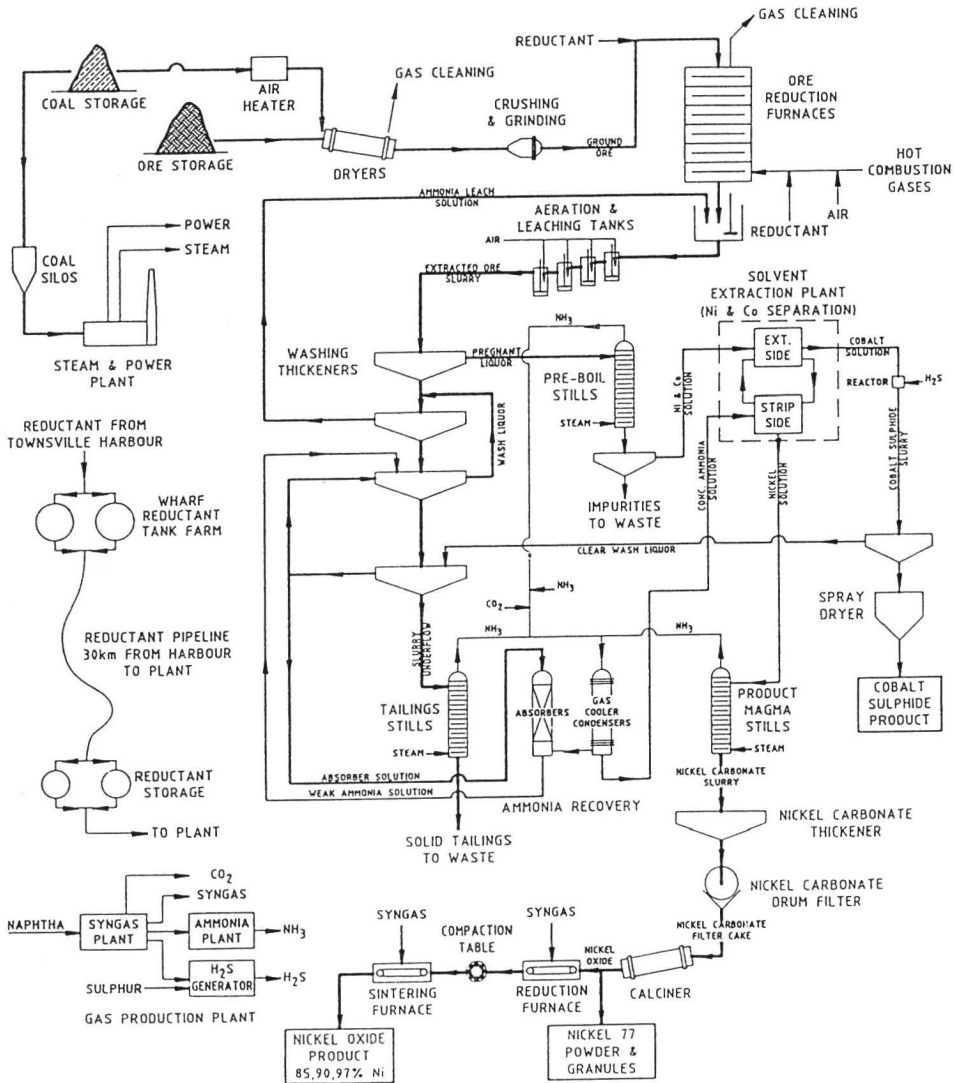


Fig. 2 Flowsheet of Yabulu Treatment Plant incorporating the ASX Circuit

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SESSION 3

RARE EARTHS



3.1

SOME PROGRESS IN SOLVENT EXTRACTION OF RARE EARTH IN CHINA

Guang-Xian XU, Chun-Hui HUANG, Biao-Biao LI

Song GAO AND Chun-Hua YAN

Research Center of Rare Earth Chemistry

Peking University

Beijing 100871, P.R.China

ABSTRACT

A review of solvent extraction of rare earths in the Research Center of Rare Earth Chemistry, Peking University is given with 25 references. The outlines are as follows: (I) The theory of countercurrent extraction and optimized design of rare earth process; (II) A novel method for a multicomponent rare earth separation system by countercurrent extraction with three outlets; (III) The expert system for rare earth extraction process control; (IV) The systematic studies on the structure of extraction complexes and the extraction mechanism.

INTRODUCTION

China has plentiful rare earth resources. Two mineral systems are found in the north and the south of China. The former is rich in light rare earth while the latter rich in heavy. During the past few years, great progresses have been achieved in rare earth science and technology which has made China one of the most important countries in output of rare earth products in the world. Solvent extraction plays an important role. Pure products for La, Gd, Tb, Y ($\geq 99.99\%$) and other elements can be produced by solvent extraction directly.

THEORY OF COUNTERCURRENT EXTRACTION AND OPTIMIZED DESIGN OF RARE EARTH PROCESS

Alders(1959) developed a liquid-liquid extraction theory which is suitable for the separation of a two-component (A and B) system having constant degrees of extraction E_A and E_B in each stage of the extraction system. Since the hypothesis of constant degrees of extraction is not satisfied in most practical extraction systems commonly used in rare earth industry, we have further developed Alders' theory by removing this hypothesis and derived a set of new equations for calculating the number of minimum and optimized extraction and scrubbing stages, as well as the optimized ratio of flow rate of the feed, extractant and scrubbing solution (Xu, 1978a, 1978b, 1979, 1982; Jin, 1979). Based on this theory and a mathematical model, a set of

programs has been established for simulating the "separating funnel method" experiment (Li, 1980a,1980b,1982,1985a,1985b,1986; Yan, 1989). The programs are applicable to systems using saponified acid extractants and may provide much more information than the laboratory "separating funnel method" does in a very short time, while the "separating funnel method" experiment requires several months to accomplish the task. Therefore, the period for a new process developed from experimental research to industrial practice has been greatly reduced. In addition, since its reliability has been extensively demonstrated by practice, the trial enlarged experiment is not necessary when a new process is designed for application in industry. Fig.1 is the comparison of purity distribution for each component between calculation and industrial practice (Yan, 1991).

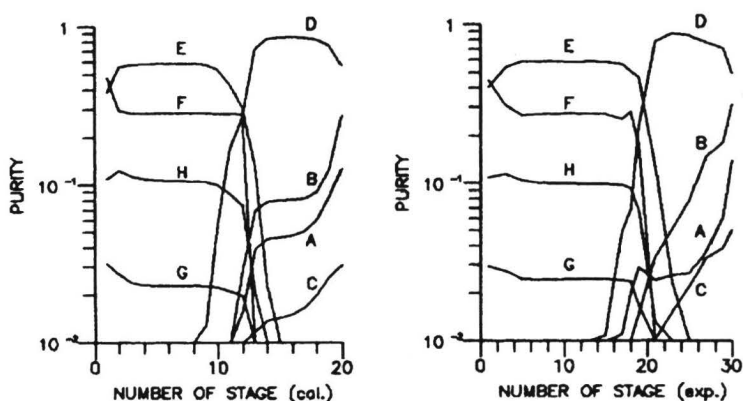


Fig.1 The comparison of purity distribution between calculation and industrial results

A NOVEL METHOD FOR A MULTICOMPONENT RARE EARTH SEPARATION SYSTEM BY COUNTERCURRENT EXTRACTION WITH THREE OUTLETS

Usually, a countercurrent extraction system has two outlets, extract and raffinate. Only one pure product and one mixture can be obtained by a single process, if more than two components exist in the feed solution. Recently, a novel method for a multicomponent rare earth separation system by countercurrent extraction with three outlets, "three outlet fractional extraction process", was developed in our research center (Li, 1989,1992). As is well known, a saponified acid extraction system possesses constant mixed degrees of extraction E_M and E_M' . The intensive theoretical analysis and software for computer simulation were developed. When the feed composition, the separation factors for those elements of interest for separation, and the quality index of products are given, the outlet fractions, the position of the third outlet, the flows, and the number of stages for both extraction and scrubbing sections can be exactly calculated and the optimized parameters can be given for general process design.

For example, in a mixture of Sm-Eu-Gd, Eu is not only the most valuable element but also the smallest amount in content. By using a three outlet process, we can obtain high purity of Gd_2O_3 and Sm_2O_3 simultaneously and also can obtain a concentrate of Eu with high yield.

TABLE 1

The relations between S and n,m,i

S \ Stage	i	n	m	n+m	i-n
1.40	39	22	63	85	17
1.50	36	21	55	76	15
1.75	32	19	47	66	13
2.00	30	18	42	60	12
2.25	29	18	39	57	11
2.50	28	17	38	55	11

In the Table 1, i is the stage of the third outlet, n and m are the number of stages for extraction and scrubbing section respectively, S is the mass flow rate. Data show that the numbers of stages for extraction and scrubbing sections, and the position of the third outlet depend on the mass flow rate selected. This new technology has been widely and successfully used in the rare earth industry in China to establish new factories or optimize old ones.

THE EXPERT SYSTEM FOR RARE EARTH EXTRACTION PROCESS CONTROL

On the basis of the studies of countercurrent extraction theory and the industrial practice in the past fifteen years, we can take the optimized design for the process of rare earth separation, and have accumulated much experience in the starting and control of an extraction system. It is possible to establish an expert system for rare earth extraction process control (REPC) utilizing the results of theoretical study and the experiences of industrial practice. The main structure of our expert system (REPC) is illustrated in Fig.2.

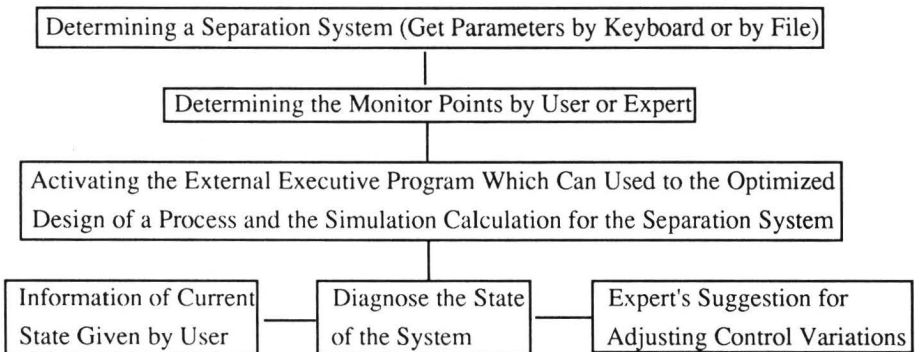


Fig.2 The main structure of expert system (REPC)

The functions of REPC are: (1) take optimized design for any process with two-outlets or three-outlets, so as to readjust the process parameters timely; (2) make a diagnosis of the state of the system and give a suggestion for the increment of each control variable.

THE SYSTEMIC STUDIES ON STRUCTURE OF EXTRACTION COMPLEXES AND THEIR EXTRACTION MECHANISM

The extraction chemistry is the coordination chemistry between two phases. In the past more than 20 years, attention has been concentrated on thermodynamic and kinetic studies in solutions, which can provide the composition and stability of the extracted species, but not their exact molecular structure. In order to obtain a deeper insight and provide a basis for the molecular design of more efficient extractants for rare earths, we started a program of systematic study to synthesize and isolate the extracted rare earth complexes with various types of extractants and to determine their crystal and molecular structure by X-ray diffraction. In these studies, the emphasis has been given not only on the solid but also on the related solutions; not only on the model molecules but also on the extractants used in practice.

For example: Naphthenic acid and mixtures of aliphatic carboxylic acids are used for separation of yttrium in high purity. Among the lanthanide elements, La is the most difficult to separate from Y. We have found by experiment that when La is the predominant component of the mixture, Y is more extractable than La, on the contrary, when Y is the predominant component, Y is less extractable than La. This peculiar behavior may be explained by co-extraction of Y and La in the organic phase. Indeed we have carried out a thermodynamic study which shows the existence of a La-Y carboxylic acid dinuclear complex, whose stability constant is larger than those of La-carboxylic acid complex and Y-carboxylic acid complex. In order to provide a direct evidence of the dinuclear complex, $\{[LaYA_4(HA)_4] \cdot Cl_2 \cdot (CH_3COCH_3)_3\}_n$ was synthesized, where HA is cyclohexyl carboxylic acid. Based on the above results, a new process for separation of 99.99% Y_2O_3 was developed and patented (Huang, 1992).

Di-(2-ethyl hexyl) phosphate (HD2EHP) is one type of extractant which is extensively used in industry. Mimicking HD2EHP, the single crystal of $\{[(C_2H_5O)_2POO]_3Pr\}_n$ was synthesized. Structural data show that every Pr atom is connected with other two Pr atoms through three "O-P-O" bridging groups to form a long chain polymer (Huang, 1990). Comparing the structure of $\{[(C_2H_5O)_2POO]_3Ce\}_n$ and $\{[(CH_3O)_2POO]_3Pr\}_n$, the conclusion is that the extracted complex has a net structure (Fig.3(a)) when $n=1$ in the organo-phosphoric acid $(C_nH_{2n+1}O)_2POOH$, but the net structure is not stable when $n>1$ and will convert to a long chain polymer as shown in Fig.3(b). This is the reason why HD2EHP prefers to form the third phase with rare earths when the ratio of phosphate radicals to rare earth elements is smaller than 6 in the extraction process.

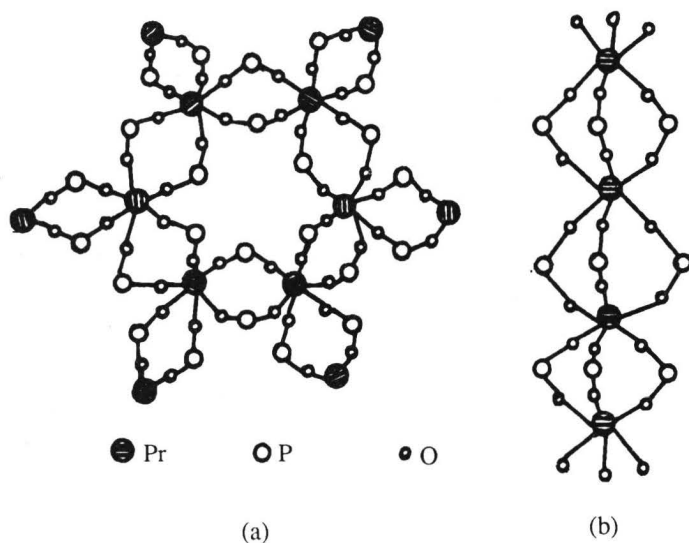


Fig.3 The net structure of $\{[(\text{CH}_3\text{O})_2\text{POO}]_3\text{Pr}\}_n$ (a)
and the long chain structure of $\{[(\text{C}_2\text{H}_5\text{O})_2\text{POO}]_3\text{Pr}\}_n$ (b)

The structure of the extracted complex NdA_3 , where $\text{HA} = \text{R}(\text{RO})\text{POOH}$, $\text{R} = \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}(\text{CH}_2\text{CH}_3)\text{-CH}_2\text{-}$, in $n\text{-C}_6\text{H}_{14}$ solution with different concentrations were studied by subtractive IR spectroscopy and osmometry. The solubility of NdA_3 in $n\text{-C}_6\text{H}_{14}$ at 37°C is 1.2mM , under this condition, the aggregation degree is 7. O-P-O takes bridging mode to coordinate to the central ion. The bridging mode will be partly replaced by monodentate mode $\text{O}=\text{P}-\text{O}$ along with reduction of the aggregation degree. When the mole ratio $\text{HA}/\text{NdA}_3 \geq 3$, the bridging coordination mode of the organo-phosphonic group was replaced by the monodentate mode throughout and the aggregation degree approached one (Li, 1991).

By using tetrabutyl ammonium nitrate as model molecule, a series of rare earth extraction complexes has been synthesized. The general formula can be presented as $[(\text{C}_4\text{H}_9)_4\text{N}]_X\text{RE}(\text{NO}_3)_{3+X}$, where $X = 3$ when $\text{RE} = \text{La}, \text{Pr}$ or Nd , and $X = 2$ when RE is Eu-Lu or Y . The complex of Sm can be of both constitutions according to the condition of synthesis. The structures of $[(\text{C}_4\text{H}_9)_4\text{N}]_3\text{Nd}(\text{NO}_3)_6$ (Huang, 1984) and $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{Er}(\text{NO}_3)_5$ (Huang, 1985) have been determined by single crystal diffractometry. The vibration frequency of RE-O changes from $\sim 190\text{ cm}^{-1}$ to $\sim 220\text{ cm}^{-1}$, when the coordination number changes from 12 to 10. In order to demonstrate that the information obtained from a single crystal makes sense in solution, a series of pregnant organic phases made by Aliquat 336 kerosene solution were examined by far IR spectrometry. It was surprising to find that the curves of vibration frequency of RE-O

against atomic number are highly similar (Huang, 1986).

Di-(1-methyl-heptyl) methyl phosphonate (trade name P350) developed in China is an efficient extractant for separation of La in high purity from other rare earths. Using triphenylphosphine oxide (B) as a model molecule for P350, a series of extraction complexes such as $\text{Nd}(\text{NCS})_3 \cdot 4\text{B}$, $[\text{Nd}(\text{ClO}_4)_2 \cdot 4\text{B}]\text{ClO}_4$ and $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{B} \cdot \text{C}_2\text{H}_5\text{OH}$ have been synthesized, whose structures were determined. Using a kerosene solution of P350 as the organic phase, the neodymium salts with different anions were extracted and ΔH , K and ΔS were determined. Comparing the IR shifts of $\text{P}=\text{O}$ both in model molecules and the corresponding pregnant organic phases, the influences of anions on the extraction reactions were given (Xu, 1988; Huang, 1989).

In the respect of synergic extraction systems, different structures of β -diketone with triphenylphosphine oxide (TPPO) reactions were studied. Among them a strong synergistic effect is found between 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HA) and TPPO. The extraction complexes of $\text{NdA}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NdA}_3 \cdot 2\text{TPPO}$ have been isolated and their structures have been determined by X-ray diffraction. The synergistic effect, clear direct evidence was given at molecular level, was caused by the replacement of the two water molecules in $\text{NdA}_3 \cdot 2\text{H}_2\text{O}$ by the hydrophilic molecules of TPPO in $\text{NdA}_3 \cdot 2\text{TPPO}$. The increase of the solubility of the extracted complex in the organic phase reflects the increase of the equilibrium constant $\log K$ from -4.63 ($\log K_{\text{HA}}$) to 4.32 ($\log K_{\text{HA-B}}$) (Huang, 1988).

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NOMENCLATURE

i	stage of the third outlet
n	number of stages for extraction section
m	number of stages for scrubbing section
S	mass flow rate
ΔH	change of enthalpy
ΔS	change of entropy

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SOLVENT EXTRACTION OF RARE EARTH ELEMENTS WITH BIS(4-ETHYLCYCLOHEXYL)PHOSPHORIC ACID

Kazuharu YOSHIKAZUKA, Masashi KOBA and Katsutoshi INOUE
Department of Applied Chemistry
Saga University
Honjo 1, Saga 840, Japan.

ABSTRACT

Bis(4-ethylcyclohexyl)phosphoric acid (D4EHPA) was synthesized to investigate its extraction behavior for rare earth elements from acidic aqueous chloride and nitrate media, together with the apparent molecular weight of D4EHPA in toluene as a diluent. D4EHPA was found to exist as dimeric species in toluene. From the concentration dependencies of the reactant species, i.e., hydrogen ion and extractant on the distribution ratio of these metals, it was concluded that the metals (M^{3+}) were extracted with D4EHPA (HR) as $MR_3 \cdot 3HR$ into the organic phase and the extraction equilibrium constants were evaluated. The selectivities between the adjacent rare earth elements are nearly the same as those with bis(2-ethylhexyl)phosphoric acid (D2EHPA). However, the extraction takes place at higher pH with this extractant than with D2EHPA, owing to its higher pK_a and the loading capacity of metals into the organic phase is excellent compared with that of D2EHPA due to prevention of gelation of the organic phase.

INTRODUCTION

Dialkylphosphoric acids have found extensive use in the hydrometallurgical recovery and refining processes of metals such as cobalt, nickel, zinc, actinides and lanthanides. The commercial separation and refining of rare earth elements have been mainly carried out by solvent extraction with dialkylphosphoric acids, especially bis(2-ethylhexyl)phosphoric acid (henceforth, abbreviated to D2EHPA), and many fundamental studies on the extraction of rare earth elements have been conducted (Bauer et al., 1972; Bhattacharyya and Ganguly, 1986; Coleman and Roddy, 1971; Danesi and Cianetti, 1982; Hirato and Toguri, 1989; Imai and Furusaki, 1987; Inoue and Nakashio, 1982; Kolarik et al., 1974; Pierce and Peck, 1963; Sato, 1989).

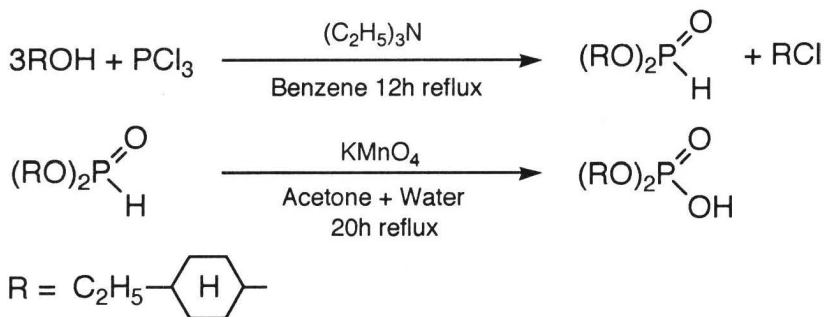
In the present study, bis(4-ethylcyclohexyl)phosphoric acid (henceforth D4EHPA, abbreviated as HR for monomeric species, and H_2R_2 for dimeric species) was synthesized to investigate the extraction behavior for rare earth elements from acidic aqueous chloride and nitrate media, together with the apparent molecular weight of the extractant in toluene by means of vapor phase osmometry. From the concentration dependencies of the reactant

species on the distribution ratios of these metals, the extraction equilibrium constants were evaluated, in order to elucidate the separation efficiencies of rare earth elements.

EXPERIMENTAL

Synthesis of D4EHPA

D4EHPA was synthesized according to the reaction expressed as follows:



4-Ethylcyclohexanol and phosphorus trichloride were mixed together in dehydrated benzene using triethylamine as a catalyst. The mixture was refluxed for 12 hours under a nitrogen atmosphere. The mixture was then washed with water, 0.5 M sulfuric acid several times and finally with water to neutral pH. The water phase was discharged and the organic phase was evaporated to remove benzene and by-product (4-ethylcyclohexyl-chloride), and to obtain the intermediate product. The intermediate product was refluxed for 20 hours in the mixture of acetone and water with potassium permanganate as a catalyst. After ethanol was added to the solution, the solution was filtered and evaporated. Benzene was added to the residue and this solution was washed with water, 0.5 M sulfuric acid and hydrogen peroxide several times and finally with water to neutral pH. The water phase was discharged and the organic phase was evaporated to remove benzene and to obtain the final product. The final product was recrystallized from ethyl acetate. The identification of the product was carried out by infrared and ^1H -n.m.r. spectroscopies. The elemental analysis of the product was obtained as follows; Found: C, 60.43; H, 9.80 %. Calcd. for $\text{C}_{16}\text{H}_{31}\text{O}_4$: C, 60.36; H, 9.81 %. The organic solution was prepared by dissolving D4EHPA in reagent grade of toluene to a required concentration gravimetrically. The aqueous solutions were prepared by dissolving oxides of the corresponding rare earth elements in the aqueous mixtures of 1 M hydrochloric acid – sodium chloride or 1 M nitric acid – sodium nitrate. The initial metal concentrations of these aqueous solutions were about 0.01 mol/dm³.

Measurement of apparent molecular weight of D4EHPA

Apparent molecular weight of D4EHPA in toluene was measured with a Hitachi model 117 vapor-phase osmometer, using benzil as a standard material.

Extraction equilibria

The experiments on extraction equilibria of rare earth elements were carried out batchwise by the conventional method (Yoshizuka et al., 1992). The two phases were shaken for 24 hours using a water bath incubator maintained at 30 °C to attain equilibrium. The metal concentration was measured by a chelating titration with EDTA solution using Xylenol Orange {3,3'-bis[*N,N*-di(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein} as an indicator and/or FIA (flow injection analysis) method using Neo-Thorin {2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)arsonic acid} as an indicator. The amount of metal extracted was calculated from the difference of the metal concentration before and after equilibration. Distribution ratio of metals, D , was defined the ratio between the concentration of metal extracted into the organic phase and that in the aqueous phase.

RESULTS and DISCUSSION

Dimerization of D4EHPA

It is considered that D4EHPA dimerizes in a nonpolar diluent such as toluene as well as D2EHPA (Coleman and Roddy, 1971; Danesi and Cianetti, 1982; Hirato and Toguri, 1989; Imai and Furusaki, 1987; Kolarik et al., 1974; Pierce and Peck, 1963; Vandegrift and Horwitz, 1977).

The dimerization equilibrium of the extractant in the organic phase is expressed as follows:



From the above equation, the dimerization constant, K_d , and the number-averaged aggregation number, m , are given by the following equations:

$$K_d = \frac{[\overline{\text{H}_2\text{R}_2}]}{[\overline{\text{HR}}]^2} = \frac{(C_{\text{HR}} - C^*)}{(2C^* - C_{\text{HR}})^2} \quad (2)$$

$$m = C_{\text{HR}}/C^* \quad (3)$$

where $C_{\text{HR}} (= 2[\overline{\text{H}_2\text{R}_2}] + [\overline{\text{HR}}])$ and $C^* (= [\overline{\text{H}_2\text{R}_2}] + [\overline{\text{HR}}])$ are the analytical concentration of D4EHPA and the total concentration of the monomeric and dimeric species in toluene measured experimentally, respectively.

Figure 1 shows the relation between C_{HR} and C^* according to Eq.(3). From the linear relationship, the number-averaged aggregation number of D4EHPA, m , was found to be equal to 2 under the present experimental conditions. However the dimerization constant cannot be obtained because the difference between $2C^*$ and C_{HR} is negligibly small. It can be concluded that D4EHPA is completely dimerized in toluene.

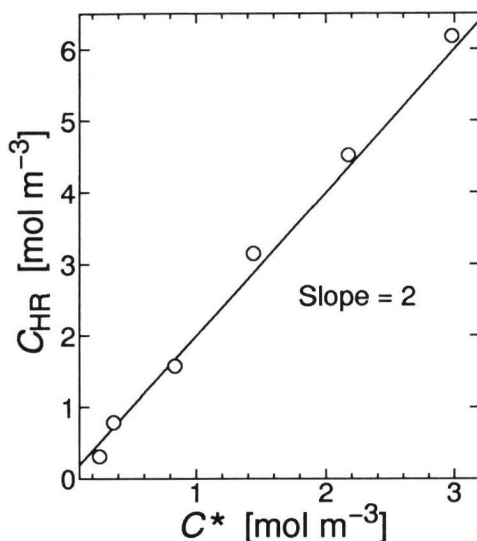


Fig. 1. Relation between C_{HR} and C^* .

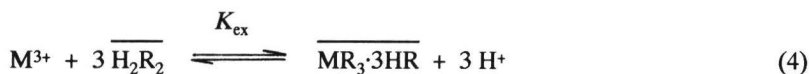
Extraction equilibria

Part a and b of Figure 2 show the effects of pH on the distribution ratios of rare earth elements, D , from the aqueous chloride and nitrate media, respectively. The plotted points lie on a straight line with the slope of 3 for all rare earth elements. This suggests that the extraction of rare earth elements with D4EHPA has inversely third order dependency on the hydrogen ion activity.

Part a and b of Figure 3 show the effects of concentration of the dimeric species D4EHPA in organic phase, $[\overline{H_2R_2}]$, on the distribution ratio of rare earth elements, D , from aqueous chloride and nitrate media, respectively.

The plotted points lie on a straight line with slope of 3 for all rare earth elements. This suggests that the extraction of these metals shows third order dependency on $[\overline{H_2R_2}]$.

From the results described above, it can be considered that all of the rare earth elements are extracted with D4EHPA according to the following extraction reaction:



The extraction equilibrium constant, K_{ex} , is expressed by:

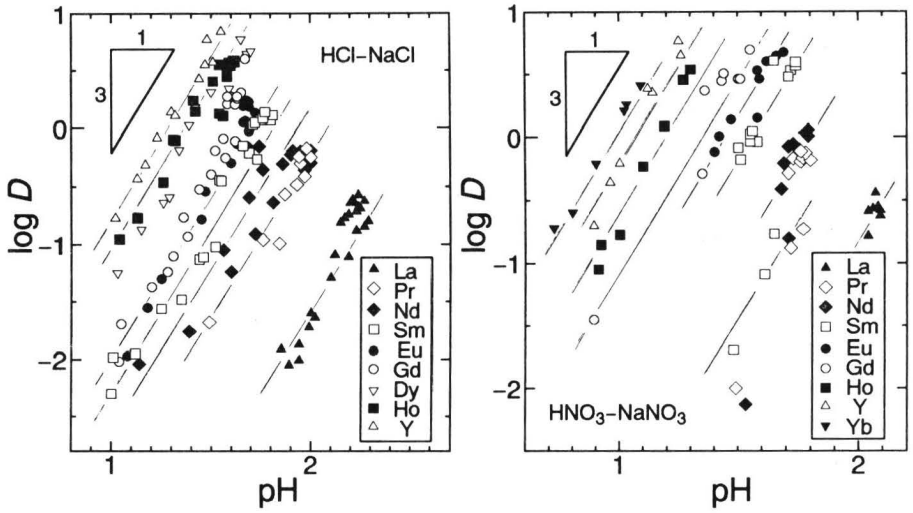


Fig. 2. (a, left) Effects of pH on D of rare earth elements from aqueous chloride media. (b, right) Effects of pH on D from aqueous nitrate media.

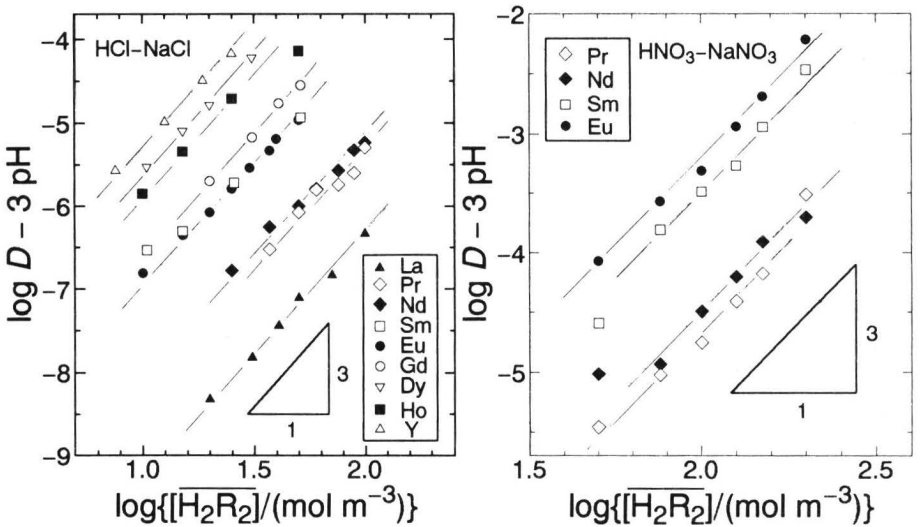


Fig. 3. (a, left) Effects of $[\text{H}_2\text{R}_2]$ on D of rare earth elements from aqueous chloride media. (b, right) Effects of $[\text{H}_2\text{R}_2]$ on D from aqueous nitrate media.

$$K_{\text{ex}} = \frac{[\overline{\text{MR}_3 \cdot 3\text{HR}}] \cdot a_{\text{H}^+}^3}{[\text{M}^{3+}] [\overline{\text{H}_2\text{R}_2}]^3} = D \cdot \frac{a_{\text{H}^+}^3}{[\overline{\text{H}_2\text{R}_2}]^3} \quad (5)$$

Eq.(5) can be rearranged as follows:

$$\log D = 3 \text{ pH} + 3 \log [\overline{\text{H}_2\text{R}_2}] + \log K_{\text{ex}} \quad (6)$$

Equation (6) is satisfactory for all the experimental results shown in Figs. 2 and 3 as expected. From all the experimental results, the extraction equilibrium constants of rare earth elements, K_{ex} , are obtained.

Figure 4 shows the relation between the logarithm of the extraction equilibrium constant and the order of atomic number of rare earth elements in the case of aqueous chloride and nitrate media. The extraction equilibrium constants tend to increase with increasing atomic number of rare earth elements in each media. This series was roughly divided into four groups such as La – Nd, Sm – Gd, Gd – Ho and Er – Yb groups. This phenomenon is called the "tetrad effect" (Peppard et al., 1960, 1970), which has been observed in many extraction system for rare earth elements. The extractability of rare earth elements from aqueous nitrate media is superior to that from aqueous chloride media, owing to the coordination of chloride ion with rare earth elements in the aqueous phase. The selectivity between the adjacent rare earth elements is nearly the same as those with D2EHPA. However, in comparison with the extractability of rare earth elements with D2EHPA (Mikhailichenko and Pimenova, 1969), the extraction takes place at higher pH of 1 – 2 units. This indicates that the consumption of acid for stripping of metals can be diminished by using D4EHPA instead of D2EHPA.

Furthermore, loading tests of neodymium(III) into the organic phase were carried out to compare the loading capacity of D4EHPA with that of D2EHPA. Using D4EHPA as an extractant, gelation of the organic phase was not observed over 40 % of loading conditions, while using D2EHPA, a highly viscous gel forms under 25 – 30 % loading conditions. This suggests that the steric hindrance of the bulky cyclohexyl group of D4EHPA can prevent the gelation of organic phase caused by the formation of polynuclear complexes.

CONCLUSION

Studies on the extraction equilibria of rare earth elements with bis(2-ethylcyclohexyl)-phosphoric acid (D4EHPA) were conducted at 30 °C from aqueous chloride and nitrate media, together with the aggregation state of the extractant. The following can be concluded:

(1) D4EHPA dimerizes almost completely in toluene.

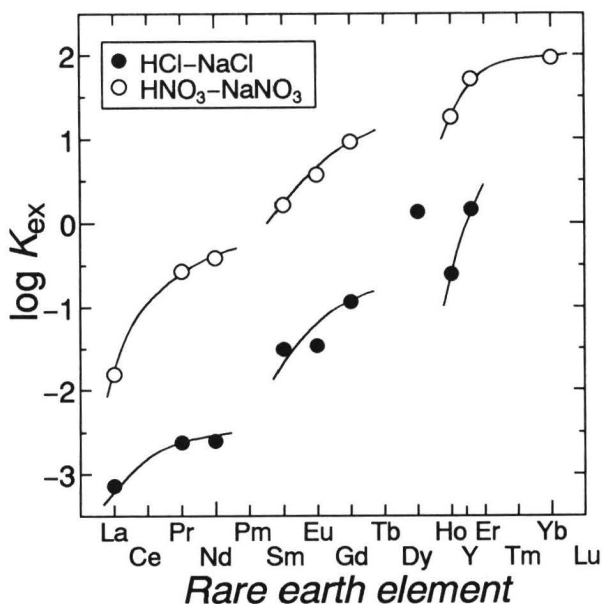


Fig. 4. Relation between logarithm of K_{ex} and order of atomic number of rare earth elements in the case of aqueous chloride and nitrate media.

(2) The extracted species of rare earth elements with D4EHPA are $MR_3 \cdot 3HR$ and the extraction equilibrium constants for rare earth elements are evaluated.

(3) The selectivities between the adjacent rare earth elements with D4EHPA are nearly the same as those with bis(2-ethylhexyl)phosphoric acid (D2EHPA). However, the extraction takes place at higher pH of 1 – 2 units with D4EHPA than with D2EHPA, owing to its higher pK_a .

(4) The loading capacity of rare earth elements into the organic phase is excellent compared with that of D2EHPA.

NOMENCLATURE

a_H	activity of hydrogen ion	$[\text{mol} \cdot \text{m}^{-3}]$
C_{HR}	analytical concentration of extractant	$[\text{mol} \cdot \text{m}^{-3}]$
D	distribution ratio of metal	$[-]$
K_d	dimerization constant of extractant	$[\text{m}^3 \cdot \text{mol}^{-1}]$
K_{ex}	extraction equilibrium constant of metal	$[-]$
$[j]$	concentration of species j ($= M^{3+}, HR, H_2R_2, MR_3 \cdot 3HR$)	$[\text{mol} \cdot \text{m}^{-3}]$
Superscript		
—	organic phase	

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3.3

**DISSOLVING ZIRCONIUM (HAFNIUM) DIBUTYLPHOSPHATES FORMED
WHEN PRODUCING THESE METALS BY EXTRACTION WITH TBP**

O.A. SINEGRIBOVA, V.P. LANIN, N.M. CHIKIRDA,
O.A. BLINOVA and V.A. BABLOEVA

The Mendeleev Institute of Chemical Technology,
Moscow, Russia

ABSTRACT

The acidic hydrolysis of TBP in the extraction technology of Zr and Hf leads to its destruction followed by the formation of dibutylphosphoric acid (HDBP) and as a result the formation of insoluble dibutylphosphates of zirconium and hafnium. The appearance of precipitates causes problems in the normal operation of the extraction process. For elimination of this negative effect the possibility of dissolving zirconium dibutylphosphates by chemical reagents was studied. The best results have been achieved for alkali-peroxide mixtures which allows dissolution of the dibutylphosphate precipitates and to generate recycled TBP forming a two phase liquid-liquid system.

INTRODUCTION

Tributylphosphate, widely used in extraction technology of rare metals, gradually undergoes destruction in acid medium with the formation of dibutylphosphoric acid as a main product of hydrolysis. The presence of HDBP for many extraction systems is a very negative factor because with some metals, specifically with zirconium and hafnium, it forms very stable compounds. The accumulation of zirconium dibutylphosphates causes a slow down in the phase separation (Gonda, Yasu, 1990), a loss of zirconium due to its unstrippability and the formation of precipitates (Utake, 1989), capable of blocking the extraction equipment. It is known (Rolf, 1961; Solovkin, 1969, 1971, 1989; Hardi, 1959), that in nitric acid solutions in the presence of HDBP and zirconium the precipitates of different composition are formed with the formulas $Zr(NO_3)_3A$, $Zr(NO_3)_2A_2$, ZrA_4 , where A - dibutylphosphate anion. These compounds are very stable, although they can be decomposed by concentrated solutions of alkali (Konunova, 1975) or hydrofluoric and sulfuric acids (Bolshakov, 1976). Such methods cannot be applied for extractant regeneration and cleaning of extraction equipment under industrial conditions because they do not permit a precipitate-free system or prevent the subsequent TBP destruction

and corrosion of extraction equipment. In extraction separation of zirconium and hafnium one may expect intensive formation of precipitates that will lead to the necessity periodically to stop the technological process and to clean the equipment mechanically. In present work we wanted to find a method of zirconium dibutylphosphate decomposition in a non-aggressive medium and with complete dissolution.

EXPERIMENTAL

To obtain the precipitate of zirconium dibutylphosphate with formula $\text{Zr}(\text{NO}_3)_2\text{A}_2$ the calculated amount of HDBP was added to the solution of zirconium nitrate in 6 mol/L HNO_3 with constant mixing. The molar ratio HDBP:Zr was 2. The precipitate formed was filtered, washed on filter paper by water to a filtrate pH of 3-4 and air-dried. Then zirconium dibutylphosphate was treated by solutions of different composition. After filtration the filtrate was analyzed for zirconium content.

RESULTS AND DISCUSSION

For dissolving zirconium dibutylphosphate solutions of alkalis, ammonium carbonate, complexing reagents, and hydrogen peroxide were used both separately and in different combinations. The extent of zirconium dibutylphosphate dissolution (E) was calculated from the total amount of zirconium and its concentration found in the solution after filtration. The results are presented in Table 1.

The data in Table 1 indicate that the alkaline solutions of hydrogen peroxide are the most effective for dissolving zirconium dibutylphosphate. The dependence of zirconium dibutylphosphate solubility in alkaline hydrogen peroxide solution on the concentration of H_2O_2 at constant NaOH concentration has been investigated. Concentration of hydrogen peroxide was varied from 0.4 to 3 mol/L. 1 g of zirconium dibutylphosphate was mixed with alkali-hydrogen peroxide solution (50 mL) for 5 min., then the concentration of zirconium in solution was determined. The results are given in Fig. 1.

The extent of zirconium dibutylphosphate decomposition depends on the concentration ratio of hydrogen peroxide and alkali: complete dissolution was observed for the ratio $\text{H}_2\text{O}_2 : \text{NaOH} > 0.5$. The influence of alkali concentration in the alkali-peroxide solution on the decomposition of zirconium dibutylphosphate was also investigated. 10 g of zirconium dibutylphosphate was treated with 100 mL solution with alkali concentration changing from 0.5 to 2.5 mol/L at constant concentration of hydrogen peroxide (Fig. 2).

The results presented in Fig. 2 show that the dependence of zirconium dissolution on the alkali concentration at constant H_2O_2 concentration is maximized when the molar ratio $\text{NaOH} : \text{H}_2\text{O}_2 = 2$. On increasing NaOH concentration the solubility of zirconium dibutylphosphate decreased. The data of Fig. 3 illustrate the dependence of transfer of zirconium from the dibutylphosphate

precipitate into solution (in %) on the time of the treatment with alkali-peroxide solution. It can be shown that the interaction of zirconium dibutylphosphate and the alkali-peroxide solution is a rapid process and the rate of dissolution is maximum again at the molar ratio $\text{NaOH} : \text{H}_2\text{O}_2 = 2$.

TABLE 1
Extent of dissolution of zirconium dibutylphosphate precipitate
in solutions of different composition, at 293K

	Composition of solution (mol/L)	The time of contacting min	The extent of dissolution %
1.	NaOH - 4.0	60	1
2.	KOH - 4.0	60	1
3.	$(\text{NH}_4)_2\text{CO}_3$ - 0.3	60	2
4.	$(\text{NH}_4)_2\text{CO}_3$ - 0.3 NaOH - 1.0	60	4
5.	$(\text{NH}_4)_2\text{CO}_3$ - 0.3 NaOH - 1.0 NaEDTA - 0.3	60	6
6.	H_2O_2 - 2.5	60	0.1
7.	H_2O_2 - 2.5 NaOH - 2.2	20	100
8.	H_2O_2 - 2.5 KOH - 2.2	20	100

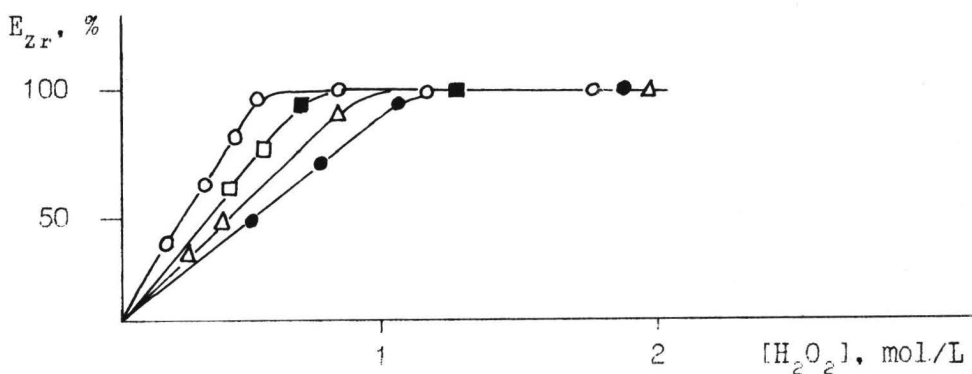


Fig. 1 The dependence of the extent of zirconium dibutylphosphate destruction in alkali-peroxide solution on hydrogen peroxide concentration
[NaOH], mol/L : 1.0 - (○); 1.5 - (■); 2.0 - (△); 2.2 - (●).

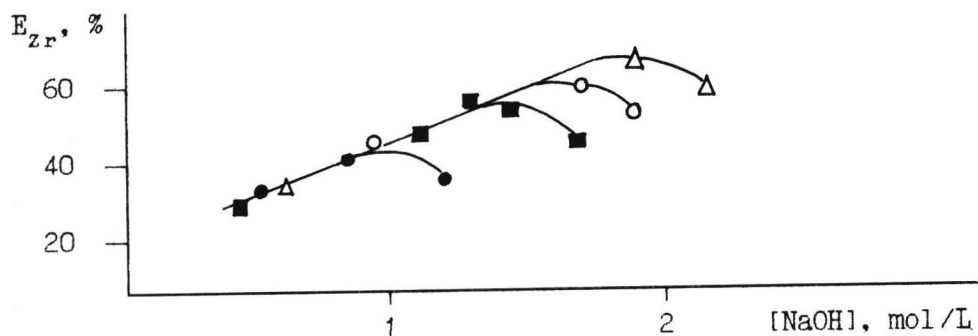


Fig. 2 The dependence of the extent of zirconium dibutylphosphate destruction in alkali-peroxide solution on hydrogen peroxide concentration of NaOH
[H₂O₂], mol/L : 0.4 - (●); 0.6 - (■); 0.8 - (○); 1.0 - (Δ)

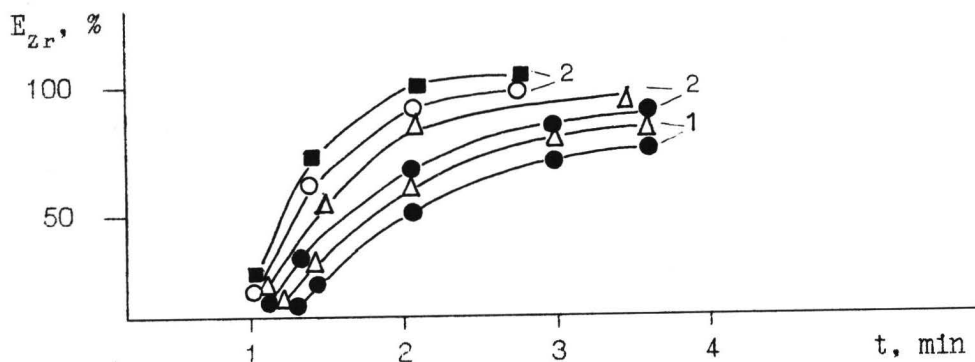
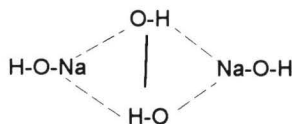
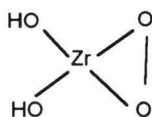


Fig. 3 The dependence of zirconium transfer into solution (in %) on the time of zirconium dibutylphosphate dissolving in the alkali-peroxide solution
[NaOH] in series 1 : 1.2 mol/L, in series 2 : 2.2 mol/L
[H₂O₂], mol/L : 0.4 - (●); 0.6 - (Δ); 0.8 - (○); 1.1 - (■).

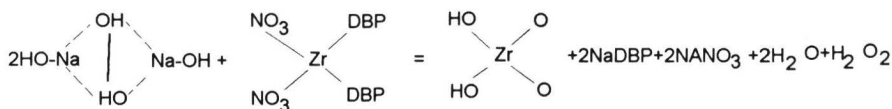
The effective dissolution of the precipitate at the molar ratio $\text{NaOH} : \text{H}_2\text{O}_2$ of 2 can be explained using the supposition about formation of the following compound:



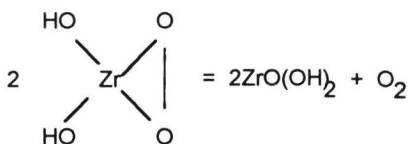
analogous to Li compound (Van Graen, 1975) in which $R_{\text{OOH}} = 104.6 \text{ nm}$, $R_{\text{OO}} = 1.46 \text{ nm}$. Bolshakov (1976) notes the existence in alkali-peroxide solution of zirconium-peroxide compound with the following structure:



Consequently the reaction of zirconium dibutylphosphate dissolution may be presented as



It is known that the peroxides are not stable compounds, transforming into hydroxides with oxygen isolation over time or at elevated temperature. So it may be expected that after the dissolution of Zr-dibutylphosphate the hydroxide of zirconium will form according to the reaction:



Indeed it was observed that after the complete dissolution of zirconium dibutylphosphate in alkali-peroxide solution the precipitate of zirconium hydrated oxide began to form. Dibutylphosphate remained in the solution as the soluble Na-salt. The maximum solubility of zirconium dibutylphosphate precipitate after its decomposition (concentration of zirconium 0.1 mol/L) was obtained when the concentrations of dissolving reagents were 2.2 mol/L NaOH and 1.4 mol/L H_2O_2 , but zirconium solution was very unstable: its hydroxide precipitated after 3-4 mins. Zirconium solution obtained after the treatment of zirconium hydroxide by alkali-

peroxide solution with a composition: 1.2 mol/L NaOH and 0.6 mol/L H_2O_2 was stable during some hours (Fig. 4), although the concentration of zirconium was a little lower (0.08 mol/L). Thus the alkali-peroxide solution of the above-mentioned composition (1.2 mol/L NaOH and 0.06 mol/L H_2O_2) is suitable for washing extraction equipment free from zirconium dibutylphosphate. It must be noted that heating of the resulting zirconium solution promotes the appearance of zirconium hydroxide precipitate.

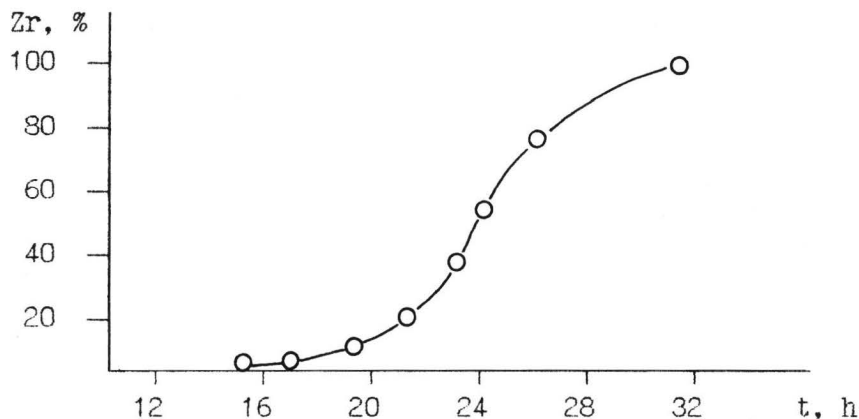


Fig. 4 The formation of zirconium hydrated oxide and dependence on time (% from initial content in solution).
[NaOH] = 1.2 mol/L, [H_2O_2] = 0.6 mol/L

The solubility of zirconium dibutylphosphate in the organic phase (70% TBP in decane) depends almost linearly on the concentration of nitric acid in the extractant. for 2.8 mol/L HNO_3 the solubility is $2.8 \cdot 10^{-3}$ mol/L Zr. this value is similar to the solubility of neptunium or plutonium dibutylphosphates under the same conditions (Fedoseev, 1988).

CONCLUSION

For dissolving zirconium dibutylphosphate precipitated in extraction equipment the use of alkali-hydrogen peroxide solution (1.2 mol/L NaOH and 0.6 mol/L H_2O_2) is recommended. The solution obtained containing zirconium peroxide and sodium dibutylphosphate is stable during some hours. Then the formation of hydrated oxide of zirconium takes place.

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3.4

REFINING OF CERIUM FROM MONAZITE BY SOLVENT EXTRACTION

I.S. EL-YAMANI and E.N. ABD EL-MESSIEH
Nuclear Chemistry Department, Nuclear Research Centre,
Atomic Energy Authority, Cairo (Egypt)

ABSTRACT

The distribution of cerium (IV) nitrate, processed from monazite, by di-(2-ethyl hexyl)-phosphoric acid is described. The dependence of extraction on aqueous acidity and extractant concentration was investigated. The possible extraction mechanism is discussed in the light of results obtained. A flowsheet for production of nuclear-grade cerium from monazite is suggested.

INTRODUCTION

The importance of rare earths and their alloys in nuclear reactors is increasing with recent progress in nuclear reactor technology. Organophosphorous compounds have received widespread attention in analytical and hydrometallurgical aspects of nuclear materials refining. Cerium generally constitutes about 45% of the total rare earths of monazite. Although the extraction of Ce(IV) from nitrate solutions by di-(2-ethyl hexyl)-phosphoric acid has been extensively investigated at trace concentrations (Peppard et al., 1957; McCown, Larsen, 1960; Mikhailichenko et al., 1970), observations at macro concentrations are few. The present investigation pertains to production of high-grade cerium from monazite through extraction with di-(2-ethyl hexyl)-phosphoric acid; extraction is achieved from nitric acid medium.

EXPERIMENTAL**Reagents**

Di-(2-ethyl hexyl)-phosphoric acid, HDEHP, a product of Union Carbide Corporation, was purified as reported elsewhere (Sato, 1970). ^{141}Ce isotope was prepared by neutron-irradiation of analytical grade oxide. The irradiated target was dissolved in HNO_3 , evaporated almost to dryness then diluted to volume. Cerium solution was oxidised to Ce(IV) by addition of a few drops of sodium bromate solution (IM). The radiochemical purity of the isotope was checked by γ -ray spectrometry. Odourless kerosene (aliphatic) obtained from the Misr Petroleum Co. was used as a diluent. Other chemicals were of reagent grade.

Procedure

The organic phase was prepared by adding the appropriate amount of the extractant to kerosene. The cerium stock aqueous solution was prepared from monazite nitrate liquor, processed through soda leaching of the ore. Th and U(IV) are removed at pH 5.8 and crude Ce(IV) nitrate is evaporated to a small volume, analysed and stored. The analysis of the stock solution was as follows: CeO₂, 44.5%; RE₂O₃, 54.7% (RE₂O₃, rare earth oxides other than cerium); ThO₂, 0.6%; U₃O₈, 0.04%; Fe₂O₃, 0.05% and TiO₂, 0.02%. The concentration of Ce(IV) in the aqueous stock solution was made up to 0.05M and the exact metal content was determined volumetrically by ammonium ferrous sulphate and ferroin indicator (Vogel, 1961) while the total tri-valent rare earths was determined complexometrically (at pH 4.5 - 6) by EDTA and xylenol orange as indicator (Kinnunen, Wennerstrand, 1957). Since Ce(IV) and trivalent rare earths were present together in one system, two parallel series of experiments were carried out and only one series was labelled with ¹⁴¹Ce. The concentration of trivalent rare earths in both the feed and aqueous phase was determined by complexometry (as mentioned) and that in the organic phase by difference. Equal volumes (5 mL) of both the aqueous phase (containing the tracer-labelled or the unlabelled species, the latter being the total trivalent rare earths) in HNO₃ of appropriate concentration and of the organic phase, were shaken mechanically in glass-stoppered tubes at room temperature (20 ± 3°) for 20 minutes to ensure complete equilibration. After centrifugation, aliquots of both phases were taken and γ-activity was counted on a multi-channel analyser, coupled to a Ge detector. The concentration of trivalent rare earths in both phases was determined complexometrically as mentioned above. Experiments were conducted in duplicate and the distribution ratio, D, defined as the ratio of the activity of the tracer (or total rare earths concentration) in the organic phase to that in the aqueous phase and the separation factor, S, was estimated from $S = D_{\text{Ce(IV)}}/D_{\text{RE(III)}}$.

RESULTS AND DISCUSSION

Effect of initial HNO₃ concentration

The extraction of Ce(IV) and other rare earths from crude Ce(IV) nitrate solution with 0.3 and 0.73M HDEHP in kerosene was examined at various acidities (0.1 - 12M); results are shown in Figure 1 and Table 1. D decreases linearly with rise of acidity, attaining a minimum value (at about 1 and 5M for Ce(IV) and other rare earths, respectively) then increases. For Ce(IV) solutions, a peak value is obtained at 8.5M then decreases thereafter. In the region of lower acidity (<1M), straight lines with slopes of about three were obtained, a result consistent with that of some trivalent rare earths (Svantesson et al., 1980).

TABLE 1
Effect of acidity on separation factor

Initial HNO ₃ concn., M	S	
	0.3M HDEHP	0.75M HDEHP
0.1	3.4	5.0
0.5	7.4	8.0
1.0	13.5	16.0
3.0	37.5	40.0
8.5	213.3	300.0
10.0	150.0	200.0
12.0	112.0	112.5

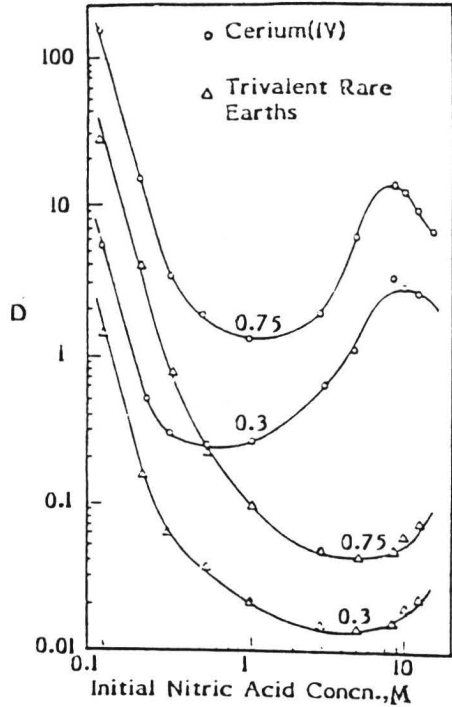


FIGURE 1
Effect of Nitric Acid Concentration on the
Extraction of Cerium(IV) by HDEHP in
Kerosene (Numerals on Curves are HDEHP
Concentrations, M)

As $D_{\text{Ce(IV)}}$ diminishes monotonically with rise of aqueous acidity (up to 1M), it is considered that extraction is principally dominated by ion-exchange reaction in which hydrogen is liberated. At higher acid concentration, D increases gradually and extraction is presumably achieved by solvation. This explanation is confirmed when HNO_3 in the aqueous phase is replaced with various concentrations of NaNO_3 (Table 2). D of HNO_3 - NaNO_3 mixture increases continuously with the total concentration of nitrate ion, analogous to that in the presence of HNO_3 . The gradual increase in D with rise of nitrate concentration suggests the formation of extractable species at higher aqueous acidity (1-8.5M). Acidity is optimized at about 8.5M whereby best separation factor is obtained (300)(Table 1). The extraction of contaminants (U(VI), Th, Ti and Fe(III)) at such condition is low ($D < 0.1$).

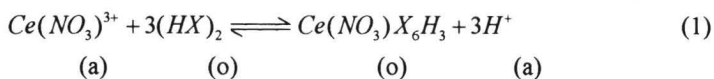
TABLE 2
Extraction of Ce(IV) from HNO₃ in the presence of
NaNO₃ concentrations with 0.2M HDEHP in kerosene

NaNO ₃ concn., M	D	
	3M HNO ₃	5M HNO ₃
---	0.84	1.21
0.5	1.54	2.53
0.75	1.72	3.10
1.25	1.80	3.20
2.25	1.80	3.30
3.75	1.90	3.35

Effect of metal and extraction concentration

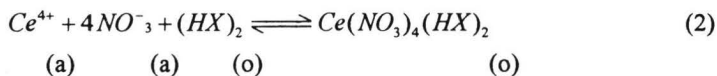
The dependence of D on Ce(IV) concentration in initial aqueous phase was examined by 0.5 and 0.75M HDEHP in kerosene from 8.5M HNO₃ solutions. The sharp decrease in D with rise of Ce(IV) concentration not only gives evidence for the formation of polymeric forms of Ce(IV) complexes in the aqueous phase but also represents a general feature in solvent extraction (at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.65 cerium(IV), D is 6.1, 3.9, 2.3, 1.6, 1.15, 0.81 and 0.66 for 0.5M HDEHP, while D is 14.7, 5.0, 3.0, 2.0, 1.8, 1.6 and 1.25 for 0.75M HDEHP respectively). Polymerisation of Ce(IV) complexes is mentioned in literature (Froaeus, Ostman, 1956). An extraction isotherm was plotted for refining of Ce(IV) from 8.5M HNO₃ by 0.5 and 0.75M HDEHP in kerosene; results are shown in Figure 2. Maximum loading charges of about 32 and 51 g/L Ce(IV) in organic phase were obtained for 0.5 and 0.75M HDEHP respectively, indicating two extractant molecules to be associated with each Ce(IV) ion. This association number is supported by the dependence of D on the concentration of HDEHP. Extraction was conducted by aqueous Ce(IV) solutions and organic phases of various molarities (0.05-0.8M); results are given in Figure 3. The equilibrium concentration of HDEHP was calculated on the assumption that: $C_{\text{HDEHP}} = C_s - n C_{\text{Ce(IV)}}$, where C_s is the initial concentration of the extractant; $C_{\text{Ce(IV)}}$, the concentration of Ce(IV) in the organic phase and $n(=2)$ as calculated above. A straight line relationship with approximate slope of 3 was obtained for 0.1M HNO₃ and 1 for 5 and 8.5M HNO₃. Although no satisfactory agreement has been reported on the mechanism of HDEHP with metal nitrates which explains what organic complexes exist (Kosinski, Bostian, 1969), under the above-mentioned conditions, the extraction mechanism may be expressed as follows:

i) At lower acidities (<1M):



where X represents the anion $(C_8H_{17}O)_2 PO_2^-$, $(HX)_2$ refers to the dimeric extractant and (a) and (o) are aqueous and organic phases respectively.

ii) At higher acidities:



Similar stoichiometries have been proposed for thorium ions (Tedesco, Rumi, 1966; Sato, 1967). From the extraction isotherm (Figure 2), the number of theoretical stages concluded was four and counter-currently five, the fifth was proposed for security.

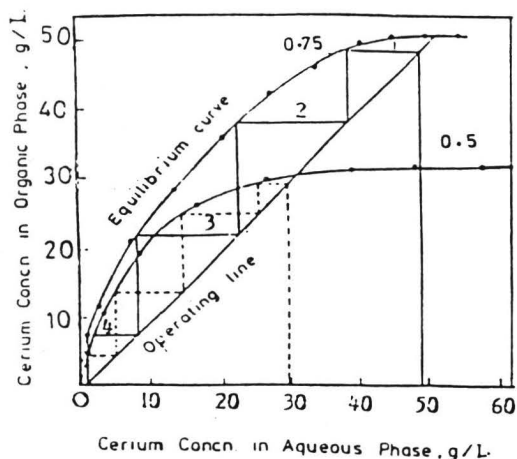


Figure 2 - McCabe-Thiele Diagram for the Extraction of Cerium(IV) from 8.50M Nitric Acid Solutions Using HDEHP in Kerosene (Numerals on Curves are HDEHP Concentrations, M)

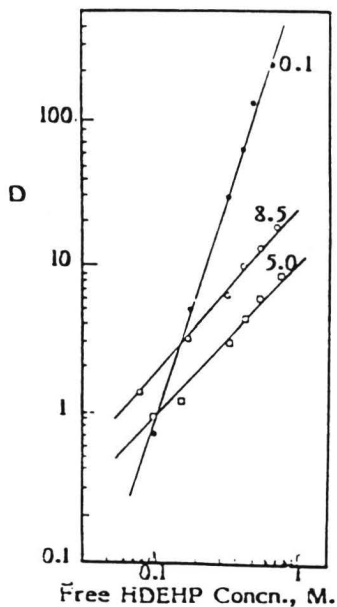


Figure 3 - Distribution Ratio for the Extraction of Cerium(IV) from Nitric Acid Solutions as a Function of HDEHP Concentration in Kerosene (Numerals on Curves are Nitric Acid Concentrations, M)

Examination of the compounds produced

Cerium nitrate was recrystallised from the strip solution and the purity of the $Ce(NO_3)_3 \cdot 6H_2O$ product was ascertained by thermal analyses and X-ray diffraction.

The curves of thermal analyses of the cerium(III) nitrate hexahydrate produced from monazite and the standard sample of this compound, are compared in Figure 4. Both compounds appear to undergo thermal decomposition along the same general pattern, exhibiting fusion of the hexahydrate at 70° followed by stepwise dehydration at 100, 160, 180, 190 and 200° with pronounced endotherms then rapid conversion to CeO_2 , accompanied by a sharp endothermic peak at 300°. The thermograms also show that the endothermic reactions are essentially complete at 350-400° and no other thermal affects are noted until the temperature reaches 700°. The comparison of differential thermal analysis of the cerium product obtained and the standard sample of pure cerium(III) nitrate hexahydrate (Figure 4), shows fairly good agreement of the peak temperatures.

The TG curve indicates that the weight loss of the sample starting from 70 to 200° is about 26% of the total weight. A sharp decrease in weight (32%) is noticed between 180 and 300° followed by a slight decrease (2%) up to 450° and no further changes occur till 700°. The observed total weight loss is 99.4% of the theoretical value for the thermal decomposition of the cerium product. X-ray study of the cerium product reveals that the sample at 20° is triclinic with the formula $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. X-ray diffraction spectra of the sample, heated at 100°, loses one molecule of water and becomes $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. If heated at 300°, the sample consisted of anhydrous cerium(III) nitrate contaminated with CeO_2 . Further heating to 500° converted the sample to the cubic CeO_2 .

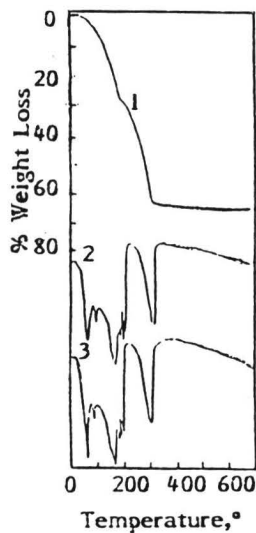


Figure 4 - 1. TGA of Cerium(III) Nitrate Hexahydrate Product; 2. DTA of Cerium(III) Nitrate Hexahydrate Product; 3. DTA of Pure Cerium(III) Nitrate Hexahydrate.

Production of nuclear grade cerium

Extraction of cerium from crude cerium(IV) nitrate feed solution was carried out using 0.75M HDEHP in kerosene. The loaded HDEHP was scrubbed with 8M HNO_3 -1M KBrO_3 while cerium from the back-washed extract was stripped with 8M HNO_3 - H_2O_2 . Nuclear pure ceria (ascertained spectrographically) with more than 90% recovery was obtained after precipitation

of cerium with oxalic acid and calcination to the oxide. A diagrammatic flow sheet for the suggested process of cerium refining is presented in Figure 5.

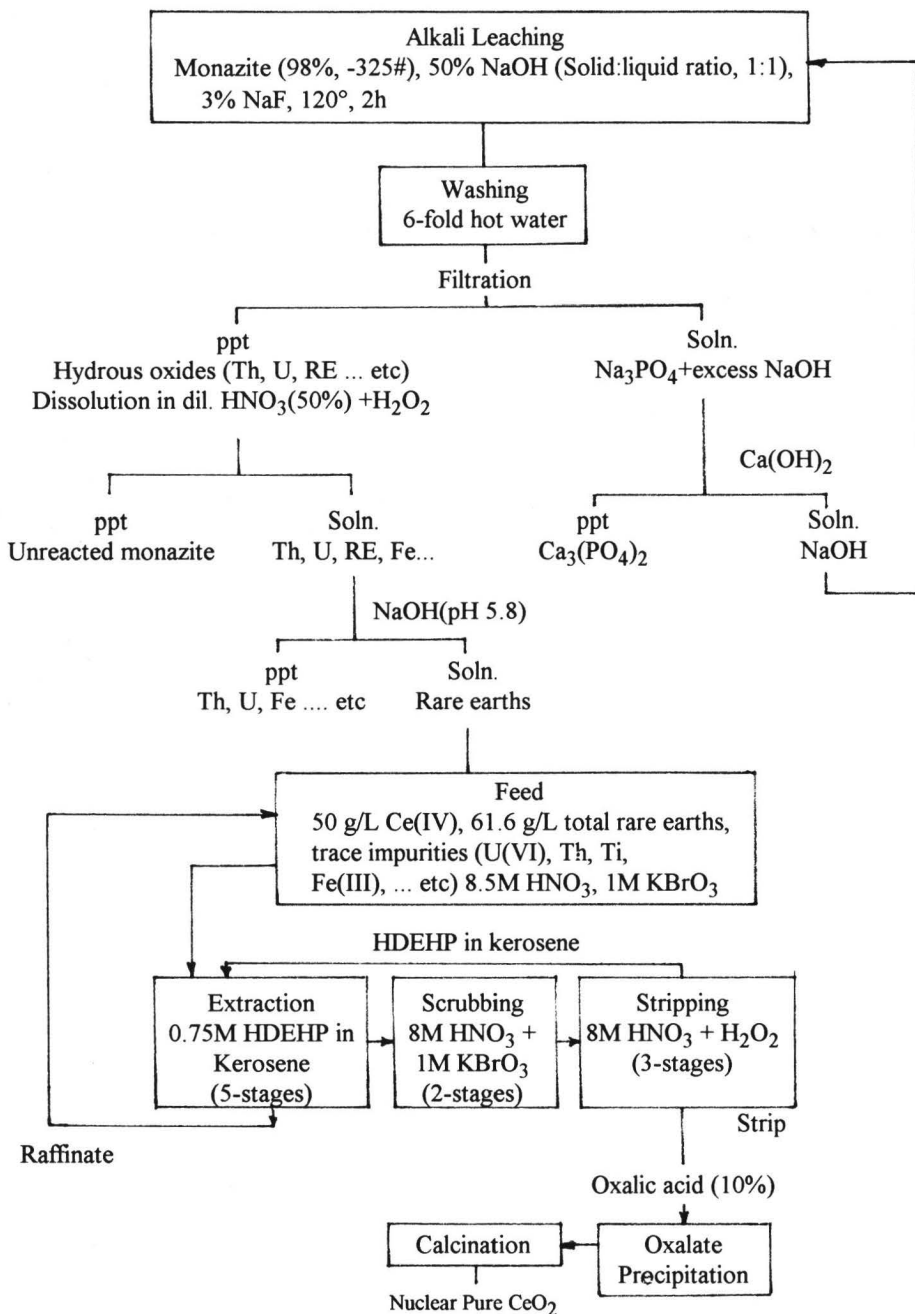


Figure 5 - Diagrammatic Flow sheet for Refining of Cerium from Egyptian Monazite

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Prof. Dr. A.B. Basily, National Research Centre, Cairo, Egypt, for spectroscopic analyses conducted. Thanks are also due to the Nuclear Materials Corporation, Cairo, Egypt, for X-ray and thermal analysis measurements.

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3.5

ZIRCONIUM SOLVENT EXTRACTION WITH CYANEX 923**D. SURIYACHAT AND P.A. DISTIN**

Department of Mining and Metallurgical Engineering,
McGill University,
Montreal, Que., H3A 2A7, Canada

ABSTRACT

Zirconium extraction from acidic chloride solutions into Cyanex 923 has been investigated. Parameters studied were hydrochloric acid, total chloride and zirconium concentrations in the aqueous phase, and extractant level in the organic phase. Results are also given comparing Cyanex 923 (straight chain alkylated phosphine oxide) with a branched chain analogue (Cyanex 925). All data were derived from laboratory-scale batch contacts.

INTRODUCTION

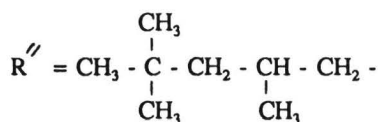
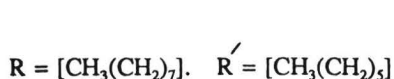
Since natural sources of zirconium always contain some hafnium, these metals must be separated when hafnium-free zirconium is produced for nuclear applications. Due to the chemical similarity of these metals, their separation is a difficult procedure for which solvent extraction is now widely recognized as the best approach. In the most extensively used solvent extraction process, methyl-isobutyl ketone (MIBK) selectively extracts hafnium as its thiocyanate complex from a solution of hafnium and zirconium thiocyanates in hydrochloric acid. The use of Cyanex 923 (Cyanamid Ltd.), an alkylated phosphine oxide mixture, offers several potential advantages over reagents such as MIBK, including greater hydrolytic stability, lower aqueous solubility and a higher flash point for the former extractant.

Before separations are attempted, knowledge is required of the solvent extraction of both zirconium and hafnium when present individually in separate solutions. The present work describes results for batch 'shake out' tests of the loading of zirconium, in the absence of hafnium and thiocyanate, from acid chloride solutions. This is the first phase of an overall project to develop a hafnium/zirconium separation process using Cyanex 923.

The aqueous chemistry of zirconium is strongly influenced by polymerization and hydrolysis reactions. In acid chloride solutions, the general tendency is for hydrolysed polymeric cations to predominate at low acidity. An increase in acid level promotes depolymerization (Kraus and Johnson, 1953; Johnson and Kraus, 1956; Johnson, Kraus and Holmberg, 1956). Simultaneously, hydroxide ions are displaced by chloride ions in zirconium-containing species. This depolymerization/chlorination process results in formation of complexes such as $ZrCl_4$ at high acid concentrations.

Since Cyanex 923 is a mixture of tri-alkyl phosphine oxides, zirconium would be expected to extract from hydrochloric acid solutions by a mechanism similar to that found for analogous reagents such as tri-butyl phosphate (TBP). In this latter case, zirconium is extracted by solvation, primarily as the neutral tetrachloride complex (Levitt and Freund, 1956; Sato 1970). Thus, the parameters studied in the present work include hydrochloric acid, chloride (through lithium chloride addition) and zirconium levels in the aqueous feed, and Cyanex 923 concentration in the organic phase.

In addition, a few comparative tests with Cyanex 925 were carried out. Although this extractant is also a mixture of trialkyl phosphine oxides, most alkyl groups are branched while all those of Cyanex 923 have straight chains. The structures of the two reagents are shown as follows:



EXPERIMENTAL

Aqueous feed solutions were made up from zirconium chloride octahydrate dissolved at the required hydrochloric acid level. Concentrations were from 0.002 M to 0.05 M Zr, and 1.0M to 6.0 M.HCl. In some cases, part of the acid content was replaced by lithium chloride such that a series of tests could be run at various LiCl/HCl ratios but at constant total chloride concentration.

The organic phase was prepared as 1.0% to 5.0% by volume (about 0.023 M to 0.12 M) Cyanex 923 (or 925) in kerosene, without modifier addition. Batch loading tests were performed at a phase ratio of 1.0 with a contact time of 30 minutes, preliminary tests having

shown that apparent equilibrium was reached in 10-15 minutes.

Zirconium analyses were performed on feed and raffinate solutions using a complexometric method (Kinnunen and Wennerstrand, 1957), in which a known excess of EDTA was added followed by boiling of the solution. This excess was then back-titrated, at pH 1.6 - 2.0, with bismuth nitrate using xylenol orange as indicator.

RESULTS AND DISCUSSION

Figures 1 - 3 show results for the effect of hydrochloric acid level on zirconium extraction at various initial metal contents of the aqueous phase. In all cases, the general trend is an increase in zirconium recovery with increasing acidity, this being consistent with extraction as a chloride species rather than through a cation exchange reaction.

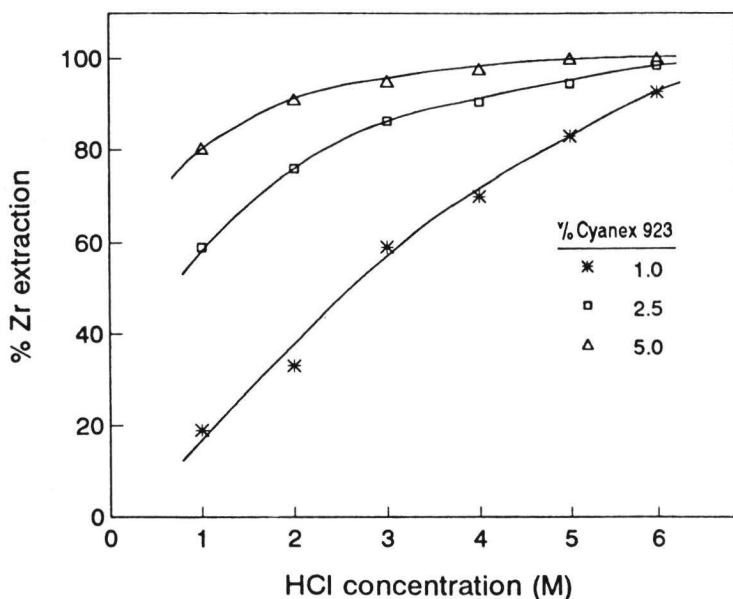


Fig. 1 Effect of HCl concentration on Zr extraction from 0.002 M. Zr solutions into Cyanex 923.

If zirconium is loaded as a chloride complex, the controlling factor should be chloride level rather than acidity, provided sufficient acid is present to prevent hydrolysis and polymerization reactions giving unextractable species. In tests carried out to check the importance of chloride content in the aqueous phase, zirconium was loaded into 5% Cyanex 923 from 0.02 M Zr solutions containing 1.5 M, 2.0 M and 3.0 M total chloride at various LiCl/HCl ratios. As shown in Figure 4, extraction decreases if the acidity drops below a value characteristic of the total chloride concentration. The higher the total chloride content, the lower may the acid level be before the effects of hydrolysis and polymerization appear.

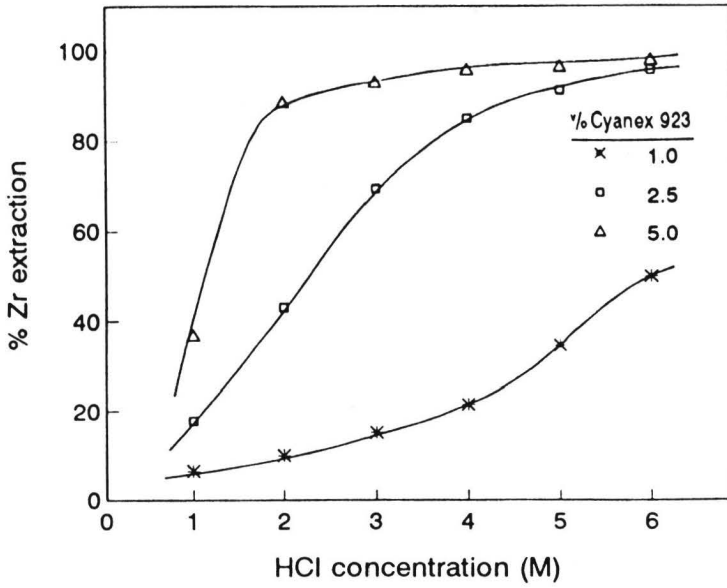


Fig. 2 Effect of HCl concentration on Zr extraction from 0.02 M Zr solutions into Cyanex 923.

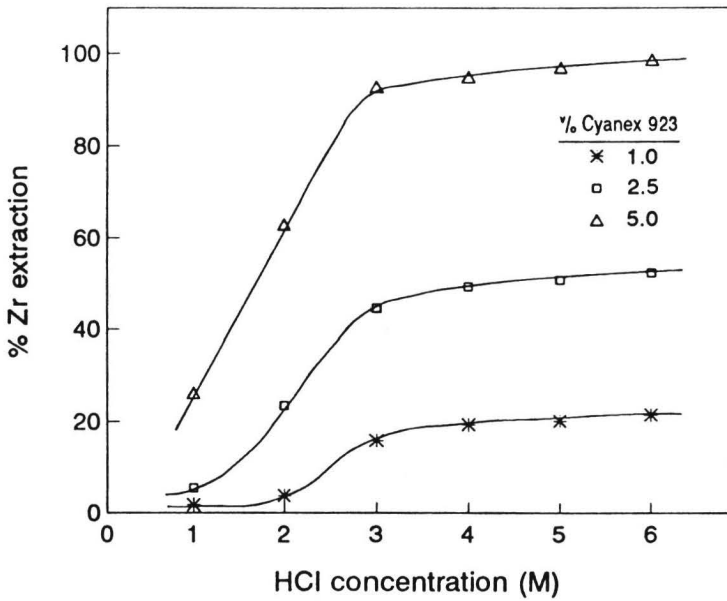


Fig. 3 Effect of HCl concentration on Zr extraction from 0.05 M Zr solutions into Cyanex 923.

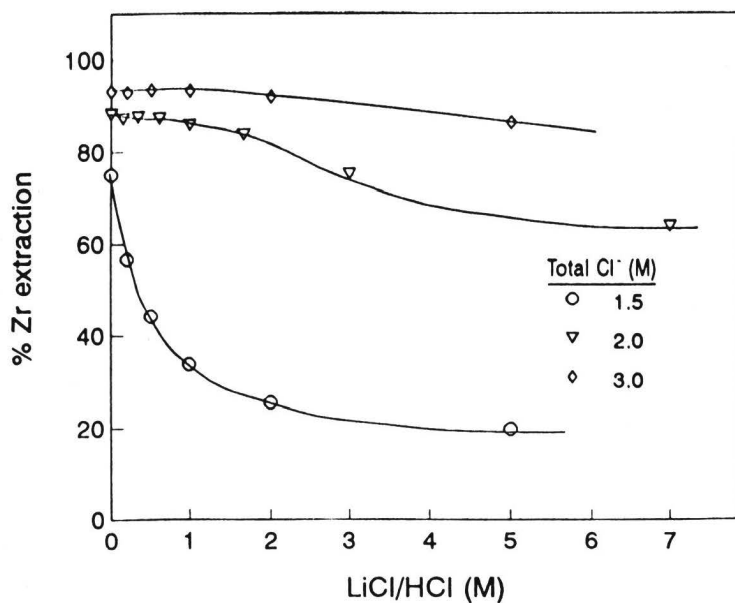


Fig. 4 Effect of LiCl/HCl ratio on Zr extraction from 0.02 M. Zr solutions into 5 vol.% Cyanex 923.

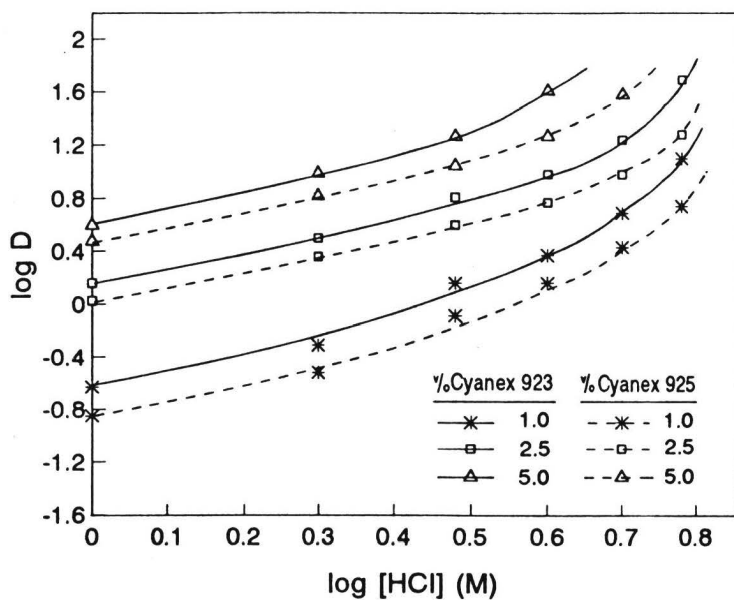


Fig. 5 Log D vs. log HCl plots for Zr extraction from 0.002 M Zr solutions into Cyanex 923 or Cyanex 925.

The data of Figure 1 for extraction from 0.002 M Zr solutions are presented as log D vs. log HCl plots in Figure 5, D being the distribution coefficient. Also included for comparison are the equivalent results for Cyanex 925. Extractions into Cyanex 925 are up to 15% less than for Cyanex 923 for comparable conditions. These differences in recovery reflect the alkyl chain branching present in the former extractant, which in general is more selective than straight chain analogues.

The effects of chloride ion level and acidity on zirconium extraction are similar to those observed in the parallel system using TBP as extractant (Levitt and Freund, 1956; Sato 1970). However in general, recovery using TBP requires markedly higher chloride ion levels than necessary with Cyanex 923. For example at a phase ratio of one, 5% TBP (0.18 M) extracts 8% Zr from 0.02 M Zr in 6M HCl (Sato, 1970), while in the present work, 5% Cyanex (0.12 M) gives 98% Zr extraction from the same aqueous phase. In these previous studies with TBP, it was concluded that zirconium was loaded by solvation as the neutral tetrachloride complex. Assuming this applies to the present work, the loading reaction may be represented as:



Although Cyanex 923 is in reality a mixture of four trialkyl phosphine oxides, representation of the extractant as a single compound in equation 1 is considered reasonable in view of their structural similarities.

The 'slope analysis' method has been used previously (Levitt and Freund, 1956; Sato, 1970) to study the stoichiometry of reaction 1, with TBP as extractant. Applying this technique to the present case, it can be readily shown that:

$$\log D = n \log [\text{R}_3\text{PO}] + \log K \quad (2)$$

where K is the equilibrium constant for reaction 1, defined in terms of concentrations. A plot of log D vs. log $[\text{R}_3\text{PO}]$ would therefore give a straight line of slope n, assuming that equilibrium is reached and activity coefficients remain constant, while only one zirconium species is extracted and formation of non-extractable complexes is negligible. These plots are shown in Figure 6 for initial zirconium levels of 0.002 M and 0.004 M in the aqueous phase containing 2M HCl. A large molar excess of Cyanex 923 over zirconium was present in each case, so that free extractant concentration remains essentially constant during extraction. Reasonably straight lines of slope approximating 1.8 are followed for the range 0.5% to 2.5% Cyanex 923. Straight lines of slopes approaching 2 were also obtained in equivalent plots from the earlier work with TBP cited above, where the disolvate was thus

considered to form. Given the assumptions made, it is reasonable to conclude that zirconium is also extracted primarily as the disolvate in the present system, at least under the conditions of Figure 6. Evidence of polymerization in the aqueous phase can also be seen in Figure 6, where D decreases with increasing initial zirconium concentration at constant acid and Cyanex 923 levels.

Not surprisingly, use of water to strip loaded organic leads to emulsion and phase separation problems, with fine precipitates forming at high zirconium levels. Loaded organic can be readily stripped with hydrofluoric acid solutions. However, alternative stripping systems are currently being investigated, including the possible use of sulphuric acid, dilute hydrochloric acid, ammonium carbonate or ammonium bicarbonate solutions.

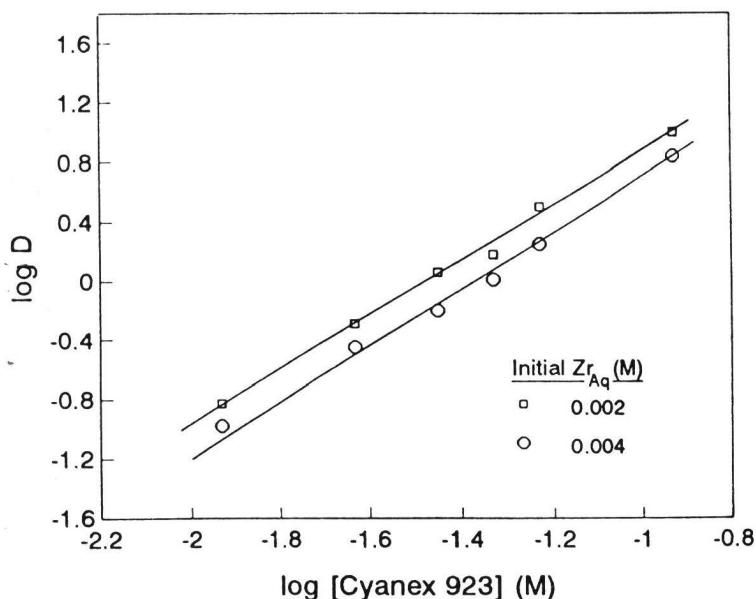


Fig. 6 Log D vs. log [Cyanex 923] plots for Zr extraction from 2M HCl solutions

CONCLUSIONS

Zirconium is extracted from chloride solution into Cyanex 923 as the tetrachloride complex forming a disolvate. Apparent equilibrium was reached in 5 to 10 min. The extraction level is maintained if, at constant total chloride, hydrochloric acid is partially replaced by lithium chloride, provided sufficient acid is present to prevent hydrolysis. Evidence of polymerization in the aqueous phase was provided by a decrease in distribution coefficient with increasing zirconium concentration under otherwise identical conditions. Zirconium extracts less readily into Cyanex 925 than Cyanex 923, probably because the branched chain

alkyl groups of the former offer 'steric hindrance' not present with the straight chain configuration of the latter.

Further evaluation is progressing on a parallel study of hafnium extraction, and on an investigation of loading characteristics for both metals when complexed by thiocyanate ion.

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3.6

**SOLVENT EXTRACTION BEHAVIOUR OF P-*TERT*-
BUTYLCALIX[N]ARENE CARBOXYLIC ACID DERIVATIVES TOWARDS
TRIVALENT LANTHANIDES AND SODIUM**

Rainer LUDWIG *, Katsutoshi INOUE, Seiji SHINKAI ** and Karsten GLOE ***

Saga University, Dept. of Applied Chemistry, Saga 840, Japan

* new address as **

** Shinkai Chemirecognics Project, Research Development Corporation of Japan,
Aikawa 2432-3 Kurume, Fukuoka 830, Japan

*** Technische Universität Dresden, Institut für Anorganische Chemie, 8027 Dresden,
Germany

ABSTRACT

In this paper we describe the solvent extraction behaviour of two cyclophane-type hosts, abbreviated L1 and L2, towards trivalent lanthanides Ln^{3+} ($\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Er}$ and Yb) and the influence of sodium ions coexisting in the aqueous phase. The extraction mechanism of Ln^{3+} was established and the corresponding extraction constants were determined. Additionally, monolayers of L1 and L2 at the air-water interface were prepared and their interaction with sodium ions was studied.

INTRODUCTION

The solvent extraction behaviour of calixarene compounds, which belong to the class of (1,n)-cyclophanes, towards organic molecules and metal ions has been studied within the last few years. However, the metal ions investigated in terms of host-guest interaction were mostly alkaline and alkaline earth ions. A few studies have dealt with lanthanide extraction and complexation, Atwood (1991), Bünzli (1991), Ungarao (1991), Harrowfield (1991), Froidevaux (1991), Soedarsono (1991) and Ohto (1991). Since the properties of calixarenes can be varied greatly, e.g. by introducing substituents onto the skeleton formed by the phenyl units or by fixing the molecule in a definite, e.g. *cone*-shape conformation, it was of interest to study rather simple calixarene derivatives as model compounds. For the present study, *p-tert*-butylcalix[6]arene hexa-acetic acid (L1) and *p-tert*-butylcalix[4]arene tetra-acetic acid (L2) were used to continue earlier investigations, Ludwig (1991). Since Markowitz (1989) and Nakamoto (1989) found that some calixarenes form stable monolayers at the air-water interface, pressure-area isotherms

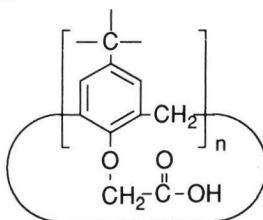
of the compounds used in the present study were measured as well as the effect of sodium ions on the monolayer properties.

EXPERIMENTAL

L1 and L2 were synthesized according to the method of Shinkai (1989) from the parent calix[n]arenes ($n=6, 4$), which are commercially available. The products were analyzed and proved by means of IR, ^1H NMR, ^{13}C NMR, m.p. and elemental analysis. Traces of N in the final products were removed with hot HCl. Chloroform was used as diluent. The extractant concentration was equal to or less than 0.5 mM. At this concentration, L1 was measured osmotically to be a monomer.

The extraction experiments were carried out in stoppered flasks at 25 °C using equal phase volumes of 15 mL. The aqueous phase contained 5 lanthanide perchlorates co-existing with an initial concentration of 0.01 mM of each. The lanthanide stock solutions were prepared from the corresponding oxides of 99.999 % purity and were calibrated with standard solutions. The pH was adjusted with HClO_4 . NaClO_4 was added as indicated in the text. The equilibria were attained within 2 hours of slow shaking. Complete stripping was achieved by using HCl of pH 1.8. The distribution coefficients D were calculated after analyzing the metal contents in the aqueous and in the stripping phase by means of ICP-AES.

Monolayers were studied at 20 °C by using a computer-controlled film balance type FSD-50 at a barrier speed of 0.4 mm/s. Chloroform was used as spreading solvent. The incubation time was 10 minutes. The subphase was ion exchanged and bidistilled water containing HNO_3 to adjust the pH. NaClO_4 was added as indicated in the text.



Scheme 1: Calixarene-type extractants used for this study. L1: $n = 6$; L2: $n = 4$

RESULTS AND DISCUSSION

Solvent Extraction Behaviour of L1 and L2

In the case of extractant L1, the values of $\log D$ vs. pH lie on straight lines with a slope of 3.0 at a pH ranging from 2.1 to 3.7, which is in agreement with the metal ion charges.

The order of extractability is $\text{Eu, Nd} > \text{La} > \text{Er, Yb}$. This order is similar to the one observed by Ohto (1991) when he used *p*-*tert*-octylcalix[6]arene hexa-acetic acid as extractant dissolved in toluene: $\text{Eu} > \text{Nd} > \text{Er}$. It is equal to the order of stability constants between

p-tert-butylbenzo-15-crown-5 and $\text{Ln}(\text{CF}_3\text{SO}_3)_3$ in propylene carbonate, determined by Bünzli (1984). The plot of $(\log D_{\text{Ln}} - 3\text{pH})$ vs. $\log c_{\text{L}}$, with c_{L} being the ligand concentration, at pH below 3.7 is depicted in Fig. 1 for La and Nd as examples. A slope of 2.0 ± 0.1 was observed for all of the investigated lanthanides. From these results we conclude the extracted species to have the composition $\text{Ln}(\text{L}1)_2$. The extraction mechanism (eqn. (I)) and calculated extraction constants K_{ex} for Ln^{3+} are summarized at the end.

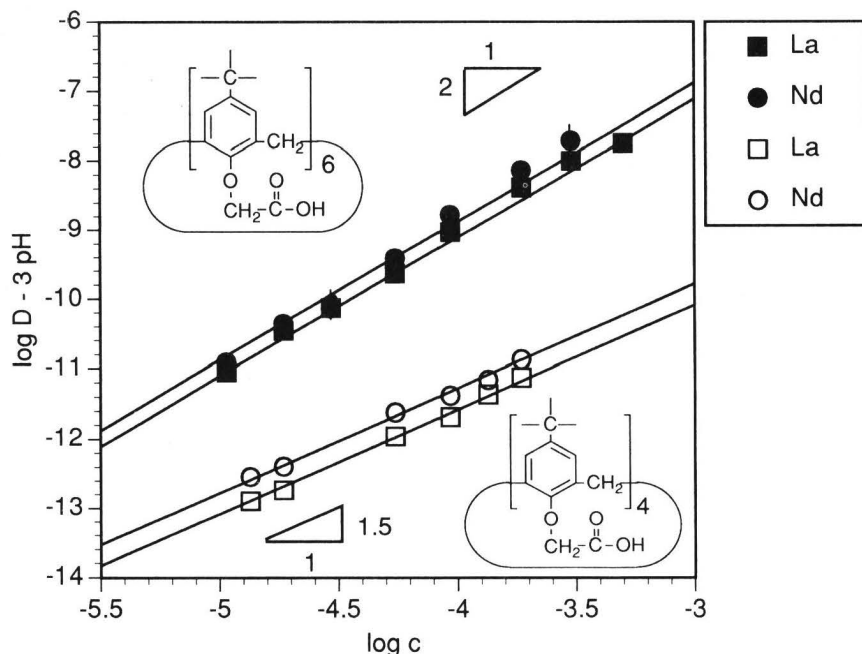


Fig. 1 Plot of $\log D_{\text{Ln}} - 3\text{pH}$ vs. $\log c_{\text{L}}$

Aqueous phase: $50 \mu\text{M} \text{Ln}(\text{ClO}_4)_3 + \text{HClO}_4$. Organic Phase:
 0.5 mM L1 (closed symbols) or 0.5 mM L2 (open symbols) in CHCl_3

By using L2 as extractant, the values of $\log D_{\text{Ln}}$ are lower about two orders of magnitude compared with L1 at pH 2 to 4. The slope in the $\log D$ vs. pH-diagram is not constant but ranges from 2 to 3.5, with higher slopes being observed at higher pH. This behaviour may be caused by partial dissociation of the extracted species due to weak acidity of the extractant. For La and Nd, the slope is 3.0 between pH 3.5 and 4.

The plot of $(\log D_{\text{Ln}} - 3\text{pH})$ vs. $\log c_{\text{L}}$ measured at pH 3.5 to 4 lies on straight lines with a slope of 1.5, as shown in Fig. 1 for La and Nd. Co-extraction of 1:1 and 1:2 metal:reagent complexes may be responsible for this behaviour.

Solvent Extraction of Lanthanides With L1 and L2 in the Presence of an Excess Amount of Sodium Ions in the Aqueous Phase.

Fig. 2 depicts typical results obtained with extractant L1 for La, Nd and Er when the aqueous phase contained the 5 lanthanides as well as 0.1 M NaClO₄. The distribution coefficients of the lanthanides D_{Ln} are decreased about one order of magnitude in the presence of sodium and the values of $\log D$ deviate from the straight lines with a slope of 3.0 at pH-values above 3.5. One reason for this non-linearity may be the co-extraction of Na. Na was extracted as a 1:1 complex as shown by a slope of 1.0 in the plot of $\log D_{Na}$ vs. $\log c_{L1}$. However, the distribution coefficient of sodium D_{Na} was independent of the pH, as shown in Fig. 2. This leads to the conclusion, that Na⁺ is bound to the neutral oxygen atoms rather than to O⁻. In the corresponding ethyl ester, Na⁺ is octaedrally bound to the same donor atoms, Shinkai (1991). The order of lanthanide extraction with L1 remains unchanged. The lanthanides are extracted as 1:1 complexes [Ln(L1)] at a ligand concentration lower than the sum of the initial lanthanide concentrations in the aqueous phase. At ligand concentrations between 50 and 200 μ M the slope of ($\log D - 3pH$) vs. $\log c_L$ is higher than 1.0 indicating the co-extraction of [Ln(L1)] and [Ln(L1)₂]. The distribution coefficients of the lanthanides are high compared with sodium, probably because of strong electrostatic interactions with the dissociated acid groups in L1. The calculated values of K_{EX} for the extraction of 1:1 metal:reagent complexes according to eqn. (II) are summarized in Table 1.

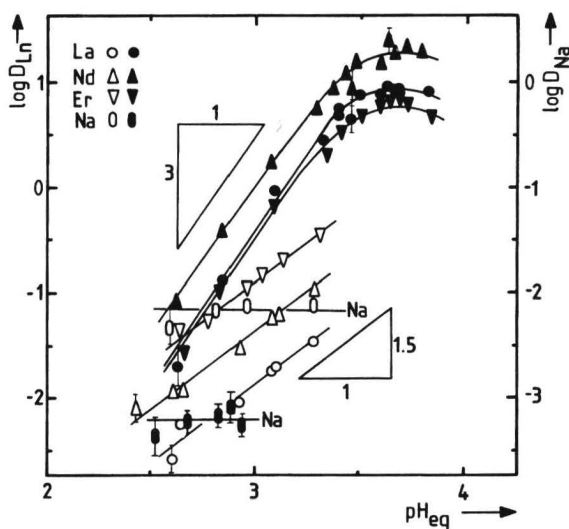


Fig. 2 Distribution coefficients of lanthanides $\log D_{Ln}$ and of sodium $\log D_{Na}$ at different pH-values. Aqueous phase: 0.1 M NaClO₄ + HClO₄ + 50 μ M Ln(ClO₄)₃. Organic phase: CHCl₃ + 0.5 mM L1 (closed) or 0.5 mM L2 (open symbols)

A very different result is obtained when L2 is used as extractant for co-existing Ln^{3+} and Na^+ . The plot of $\log D$ vs. pH gives straight lines with a slope of 1.5. In Fig. 2 the results for La, Nd and Er as well as Na are depicted. The distribution coefficients D_{Ln} are increased about one order of magnitude at lower pH compared with the extraction in the absence of sodium. The order of extraction is different from the one observed in the case of L1. The reagent preferably extracts the heavy to medium lanthanide ions. The selectivity is much higher compared with the sodium-free system. On the other hand, the extraction of sodium was again independent of the pH, but about one order of magnitude higher compared with L1. These results can be interpreted in terms of conformational fixing of the host molecule by sodium ions bound to ethereal oxygen atoms, thereby enhancing the extraction of certain lanthanides, which fit well into the cavity formed by the carboxylic groups.

Monolayer Behaviour of L1 and L2.

The different influence of sodium ions on the extraction behaviour of L1 and L2 is reflected by a different influence on the monolayer properties. Compound L1 forms a stable monolayer within the investigated pH-range from 1.7 to 6.8. At pH=2.8 the monolayer collapses at 54 mN/m and an area of 1.24 nm²/molecule. The extrapolated area at zero-pressure is 1.72 nm²/molecule. The collapse pressure is slightly decreased to 52 mN/m upon the addition of 0.1 M NaClO₄ to the aqueous phase, while the monolayer becomes somewhat expanded.

The monolayer of compound L2 is less stable compared with L1. The pressure-area isotherm at pH 2.8 is depicted in Fig. 3 as the lower curve. The film collapses at 21 mN/m and an area of 1.0 nm²/molecule. The molecular area at zero-pressure is 1.15 nm²/molecule. Upon addition of 0.1 M NaClO₄ to the subphase, the collapse-pressure increases to 32 mN/m (upper curve in Fig. 3). This leads to the conclusion that sodium ions strongly interact with the monolayer molecules in agreement with the conclusions drawn from the extraction data.

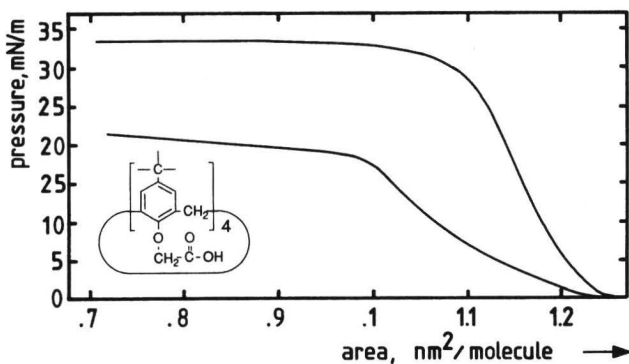


Fig. 3 Pressure-area isotherms of L2 at pH 2.8 in the absence (lower curve) and presence of 0.1 M NaClO₄ (upper curve) in the aqueous subphase.

SUMMARY

The investigated lanthanides were extracted by L1 according to eqn. (I) in the absence of Na and according to eqn. (I) and (II) in the presence of an excess amount of Na. The calculated extraction constants for these equilibria are listed in Table 1.

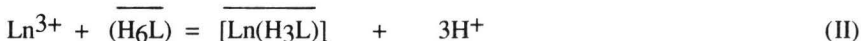
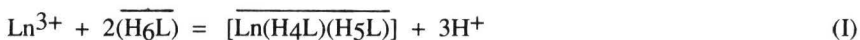


TABLE 1

Extraction constants for complexes between L1 and Ln^{3+} at 20 °C and pH 2.1 - 3.7

Metal ion	log K_{ex} of the 1:1 complex in the presence of sodium	log K_{ex} of the 1:2 complex in the absence of sodium
Ln^{3+}		
Ln = La	-5.44 ± 0.02	-1.11 ± 0.01
Nd	-5.25 ± 0.02	-0.91 ± 0.04
Eu	-5.32 ± 0.02	-0.95 ± 0.03
Er	-5.81 ± 0.03	-1.58 ± 0.04
Yb	-5.87 ± 0.03	-1.64 ± 0.02

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3.7

**GROUP SEPARATION OF RARE EARTHS BY SOLVENT EXTRACTION
USING IONQUEST® 801 METAL EXTRACTANT**

F. DELMAS, C. NOGUEIRA, F. RODRIGUES

Departamento de Tecnologia de Materiais
Instituto Nacional de Engenharia e Tecnologia Industrial (INETI)
Estrada do Paço do Lumiar, 1699 Lisboa Codex, Portugal

J. DUARTE NETO

Companhia Vale do Rio Doce (CVRD)
R. S. Paulo 351, CEP 30.170, Belo Horizonte, Brasil

ABSTRACT

IONQUEST 801 metal extractant was evaluated in rare earth fractionation from didymium chloride solutions, in a bench-scale continuous battery of mixer settlers.

The cascade was based on 4 extraction stages, 5 scrubbing stages, 4 stripping stages and 1 washing stage at combined aqueous plus organic flow rates of about 10 L/h.

Three main types of runs were performed to attain the targeted results in fractionation: (1) heavy from medium and light rare earths separation; (2) medium from light rare earths separation and (3) lanthanum from praseodymium and neodymium separation.

Rare earth carbonates of all the separated fractions were obtained. The purity and recovery yields of products, expressed in rare earth oxides, when obtained under best conditions are: lanthanum (La) 97.3%, 99% recovery; praseodymium and neodymium (Pr and Nd) 96.6%, 98% recovery; medium rare earths (Sm, Eu, Gd, Tb) 97.7%, 96% recovery and heavy rare earths (Dy, Ho, Er, Yb and Y) 95.5%, 61.5% being Y, 93% recovery.

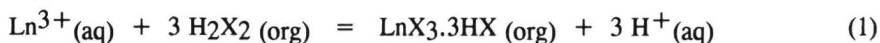
INTRODUCTION

Rare earth (RE) elements and yttrium have been used in several applications, namely in chemical industry as catalysts, in ceramics, in electronic industry and in high-performance materials. Usually both metallic and oxide forms of rare earths are used for such applications. To obtain the high purity compounds (or elements) suitable for these advanced technologies, a very large and complicated separation process is needed (Kaczmarek, 1981 and Narayanan, 1988).

The purification of the solutions containing lanthanides aiming at obtaining high purity individual elements or groups is most commonly accomplished using solvent extraction processes. The separation of rare earths by this method is usually carried out with acidic

alkylphosphorus extractants (Marcus, 1983 and Preston, 1990), di-(2-ethylhexyl)phosphoric acid - D2EHPA - being the most common extractant used, since the pioneer work of Peppard and Mason, 1957. This extractant has the advantage over other diesters of phosphoric acid that it is commercially and readily available, easily purified and has very low solubility in the aqueous phase. In this work an alternative extractant of D2EHPA is tested, the mono(2-ethylhexyl)-2-ethylhexyl phosphonic acid - EHEHPA - which has already been mentioned by other authors (Li, 1980 and Bennedetto et al, 1992). The alkylphosphonic acids are usually less effective regarding extraction of the rare earth cations than the corresponding alkylphosphoric acids (Marcus, 1983). However, higher separation factors can be obtained with the phosphonic acids. Furthermore, EHEHPA allows easier stripping and has good hydrodynamic behaviour.

The extraction mechanism usually assumed for these extractants is a cation-exchange with the formation of a stable metal complex in the organic phase, probably solvated by 2 or 3 molecules of free extractant, according to the following equation, where H_2X_2 represents the organophosphorus acid in its dimeric form and Ln is the lanthanide,



At high acidities some of the organophosphorus acids are able to extract RE by a solvating complexant mechanism.

The main objective of this work was the development of a continuous solvent extraction process to separate the rare earths in 4 groups, starting from a Brazilian didymium carbonate and using EHEHPA as extractant in a bench-scale battery of mixer-settlers, aiming at obtaining the following RE fractions: (1) heavy rare earths (Dy, Ho, Er, Yb) and yttrium; (2) medium rare earths (Sm, Eu, Gd, Tb); (3) praseodymium and neodymium; and (4) lanthanum. The conditions selected were based on previous batch work carried out in CVRD, Brazil and in INETI, Portugal, using the Kremser equation approach (Treybal, 1985). The purity envisaged for all the fractions was over 95% together with a minimum recovery of 90%.

EXPERIMENTAL

The initial feed solution containing 100 g/L of rare earth oxides (REO) was prepared by dissolving the didymium carbonate in hydrochloric acid. The organic phase was the commercial extractant IONQUEST®801 (EHEHPA), made available by Albright & Wilson Americas Inc., diluted to 1M in the aliphatic diluent Shell D70. The scrubbing and stripping solutions were prepared using commercial grade hydrochloric acid. Acidity control in extraction was achieved adding 2.8M caustic soda directly to the feed stage.

The bench-scale continuous solvent extraction plant consisted of a battery of mixer-settlers built in PVC-glass. Square mixers and rectangular settlers were used. The total throughput in

the mixer-settlers was about 10 L/h. Peristaltic pumps and pump-mix impellers assured the flows of organic and aqueous phases through the several mixer-settlers. Tip velocity in stirrers was adjusted in order to obtain good dispersion and the organic phase as the continuous phase. Figure 1 shows the typical configuration of the solvent extraction plant. The variables tested in each part of the separation tests were the cascade configuration (number of mixer-settlers in each section), the acidities of feed, scrubbing and stripping solutions, and the flow of the neutralizing agent, as can be seen in Table 1.

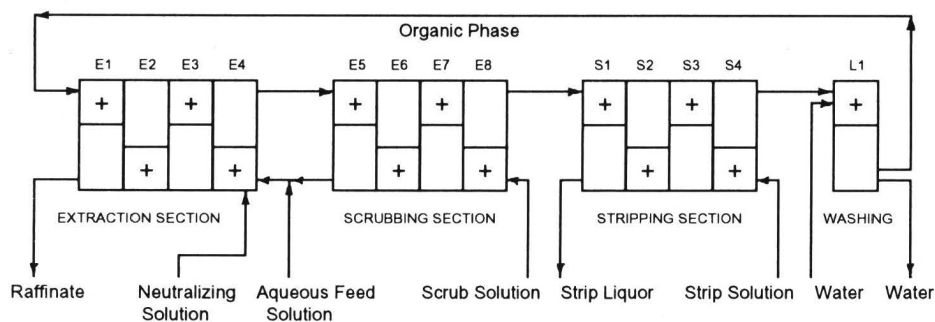


Fig. 1 Flow diagram of the continuous solvent extraction plant used in the test runs.

TABLE 1
Experimental conditions in the different parts of the separation process

Conditions		Part 1	Part 2	Part 3
Configuration	extr. stages	4 (or 5)	4	4
	scrub. stages	6 (or 5)	5	5
	strip. stages	4	4	4
Aqueous feed solution	Ln_2O_3 , g/L	100	100	90
	Acidity	0.8 to 1.2 M	pH=1.5	pH=1.5
	Flow, mL/min	25	25	25
Scrubbing solution	HCl, M	0.6	0.5	0.25 and 0.36
	Flow, mL/min	25	25	25
Stripping solution	HCl, M	6	5	5
	Flow, mL/min	25	25	25
Neutralizing solution	NaOH, M	not used	2.8	2.8
	Flow, mL/min		1.1 to 2.6	6 to 8.5
Organic phase	Composition	EHEHPA 1 M in Shell D70		
	Flow, mL/min	100		
Mixer conditions	O/A	2 (extr. section) and 4 (scrub. and strip. sections)		
	Residence time, min	3.5 (extr. section) and 4 (scrub. and strip. sections)		
Settler conditions	O/A	1 (extr., scrub. and strip. sections)		
	Residence time, min	8 (extr. section) and 10 (scrub. and strip. sections)		

Total rare earths were determined by complexometry with EDTA using xylenol orange as indicator, and the individual rare earths were analysed by ICP-AES or AAS spectrometries. The organic phases were back-extracted with hydrochloric acid 6M prior to analysis. Samples from each mixer-settler, feed solution, raffinate and strip liquor were analysed periodically.

The testwork was divided into 3 parts. In the first part, the heavy rare earths were separated from the other rare earths. In the second part, the separation of medium from light rare earths was made. In the third part the light rare earths were processed to separate lanthanum from praseodymium and neodymium. All the fractions obtained were precipitated in the carbonate form by adding commercial grade sodium carbonate.

RESULTS AND DISCUSSION

Separation of the heavy rare earths and yttrium from the other rare earths

In this part of the separation process (part 1), three test runs were carried out modifying the configuration of the plant and the acidity of the feed solution (0.8, 1.0 and 1.2 M in HCl).

The results are presented in Table 2. Overall extractions were calculated based on the concentrations and flow rates of raffinates and strips. As can be seen, at the higher acidity (1.2 M) the extraction of the heavy RE, yttrium included, was only 75%. The maximum extraction was 93% in test 1, but an undesirable co-extraction of 20% of terbium and about 6% of gadolinium were found. In test 2, the co-extraction of medium RE was lower (13% of terbium) but the recovery of the heavy RE and yttrium decreased to 85%. The conditions of test 1 seem to be the more appropriate concerning the maximum recovery of the heavy rare earths. Under these conditions the recovery of the total heavy RE + yttrium is 93%, and >90% for all the heavy RE and yttrium individually. The raffinate obtained is >99.9% pure in light+medium RE and the strip liquor is 95% pure in heavy RE+yttrium.

Separation of the medium rare earths from the light rare earths

In part 2 of the experimental work, the feed solution used was the raffinate produced in the previous tests, after being concentrated by evaporation and pH adjustment. Three test runs were considered, the variable tested being the flow of the neutralizing agent (1.1, 2.1 and 2.6 mL/min). The other experimental conditions are presented in Table 1.

As can be seen in Table 3, the extraction of the rare earths increased with the flow of the neutralizing agent, as expected from the extraction mechanism assumed (equation (1)). The acidity conditions in test 4 were not satisfactory resulting in low recovery of the medium rare earths (72.5%), although producing a high purity strip solution. On increasing the flow of the NaOH solution the extraction of the medium rare earths increased to 96.5% in test 5, without significant co-extraction of the light RE. The strip solution obtained contained 98.4% of medium RE and less than 1% of light RE, while the raffinate was 99.7% light RE.

TABLE 2

Compositions and extraction efficiencies in the different test runs of Part 1:
Separation of the heavy rare earths and yttrium from the other rare earths.

Test	Conditions		RE oxides	Composition of streams (%)			Overall Extraction %
	Feed acidity HCl, M	Stages extr./scrub		Feed	Raffinate	Strip	
1	0.8	4 / 6	Light	91.4	93.0	0	0
			Sm ₂ O ₃	4.11	4.17	0	0
			Eu ₂ O ₃	0.10	0.10	0	0
			Gd ₂ O ₃	2.40	2.47	0.84	5.83
			Tb ₄ O ₇	0.37	0.24	4.46	20.0
			Medium	6.98	6.98	5.30	1.26
			Dy ₂ O ₃	0.45	0	27.1	100
			Ho ₂ O ₃	0.05	0	2.83	94.0
			Er ₂ O ₃	0.05	0	2.83	94.0
			Yb ₂ O ₃	0.005	0	0.30	100
			Y ₂ O ₃	1.13	0.03	61.5	90.3
			Heavy+Y	1.69	0.03	94.6	92.9
2	1.0	4 / 6	Light	90.6	92.2	0	0
			Sm ₂ O ₃	5.13	5.12	0	0
			Eu ₂ O ₃	0.10	0.10	0	0
			Gd ₂ O ₃	2.15	2.15	0.67	0.48
			Tb ₄ O ₇	0.39	0.28	3.42	13.4
			Medium	7.77	7.65	4.09	0.80
			Dy ₂ O ₃	0.46	0.09	24.5	81.1
			Ho ₂ O ₃	0.05	0.01	2.75	82.0
			Er ₂ O ₃	0.05	0	3.29	98.0
			Yb ₂ O ₃	0.005	0	0.34	100
			Y ₂ O ₃	1.16	0.07	65.1	85.8
			Heavy+Y	1.73	0.17	96.0	84.6
3	1.2	5 / 5	Light	91.1	92.2	0	0
			Sm ₂ O ₃	5.01	5.07	0	0
			Eu ₂ O ₃	0.10	0.10	0	0
			Gd ₂ O ₃	2.10	2.13	4.03	2.19
			Tb ₄ O ₇	0.33	0.20	4.21	14.5
			Medium	7.54	7.50	8.24	1.25
			Dy ₂ O ₃	0.45	0.19	23.2	59.1
			Ho ₂ O ₃	0.05	0.02	2.54	58.0
			Er ₂ O ₃	0.05	0.02	2.98	68.0
			Yb ₂ O ₃	0.005	0.002	0.35	80.0
			Y ₂ O ₃	0.83	0.07	63.1	86.7
			Heavy+Y	1.39	0.30	92.2	75.5

Note: Approx. concentr. of streams, in REO: Feed=100g/L ; Raffinate=49g/L; Strip=1.5g/L

An increase of the neutralizing flow rate decreases the purity of the strip solution. So, the results of the test 5 are the best obtained in this part of the separation process.

TABLE 3

Compositions and extraction efficiencies in the different test runs of Part 2:
Separation of the medium rare earths from the light rare earths.

Test	Conditions Flow of NaOH 2.8M, mL/min	RE oxides	Composition of streams (%)			Overall Extraction %
			Feed	Raffinate	Strip	
4	1.1	La ₂ O ₃	45.4	46.7	0.03	0
		CeO ₂	1.51	1.55	0	0
		Pr ₆ O ₁₁	10.2	12.5	0.07	0.03
		Nd ₂ O ₃	36.1	36.8	0.25	0.04
		Light	93.2	97.6	0.35	0.02
		Sm ₂ O ₃	4.11	2.37	42.9	54.0
		Eu ₂ O ₃	0.10	0	1.90	95.0
		Gd ₂ O ₃	2.35	0.06	52.2	98.2
		Tb ₄ O ₁₁	0.13	0	2.15	100
		Medium	6.68	2.43	99.2	72.5
		Y ₂ O ₃	0.07	0	0.47	100
5	2.1	La ₂ O ₃	47.1	49.9	0.07	0.01
		CeO ₂	1.13	1.22	0	0
		Pr ₆ O ₁₁	9.77	10.6	0.08	0.06
		Nd ₂ O ₃	34.7	38.0	0.58	0.12
		Light	92.7	99.7	0.73	0.06
		Sm ₂ O ₃	5.05	0.25	65.5	95.5
		Eu ₂ O ₃	0.09	0	1.27	97.9
		Gd ₂ O ₃	2.01	0.04	30.3	98.3
		Tb ₄ O ₁₁	0.10	0	1.36	100
		Medium	7.25	0.29	98.4	96.5
		Y ₂ O ₃	0.07	0	0.92	100
6	2.6	La ₂ O ₃	47.1	52.3	0.08	0.02
		CeO ₂	1.13	1.24	0	0
		Pr ₆ O ₁₁	9.77	10.5	0.14	0.13
		Nd ₂ O ₃	34.7	35.8	4.74	1.22
		Light	92.7	99.8	4.96	0.46
		Sm ₂ O ₃	5.05	0.11	64.8	98.2
		Eu ₂ O ₃	0.09	0	1.17	98.0
		Gd ₂ O ₃	2.01	0.04	27.0	98.5
		Tb ₄ O ₁₁	0.10	0	1.21	100
		Medium	7.25	0.15	94.2	98.4
		Y ₂ O ₃	0.07	0	0.83	100

Note: Approx. concentr. of streams, in REO: Feed=100g/L; Raffinate=44g/L; Strip=7.5g/L

Separation of lanthanum from praseodymium and neodymium

The raffinate from part 2 of the process containing the light rare earths was concentrated by evaporation and the pH adjusted to be used as feed solution in the experimental work carried out in this part of the separation process. The variables tested were the flow of NaOH (6, 7 and 8.5 mL/min) and the acidity of the scrub solution (HCl 0.25 and 0.36 M).

In Table 4 the results of part 3 of the separation process are presented. In the three initial tests, the flow of the neutralizing solution was increased from 6 to 8.5 mL/min, maintaining the same scrub solution. The extraction of the rare earths increased with the flow of the NaOH solution, as expected. In test 9, about 97% of Pr+Nd was recovered, but an important co-extraction of La (7%) was observed. In order to maximise the recovery of Pr+Nd and simultaneously to decrease the La co-extraction, a more acidic scrub solution was used in test 10, maintaining the flow rate of caustic soda at the same level of test 9.

The results obtained were very satisfactory: almost 98% of Pr+Nd was recovered, leading to a strip solution with 0.4% of La and 96% of Pr+Nd, and a raffinate containing 97.5% of La and 2% of Pr+Nd. The element cerium was not considered important in this test, because its content is only residual and can be removed easily by classical methods.

TABLE 4

Compositions and extraction efficiencies in the different test runs of Part 3:
Separation of lanthanum from praseodymium and neodymium

Test	Conditions		RE oxides	Composition of streams (%)			Overall Extraction %
	Flow of NaOH 2.8M, mL/min	Scrub solution HCl, M		Feed	Raffinate	Strip	
7	6	0.25	La₂O₃	47.6	87.6	0.15	0.15
			CeO ₂	1.52	1.40	1.40	47.3
			Pr ₆ O ₁₁	11.1	4.50	20.3	80.5
			Nd ₂ O ₃	38.4	6.50	75.7	91.3
			Pr+Nd	49.5	11.0	96.0	88.8
			Sm ₂ O ₃	1.40	0	2.40	100
8	7	0.25	La₂O₃	46.5	94.3	0.23	0.25
			CeO ₂	1.62	0.96	2.05	68.5
			Pr ₆ O ₁₁	10.9	2.17	20.9	90.8
			Nd ₂ O ₃	37.7	2.54	71.4	96.7
			Pr+Nd	48.6	4.71	92.3	95.3
			Sm ₂ O ₃	3.25	0	5.37	100
9	8.5	0.25	La₂O₃	49.0	96.2	6.34	6.86
			CeO ₂	1.25	0.57	1.89	78.6
			Pr ₆ O ₁₁	11.0	1.42	20.7	94.2
			Nd ₂ O ₃	37.5	1.84	69.0	97.7
			Pr+Nd	48.5	3.26	89.7	96.8
			Sm ₂ O ₃	1.20	0	2.10	100
10	8.5	0.36	La₂O₃	49.0	97.5	0.39	0.40
			CeO ₂	1.25	0.46	1.77	79.5
			Pr ₆ O ₁₁	11.0	1.04	22.2	95.6
			Nd ₂ O ₃	37.5	1.04	73.6	98.6
			Pr+Nd	48.5	2.08	95.8	97.9
			Sm ₂ O ₃	1.20	0	2.04	100

Note: Approx. concent. of streams, in REO: Feed=90g/L ; Raffinate=20g/L ; Strip=46g/L

Production of rare earth carbonates

Rare earth carbonates were produced from the best fractions obtained in the different parts of the separation process. The compositions of these carbonates are shown in Table 5. All the products have purities over 95%.

TABLE 5
Compositions of the rare earth carbonates

	LANTHANUM CARBONATE	PRASEODYMIUM + NEODYMIUM CARBONATE	MEDIUM RARE EARTHS CARBONATE	HEAVY RARE EARTHS CARBONATE
COMPOSITION	97.3% La	0.39% La	0.05% La	0.80% Gd
(% REO)	0.64% Ce	2.42% Ce	0.08% Pr	3.70% Tb
	0.98% Pr	20.9% Pr	0.57% Nd	27.9% Dy
	1.08% Nd	75.7 % Nd	64.4% Sm	2.90% Ho
		0.48% Sm	1.32% Eu	2.90% Er
		0.004% Eu	28.8% Gd	0.30% Yb
		0.11% Gd	3.20% Tb	61.5% Y
			0.05% Ho	
			0.05% Er	
			1.48% Y	
PURITY (%REO)	97.3% La	96.6% Pr+Nd	97.7% Medium	95.5% Heavy+Y

CONCLUSIONS

IONQUEST 801 metal extractant seems to be a good alternative to D2EHPA for separating rare earths in groups from didymium chloride solutions. Fractions of lanthanum, praseodymium + neodymium, medium rare earths and heavy rare earths + yttrium, more than 95% purity and over 93% recovery were achieved by the process described.

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SOLVENT EXTRACTION AND SEPARATION OF SOME ELEMENTS OF GROUPS III-IV WITH TRIBUTYL PHOSPHATE FROM FLUORIDE-NITRATE MEDIA

S.A. SEMENOV, A.M. REZNIK, I.F. POLETAEV, V.V. VYGOVSKY

Department of Rare and Dispersed Elements
Lomonosov Moscow Institute of Fine Chemical Technology
Vernadsky Prospect 86, Moscow 117571, Russian Federation

ABSTRACT

The influence of yttrium, zirconium and thorium complex formation with fluoride ion on their solvent extraction and separation with 100% tributyl phosphate (TBP) from nitric acid media has been investigated. A mathematical model of yttrium and zirconium solvent extraction has been proposed. Yttrium and zirconium solvent extraction in the presence of iron and aluminium has been studied.

The process of complex formation is of great importance for solvent extraction separation of elements. In this study the influence of yttrium, zirconium and thorium complex formation with fluoride ion on their solvent extraction and separation with 100% tributyl phosphate from nitric acid media has been investigated. The analysis of zirconium distribution coefficient (D_{Zr}) dependence upon initial concentration ratio c_F/c_{Zr} has indicated that the reaction of zirconium with fluoride ion leads to formation of a well extracted adduct at $c_F/c_{Zr} = 1$ (Fig. 1) (Korovin et al., 1962; Yagodin et al., 1963). The yttrium fluoride complex ions are not extracted, confirmed with the decrease of D_Y with the increase in c_F/c_{Zr} (Semenov et al., 1991a). The yttrium and zirconium separation factor ($\beta_{Y/Zr} = D_Y/D_{Zr}$) dependence upon c_F/c_{Zr} has a minimum which coincides in position with the $D_{Zr} = f(c_F/c_{Zr})$ function maximum. A mathematical model of yttrium and zirconium solvent extraction with TBP from fluoride-nitrate media has been proposed (Semenov et al., 1991a). Such species as H^+ ; TBP; NO_3^- ; F^- ; Zr^{4+} ; Y^{3+} with initial concentrations (M): 2-6; 3.66; 2.08-6.16; 0-0.16; 0.02-0.06; 0.02-0.06 were accepted as the system components. Three-dimensional representation of the response surface has been used for analysis of principal mechanisms in component reactions (Figs. 2,3). The proposed model of yttrium and zirconium solvent extraction and separation describes the basic regularities of the process correctly and may be used for calculation of yttrium and zirconium extraction parameters in the examined system.

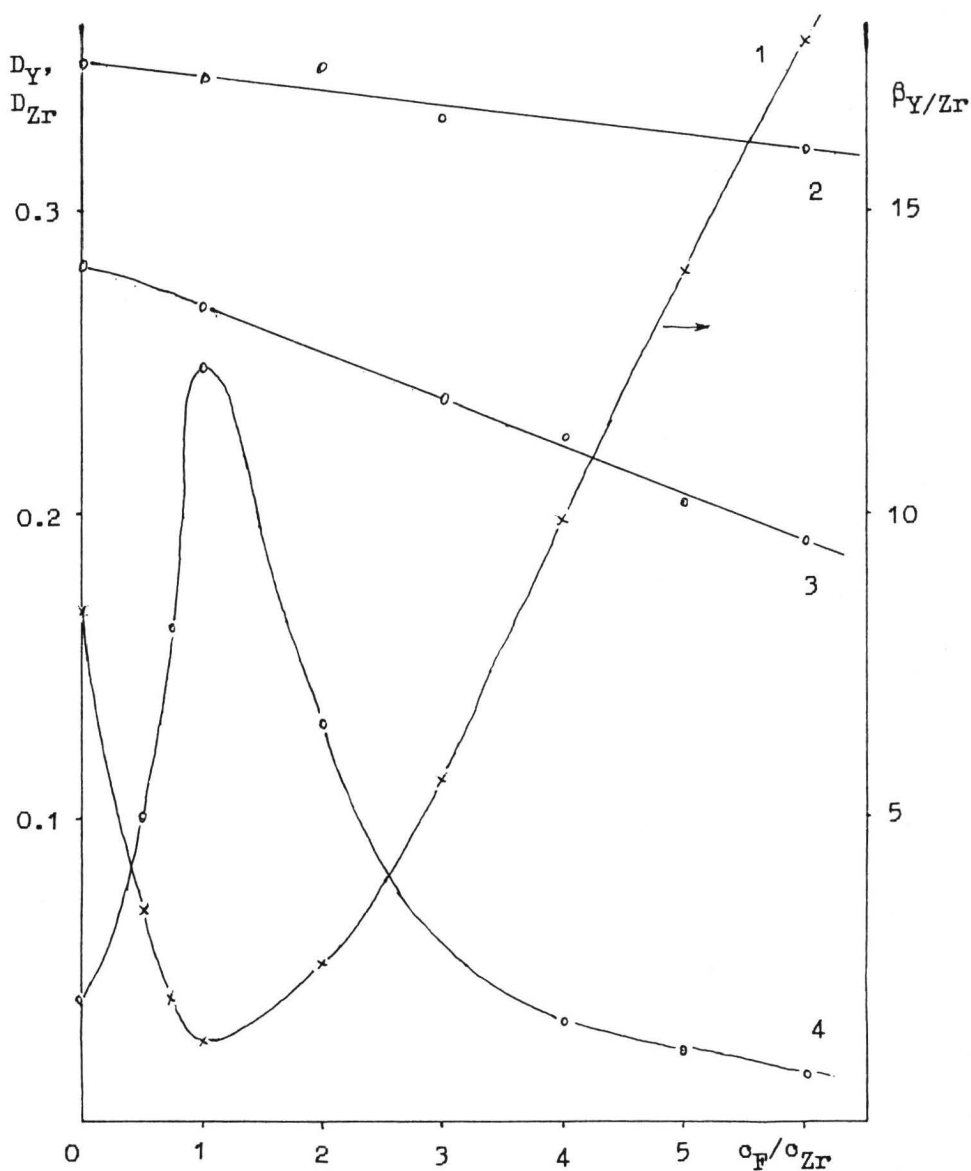


Fig. 1 Plots of D_Y , D_{Zr} and $\beta_{Y/Zr}$ vs c_F/c_{Zr}

$c_{Zr} = 0.0548$ M; $c_Y = 0.272$ M; $c_{HNO_3} = 3$ M; 1 - $\beta_{Y/Zr}$; 2, 3 - D_Y (2 - in zirconium presence; 3 - in zirconium absence); 4 - D_{Zr} (in yttrium absence)

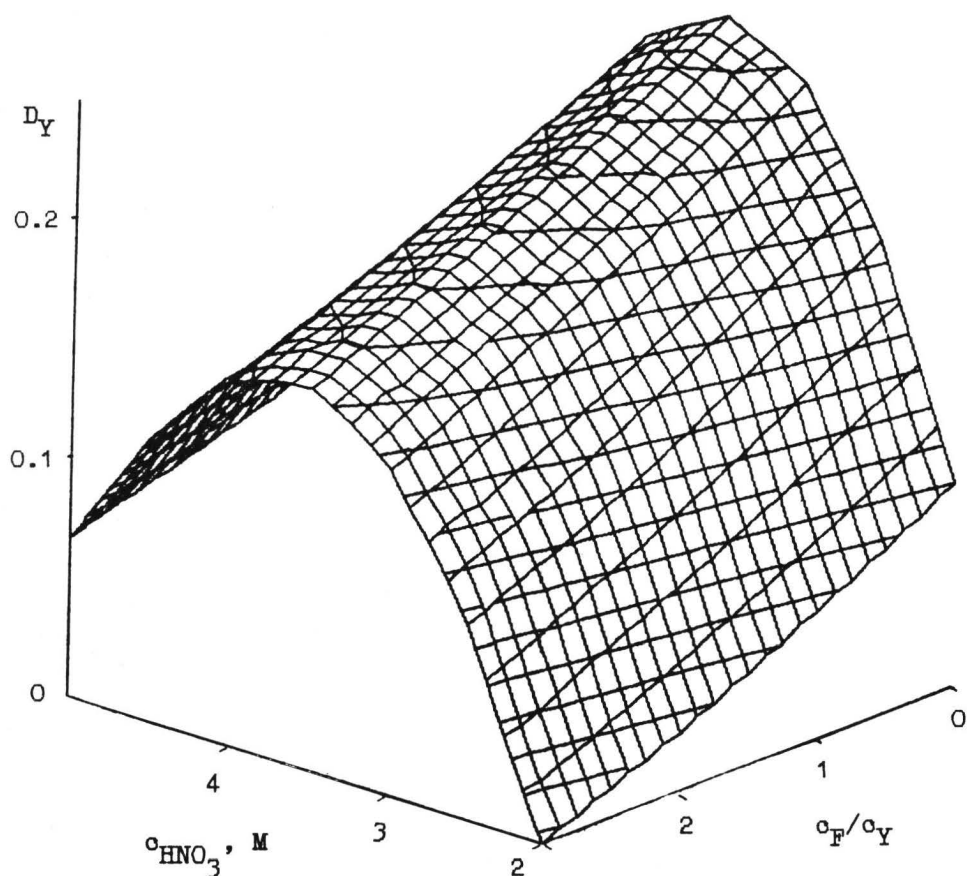


Fig. 2 Plot of D_Y vs c_F/c_Y and c_{HNO_3}

The iron and aluminium influence on yttrium and zirconium solvent extraction and separation from fluoride-nitrate media has been investigated. The shape of curves (2) (Fig. 4) and (1) (Fig. 6) is determined by iron and aluminium salting out effect. The shape of the curves (1) (Fig. 4) and (2) (Fig. 6) depends on aluminium and iron properties as salting out complexing agents. However, in comparison with aluminium, complexing properties of iron are displayed to a lesser degree. On the basis of constructed diagrams of zirconium fluoride complex ions distribution dependence upon the ratio c_{Al}/c_{Zr} (Fig. 5) and that of c_{Fe}/c_{Zr} (Fig. 7) it has been found that in systems with aluminium the fluoride ion redistribution between zirconium and aluminium takes

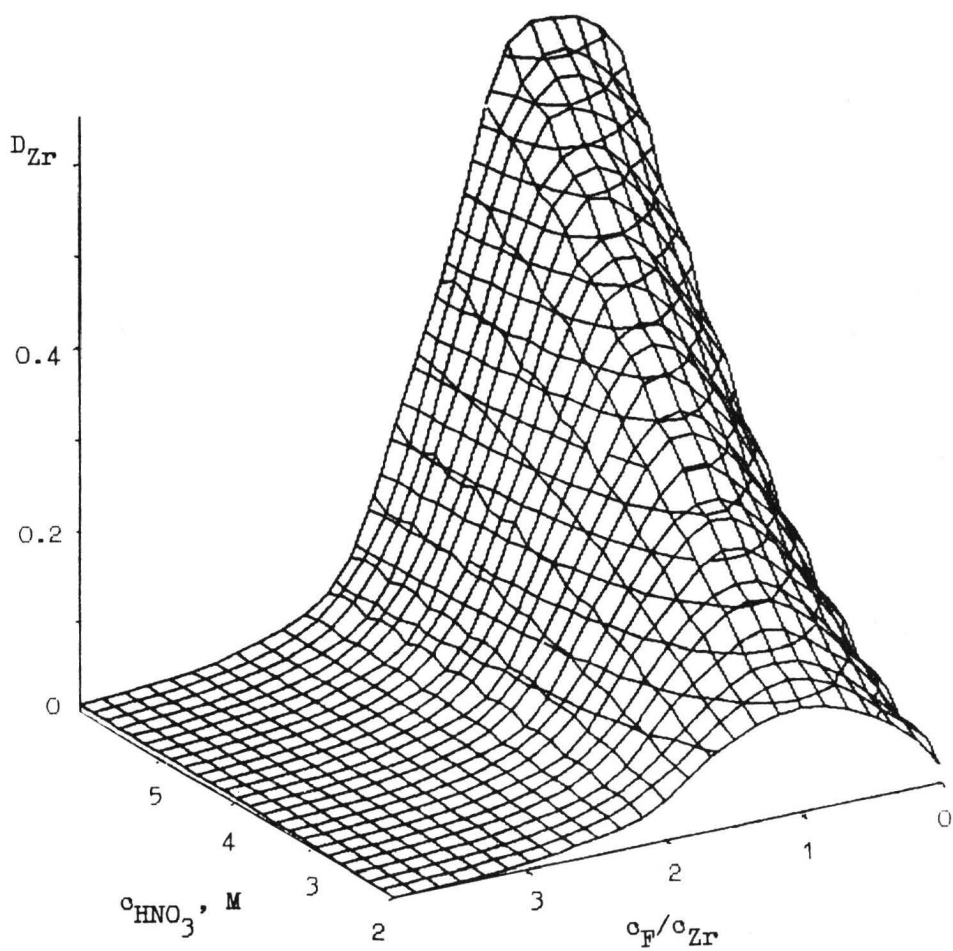


Fig. 3 Plot of D_{Zr} vs c_F/c_{Zr} and c_{HNO_3}

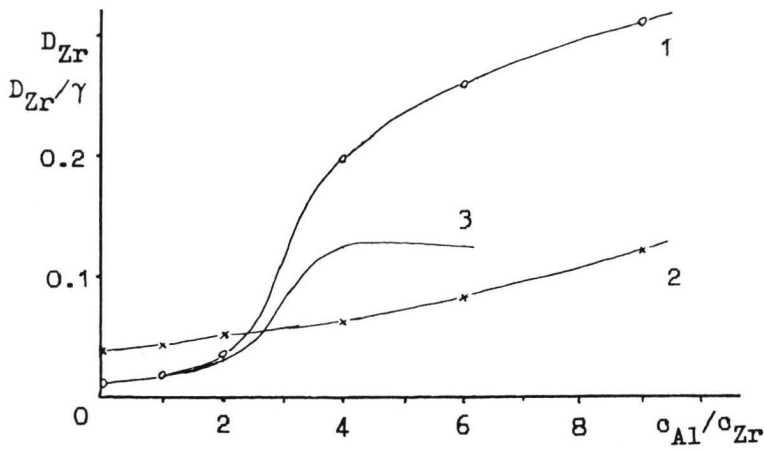


Fig. 4 Plots of D_{Zr} and D_{Zr}/γ vs c_{Al}/c_{Zr} ; $c_{Zr} = 0.0548$ M;
 $c_{HNO_3} = 3$ M; 1, 3 - $c_F/c_{Zr} = 6$; 2 - $c_F = 0$; 3 - D_{Zr}/γ ; $\gamma = D_{Zr}/D^{\circ}_{Zr}$
 in fluoride ion absence; D°_{Zr} - in aluminium absence

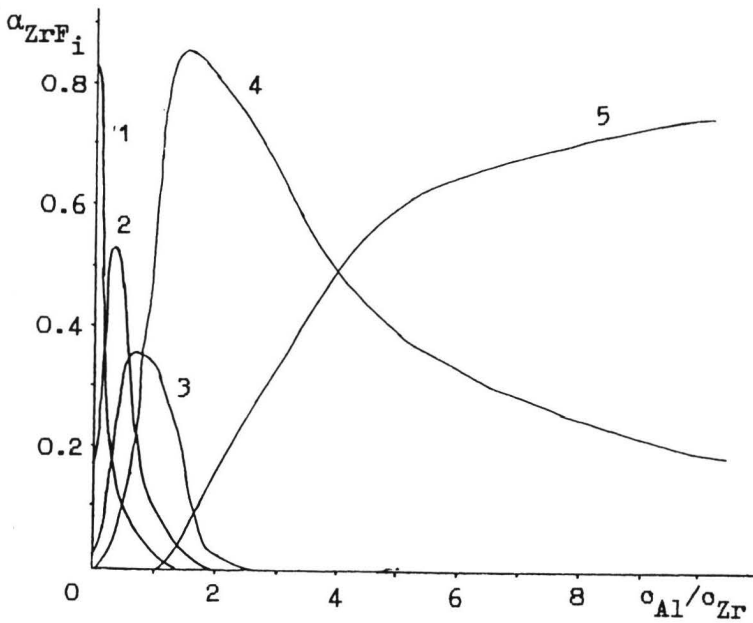


Fig. 5 Plots of species distribution vs c_{Al}/c_{Zr} ; $I = 0.5$;
 $c_F/c_{Zr} = 6$; 1 - ZrF_6^{2-} ; 2 - ZrF_5^- ; 3 - ZrF_4 ; 4 - ZrF_3^+ ; 5 - ZrF_2^{2+}

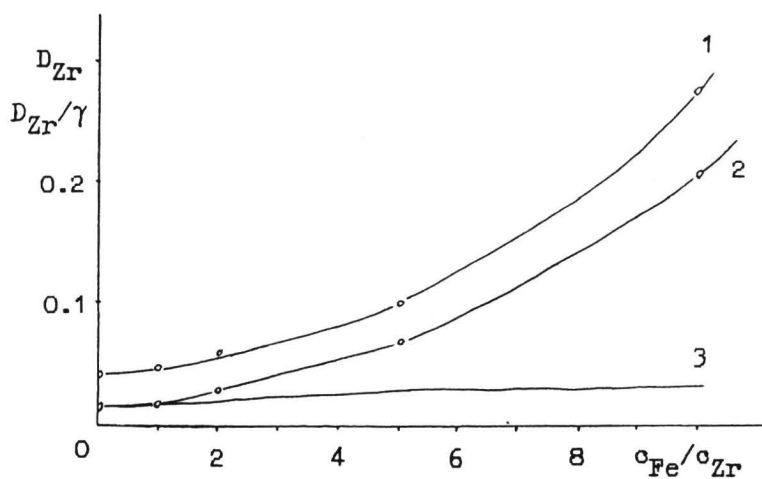


Fig. 6 Plots of D_{Zr} and D_{Zr}/γ vs c_{Fe}/c_{Zr} ; $c_{Zr} = 0.0548$ M;
 $c_{HNO_3} = 3$ M; 1 - $c_F = 0$; 2, 3 - $c_F/c_{Zr} = 6$; 3 - D_{Zr}/γ ; $\gamma = D_{Zr}/D_{Zr}^o$
 in fluoride ion absence; D_{Zr}^o - in aluminium absence

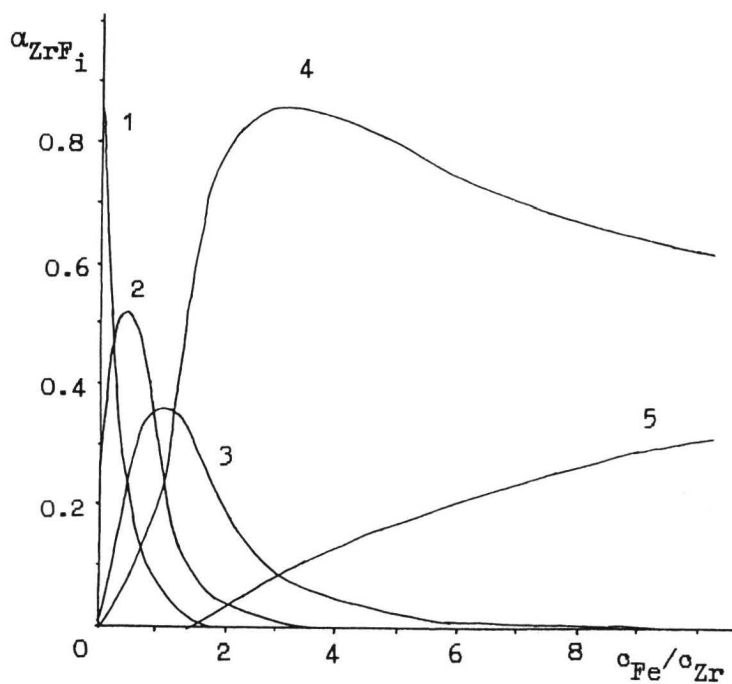


Fig. 7 Plots of species distribution vs c_{Fe}/c_{Zr} ; $I = 0.5$;
 $c_F/c_{Zr} = 6$; 1 - ZrF_6^{2-} ; 2 - ZrF_5^- ; 3 - ZrF_4 ; 4 - ZrF_3^+ ; 5 - ZrF_2^{2+}

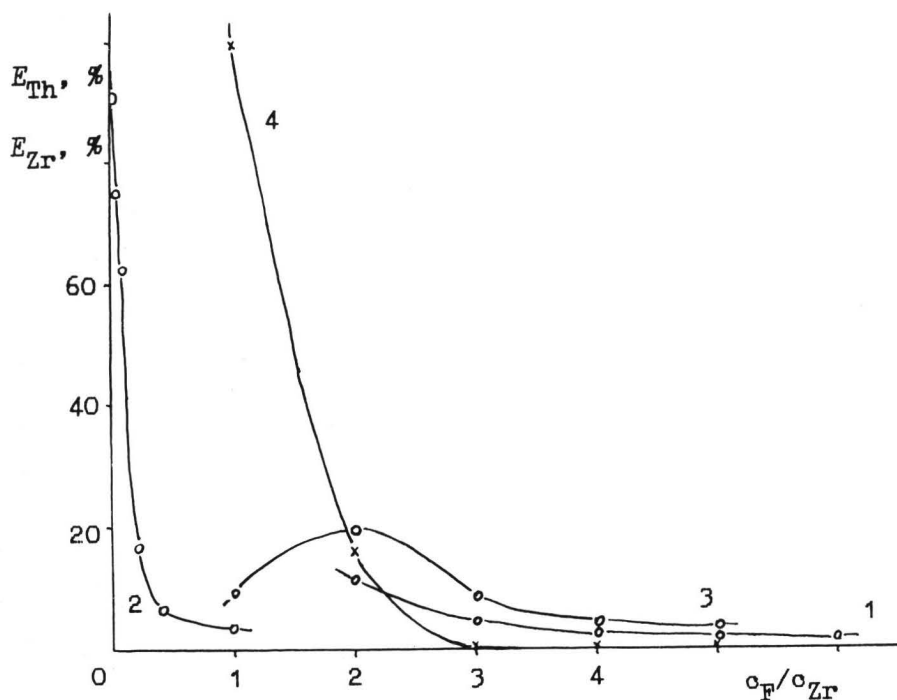


Fig. 8 Plots of zirconium and thorium extraction degree vs c_F/c_{Zr} :

$c_{Zr} = 0.110$ M; $c_{Th} = 4.31 \cdot 10^{-3}$ M; $I = 1.89$ (HNO_3); 1, 3 - Zr;

2, 4 - Th; 1 - in thorium absence; 2 - in zirconium absence

place, having influence on zirconium solvent extraction (Semenov et al., 1991b). In the case of iron the fluoride ion redistribution is expressed to a lesser degree and has no essential influence on zirconium solvent extraction (Semenov et al., 1991c). The increase in c_M/c_{Zr} , where M is Al or Fe, decreases $\beta_{Y/Zr}$, especially in the case of aluminium. A relationship between thorium and zirconium mutual influence regularities and the processes of their complexation in water phase is revealed (Fig. 8) (Semenov et al., 1991d). The increase of fluoride ion concentration leads to thorium and zirconium extraction decrease. This is caused by formation of stable fluoride complexes in water phase (Martell et al., 1976). In the case of zirconium the soluble complexes are formed in the whole studied range of the c_F/c_{Zr} ratio. In thorium solutions ThF_4 sediment is precipitated at $c_F/c_{Th} = 2$, corresponding to the ratio $c_F/c_{Zr} = 0.078$. With zirconium present ThF_4 sediment is precipitated at $c_F/c_{Zr} = 3$. The obtained conditions of ThF_4 sediment formation are confirmed by the relevant calculations, which indicate the possibility of *a priori* information on complex formation processes (Semenov et al., 1991d). The effect of the increase of the c_F/c_{Zr} ratio in which ThF_4 is precipitated is accounted for by the fluoride ion

binding with zirconium. At the moment of ThF_4 sediment formation the degree of thorium extraction is decreased to zero (Fig. 8). In common presence of thorium and zirconium the degrees of their extraction increases in comparison with those in the case of their individual solutions (at the same fluoride ion concentration). This is caused by ligand redistribution between the complexing agents. An especially significant increase of extraction degree is observed in the case of thorium.

The results form a well founded approach to the choice of yttrium, zirconium and thorium separation conditions and to reception of required composition materials.

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3.9

THE SEPARATION OF RARE EARTH AND NON-RARE EARTH ELEMENTS

Chun-Hui HUANG, Biao-Guo LI, Tian-Zhu JIN, Chun-Hua YAN,
Yong-Fen ZHOU, Zhao-Jie WEI, Wei-Dong SHI AND Guang-Xian XU
Research Center of Rare Earth Chemistry
Peking University
Beijing 100871, P.R. China

ABSTRACT

The separation of rare earth and non-rare earth impurities is discussed in this paper. The hydrolysis, precipitation and solvent extraction of the impurities were introduced into the dissolution of rare earth oxide concentrate, preparation of the feed and the further purification of products. All the above processes have been used in rare earth extraction industries in China with satisfactory results.

INTRODUCTION

The extensive applications of rare earths in high-technology fields require that most of the rare earths are single elements and in high purity grade. This purity not only involves rare earths impurities, but also non-rare earth impurities. Rare earths can improve the functions of many materials and their purities are closely related to these functions. For example, the transfer loss of the optical fibre containing high purity lanthanum fluoride is 0.001db/km and better than the best quartz glass fibre by nearly 100 times, but if LaF_3 contains $0.18\mu\text{g/kg Sm}^{2+}$, the transfer loss of the fibre is increased greatly. When yttrium oxide is applied to colour TV fluorescent material, if it contains 3~5mg/kg heavy metal elements, the screen brightness is decreased remarkably. There are many studies concerning the rare earths separation, but in this paper we will emphasize the separation between rare earths and non-rare earth elements.

PRE-SEPARATION OF RARE EARTH AND NON-RARE EARTH

The natural rare earth is mostly intergrown with other minerals. Although the production process of rare earth concentrate has the separation function between rare earth and non-rare earth elements, this concentrate still contain a large amount of impurities. In the ionic absorptive type rare earth concentrate, which is produced in the South of China, the soluble rare earth oxide is only 87~92%, while the moisture and other impurities are 13~8%, in which Fe_2O_3 , Al_2O_3 , SiO_2 and CaO are about 0.1%, 0.02%, 4% and 2%, respectively. If the concentrate is not precipitated

by $\text{H}_2\text{C}_2\text{O}_4$ but $(\text{NH}_4)_2\text{CO}_3$, the impurity is even greater.

The non-rare earth impurities not only affect the qualities of products, but also the separation process. In order to prepare the feed for solvent extraction, the pre-separation of rare earth and non-rare earth is needed, which might utilize following properties or reactions (Jin, 1978).

The basicities of the oxide

It is well known that the basicity order of the above-mentioned oxides is $\text{CaO} > \text{RE}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{SiO}_2$, so we can control the oxide dissolving process at the optimum acidity and temperature, and keep SiO_2 , Fe_2O_3 and Al_2O_3 from dissolving as litter as possible.

Hydrolysis

Using the different hydrolysis acidities of Fe^{3+} , Si^{4+} and RE^{3+} ion, most of Fe^{3+} and part of Si^{4+} impurities can be removed from the rare earth solution.

TABLE 1
Separation of Fe^{3+} , Si^{4+} from RE^{3+} by hydrolysis

Sample	Initial solution		Ageing time (day)	Final solution	
	RE^{3+} , mol/L	pH		Precipitate	Colour
1	2.15	4.10	15	No	orange
2	1.83	4.75	7	Yes	pink
3	1.63	5.10	0.5	Yes	pink
4	1.59	5.32	0.5	Yes	pink

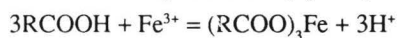
Table 1 shows the results of the hydrolysis. So long as the acidity is controlled at $\text{pH} 4.75 \sim 5.40$ and the solution is aged more than 12 hours, the content of Fe^{3+} might be decreased from 231 mg/L to 18mg/L, and Si^{4+} decreased from 10.7mg/L to 5mg/L. However, the hydrolysis reaction can not decrease the content of Al^{3+} , which still remains in the rare earth feed solution.

Precipitation

It is possible to separate some non-rare earth impurities from rare earth solution by precipitation. For example, impurity Pb^{2+} can be precipitated by $(\text{NH}_4)_2\text{S}$, and Ba^{2+} can be removed by $(\text{NH}_4)_2\text{SO}_4$, and so on.

Pre-extraction

Under normal conditions, the rare earth solution could be feed to the solvent extraction after the above-mentioned processes. But in the solvent extraction process for fluorescent grade Y_2O_3 with naphthenic acid, the Fe^{3+} would cause emulsification of the organic phase and worsen the separation efficiency, so we had to further separate Fe^{3+} by pre-equilibrium extraction as follows:

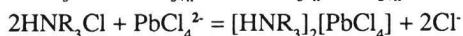


Here, RCOOH is naphthenic acid, and the reaction mechanism is cation exchange. Because Fe^{3+} exists in $[\text{Fe}(\text{OH})]^{2+}$ and $[\text{Fe}(\text{OH})_2\text{Fe}]^{4+}$ at $\text{pH} > 3$, and naphthenic acid would extract RE^{3+} at high pH also, this pre-extraction must be done at $\text{pH} = 2 \sim 4$.

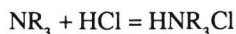
SEPARATION OF MICRO-IMPURITIES FROM RARE EARTH PRODUCTS

Separation of the impurities Fe^{3+} and Pb^{2+} from RE^{3+} with Alamine 336

The extracting reaction of Fe^{3+} , Pb^{2+} with Alamine 336 can be shown as follows:



Here, NR_3 [$\text{R} = -\text{CH}_2(\text{CH}_2)_{6-10}\text{CH}_3$] represents Alamine 336, which must be acidified to produce HNR_3^+ so that FeCl_x^{3-x} , PbCl_4^{2-} could be removed from RE^{3+} completely through ion pair mechanism.



Under the countercurrent extraction with two extracting and six scrubbing stages, the contents of Fe^{3+} and Pb^{2+} might be decreased from more than 100mg/L to less than 5mg/L. In this system, the organic phase was composed of 30% Alamine 336, 10% iso-octyl alcohol, and 60% sulphonated kerosene, which must be acidified with 2.0mol/L HCl in suitable volume. The aqueous feed was composed of 1.5~1.8 mol/l rare earth and 0.6~1.5 mol/L HCl, in which the concentration of Cl^- was more than 6.0mol/L (Li, 1989).

Separation of non-rare earth impurities with HEHEHP

The extraction order in mono 2-ethyl hexyl 2-ethyl hexyl phosphonic acid (HEHEHP) system is $\text{Ce}^{3+} > \text{La}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+} > \text{Ni}^{2+}$. Among them the couple of La^{3+} and Pb^{2+} is the most difficult to separate. Table 2 shows the separation factor $\beta_{\text{La/Pb}}$ in LaCl_3 - PbCl_2 -HCl- H_2O -1.5M HEHEHP (kerosene) system (Li, 1984).

TABLE 2

The relations between $\beta_{\text{La/Pb}}$ and the content of Pb^{2+}

Pb^{2+} , mg/L	1500	1000	300	100	30
$\beta_{\text{La/Pb}}$	40	40	30	25	25

According to the Theory of Countercurrent Extraction(Xu, 1985), we have desinged an industrial process for separating La^{3+} and Pb^{2+} , and obtained the satisfactory results (Table 3).

TABLE 3

The results of separating La^{3+} and non rare earth impurities

Impurity	PbO	CuO	CoO	NiO	CaO
Initial content (mg/L)	500	100	100	100	5000
Final content (mg/L)	<1	<1	<1	<1	5~11

SEPARATION OF RARE EARTH AND TRACE IMPURITIES

According to the Hard-Soft Acid-Base Rule of Pearson, extractant containing S or N atoms as ligands, will coordinate with heavy metal elements easily and but not with rare earths. Using this property we could select extractants such as (I) dialkyldithiophosphinic acid (Cyanex 301), (II) 7-alkyl-8-hydroxy quinoline, etc., to extract Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Pb^{2+} from rare earths and purify the rare earth products. Table 4 shows the results of cross-current extraction with Extractant I and II. In Extractant I, $\text{R} = -\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)_3$, its average molecular weight is $\overline{\text{M}}=322$. The Extractant II was a mixture, in which $\overline{\text{M}}=311$, $\text{R} = -\text{CH}(\text{CHCH}_2)-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_3$ or $\text{R} = -\text{CH}_2-\text{CH}(\text{CHCH}_2)-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_3$.

TABLE 4

The separation results with Extractant I and II

Extractant	stage	Cu^{2+} ,mg/L	Fe^{3+} ,mg/L	Co^{2+} ,mg/L	Ni^{2+} ,mg/L
I	1	0.015	24.0	7.0	0.06
	2	0.015	4.15	0.02	0.06
II	1	0.015	4.00	57.0	60.0
	2	0.015	0.25	51.0	57.0
I + II	once each	0.015	0.35	0.23	0.06

Extractant I and II were diluted to 0.49mol/L and 0.12mol/L by n-octane respectively. The aqueous feed was composed of 0.5~1.0mol/L RECl_3 , and Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} were each 50 mg/L. The phase ratio was $\text{O/A}=1$. The data were analyzed by ICP atomic absorption spectrophotometer. It is quite evident that Extractant I can selectively separate Cu^{2+} , Co^{2+} and Ni^{2+} , and Extractant II was effectual for removing Fe^{3+} and Cu^{2+} from the rare earth. When used together, the above heavy metals would be decreased to less than 0.5mg/L (Huang, 1992).

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3.10

SCANDIUM EXTRACTION BY TVEX—TBP FROM TITANIUM—MAGNESIUM PRODUCTION WASTES

KOROVIN, V. Yu., POGORELOV, Yu. N., CHIKODANOV, A. I.

“Sorbent” Scientific-Pedagogic Center
of the Ukraine Academy of Sciences,
Dnieprostoevskaya 2, Dneprodzerdzinsk, Ukraine

ABSTRACT

The process of scandium extraction from hydrochloric media by solid extractant (TVEX) using tributylphosphate (TBP) base was investigated. The extraction mechanism was determined by ^{31}P and ^{45}Sc NMR method, and comparison with solvent extraction was carried out. It is shown that TVEX polymer styrene-divinylbenzene matrix influences scandium extraction by TBP, changing the composition and relative quantity of scandium hexacoordinated chlorine-aquacomplexes in organic phase. The technological scheme of scandium removal from titanium- magnesium production wastes by TVEX-TBP is given.

INTRODUCTION

Extraction of scandium is a difficult problem, closely connected with its selective removal and separation from impurities. One of the most important scandium raw materials are the chloride wastes from titanium-magnesium production. As a result of their recovery the highly mineralized chloride pulps are produced with scandium concentration 80-100 mg/L. The presence of much silicon in the pulp makes difficult the use of solvent extraction owing to the formation of true emulsions and large loss of organic phase. Therefore the development of scandium extraction methods directly from chloride pulps acquires importance. Nowadays materials combining the properties of sorbents and selective solvent extractants have the wide use in technology of rare and rare-earth elements [Korovin V., Randarevich S., 1991]. These type materials were created for the first time simultaneously in Ukraine [Bolotov A. et al, 1975] and in German Federal Republic [Kroebe R, 1974]. They were called solid extractants (TVEX) in our state and as “Levextrel type resins” abroad. Solid extractants are produced by extractant introduction into the polymer matrix during the synthesis, during suspension co-polymerization of styrene (or other monomer) with mono-

or divinylbenzene compounds, for example, divinylbenzene, in the presence of radical polymerization initiator. As a result lustreless spherical granules containing solvent extractant are made.

The results of comparative investigation by ^{31}P and ^{45}Sc NMR method of scandium complexes composition, extracted from hydrochloric solution by 100% TBP and by solid extractant (TVEX-TBP) with 50% TBP content are given in this paper. The solid extractant use for selective scandium removal from chloride wastes is shown.

SCANDIUM EXTRACTION BY TBP AND TVEX—TBP ACCORDING TO ^{31}P AND ^{45}Sc NMR DATA

Figure 1 shows the isotherms of scandium extraction by 100% TBP and TVEX-TBP (in terms of 100% TBP). As one may see, the isotherms practically coincide at low equilibrium metal concentrations, but the extractant introduced in the TVEX polymer matrix has higher capacity compared to liquid TBP for high equilibrium metal concentrations. The difference observed in the scandium equilibrium distribution between tri- butylphosphate liquid and introduced in TVEX, is probably caused by exchange of composition of extracted metal

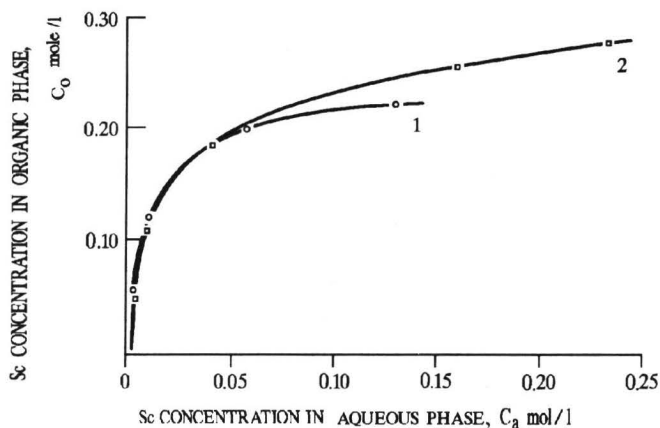


Fig. 1. The isotherms of scandium extraction from 8 M HCl by liquid TBP (1) and by TVEX-TBP (2).

complexes because of polymer matrix influence.

The kinetic investigations of scandium extraction by TVEX-TBP from 8 M HCl were carried out by the method of phase limited volume. It was determined that 80-90% of Sc is extracted within 45 minutes. The diffusion coefficient of metal in TVEX granules is $3,6 \cdot 10^{-12} \text{ m}^2/\text{s}$, higher than for Sc sorption by ion-exchange resins [Laskorin B. et al, 1990].

The ^{31}P NMR spectra of scandium extracts by 100% TBP and TVEX-TBP

contain the A, B and C group of signals. The intensities distribution of signals and value of average solvate number (ASN) depending upon scandium concentration in extracts are given in Table 1.

The A signal, according to its position in NMR spectra (the chemical shift is 1 ppm relatively 85% H_3PO_4) is caused by non-coordinated with Sc complex

TABLE 1
Parameters of ^{31}P NMR spectra and scandium ASN in extracts

N	TBP mole/Sc mole ratio	Signal intensities in ^{31}P ratio NMR spectra, %			ASN
		A	B	C	
Liquid TBP					
1	87.28	98.07	1.93	less than 0.1% the same	1.68
2	41.16	92.35	7.65		3.15
3	23.21	85.40	14.60	—	3.38
4	13.59	76.70	23.30	—	3.17
5	9.05	66.70	33.30	—	3.01
6	6.68	55.80	44.20	—	2.95
7	5.45	48.90	52.10	—	2.83
8	5.18	40.80	59.20	—	3.07
TVEX-TBP					
9	33.59	93.37	6.67	—	2.23
10	15.70	82.52	13.20	4.26	2.75
11	9.60	73.00	21.00	6.00	2.59
12	6.53	62.80	31.70	5.50	2.43
13	5.60	60.93	30.25	8.80	2.19
14	4.53	57.37	33.26	9.36	1.93
15	4.37	57.20	33.60	9.18	1.87
16	3.95	56.30	34.02	9.50	1.72

TBP. The B signal (-4 ppm), the intensity of which increases in proportion to scandium concentration in organic phase, corresponds to tributylphosphate, coordinated to metal ion. The integral intensity of C group resonance lines (-10 — -14 ppm) depends insignificantly upon scandium content in extracts, but increases with time. This allows these signals to be related to the products of tributylphosphate hydrolysis - dibutylphosphoric (DBPA) and monobutylphosphoric (DBPA) acids, bound with metal. The large- two times - solvate shift of C group signals compared to B signal testifies that tributylphosphate hydrolysis products are fixed with scandium at the same time by ion and coordination bonds, forming the different polynuclear complexes in extracts; the availability of several signals in the C group indicates the variety of polymer forms in the extract.

The value of average solvate number (ASN) was calculated for the different extracts upon the relation between the tributylphosphate free and bonded with scandium (see Table 1). The average solvate number differs essentially for

extraction by TBP and TVEX-TBP and has fractional value, which testifies to the formation of several complexes in organic phase and the different relations between them. The ASN value depends upon metal concentration in extract, and the ASN value decreases for TVEX-TBP with scandium content increase. This may be used to explain the observed increase of TBP equilibrium capacity for high scandium concentration in aqueous phase (Fig.1).

The ^{45}Sc NMR spectra were recorded for each isotherm point, some of which are given on Figure 2. We determined earlier [Korovin et al, 1988] on the basis of ^{31}P and ^{45}Sc NMR study of scandium extracts by TBP and TVEX-TBP from

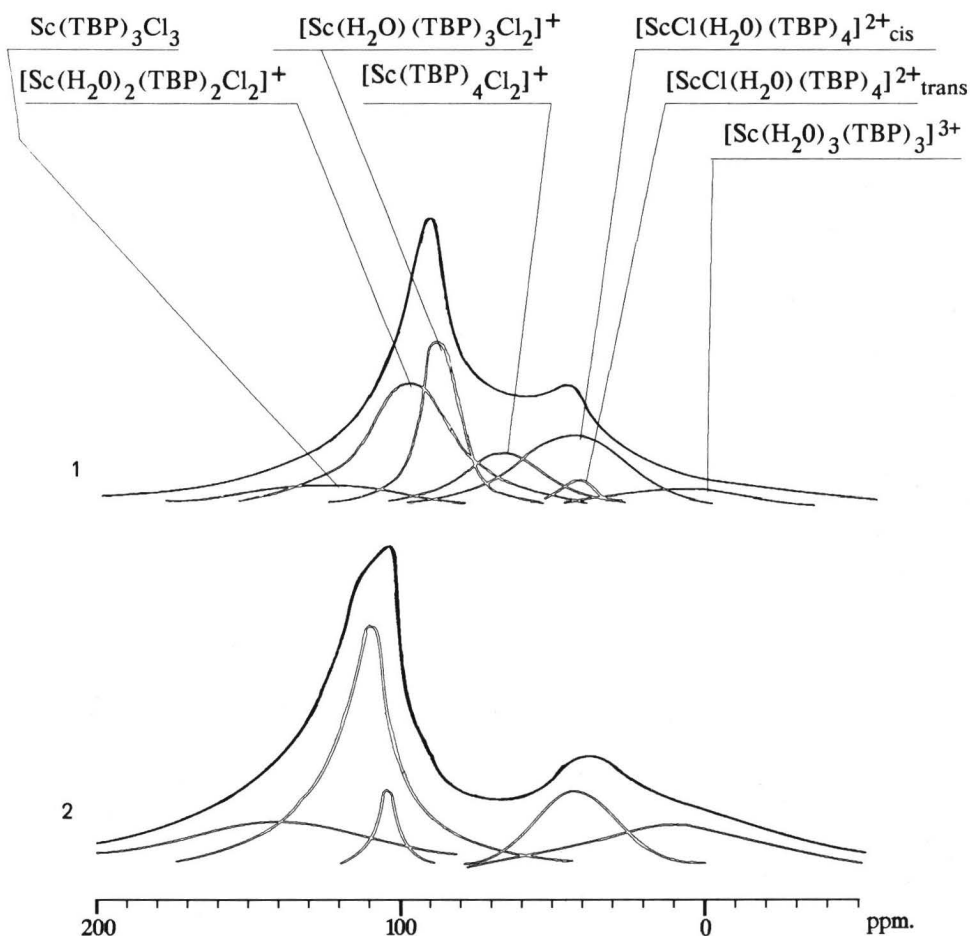
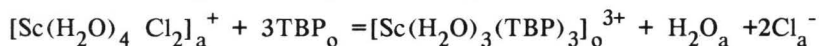
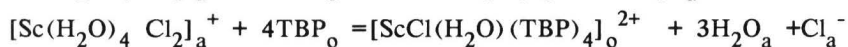
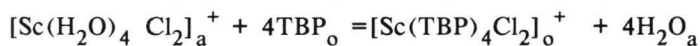
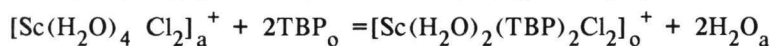
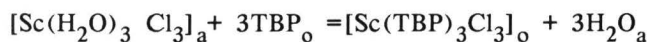


Fig. 2. ^{45}Sc NMR spectra of scandium extracts from 8 M HCl by liquid TBP, sample No 2 from Table 1 (1) and by TVEX-TBP, sample No 9 from Table 1 (2)

hydrochloric solutions that a several different complexes, containing water molecules, are present in this system. One may see from the Figure 2 that the relation between extracted forms is different for TBP and TVEX-TBP. The large number of signals in the spectra may be explained by high ligand lability in scandium coordination sphere, testifying to the difficulty of the systems studied.

We related signals in ^{45}Sc NMR spectra of TBP and TVEX-TBP extracts (Fig.2) to the following complexes, taking into consideration the chemical shifts of the $[\text{Sc}(\text{TBP})_{6-n}\text{Cl}_n]^{3-n}$ complexes and their isomers, given in [Kirakosyan G. et al,1989]: $\text{Sc}(\text{TBP})_3\text{Cl}_3$ (130ppm.), $[\text{Sc}(\text{H}_2\text{O})_2(\text{TBP})_2\text{Cl}_2]^+$ (100 ppm.), $[\text{Sc}(\text{H}_2\text{O})(\text{TBP})_3\text{Cl}_2]^+$ (91 ppm.), $[\text{Sc}(\text{TBP})_4\text{Cl}_2]^+$ (67 ppm.), $[\text{ScCl}(\text{H}_2\text{O})(\text{TBP})_4]^{2+}_{\text{cis}}$ (43 ppm.), $[\text{ScCl}(\text{H}_2\text{O})(\text{TBP})_4]^{2+}_{\text{trans}}$ (41 ppm.) and $[\text{Sc}(\text{H}_2\text{O})_3(\text{TBP})_3]^{3+}$ (-9 ppm.). Taking into account the scandium state in aqueous solutions [Kirakosyan G. et al, 1982] the extraction equilibria may be recorded as:



It is necessary to note the following laws of Sc extraction from hydrochloric solution by tri-butylphosphate liquid and introduced in TVEX polymer matrix. The extraction equilibrium upon extraction by liquid TBP is displaced to the formation of complexes with the charge from +1 to +3, and the forms with water molecules in the coordination sphere prevail.

In the case of Sc extraction by TVEX-TBP the TVEX hydrophobic polymer matrix influences scandium extraction by TBP, displacing the equilibrium relation of Sc complexes to the compounds with small charge and lesser quantity of H_2O molecules. Probably, the presence of hydrophobic polymer matrix prevents the water molecules transition to organic phase together with Sc^{3+} ions.

The data obtained testify that TVEX-TBP may be used for scandium removal from chloride solutions.

THE USE OF TVEX-TBP FOR SCANDIUM REMOVAL FROM CHLORIDE WASTES

We elaborated and introduced to titanium-magnesium integrated works the highly effective technology (Fig.3) of selective scandium removal from hydrochloric

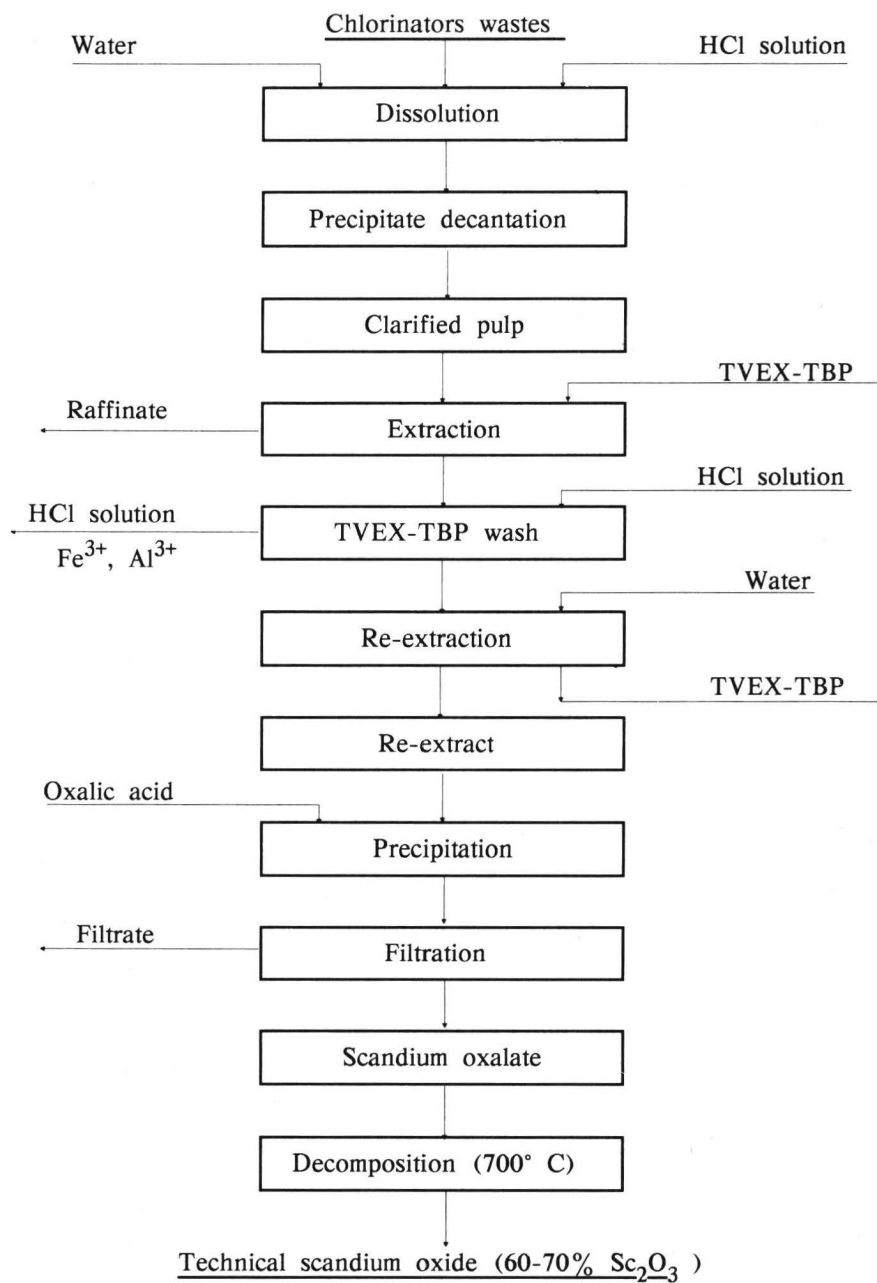


Fig. 3. The scheme of "TVEX-Sc process".

pulps, produced by dissolving titanium production mine and salt chlorinators wastes. We called this technology "TVEX-Sc-process".

The initial technology stage includes the wastes dissolution with formation of hydrochloric pulp with density 1300 kg/m^3 and low HCl content; desiliconization and precipitate decantation gave clarified pulp. The clarified pulp then goes to scandium extraction by TVEX-TBP, which is carried out in several cycles in a reactor with continuous agitation. TVEX-TBP then is washed by concentrated hydrochloric acid. The preliminary scandium purification from a number of impurities is attained at this stage.

Re-extraction is carried out by water with further precipitation of scandium oxalate by oxalic acid. The technical scandium oxide is produced after filtration and oxalates decomposition, containing 60-70% of required product.

For the production of scandium oxide with higher purity the technical oxide is dissolved in hydrochloric acid, solvent extraction by tributylphosphate is carried out with scandium re-extraction and its further precipitation as oxalate and decomposition to oxide. The additional iodate purification may be carried out for thorium, zirconium and titanium removal. The use of this additional purification step gives the opportunity to obtain scandium oxide with 99,9% purity.

It should be noted that due to TVEX-TBP use we removed the filtration of pulps, reduced tributylphosphate consumption, avoided loss with emulsions, decreased the labor expenditure, and increased the extraction degree of the required product.

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3.11

**THE PURIFICATION OF TBP FROM HDBP IN RE EXTRACTION
FROM LOPARITE CONCENTRATE**

BLINOVA O.A., LANIN V.P., PUSHKOV A.A.,

Mendeleev Institute of Chemical Technology,

Miusskaya pl.9, 125190 Moscow, Russia.

KUZNETSOV G.I., NIKOLAEV YU.M.,

NPO NIKIMT, Altuf'evskoe shosse 43, 127106 Moscow, Russia.

ANTONOV B.I., GURYANOV A.S., RYBALKIN A.I.,

Chemical Metallurgical Industrial Association, Sillamj e, Estonia.

ABSTRACT

The mechanism of TBP hydrolysis is proposed. The hydrolysis rate constants in the presence of HNO_3 and some rare metals are calculated. The value of the constants are satisfactorily correlated with the value of frequency shifts of $\text{P}=\text{O}$ group valent vibrations. The HDBP accumulation in the processes of different RE concentrate production from loparite is estimated. The effect of phase contact time in centrifugal extractors on stage efficiency in TBP washing by ammonium carbonate with complexing agent is established. The possibility of using centrifugal extractors for this operation is demonstrated.

INTRODUCTION

TBP is widely used in RE processing. When TBP is in contact with aqueous solutions, it undergoes hydrolysis with formation of HDBP, H_2MBP , the quantity of H_2MBP being 6 to 10 times less than HDBP (Solovkin et al, 1985). The products of the hydrolysis cause the definite difficulties in extraction processes by forming stable compounds with a number of metals. HDBP-metal complexes decrease the decontamination factor of extracted metals, increase their losses with raffinates, cause solid phase and stable emulsion formation and contamination of product by phosphorus. The presence of HDBP leads to a interfacial tension decrease (Nikolotova, Kartashova, 1978), which is the reason for deterioration of phase separation and increase in mutual phases entrainment.

It is considered that TBP hydrolysis in acidic solutions proceeds by carbon-oxygen bonds breaking. The hydrolysis rate constant is calculated in accordance with the equation:

$$K_h^H = - \frac{d[\text{TBP}]}{dt} [\text{TBP}]^{-1} [\text{HNO}_3]^{-1} \quad (1),$$

where $[\text{TBP}]$, $[\text{HNO}_3]$ – concentrations in organic phase.

When HNO_3 concentration in organic phase changes from 0.5 to 5 mol/L, K_h^H changes from $1.8 \cdot 10^{-3} \text{ h}^{-1}$ to $1.4 \cdot 10^{-2} \text{ h}^{-1}$.

Supposing that only TBP molecules linked into complexes with HNO_3 are subjected to hydrolysis, the authors of the paper (Sinegribova et al, 1990) proposed the following equation to calculate K_h^H :

$$K_h^H = \frac{d[\text{HDBP}]}{dt} [\text{TBP}]_*^{-1} [\text{H}_2\text{O}]_0 \quad (2),$$

where $[\text{H}_2\text{O}]_0$ – concentration of water in organic phase; $[\text{TBP}]_*$ – concentration of TBP, linked in complexes with HNO_3 , its concentration being determined in accordance with the paper (Stoyanov et al, 1990). Thus calculated K_h^H in interval of HNO_3 concentration in organic phase from 0.5 to 4.1 mol/L is constant and equal to $3.6 \cdot 10^{-10} \text{ L/mol} \cdot \text{s}$

The effect of extracted metals on the TBP hydrolysis is of great practical interest. The data on TBP hydrolysis in the presence of uranium (IV, VI), thorium and zirconium which are published in the review (Solovkin et al, 1985), are not consistent and do not allow estimation of this effect quantitatively.

EXPERIMENTAL WORK

The purification of TBP from HDBP was carried out by repeated washing with 5% soda solution. The effect of rare metals nature on TBP hydrolysis and the rate of this process was studied using model solutions from these metals extracts. The RE extracts were prepared by the extraction of these metals with 100% TBP from aqueous nitric acid solutions. Thorium and zirconium extracts were obtained by extraction with TBP, in equilibrium with 4 mol/L HNO_3 . Concentration of H_2O in organic phase was determined using Fisher's method. Metal concentration was measured by volumetric titration with Complexon III, HNO_3 concentration in alkalimetric manner. The rate of TBP hydrolysis in the model solution is calculated on the basis of data on HDBP accumulation in definite intervals of time at $298 \pm 2 \text{ K}$, HDBP concentration was found by extraction – spectrometric method with Saphroninum-T (Klygin et al, 1977). IR spectra of metal extracts were measured by IR-spectrometer SPECORD/M80 in KRS glass.

RESULTS AND DISCUSSION

We supposed that only those TBP molecules which are linked in complexes with HNO_3 and nitrate of appropriate metal mainly undergo hydrolysis. For this reason we considered HDBP concentration received experimentally as a summary one. One part of HDBP is formed as a result of TBP hydrolysis under the effect of metal, another part – under the effect of HNO_3 . The quantity of HDBP formed in the latter case can be estimated using the constant of TBP hydrolysis in the presence of HNO_3 (Sinegribova et al, 1990). Composition of model solutions and experimental results are given in Table 1.

TABLE 1
HDBP concentration in model solutions

N	Me	τ_k , days	$C_5 \cdot 10^4$	$C_6 \cdot 10^4$	$C_7 \cdot 10^4$	$K_h^M \cdot 10^{10}$ L/mol·s
For RE: $C_1=0.1$ mol/L; $C_2=0.1$ mol/L; $C_3=0.3$ mol/L For Th and Zr: $C_3=0.2$ mol/L						
1	Gd	71	6.76	3.88	2.88	0.9
2	Dy	56	3.70	2.62	1.07	0.5
3	Y	60	7.43	2.86	4.56	1.9
4	Yb	61	9.60	2.76	6.84	3.0
5	Th	49	58.1	2.69	55.4	40
6	Zn	35	18.4	2.12	16.3	20
For RE: $C_1=0.2$ mol/L; $C_2=0.2$ mol/L; $C_3=0.6$ mol/L For Th and Zr: $C_3=0.4$ mol/L						
7	La	67	13.2	5.10	8.12	1.9
8	Nd	67	14.5	5.39	9.68	2.0
9	Eu	70	15.6	5.85	9.76	2.0
10	Gd	70	15.0	4.98	9.97	2.4
11	Y	69	20.6	5.17	15.5	3.6
12	Yb	50	19.6	4.52	15.1	4.0
13	Yb	63	24.3	5.70	18.6	3.9
14	Th	40	68.8	3.30	65.5	40
15	Zr	35	49.6	4.19	45.4	20

C_1 – metal concentration in organic phase;

C_2 – concentration of HNO_3 ;

C_3 – concentration TBP linked in complex with metal nitrate;

C_4 – concentration TBP linked in complex with HNO_3 ;

C_5 – HDBP summary concentration;

C_6 – concentration of HDBP formed by hydrolysis under effect of HNO_3 ;

C_7 – concentration of HDBP formed by hydrolysis under effect of metal; mol/L

As the result of the study the following values of the TBP hydrolysis rate constants under the effect of metals were estimated: La - $1.9 \cdot 10^{-10}$, Nd - $2.0 \cdot 10^{-10}$, Eu - $2.0 \cdot 10^{-10}$, Gd - $1.7 \cdot 10^{-10}$, Dy - $0.5 \cdot 10^{-10}$, Y - $2.8 \cdot 10^{-10}$, Yb - $3.6 \cdot 10^{-10}$, Th - $0.4 \cdot 10^{-8}$, Zr - $0.2 \cdot 10^{-8}$ L/mol·s.

It is known (Moskvin, 1975), that stability of extracted complexes correlates with the shift of frequency of P=O group valent vibrations. One can suppose that TBP hydrolysis under the effect of metal is the more active the more stable an extracted complex is. The frequency (ν , nm^{-1}) of P=O group valent vibrations is: for dried TBP - 1274; TBP saturated with water - 1260; the extracts of: La - 1212, Nd - 1198, Eu - 1204, Gd - 1208, Dy - 1207, Y - 1212, Yb - 1220, Th - 1182, Zr - 1160. The frequency shift ($\Delta\nu$, nm^{-1}): for TBP saturated with water - 14, for extracts: La - 62, Nd - 76, Eu - 70, Gd - 66, Dy - 67, Y - 62, Yb - 54, Th - 92, Zr - 114.

These data satisfactorily correlate with the obtained TBP hydrolysis constants in the presence of these metals. They are close to the values in the presence of HNO_3 . The constants for Th and Zr differ considerably from the constants for RE.

The rate of TBP hydrolysis in processing RE at Sillamyae chemical and metallurgical Plant was calculated using these values K_h^H and K_h^M . Nitric acid solutions of RE are processed in 4 extraction cycles with 100% TBP in ESCAR mixer-settlers (Sklokin et al, 1988).

Quantitative extraction of RE from aqueous solution with their simultaneous purification from alkaline-earth elements and ammonium ions are carried out in the first cycle. Lanthanum and cerium concentrates are produced in the second cycle. Diodymium concentrate is done in the third cycle, neodymium and RE of the middle group - in the fourth cycle. The number of mixer-settlers stages in these cycles is: 1-16, 2-87, 3-65, 4-70. Feed aqueous solutions of each of the following cycles are strip products from the preceeding extraction operation, the volume of which is reduced several times by evaporation. RE and HNO_3 concentrations in organic phase of all mixer-settlers are approximately 120-140 g/L and 20 g/L; the phase ratio (O/A) is 1.5 to 2. The total residence time of organic phase in tanks is about 3000 s, mixing chambers - 150-300 s and in separating chambers 800-1500 s.

Taking into account the percentage composition of RE in each extraction cycle, the number of mixer-settler stages and the volumes of organic solutions in all equipment, the rates of HDBP accumulation in the process considered are: for the first cycle $2.2 \cdot 10^{-13}$, the second - $0.9 \cdot 10^{-13}$, the third - $2.6 \cdot 10^{-13}$ and the fourth - $3.5 \cdot 10^{-13}$ g/L·s.

The solubility of HDBP-metal complexes in organic phase perhaps is determined by HNO_3 concentration. The solubility of Nd and Y dibutylphosphates in TBP containing different quantities of HNO_3 is also obtained here. Results are presented in Table 2.

TABLE 2

Solubility (g/L Me) of neodymium and yttrium dibutylphosphates in TBP, containing HNO_3 .

Concentration HNO_3 in TBP, mol/L	0.09	0.24	0.47	0.66	0.94	1.10
Concentration Nd, g/L	6.0	14.5	28.3	39.5	55.5	65.0
Concentration Y, g/L	—	—	1.3	2.7	5.6	8.8

The products of TBP hydrolysis can be removed by ammonium carbonate washing, as HDBP ammonium salt is soluble in aqueous solution. However, RE carbonates formed under this washing have low solubility. To prevent the formation of RE precipitates it is necessary to add a complexing agent into the washing solution. We used EDTA (Table 3).

TABLE 3

Stripping of Nd from organic phase by ammonium carbonate solutions in presence of EDTA.

Feed organic phase: 100% TBP; 0.4 g/L HDBP; 1.09 g/L Nd.

O/A = 1, T = 298 K, τ_k = 10 min.

N	Feed washing solution	Solution after washing	
	ammonium carbonate,g/L	EDTA, g/L	Nd, g/L
1	100	0.43	0.45
2	100	0.86	0.67
3	100	1.29	0.75
4	100	1.72	0.78
5	100	4.30	0.80
6	100	6.45	.81
7	100	8.60	0.83
8	75	8.60	0.82
9	50	8.60	0.82
10	25	8.60	0.77

As the densities of organic and aqueous phase are almost the same, 100% TBP washing by ammonium carbonate was done in centrifugal extractors EC-33 (Kuznetsov et al, 1986). the data on the dependence of stage efficiency (Treybal, 1966) upon phase contact time are given in Table 4.

TABLE 4

Effect of phase contact time (τ_k) on centrifugal extractor efficiency (E) and stripping of neodymium.

Centrifugal extractor EC-33, T - 298 K

Feed solutions: organic - 100% TBP, Nd - 1.09 g/L, HDBP - 1.3g/L;

aqueous - ammonium carbonate - 100g/L, EDTA - 8.6 g/L.

N O/A			E				Solution after washing Nd,g/L				
			τ_k, s				τ_k, s				
			2	5	10	15	2	5	10	15	600
1	2.5	0.63	0.82	0.92	—	—	0.7	0.79	0.92	—	1.0
2	2.0	—	0.55	0.75	0.90	—	—	0.55	0.80	0.95	1.0
3	2.0	0.55	0.68	0.78	0.80	0.80	0.5	0.63	0.75	0.75	0.98
4	1.0	0.28	0.52	0.83	0.85	0.85	0.36	0.55	0.77	0.86	0.98

These results indicate the possibility of centrifugal extractors application for washing 100% TBP with ammonium carbonate solution in RE extraction from loparite concentrate.

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3.12

**DETERMINATION OF EXTRACTION MECHANISMS OF IMIDO-
DIPHOSPHORYL EXTRACTANTS BY TWO-PHASE POTENTIOMETRY**

Neil V. JARVIS

Department of Process Technology, Atomic Energy Corporation of South Africa Ltd,
PO Box 582, Pretoria, 0001, South Africa.

Leon KRÜGER and Jan G. H. DU PREEZ

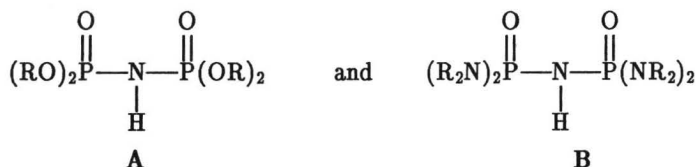
Uranium Chemistry Research Unit, University of Port Elizabeth, PO Box 1600, Port
Elizabeth, 6000, South Africa.

ABSTRACT

Imidodiphosphoryl extractants with the structures $[(R_2N)_2P(O)]_2NH$ and $[(RO)_2P(O)]_2NH$ have been studied as possible extractants for trivalent f-transition metal ions with applications in the nuclear and rare earth industries. The extractants show promise but structures will have to be optimised. Extraction mechanisms for trivalent rare earth metal ions were determined by two-phase potentiometry. Data were analysed in a new way using the programs SUPERQUAD and ESTA which were originally written for determining formation constants in aqueous solutions from potentiometric data. It was found that the programs could be used to model two-phase systems if experimental conditions were carefully chosen and corrections were made. It was shown that formation functions defined for single phase systems could be used in model selection in two-phase systems. Extraction mechanisms found were complicated with a number of species being formed in the organic phase. Besides extraction equilibrium constants and separation factors, the extraction aggregation and partition constants could be calculated. Acid dissociation constants needed in the calculations were determined using water-soluble analogues of the hydrophobic extractants.

INTRODUCTION

Imididiphosphoryl complexing agents of the following two forms were investigated:

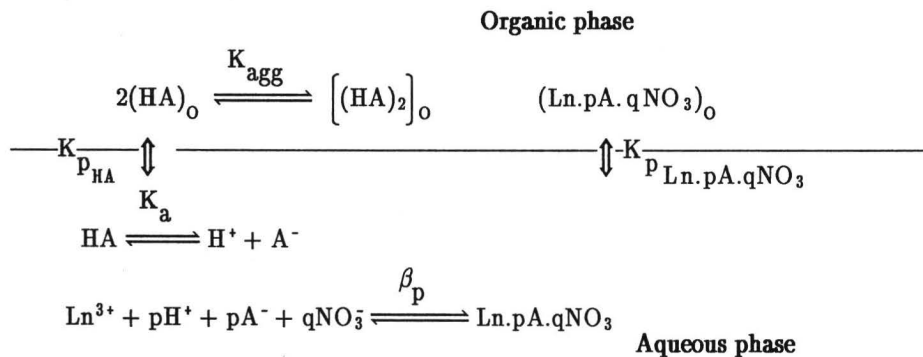


Two-phase potentiometry was used to elucidate extraction mechanisms for trivalent lanthanides as well as to calculate the fundamental constants of the extractants themselves. The data were submitted to the programs SUPERQUAD (A) and ESTA (B). This represents a novel use of these programs which were originally written to calculate formation constants from potentiometric data obtained from aqueous experiments.

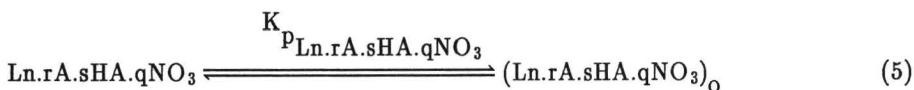
The work reported here was done using R = dodecyl for A (ITDDPP) and R = butyl for B (OBIPA). Water-soluble analogues used to determine pK_a 's were R = ethyl for A (ITEPP) and R = methyl for B (OMIPA).

THEORY

The extraction mechanism may be schematically represented as:

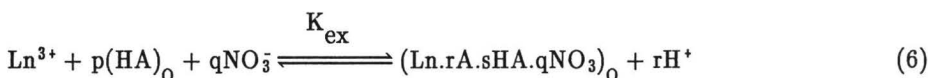


The equilibria involved are:



where $r + s = p$.

The extractant complete with its imidic proton is denoted by HA. Subscript o means the species is in the organic phase. The overall reaction is given by:



where K_{ex} is the extraction equilibrium constant, $r + s = p$ and $r + q = 3$. The latter sum must be such that organic phase species must be neutral in order to be soluble in organic diluents such as toluene which have low dielectric constants.

EXPERIMENTAL

Two-phase potentiometric titrations in the absence and presence of metal ions were carried out using a Metrohm Titroprocessor 670 with Metrohm single glass and reference electrodes. Experimental conditions were carefully chosen in order to minimise error sources in the data used by the programs. Organic to aqueous ratios were in the order of 1:10, temperature was 20 °C, $I = 1.0 \text{ M NaNO}_3$ and titration

volumes were 20 ml or until third-phase formation in the case of ITDDPP. Various ratios extractant:nitric acid or extractant:metal ion were used. the diluent was toluene. Aqueous solubility of the extractants was checked at various pH values by determining P in aqueous phases by ICP. Both extractants were found to be sparingly soluble. Na extraction was checked by AES and found to be negligible for ITDDPP but appreciable for OBIPA.

RESULTS AND DISCUSSION

Fundamental constants

pK_a values of the water-soluble analogues were calculated as shown in Table 1.

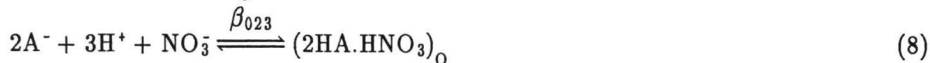
TABLE 1

Ligand	pK_{a1}	pK_{a2}	R-factor ESTA	σ SUPERQUAD	χ^2
ITEPP	4.16(0.005)			3.16	13.36
OMIPA	9.04(0.003)	3.00(0.006)	0.00694		

The pK_a of the extractants were assumed to be very similar to those of the water-soluble analogues.

The protonation formation curves for OBIPA could be obtained using the ESTA0 module. These are in Figure 1 and assisted in model selection.

Potentiometry yielded the following model for the extractants:



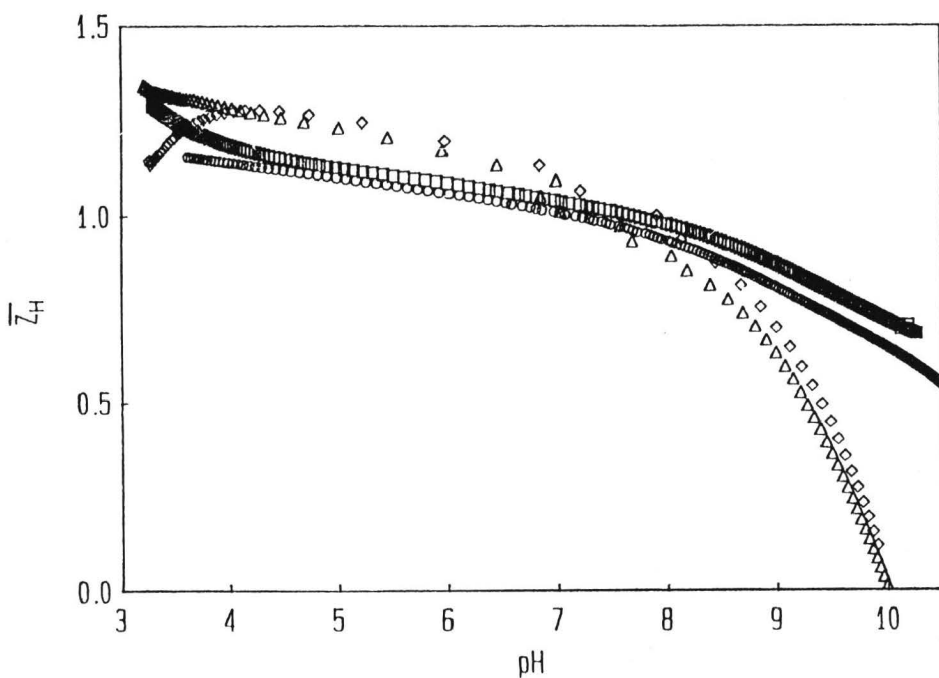


Figure 1. Protonation formation function, $\bar{Z}_H$, curves for OBIPA.

The species on the right hand side of the above equilibria must be in the organic phase even though the programs consider them to be in the aqueous phase. A simple volume correction factor of V_a/V_o may be employed in order to allow for this. The programs gave values for the constants as shown in Table 2.

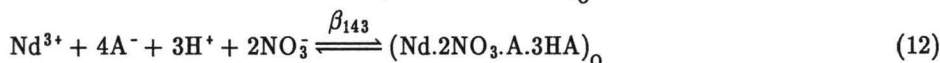
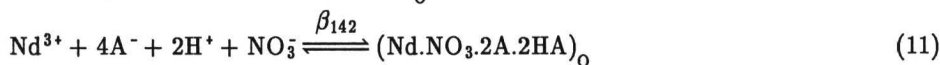
TABLE 2

Ligand	Equilibrium	$\log\beta$	σ	χ^2	R-factor
ITDDPP	011	7.80(0.01)			
	023	22.56(0.03)	5.31	32.24	
	022	18.81(0.009)	1.02	10.53	
OBIPA	011	10.17(0.01)			
	023	26.45(0.04)			
	022	22.77(0.03)			0.095

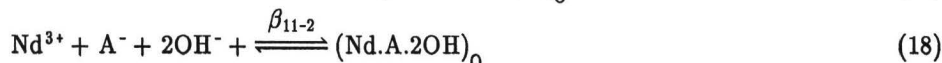
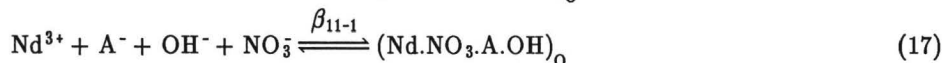
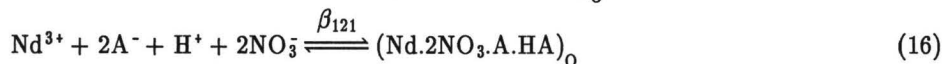
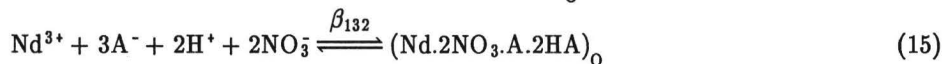
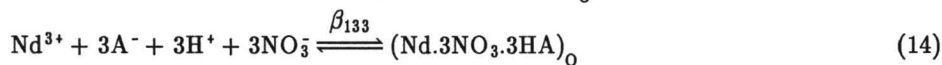
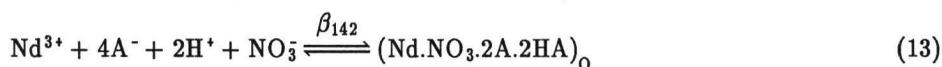
Now it can be shown that $K_{P_{HA}} = \beta_{011} \cdot K_a$ and $K_{agg} = \beta_{022} \cdot K_a^2$. Extractant partition constants were calculated to be 4.36×10^3 and 1.92×10^2 for ITDDPP and OBIPA respectively. Using results of P analyses of both phases, $K_{P_{HA}}$ was found to be $(2.23 \pm 0.251) \times 10^2$ for OBIPA which is in close agreement. Extractant dimerisation constants were found to be 2.95×10^{10} and 18.5 M^{-1} for ITDDPP and OBIPA respectively. K_{ex} constants could be calculated for the 023 complex from the formula $K_{023} = \beta_{023} \cdot K_a^2 / K_{P_{HA}}^2$. These were found to be 1.22×10^8 and $7.54 \times 10^3 \text{ M}^{-3}$ respectively for ITDDPP and OBIPA.

Extraction of trivalent lanthanides

For ITDDPP, the following model was obtained for Nd(III):



For OBIPA, the following model was obtained for Nd(III) (similar models were also obtained for Y(III), Yb(III) and Eu(III) but only the Nd(III) results will be presented here in order to compare with the ITDDPP results):



For ITDDPP, SUPERQUAD gave values for the constants as shown in Table 3.

TABLE 3

Complex	$\log\beta$	σ	χ^2
141	35.89(0.005)	1.657	14.40
142	39.69(0.003)		
143	42.95(0.007)		

This model was successfully checked by simulating experimental distribution curves.

For OBIPA, ESTA gave values for the constants as given in Table 4. Hydrolysis constants, $\log\beta_{011}$, $\log\beta_{023}$ and $\log\beta_{022}$ values obtained above were included in the models and fixed during refinement procedures. The OBIPA model could be checked using the QBAR task in ESTA1. This module calculates the $\overline{Q}$ (deprotonation function) for both experimental and calculated data. A good fit was obtained bearing in mind that ESTA could not make volume corrections for species in the organic phase. The results are given in Figure 2 (points = experimental, solid lines = calculated from model, dotted line = protonation formation curve of OBIPA in the absence of metal).

TABLE 4

Complex	$\log\beta$	R-factor
142	39.76(0.02)	0.0205
133	39.09(0.02)	
132	33.47(0.03)	
121	20.27(0.02)	
11-1	12.47(0.01)	
11-2	17.00(0.01)	

The more familiar K_{ex} constants could then be calculated. Species distribution curves obtained by the SPEC task in ESTA1 then enabled the calculation of distribution constants and curves as well as separation factors.

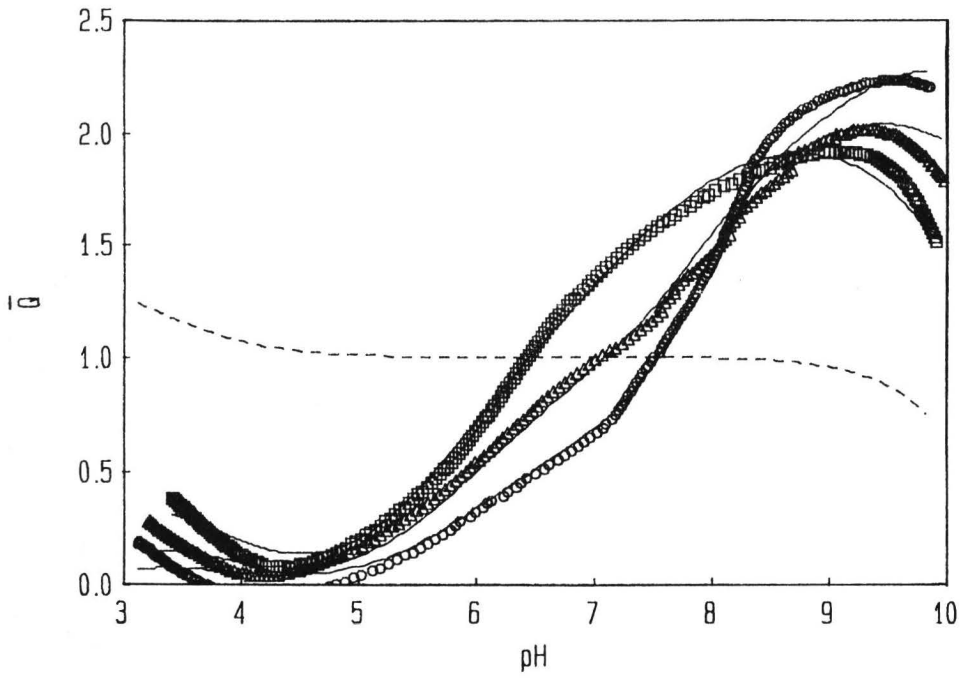


Figure 2. Model fitting for Nd(III) extraction by OBIPA.

3.13

**EQUILIBRIUM AND EXTRACTION KINETICS OF Eu(III) AND Gd(III)
BY DI-(2-ETHYLHEXYL) PHOSPHORIC ACID IN BENZENE
FROM PHOSPHATE MEDIUM**

J.A.DAoud, S.M.KHALIFA, M.GASSER AND H.F.ALY

Hot Laboratories Centre
Atomic Energy Authority
Post Code 13758, Egypt

ABSTRACT

The extraction of radioactive europium(III) and gadolinium(III) from buffered phosphate medium of low pH by di-(2-ethylhexyl) phosphoric acid (HDEHP) in benzene has been investigated. The effect of the different parameters affecting the extraction of both cations was studied and the stoichiometry of the extracted species was elucidated. The kinetics of Eu(III) extraction has been carried out using a stirred Lewis cell. The effect of the rate of stirring, [buffer], [HDEHP] and $[H^+]$ as well as temperature on the rate of extraction were studied.

INTRODUCTION

Phosphoric acid produced from phosphate ores by the wet process contains small amounts of uranium together with some lanthanides. The extraction of these lanthanides is of major importance for the recovery of high purity uranium. HDEHP has been proved an effective extractant in the separation of lanthanides and actinides from hydrochloric and nitrate media, Liljenzin et al. (1979), Haiduc et al. (1986), Lin and Huang (1988). However, little work is reported on its extraction from phosphoric acid. Rao et al. (1986) have shown from their study on the phosphate complexation of Am(III) that different phosphate species are present at different pH of the medium. Jia et al. (1989) studied the kinetics of extraction of U(VI) from phosphoric acid solution using a Lewis cell and showed

that the extraction rate of uranium is controlled by the chemical reaction at the interface.

The present work is directed to study the equilibrium of extraction of radioactive Eu(III) and Gd(III) by HDEHP in benzene from phosphate medium of low pH. Kinetic investigations were carried out on Eu(III) to learn about its mechanism of extraction.

EXPERIMENTAL

Chemicals and reagents

All chemicals used were of analytical reagent grade and used without further purification. Bis-(2-ethylhexyl)phosphoric acid (HDEHP) was supplied by Union Carbide Corporation, USA. Benzene was an AR product of BDH, England. The aqueous medium was a buffer solution of sodium dihydrogen phosphate (BDH) and phosphoric acid (BDH) in equal molar concentrations giving a pH=2. $^{152+154}\text{Eu}$ was prepared by neutron irradiation of spectroscopically pure europium oxide while ^{153}Gd was supplied by Amersham (England) and these were used in concentrations less than 10^{-6}M .

Procedure

Equal volumes of a benzene solution containing HDEHP and an aqueous phosphate solution were pre-equilibrated before the addition of the radioactive tracer. The two phases were then mechanically shaken at constant temperature for 30 min to reach equilibrium. Equal volumes were taken from both phases for γ -radiometric assay using a scintillation counting assembly. The distribution ratio (D) was calculated from the counting of both phases with a standard deviation of $\pm 3.5\%$.

In kinetic investigations, an equal volume of the pre-equilibrated organic phase was carefully transferred with an equal volume of the pre-equilibrated aqueous phase containing the radioactive tracer into a double-jacket Lewis cell connected to a Julabo circulator. The reaction was begun by starting the stirring motor at 350 min^{-1} . At various time intervals equal volumes were withdrawn from the two phases and

assayed radiometrically as previously reported (Daoud et al.(1991)),until constant values were reached at equilibrium.The radioactivity measured in the organic phase at time t and at equilibrium are denoted by A and A_{eq} ,respectively.The plots of $\log(A_{eq}-A)$ versus time (t) yielded straight lines indicating a first order reaction.The different values of the observed rate constant (k_{obs}) were calculated from the respective slopes of the straight lines obtained.

RESULTS AND DISCUSSION

The effect of buffer concentration on the extraction of either nuclide was studied by varying its concentration from 10^{-3} to $5 \times 10^{-2} M$ while keeping the ratio of $H_3PO_4:NaH_2PO_4$ constant at 1:1. The results represented in Fig.1 show that the distribution ratios of Eu(III) and Gd(III) have nearly the same value and remains constant up to buffer concentration $3 \times 10^{-3} M$. With further increase in the buffer concentration, the distribution ratio decreases to give straight line relations of slope -1.This decrease can be related to the formation of the non-extracted phosphate complexes of Eu(III) or Gd(III) at high buffer concentrations.

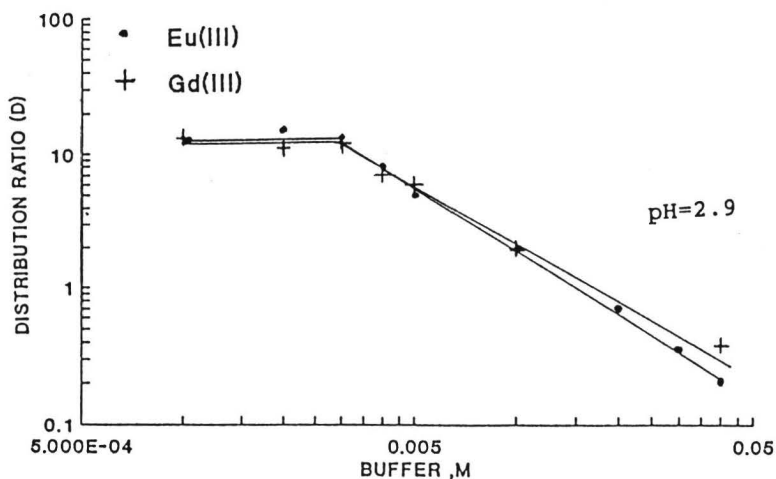


Fig. 1 Effect of [buffer]

An increase in $[H^+]$ was found to decrease the extraction of the investigated cations and linear relations of slope -1 are observed in the log-log relation, Fig. 2. However, the slope of these relations was found to decrease from -1.8 to -1 as the buffer concentration decreased from 0.01 to 0.002M in the case of Eu(III), while the slope remained -1 in the case of Gd(III) extraction. This change in the slope could be related to the formation of different extractable europium species.

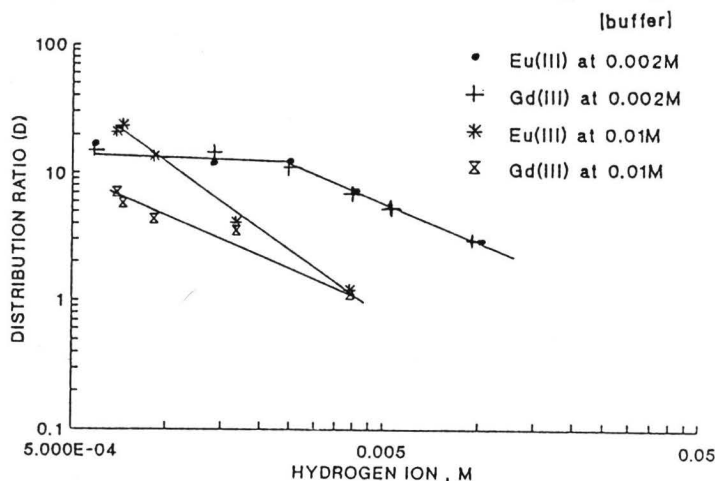


Fig. 2 Effect of $[H^+]$

The increase in [HDEHP] was found to increase the extraction of Eu(III) and Gd(III) and slopes of 3 were obtained from the log-log relations of D vs [HDEHP], Fig. 3.

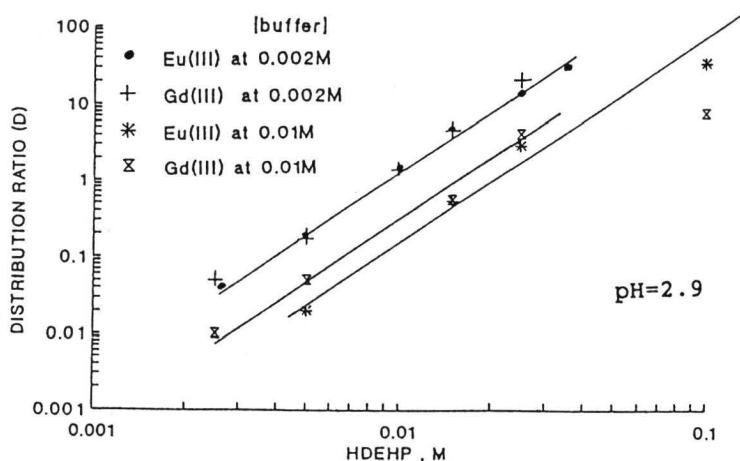
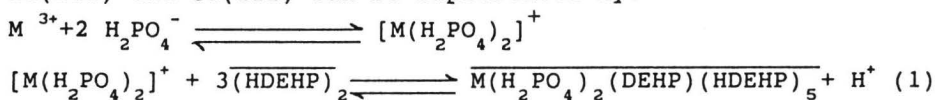


Fig. 3 Effect of [HDEHP]

According to Rao et al.(1986),the predominating species in the aqueous phosphate medium of low pH is H_2PO_4^- .Therefore, and based on the above results,the equilibrium of extraction of Eu(III) and Gd(III) can be represented by:



where $\text{M}^{3+} = \text{Eu}^{3+}$ or Gd^{3+} and bars refer to organic phase.

The extraction constant for the reaction, K_{ex} , is given by

$$K_{\text{ex}} = \frac{D [\text{H}^+]}{[(\overline{\text{HDEHP}})_2]^3} \quad (2)$$

The data obtained for K_{Eu} and K_{Gd} at different $[\text{H}^+]$ and $[\overline{\text{HDEHP}}]$ are listed in Table 1, giving mean values of $1.85 \pm 0.03 \times 10^3$ and $1.76 \pm 0.05 \times 10^3$ for Eu(III) and Gd(III), respectively. The results obtained show the possibility of extraction of the two cations to the same extent from phosphate buffer of concentration $< 3 \times 10^{-3} \text{M}$ and $\text{pH} = 2.9$ (Fig.1).

TABLE 1

Extraction constants, K_{ex} , of Eu(III) and Gd(III) extracted by HDEHP in benzene from phosphate medium.

Extracted species	$[\overline{\text{HDEHP}}]$	$K_{\text{ex}} \times 10^{-3}$	$[\text{H}^+] \times 10^3$	$K_{\text{ex}} \times 10^{-3}$
$\text{Eu}(\text{H}_2\text{PO}_4)_2(\text{DEHP})(\overline{\text{HDEHP}})_5$				
	0.005	1.81	10	1.86
	0.010	1.83	5.3	1.88
	0.015	1.83	2.5	1.87

Mean value, $K_{\text{ex}} \times 10^{-3}$		1.82		1.87
Total mean value			1.85 ± 0.03	
$\text{Gd}(\text{H}_2\text{PO}_4)_2(\text{DEHP})(\overline{\text{HDEHP}})_5$				
	0.005	1.71	9.6	1.77
	0.010	1.76	5.3	1.81
	0.015	1.76	2.5	1.76

Mean value, $K_{\text{ex}} \times 10^{-3}$		1.74		1.78
Total mean value			1.76 ± 0.03	

Kinetic investigations

Kinetic investigations were carried out on Eu(III) extraction to learn about its extraction mechanism.

The experimental results of the effect of stirring speed on the rate of extraction of Eu(III) from 50 to 400 min⁻¹ have shown that the rate of extraction becomes independent of the stirring speed in the range 300-400 min⁻¹. In this region the thickness of the diffusion film between the two phases decreases to a constant value leading to a minimal contribution of diffusion and the chemical reactions at the interface then becomes the rate controlling process, as reported by Danesi and Chirizia (1980).

The effect of [buffer], [H⁺] and [HDEHP] on the extraction rate was separately investigated and the obtained values of k_{obs} are given in Table 2. The tabulated data show that k_{obs} decreases with the increase in [buffer] and increases with the increase in [HDEHP] while the increase in [H⁺] has a negligible effect. Slope analysis of the experimental results plotted as log-log relations in Fig.4 indicates that the rate of extraction of Eu(III) is first-order dependent on [HDEHP] and inverse first-order dependent on buffer concentration.

Based on the above results, the extraction rate can be expressed as follows:

$$-d[\text{Eu(III)}] / dt = k [\text{HDEHP}] [\text{buffer}]^{-1}$$

TABLE 2

Kinetic data for Eu(III) extraction by HDEHP
from phosphate medium

A)-Dependence on [buffer]

pH=2.8

T=25°C

[HDEHP]=0.05M

rate=350 min⁻¹

[buffer], M	k_{obs} , min ⁻¹
0.001	0.155
0.0015	0.106
0.0025	0.065
0.0030	0.052

The slope of log k_{obs} vs log [buffer] relation is -1 ± 0.01
cont.

B)-Dependence on $[H^+]$

$[buffer]=0.002M$ $T=25\pm 0.01^\circ C$ $[HDEHP]=0.05M$
 $rate=350 \text{ min}^{-1}$

$[H^+], M$	k_{obs}, min^{-1}
6.3×10^{-4}	0.22
1.25×10^{-3}	0.25
2.5×10^{-3}	0.32
4.17×10^{-3}	0.38

The slope of $\log k_{obs}$ vs $\log [H^+]$ relation is 0.2 ± 0.01

C)-Dependence on $[HDEHP]$

$[buffer]=0.002M$ $T=25\pm 0.01^\circ C$ $pH=2.8$
 $rate=350 \text{ min}^{-1}$

$[HDEHP], M$	k_{obs}, min^{-1}
0.0050	0.29
0.0075	0.42
0.0100	0.61
0.0150	0.78

The slope of $\log k_{obs}$ vs $\log [HDEHP]$ relation is 1.05 ± 0.01

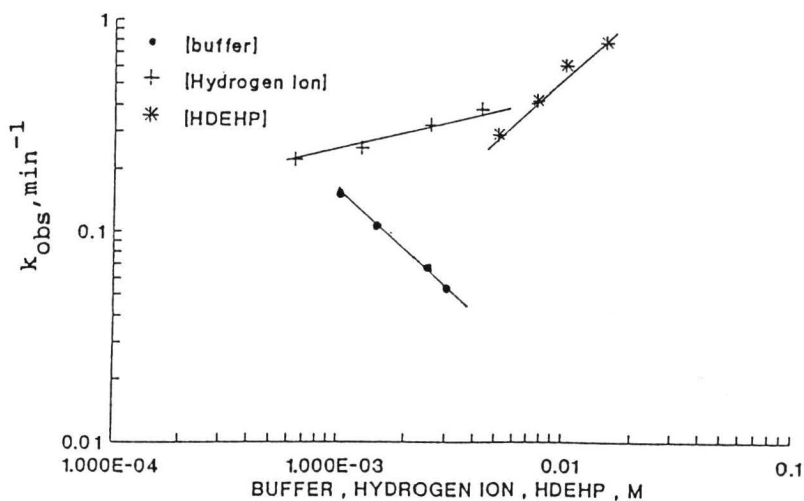


Fig. 4 Effect of $[buffer]$, $[H^+]$ and $[HDEHP]$ on the reaction rate

The effect of temperature on the extraction rate was studied to evaluate the thermodynamic parameters of the investigated

system. The data followed the usual Arrhenius equation. The energy of activation (E), the heat of activation (ΔH^*) and the entropy of activation (ΔS^*) were found to be $35.51 \pm 0.4 \text{ kJ mol}^{-1}$, $33.01 \pm 0.3 \text{ kJ mol}^{-1}$ and $-180.37 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. As reported by Laidler (1975), the effect of temperature on the rate of reaction governed by diffusion is less pronounced than that controlled by the chemical process and the activation energy in the case of the former does not exceed 20.9 kJ mol^{-1} . Consequently, the obtained value of E (35.5 kJ mol^{-1}) justifies that the chemical process is the rate determining factor in the extraction of Eu(III) under the experimental conditions used.

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3.14

EFFECT OF DILUENTS ON SYNERGISTIC EXTRACTION OF LANTHANOIDS WITH ORGANOPHOSPHORUS COMPOUNDS

Kazuo KONDO

Department of Chemical Engineering
Doshisha University
Karasuma-Imadegawa, Kamigyo-ku, Kyoto 602, JAPAN

ABSTRACT

The effect of diluents on the synergistic extraction of rare-earth elements with organophosphorus compounds and 1,10-phenanthroline was investigated. The organophosphorus compounds used were di(2-ethylhexyl)phosphoric acid, diisodecylphosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, dibutylmonothiophosphoric acid and didodecylmonothiophosphoric acid. Using these extractants, the synergistic extraction of typical rare-earths, lanthanum, europium and gadolinium were carried out in n-heptane or toluene diluent.

INTRODUCTION

A number of studies of extraction of the rare-earth metals have been carried out using acidic organophosphorus extractants. However, few studies of the synergistic extraction of lanthanide ions have been reported. Hirashima et al. (1976) studied the synergistic extraction of some lanthanide ions with a mixture of di(2-ethylhexyl)phosphoric acid (hereafter abbreviated D2EHPA) and thenoyltrifluoroacetone and concluded that the magnitude of synergistic enhancement is relatively small. Nag et al. (1977) carried out the synergistic extraction of neodymium with a mixture of 1,1,1-trifluoro-4(2-thienyl)-4-mercaptobut-3-en-2-one and some neutral donors such as dipyridyl and clarified the extracted species by synergism.

In the present study, the synergistic extraction of rare-earth metals with mixed extractants of some organophosphorus compounds and 1,10-phenanthroline (Phen) is carried out using n-heptane or toluene as the diluent. Three synergistic extraction systems are examined. One of them is the extraction of lanthanum (La) or gadolinium (Gd) with a mixture of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and Phen. The second one is the extraction of europium (Eu) with a mixture of D2EHPA or diisodecylphosphoric acid (DIDPA) and Phen. The last one is the extraction of Eu with a mixture of dibutylmonothiophosphoric acid (DBTPA) or didodecylmonothiophosphoric acid (DDTPA) and Phen.

EXPERIMENTAL

Reagents

The extractants, DBTPA and DDTPA were synthesized according to Pesin (1961) as ammonium salts by the interaction of the dialkyl phosphite and sulfur under ammoniacal atmosphere. The other extractants were kindly supplied by Daihachi Chemical Co. in Japan. Other organic and inorganic chemicals used, that is, n-heptane, toluene, Phen, hydrochloric acid, sodium acetate, hexahydrates of europium chloride and gadolinium chloride and heptahydrate of lanthanum chloride were guaranteed reagent grade.

Measurement of distribution ratio of Phen

The distribution ratio of Phen between n-heptane or toluene and water was measured. The pH of the aqueous solution was adjusted using 1 kmol/m³ hydrochloric acid-sodium acetate buffer solution containing Phen of known concentration. Equal volumes of the aqueous and organic solutions were shaken at 303K for 24 hours to attain equilibrium. After phase separation, Phen in the organic phase was redistributed into 1 kmol/m³ hydrochloric acid. The Phen concentrations in the two aqueous solutions were determined by a spectrophotometer.

Measurement of extraction equilibria of rare-earth elements

First the extraction equilibrium of the metal with each main extractant was measured at 303K. The organic phase was prepared by dissolving the extractant in the diluent. The aqueous solution was prepared by dissolving the metal chloride in 100 mol/m³ hydrochloric acid-sodium acetate solution whose pH was adjusted. Then measurement of the synergistic extraction of the rare-earth metals was carried out. The organic phase was prepared by further dissolving Phen in the diluent containing the main extractant. The concentration of the lanthanide ion was determined by the Arsenazo III method using the spectrophotometer.

RESULTS AND DISCUSSION

Distribution equilibrium of Phen

Phen is protonated to $\text{Phen} \cdot \text{H}^+$ in acidic aqueous solution. The distribution ratio of Phen, D_{ph} , is defined by Eq. (1).

$$D_{\text{ph}} = C_{\text{ph,org}} / (C_{\text{ph,aq}} + C_{\text{phH,aq}}) \quad (1)$$

where C_{ph} and C_{phH} are the concentrations of Phen and $\text{Phen} \cdot \text{H}^+$, respectively. Defining the partition constant of Phen, $K_{\text{d,ph}}$, by Eq. (2),

$$K_{\text{d,ph}} = C_{\text{ph,org}} / C_{\text{ph,aq}} \quad (2)$$

the following equation is obtained.

$$D_{\text{ph}} = K_{\text{d,ph}} / (1 + C_{\text{H}} / K_{\text{a,ph}}) \quad (3)$$

where $K_{\text{a,ph}}$ is the acid dissociation constant of $\text{Phen} \cdot \text{H}^+$. The relation between D_{ph} and pH is shown in Fig.1 in the case of n-heptane diluent. The values of $K_{\text{d,ph}}$ and $K_{\text{a,ph}}$ were obtained

from Fig.1 and are listed in Table 1 along with the results of toluene diluent.

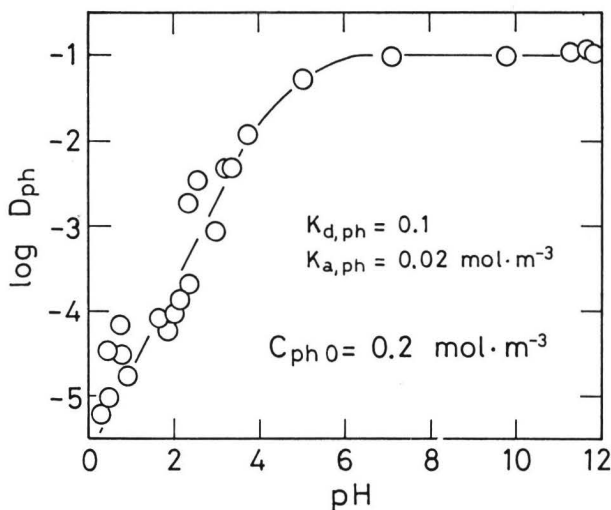


Fig.1 Distribution ratio of phenanthroline

TABLE 1

Values of $K_{d,ph}$ and $K_{a,ph}$		
Diluent	$K_{d,ph}$	$K_{a,ph} \cdot \text{mol/m}^3$
n-Heptane	0.1	0.02
Toluene	3.6	0.02

Synergistic extraction of La or Gd with a mixture of EHPNA and Phen

In the extraction of Gd, it was found that no synergistic extraction was observed in either diluent. Instead the extent of Gd extracted was lowered by addition of Phen. This may be considered to be due to the formation of a stable complex between Gd and Phen in the aqueous phase.

Typical results of La extraction are shown in Fig.2. A synergistic effect was shown in the case of toluene diluent, but no synergistic extraction was observed for n-heptane diluent. Figure 3 shows the effects of Phen concentration on the extent of La extracted. E. Toluene diluent gives a large synergism whereas n-heptane shows a negative synergistic effect. Hereafter, the synergistic extraction of La for the toluene diluent will be discussed quantitatively. First the extraction mechanism of La with EHPNA (HR) alone is considered. Assuming that lanthanum is extracted as a complex of composition, $\text{LaR}_3 \cdot x\text{HR}$, into the organic solution with the dimer of EHPNA.

(HR)₂, the extraction equilibrium can be expressed as follows.

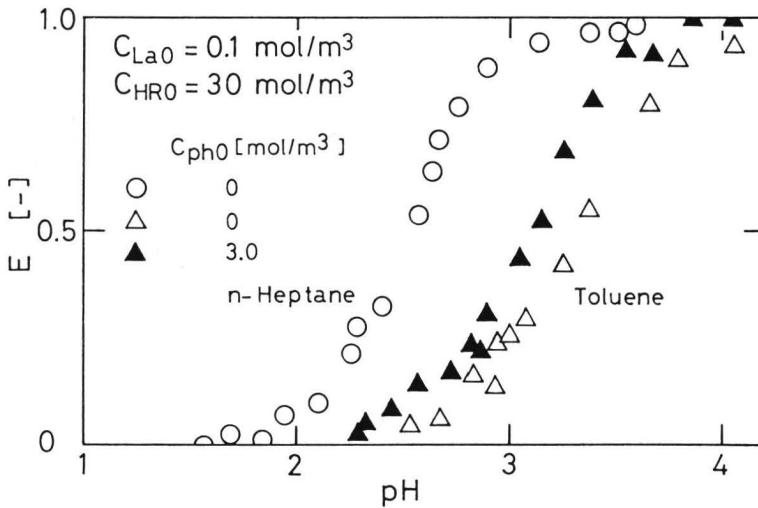


Fig.2 Synergistic extraction of La with EHPNA and Phen

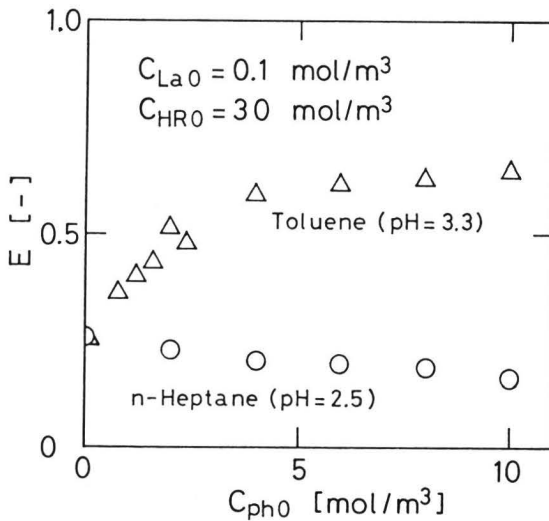
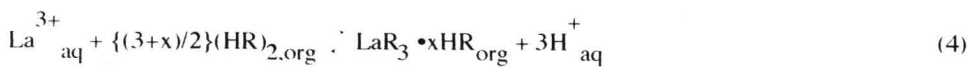


Fig.3 Effect of Phen concentration on synergistic extraction of La



The distribution ratio of La, D , is given by Eq. (5).

$$D = C_{\text{La,org}} / C_{\text{La,aq}} = K_{\text{ex}} C_{(\text{HR})_2}^{(3+x)/2} / C_{\text{H}}^3 \quad (5)$$

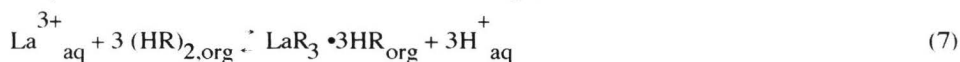
where K_{ex} is the extraction equilibrium constant. Equation (5) is rewritten as follows.

$$\log (DC_H^3) = \{(3+x)/2\} \log C_{(HR)2} + \log K_{ex} \quad (6)$$

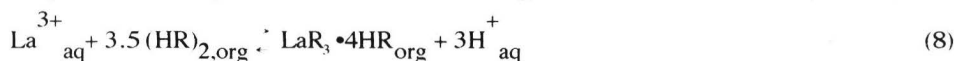
The experimental results for n-heptane diluent were plotted according to Eq. (6). It was found that the slope of the straight line is 3.5 in a high concentration range of the extractant, but that the slope is 3.0 in a low concentration range. In the case of toluene diluent, the slope was 3.5 over the whole range of the extractant concentration.

From the results mentioned above, the equation for the extraction equilibrium of La with EHPNA is represented as follows.

For n-heptane diluent (low extractant concentration range);



For n-heptane diluent (high extractant concentration range) and for toluene diluent;

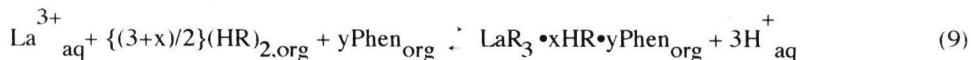


The values of the extraction equilibrium constants obtained are shown in Table 2.

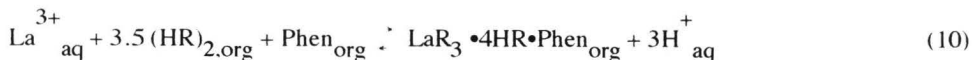
TABLE 2
Extraction equilibrium constants of La

Diluent	$C_{(HR)2}$	$K_{ex} \cdot m^{1.5} / mol^{0.5}$
n-Heptane	low	1.3×10^{-3}
n-Heptane	high	1.5×10^{-3}
Toluene	low and high	8.1×10^{-6}

Then the synergistic extraction of La will be considered. It was beforehand confirmed that extraction by Phen alone is negligibly small. Assuming that La is extracted as a monomer complex of composition, $LaR_3 \cdot xHR \cdot yPhen$, with the mixed extractants from the aqueous solution, the synergistic extraction equilibrium can be expressed as follows.



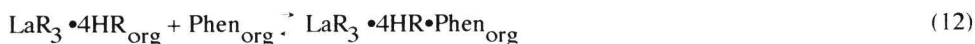
From the slope analyses of the experimental results for concentration dependencies of the distribution ratio of La on HR and Phen, it was found that $x=4$ and $y=1$. In this procedure, the concentration of Phen in the organic phase was estimated using the values of $K_{d,ph}$ and $K_{a,ph}$ listed in Table 1. These results show that the synergistic extraction of La is written as follows.



Equation (10) is rewritten as follows.

$$\log D = \log (C_{(\text{HR})2,\text{org}}^{3.5} C_{\text{H}}^{-3} C_{\text{ph,org}}) + \log K_{\text{ex,syn}} \quad (11)$$

All the experimental results are plotted in Fig.4 according to Eq. (11), from which the synergistic extraction equilibrium constant, $K_{\text{ex,syn}}$, was obtained. From Eqs. (8) and (10), the following equation is obtained.



Defining the equilibrium constant for Eq. (12) as K_{syn} , K_{syn} is written as

$$K_{\text{syn}} = K_{\text{ex,syn}} / K_{\text{ex}} \quad (13)$$

K_{syn} is considered as a measure showing the degree of synergistic effect. These values are shown in Table 3.

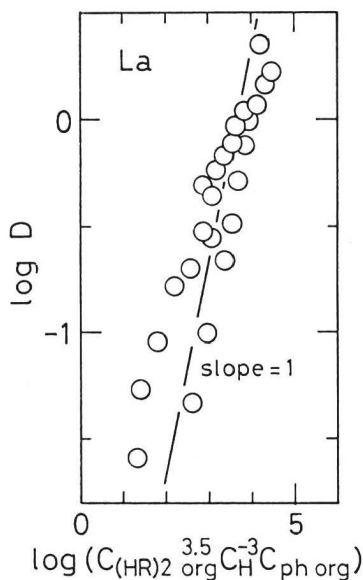


Fig.4 Rearrangement of experimental results for synergistic extraction of La

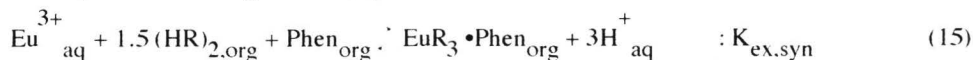
TABLE 3

Synergistic extraction equilibrium constants of La with EHPNA and Phen

Diluent	$K_{\text{ex,syn}} \cdot \text{m}^{4.5} / \text{mol}^{1.5}$	$K_{\text{syn}} \cdot \text{m}^3 / \text{mol}$
Toluene	2.2×10^{-4}	27

Synergistic extraction of Eu with a mixture of D2EHPA or DIDPA and Phen

From the same analyses of the experimental results as mentioned above, the equations of the extraction reaction for this system were found to be as follows.



The extraction equilibrium constants are listed in Table 4.

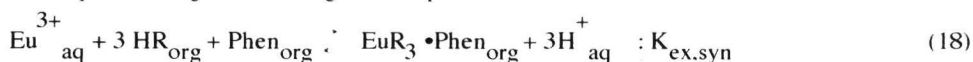
TABLE 4

Synergistic extraction equilibrium constants of Eu with D2EHPA or DIDPA and Phen

Diluent	Extractant	$K_{\text{ex}} \cdot \frac{1.5}{\text{mol}} \cdot \frac{4.5}{\text{m}}$	$K_{\text{ex},\text{syn}} \cdot \frac{0.5}{\text{mol}} \cdot \frac{1.5}{\text{m}}$	$K_{\text{syn}} \cdot \frac{3}{\text{m}} \cdot \frac{3}{\text{mol}}$
Toluene	D2EHPA	1.0	2.5	2.5
Toluene	DIDPA	7.1×10^1	8.5×10^{-1}	1.2×10^{-2}

Synergistic extraction of Eu with a mixture of DBTPA or DDTPA and Phen

Kondo et al. (1989) showed that DBTPA or DDTPA which is a dialkylmonothiophosphoric acid exists as the monomer in toluene diluent. The equations of the extraction reaction for this system were found to be as follows, from the same analyses as mentioned above.



The extraction equilibrium constants are shown in Table 5.

TABLE 5

Synergistic extraction equilibrium constants of Eu with DBTPA or DDTPA and Phen

Diluent	Extractant	$K_{\text{ex}} \cdot -$	$K_{\text{ex},\text{syn}} \cdot \frac{3}{\text{m}} \cdot \frac{3}{\text{mol}}$	$K_{\text{syn}} \cdot \frac{3}{\text{m}} \cdot \frac{3}{\text{mol}}$
Toluene	DBTPA	2.7×10^{-3}	5.7×10^1	2.1×10^4
Toluene	DDTPA	2.3×10^{-2}	2.0×10^2	8.7×10^3

CONCLUSIONS

From the results mentioned above, the following information was obtained.

1. The synergistic effect is larger when using an extractant with a shorter alkyl-chain length than a longer one.
2. The synergistic effect is larger in the extraction of a lighter rare-earth than a heavier one.
3. The synergistic effect is larger when using toluene as the diluent than n-heptane.

NOMENCLATURE

C	concentrations (mol/m^3)
E	degree of extraction (-)
K	equilibrium constant
Non-Standard nomenclature:	
D	distribution ratio (-)
K_a	acid dissociation constant (mol/m^3)
K_d	distribution constant (-)
Subscripts	
aq	aqueous phase
ex	extraction
H	hydrogen-ion
(HR) ₂	dimer of extractant
La	lanthanum
org	organic phase
ph	phenanthroline
phH	protonated phenanthroline
syn	synergism

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**SYNERGISTIC EXTRACTION OF NEODYMIUM(III) AND EUROPIUM(III)
WITH 3-PHENYL-4-BENZOYL-5-ISOXAZOLONE USING
NEUTRAL OXO-DONORS**

P.N. BANGROO, H.C. ARORA

Department of Atomic Energy

Atomic Minerals Division

West Block VII, R.K. Puram,

New Delhi - 110 066, INDIA

ABSTRACT

The solvent extraction of Neodymium (III) and Europium (III) with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) has been studied. Both Nd(III) and Eu (III) were extracted from buffered aqueous media into toluene. The value of $\log K_{ex}$, where K_{ex} refers to the equilibrium $M(III) + 3HL \rightleftharpoons ML_3 + 3H^+$, is +0.4 and +0.7 for Nd-HPBI & Eu-HPBI respectively. HPBI seems to be a better extractant for Nd(III) and Eu(III) than the commonly used β -diketones viz 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) the nitroderivative of HPMBP i.e. 1-phenyl-3-methyl-4-nitro benzoyl- 5-pyrazolone (HNMPP), theonyltrifluoroacetone (HTTA) and hexafluoroacetylacetone (HFA). The effect of various Lewis bases - tri(n) octylphosphine oxide (TOPO), tri-n butyl phosphate (TBP) and dibenzyl sulphoxide (DBSO) in combination with HPBI on the extraction of Nd(III) and Eu(III) has also been investigated. All the Lewis bases show synergistic enhancement with both the metals. Synergistic extraction constants, stability constants and the stoichiometry of the respective adducts formed during the extraction have been calculated.

INTRODUCTION

β -diketones have been used extensively for the solvent extraction of metals (De et al, 1970). Among these 4-acylpyrazolones, first introduced by Jensen (1959), have proved to be the most promising reagents for the extraction of metals. 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) has found extensive application and is a better extractant than theonyltrifluoroacetone (HTTA) and hexafluoroacetylacetone (HFA) for most metals (Rao et al, 1975). The replacement of the pyrazole moiety by isoxazole moiety in HPMBP is expected to decrease pK_a which helps in extraction of metals at lower pH values. Thus 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) would be more promising than HPMBP for the extraction of metal ions. The reagent HPBI has been earlier used in the study of extraction of Mn, Fe, Co, Ni, Zn, Cd, Pb, Rh (Jyothi et al, 1987), and Er, a member of heavy rare earths (Bangroo et al, 1991).

The present work deals with the study of extraction of Nd(III) and Eu (III) members of light and middle rare earths respectively with HPBI and comparison of its efficiency with HPMBP, 1-phenyl-3-methyl-4(p)nitro-benzoyl-5-pyrazolone (HNMP), HTTA and HFA. Also investigated is the effect of some organic Lewis bases on the extraction of Nd(III) & Eu(III) in combination with HPBI. The Lewis bases used are: tri-n-octylphosphine oxide (TOPO), tri-n-butyl phosphate (TBP) and dibenzylsulphoxide (DBSO).

EXPERIMENTAL

The ligand HPBI was prepared using 3-phenyl-5-isoxazolone and benzoic anhydride (Hantzsch, 1891) in the presence of sodium benzoate as the method of Korte and Storiko (1961). The purity of HPBI was established by elemental analysis and melting point data. The solution of requisite concentration of HPBI was prepared in toluene (A.R.).

The solutions of Nd(III) and Eu(III) were prepared using the reagent grade $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%; Fluka) and Eu_2O_3 (99.9%, Fisons, Philadelphia) respectively. The stock solutions were standardised gravimetrically after precipitation as oxalate. All other reagents used were of analytical grade.

Solvent Extraction

The initial concentrations of Nd(III) and Eu(III) in the aqueous phase were maintained at 0.35 mM and 0.33 mM respectively. The ionic strength was kept at 0.1M (H,K) Cl. Equilibrated pH of the aqueous phase was measured in all the experiments using an Elico pH meter. Equal volumes (10 cm³ each) of pre-contacted aqueous phase and toluene phase containing the ligand were placed in stoppered Pyrex glass bottles and shaken for one hour in a thermostatted mechanical shaker at $30^\circ\text{C} \pm 1^\circ\text{C}$. The distribution ratio (K_d) was calculated by monitoring the concentration of the metal in the aqueous phase by spectrophotometry by developing colour with Alizarin Red-S using a Varian-634 spectrophotometer. As the K_d is calculated from the ratio of concentrations of metal obtained by difference, the experiments were carried out in duplicate.

Similar experiments were carried out to extract Nd(III) and Eu(III) with HPBI in combination with neutral oxo-donors: TOPO, TBP and DBSO and the distribution ratios were calculated.

RESULTS AND DISCUSSION

The variation of K_d as a function of the aqueous phase acidity and as a function of the extractant concentration has been used to understand the extraction behaviour of Nd(III) and Eu(III) with HPBI. The slope value of the plot of $\log K_d$ vs $\log [\text{HPBI}]$ at constant pH is about 3 ± 0.1 for both Nd(III) and Eu(III) Fig.1. Also, the plot of $\log K_d$ vs pH at constant ligand concentration gives a slope of three for both Nd(III) and Eu(III). This indicates that during the extraction three protons are released and three moles of the ligand HPBI are involved in the formation of the extracted complexes.

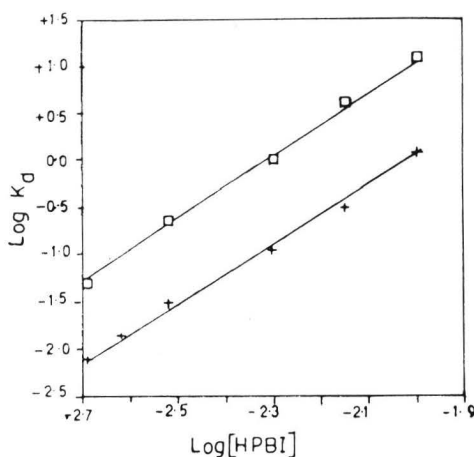
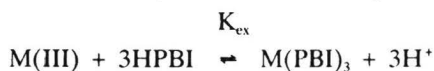


Fig. 1 Plot of $\log K_d$ vs $\log [\text{HPBI}]$
 (□ Eu - HPBI, pH = 2.0;
 + Nd - HPBI, pH = 2.2)

The extraction equilibrium can be represented as.



where M(III) represents Nd(III) and Eu(III). The equilibrium constant $\log K_{\text{ex}}$ has been calculated by using the equation:

$$\log K_{\text{ex}} = \log K_d - 3 \log [\text{HPBI}] - 3\text{pH}.$$

and the values of $\log K_{\text{ex}}$ are shown in Table 1, along with pK_a values of various ligands.

TABLE 1
 Comparison of extraction constant values ($\log K_{\text{ex}}$) of
 Nd-HPBI and Eu-HPBI systems with those for Nd(III) and Eu(III)
 complexes of HNMPP, HPMBP, HFA and HTTA

Ligand	pK_a	$\log K_{\text{ex}}$ of Nd(III) complexes	$\log K_{\text{ex}}$ of Eu(III) Complexes
HPBI	1.13 ^a	+0.4 ^b	+0.7 ^b
HNMPP	2.0 ^c	-1.6 ^c	-1.4 ^c
HPMBP	4.10 ^a	-5.63 ^d	-3.96 ^c
HFA	--	-6.15 ^f	-5.79 ^f
HTTA	6.23 ^a	-8.38 ^e	-7.86 ^h

a) (Sizonenko et al, 1969)

b) (Present work)

c) (Bangroo et al, 1989)

d) (Marcus et al, 1967)

e) (Sekine et al, 1967)

f) (Mitchell et al, 1972)

g) (Kassierer et al, 1972)

h) (Chmutova et al, 1969)

The relative values of $\log K_{ex}$ under similar conditions give an idea about the relative efficiency of the extraction with various ligands. It is clear from Table 1 that HPBI is a better extractant for Nd(III) and Eu(III) as compared to HNMPP, HPMBP, HTTA and HFA. This trend conforms to the pK_a values of various ligands, lower pK_a of the ligand signifying higher extraction.

Effect of Lewis bases (S)

The study of the effect of Lewis bases in combination with HPBI on the extraction of Nd(III) and Eu(III) was carried out by varying the concentration of the Lewis bases at constant pH and constant ligand concentration. This gives the information regarding the number of auxiliary ligands incorporated in the formation of adducts. Experiments conducted at constant pH and constant auxiliary ligand concentration show the number of ligand molecules involved during the formation of the extracted complex.

The plot of $\log K_d$ vs $\log [S]$ at constant pH and constant HPBI concentration for Nd(III) with TOPO, TBP & DBSO is shown in Fig.2.

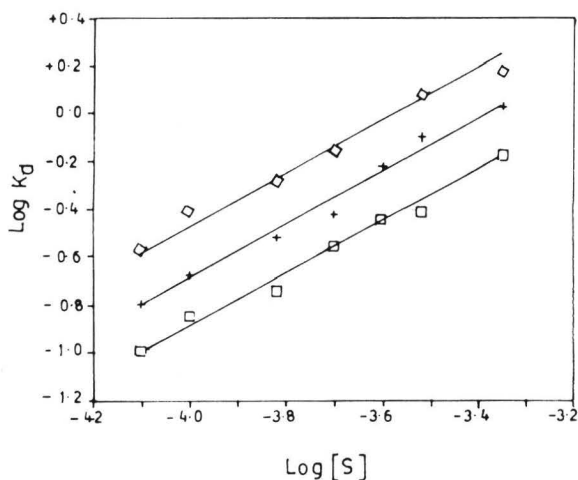


Fig.2 Plot of $\log K_d$ vs $\log [S]$
 ($\diamond$ Nd - HPBI - TOPO, pH = 2.0;
 + Nd - HPBI - TBP, pH = 1.9;
 $\square$ Nd - HPBI - DBSO, pH = 2.0;
 [HPBI] = 5 mM in toluene)

The slopes indicate that 1 mole each of TOPO, TBP and DBSO take part in the adduct formation. In the case of the Eu(III)-HPBI system also, 1 mole each of TOPO, TBP and DBSO is taken up for adduct formation (Fig.3).

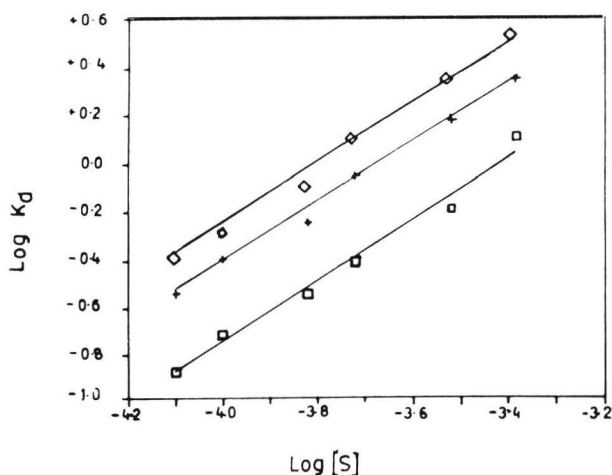
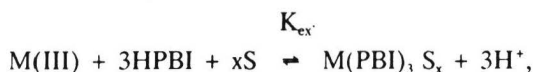


Fig.3 Plot of $\log K_d$ vs $\log [S]$
 ($\diamond$ Eu - HPBI - TOPO, pH = 1.9;
 + Eu - HPBI - TBP, pH = 2.0;
 $\square$ Eu - HPBI - DBSO, pH = 1.9;
 [HPBI] = 5 mM in toluene)

The extraction equilibrium of Nd(III) and Eu (III) in the presence of auxiliary ligands can be shown as,



where K_{ex}' refers to the extraction equilibrium constant and is calculated by the equation:

$$\log K_{\text{ex}}' = \log K_d - 3\log [\text{HPBI}] - 3\text{pH} - x \log [S]$$

Where $x = 1$ and $S = \text{TBP, TOPO or DBSO}$

The values of $\log K_{\text{ex}}'$ and adduct stability constants ($\log K_s$) are given in Table 2.

TABLE 2
 Extraction Constants and Stability Constants of Nd-HPBI-S and Eu-HPBI-S adducts

Auxiliary ligand	Nd(III) - HPBI		Eu(III) - HPBI	
	$\log K_{\text{ex}}'$	$\log K_s$	$\log K_{\text{ex}}'$	$\log K_s$
TOPO	4.5	4.1	4.7	4.0
TBP	4.3	3.9	4.4	3.7
DBSO	4.0	3.6	4.2	3.5
--	0.4	--	0.7	--

It is clear from the results that synergistic enhancement occurs in these systems and the synergism with TOPO is higher than with TBP and DBSO which is probably due to its higher basicity.

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RECOVERY OF NIOBIUM AND TANTALUM VALUES FROM A CUTTING TOOL SCRAP BY SOLVENT EXTRACTION PROCESS USING TBP-HF-H₂SO₄ SYSTEM

N.V. THAKUR, R.B. GANJANKUSH, S.M. DESHPANDE AND K.S. KOPPIKER

Uranium and Rare Earths Extraction Division
Bhabha Atomic Research Centre, Trombay,
Bombay - 400 085, INDIA.

ABSTRACT

A significant quantity of tungsten carbide cutting tool scrap is generated in India every year. This material can be considered as an important secondary source for metals such as tungsten, cobalt, niobium, tantalum and titanium. During the commercial treatment of this scrap to recover tungsten and cobalt, a hydroxide cake analysing 26% TiO₂, 21% Nb₂O₅, 40% Ta₂O₅, 6% WO₃ and 7% other impurities is rejected as residue. The present paper is concerned with this hydroxide cake as starting material for the separation of its niobium and tantalum contents by solvent extraction using the TBP-HF-H₂SO₄ system. The feed solution analysing 75 g/L total oxides(T.O.) was prepared by dissolving the hydroxide cake in an acid mixture composed of HF and H₂SO₄. Starting with this feed solution and 50% TBP in kerosene (mainly paraffinic and naphthenic hydrocarbon in C₁₀-C₁₄ range) as an extractant a solvent extraction study has been carried out to standardise the extraction and stripping steps with respect to number of stages, organic to aqueous phase ratio, composition of the stripping solutions and the acidity of the feed solution with respect to HF and H₂SO₄. It was found possible to preferentially strip Nb from the loaded solvent using water and then strip Ta using 4 M NH₄F or strip Nb and Ta together from the loaded solvent using NH₄OH. A flow sheet has been developed which can be used for large scale production of Nb and Ta.

INTRODUCTION

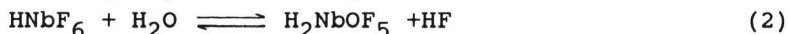
A considerable quantity of tungsten carbide cutting tool scrap is generated in industry every year. This scrap containing mainly the metals W, Co, Ti, Nb and Ta which are of commercial interest initially undergoes treatment to recover Co and W

values. W is recovered as soluble Na_2WO_4 using NaOH or Na_2CO_3 fusion technique. The cake obtained after W removal is enriched with respect to Nb and Ta values. In this investigation attempts have been made to develop a solvent extraction process to recover Nb and Ta values from this cake using 50% tributyl phosphate (TBP) in kerosene as an extractant. The use of TBP for the separation of Nb and Ta has been reported by Giganov and Yarinova(1975). It has also been reported by Fletcher, Morris and Wain(1955-56) and Nishimura, Moriyama and Kushima(1963) that TBP offers the advantages of higher separation factors and lower losses of extractant to the aqueous phase compared to methyl iso butyl ketone (MIBK).

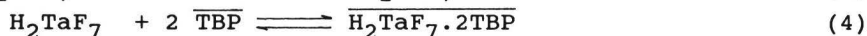
MECHANISM OF EXTRACTION

The cake obtained after separation of Co and bulk W was dissolved in HF to keep Nb and Ta in solution. The solution (feed) obtained contained about 16 g $\text{Nb}_2\text{O}_5/\text{L}$, 34 g $\text{Ta}_2\text{O}_5/\text{L}$, 20 g TiO_2/L , 5 g WO_3/L and 2 M HF. This feed solution was used for the solvent extraction studies.

The extraction studies were carried out using different initial concentrations of acidity in the feed. The extractant used was 50% TBP in kerosene. These studies indicated that if free HF in the feed is reduced to around 0.5 M then Ta is preferentially extracted over Nb due to the predominance of inextractable hydrolysed Nb species formed such as H_2NbOF_5 as shown below:



Under these conditions Ta is present largely in the form of extractable HTaF_6 and H_2TaF_7 . However, if excess of free HF (>2M) is present in the feed then Nb and Ta form the species H_2NbF_7 and H_2TaF_7 respectively and are extracted into 50% TBP as shown below:



Bars indicate the organic phase.

The extractant solvates the proton component of the extracted fluorometallic acid and not the metal ion. In this process Ti which is present in the solution to a considerable extent is also extracted in 50% TBP along with Nb and Ta. The interference of Ti needs to be avoided by keeping Ti in the aqueous phase. The effect of concentration of H_2SO_4 in the feed solution on the extraction behaviour of Ti was therefore studied. It was found that at 6.0 M H_2SO_4 Ti is least extracted without affecting the extraction behaviour of Nb and Ta. The distribution coefficient (K_d) of Ti was found to be <0.1 and of Ta and Nb >2.0 when HF was ~ 2.0 M and H_2SO_4 was ~ 6.0 M in the feed indicating that the separation factor of Nb/Ti or Ta/Ti is >20 under these conditions.

OPTIMISATION OF THE PROCESS PARAMETERS

Taking into consideration the mechanism of extraction of Nb and Ta in TBP from HF medium in the presence of 6 M H_2SO_4 the various parameters such as the organic to aqueous phase ratio in extraction and stripping cascades and the extraction and stripping stages have to be optimised to obtain the desired purity and recovery of Nb and Ta. Parameters have been optimised in such a way that Nb and Ta together are extracted first keeping all other impurities in raffinate. About 90% Nb is then stripped back along with 10% Ta from the extract in stripping cascade-I with water and Ta is stripped back in stripping cascade-II from the extract using 4 M NH_4F solution. Generally in industry the specifications for the purity of Nb and Ta to be used in cutting tools have been laid down. With the ultimate aim of using Nb and Ta in cutting tools, Nb with $\sim 90\%$ purity with respect to Ta, and Ta with 90% purity with respect to Nb is good enough, as solutions of these purities of Nb and Ta can be blended to give the desired composition of Nb and Ta for further reduction and making of tools. However, for the other impurities in the product the specifications are rigid. The parameters in the solvent extraction process determined to get 90% purity of Nb with respect to Ta and 90%

purity of Ta with respect to Nb are given below:

O/A : 2.5 in extraction cascade

O/A : 1.0 in the stripping cascade-I

O/A : 2.0 in the stripping cascade-II

No of extraction stages in the extraction cascade : 4

No of stripping stages in the stripping cascade-I : 1

No of stripping stages in the stripping cascade-II: 2

Feed acidity: 2 M HF (free) + 6 M H_2SO_4

STRIPPING OF THE LOADED EXTRACT

The extracted metals (Nb and Ta) can be stripped out of the solvent in two ways: (a) both the metals can be stripped together (b) each metal can be selectively stripped. (a) If the loaded extract is contacted with 4 M NH_4F solution, both Nb and Ta are quantitatively stripped out in a counter-current stripping process. The optimum phase ratio in the stripping cascade has been found to be 2.0. It is possible to use a dilute solution of NH_4OH for stripping. During the contact with organic phase it is converted to NH_4F . (b) If the loaded extract is contacted with water, ~ 90% Nb is stripped out (probably as H_2NbOF_5) along with ~ 10% Ta in a single stage at a phase ratio of 1.0. The residual Ta present in the extract can then be stripped out with 4 M NH_4F solution to give a product containing about 10% Nb. This can be achieved in two stages at the phase ratio of 2.0. The barren solvent then can be recycled for extraction. Based on these findings a flowsheet has been developed and shown in Fig. 1.

RECOVERY OF NH_4F AS A BYPRODUCT

The extract containing Nb and Ta is contacted with water at a phase ratio of 1.0 in a single stage. Nb (~90%) is stripped out along with 10% Ta and HF. This solution can be neutralised with NH_4OH (passing NH_3 gas into the solution) giving hydroxide precipitate of Nb (90%) and Ta (10%) which can be filtered out. The filtrate containing NH_4F is concentrated to obtain 4 M NH_4F solution which can be used for stripping Ta from the

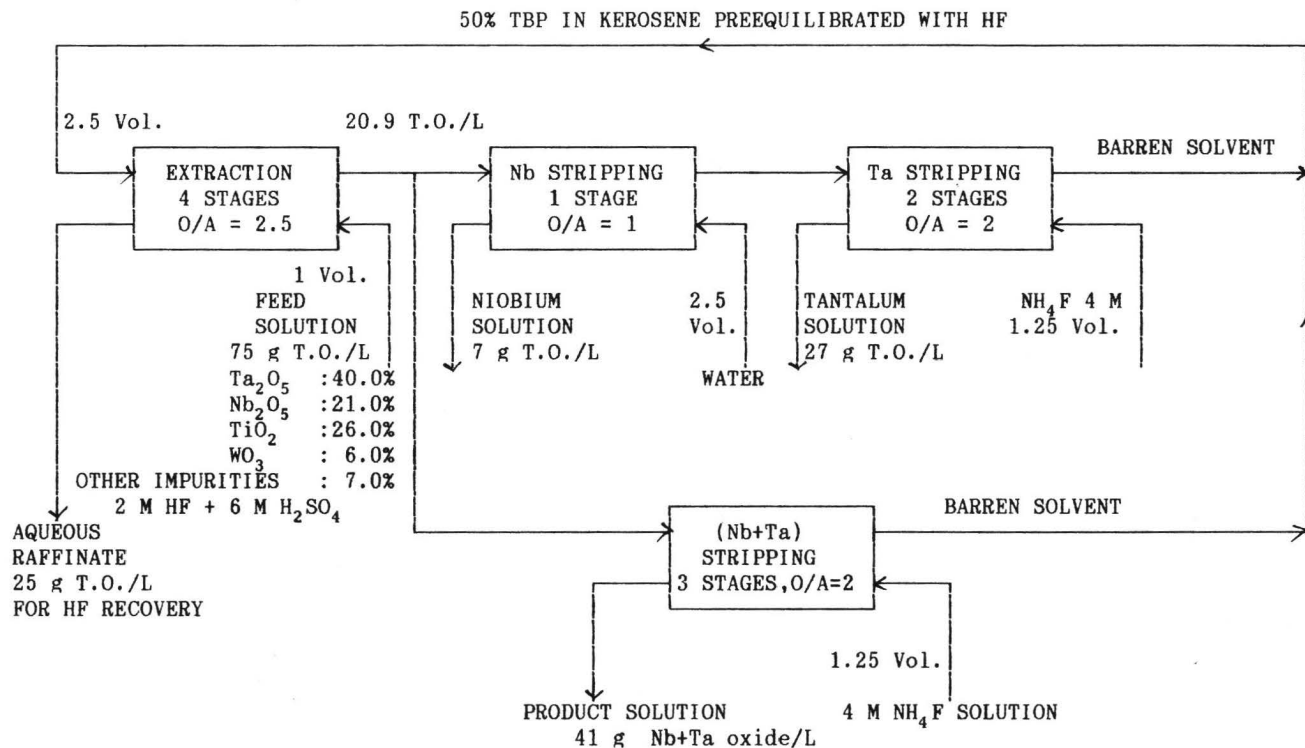


Fig. 1 Tentative solvent extraction flow sheet for recovery of Nb and Ta from cutting tool-scrap sludge solution

extract at a phase ratio of 2.0 in two stages. The stripped solution containing Ta (90%) and Nb (10%) can be neutralised with NH_4OH (passing NH_3 gas into the solution) to obtain the hydroxide precipitate which can be filtered. The filtrate containing NH_4F can be concentrated and recovered as NH_4F crystals which are a byproduct of the system.

CONCLUSIONS

The work carried out has shown the feasibility of recovering Nb and Ta from tungsten carbide cutting tool scrap with the desired purity and recovery of these metals. The optimum parameters have been determined and used in the solvent extraction process. The process is feasible on an industrial scale. From the economic consideration the degradation of TBP due to the use of high concentration of HF need to be taken into consideration.

ACKNOWLEDGEMENTS

The authors thank Shri K.N. Harindran and Shri V.N. Krishnan, Head, Quality Assurance Section for the help extended in analysing some of the samples by atomic absorption spectroscopy.

NOMENCLATURE

Kd Distribution coefficient

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3.17

DEVELOPMENT OF FOUR-EXIT PROCESS FOR SIMULTANEOUS PURIFICATION OF DYSPROSIUM AND TERBIUM FROM DYSPROSIUM CONCENTRATE USING PARTIALLY SAPONIFIED 2-ETHYL HEXYL PHOSPHONIC ACID MONO 2-ETHYL HEXYL ESTER (PC 88 A) AS AN EXTRACTANT

N.V. THAKUR and S.L. MISHRA

Uranium and Rare Earths Extraction Division,
Bhabha Atomic Research Centre, Trombay,
Bombay - 400 085, INDIA.

ABSTRACT

Extraction studies of Dy have been conducted from acidic chloride solutions using 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester (PC 88 A) in kerosene as an extractant. Distribution coefficients (K_d) of Dy were determined as a function of initial concentration of $HCl(H_2)$ for different initial concentrations (C_i) of Dy. Similar distribution data for Gd, Tb and Y were derived mathematically using the distribution data of Dy and the separation factors of Tb-Gd, Dy-Tb and Y-Dy which have been determined in this investigation. Based on these data empirical mathematical models have been made to predict the extraction behaviour of these metal ions in organic and aqueous phases at various initial acidities and metal concentrations. Incorporating these models a computer program was developed to calculate the concentrations of the metal ions in the organic and aqueous phases at various stages of extractions and scrubblings in a counter-current solvent extraction (SX) cascade. Using this program the controlling parameters of the process such as the number of extraction, scrubbing and stripping stages, initial acidity of the feed, acidities of the different scrubbing and stripping solutions and organic to aqueous phase ratios (R) in various cascades of extractions, scrubblings and strippings have been optimised to obtain the desired purity (97%) and recovery (93%) of Dy. Under these predetermined conditions counter-current extractions and scrubblings were carried out using mini mixer-settlers (50 mL capacity). The mixer-settler was run continuously and yielded four different products from its four exit points. The raffinate coming from the first exit was essentially Gd rich solution and other lighter rare earths. The fourth and final exit point was for the stripped solution

that contained 85% Y with 95% recovery. The remaining two exit points involving scrubbing stages yielded 83% pure Tb concentrate and 97% pure Dy with 93% recovery of each.

INTRODUCTION

Indian Rare Earths Ltd.(IRE), a unit of the Department of Atomic Energy, produce mixed rare earths chloride from monazite, a source of mainly light rare earths. Further fractionation of the rare earths is done using SX processes in which a concentrate containing around 57% Dy_2O_3 and 15% Tb_4O_7 along with other rare earths mainly Y and Gd is obtained as an intermediate product. From this concentrate an attempt has been made in this laboratory to separate Dy and Tb simultaneously using PC 88 A (20% saponified), a liquid cation exchanger in kerosene (mainly paraffinic and naphthenic hydrocarbon in C_{10} - C_{14} range), as an extractant. This attempt was based on the experimental data for the distribution coefficient (K_d) as a function of initial acidity (H_i) and initial concentration (C_i) of metal ions.

EXTRACTION MECHANISM

The extraction mechanism has been established as an ion-exchange reaction expressed by equation (1).



Where Ln stands for free lanthanide ion and $(HG)_2$ for dimer of PC 88 A. Bars indicate the organic phase. Charges have been omitted for simplicity. K_d of RE depends on H_i and C_i provided the extractant concentration is constant which is normally the case since it is in large excess. Hence an empirical mathematical equation showing K_d as a function of H_i and C_i would prove useful.

Extraction data

It is necessary to generate a large volume of data for each individual RE for deriving a mathematical model. The data K_d vs. H_i were experimentally determined for Dy only, varying H_i from 0.2 to 1.0 M and C_i from 0.05-0.3 M at constant $R(1.0)$. The data obtained are given in Table 1. Similar data for Gd, Tb

and Y were generated using an equation (2) derived by knowledge of separation factors (β) for various pairs of RE present in feed is essential and hence β values for Tb-Gd, Dy-Tb and Y-Dy have been determined experimentally ($\beta_{\text{Tb-Gd}} = 5.2$, $\beta_{\text{Dy-Tb}} = 2.71$, $\beta_{\text{Y-Dy}} = 3.2$). It has been observed that the separation factors are practically constant under the experimental conditions and do not change with the concentration of the mixed rare earth ions and acidity.

The distribution data generated experimentally for Dy were substituted in the following equation (Thakur, 1990),

$$[H_2]_i = \{[H_1]_i + Z * (1-\beta^{1/3})\} / \beta^{1/3} \quad (2)$$

$[H_1]_i$ is the initial acidity of the Dy solution at which the K_d value has been determined, $[H_2]_i$ is the calculated initial acidity of the solution of another RE of interest (Tb, Gd and Y) at which the K_d value for that RE would be identical to that of Dy. Data for Y were generated using the same equation as above but $[H_1]_i$ is the calculated initial acidity of Y solution and $[H_2]_i$ is the initial acidity of Dy solution. In other words this equation helps to generate sets of data, K_d vs. H_i , for each of the individual RE without carrying out any experiment, provided the experimental data of one of the rare earths are known. In the above equation β is the separation factor of the pair of elements - Dy and other rare earth of interest.

$$Z = 3 * C_i * K_{d1} * R / (K_{d1} * R + 1) = 3 * C_i * K_{d2} * R / (K_{d2} * R + 1)$$

C_i is the initial concentration of metal ion which would be the same for both the elements, and $K_{d1} = K_{d2}$. Using the equation (2) data K_d Vs. H_i have been generated for Gd, Tb and Y and recorded in Table 1. The generated data have also been verified experimentally and found to be agreeing with the derived data.

DERIVATION OF MATHEMATICAL MODELS

The data K_d vs. H_i obtained for the various RE at C_i (0.05, 0.1, 0.2 and 0.3 M) were curve fitted using least squares method with the help of a microcomputer using software 'GRAPHPAD' to get an exponential fit

$$K_d = A * \exp(B * H_i) \quad (3)$$

TABLE 1

Data of distribution coefficient(Kd) vs initial acidity(H_i) for Dy, Gd, Tb and Y at various initial metal concentrations(C_i). Extractant: 1 M PC 88 A in kerosene. Phase ratio (R): 1.0.

C_i	Kd	H_i			
		Dy*	Gd ^o	Tb ^o	Y ^o
0.05	9.290	0.220	0.012	0.119	0.388
	2.640	0.420	0.110	0.270	0.670
	1.120	0.630	0.214	0.429	0.465
	0.315	1.030	0.405	0.728	1.534
0.10	3.940	0.084	-0.105	-0.007	0.237
	2.550	0.168	-0.057	0.060	0.349
	1.720	0.252	-0.007	0.127	0.461
	0.970	0.420	0.087	0.259	0.688
	0.575	0.582	0.176	0.386	0.909
0.20	0.954	0.083	-0.137	-0.023	0.261
	0.654	0.250	-0.036	0.112	0.480
	0.250	0.680	0.211	0.453	1.050
	0.117	1.010	0.381	0.706	1.518
0.30	0.490	0.090	-0.136	-0.019	0.272
	0.390	0.190	-0.069	0.065	0.399
	0.290	0.380	0.039	0.215	0.655
	0.130	0.780	0.262	0.530	1.190
	0.050	1.170	0.459	0.827	1.740

* Initial acidities of the Dy solution for which Kd values have been determined experimentally.

o Derived acidities using equation (2) for the Kd values mentioned in the table.

Negative acidities indicate that PC 88 A in the organic phase is partially saponified to that extent.

A and B are arbitrary constants depending on the metal and C_i . The values of A and B obtained for the fitted curves showed a dependence on C_i .

Hence the data A Vs. C_i and B vs. C_i were once again fitted to the following general equations

$$A = A_1 * C_i^{A_2} \quad (4)$$

$$B = B_1 * C_i^{B_2} \quad (5)$$

A_1 , A_2 , B_1 , B_2 are arbitrary constants which depend on the metal. Substituting the equations (4) and (5) in the equation

(3) we find the overall general equation

$$K_d = A_1 * C_i^{A_2} * \exp(B_1 * C_i^{B_2}) * H_i \quad (6)$$

This is the general mathematical model derived for the extraction behaviour of RE. Based on the data generated the mathematical models derived for Gd, Tb, Dy and Y are shown in Table 2. These models have been utilised in a computer program developed for simulation studies on separation of Dy, Tb, Y and the light rare earths.

TABLE 2

Mathematical models for the extraction behaviour of Gd, Tb, Dy and Y with 1.0 M PC 88 A in kerosene

$K_d(\text{Gd})$	$= 0.0058 * (C_i^{-2.503}) * \exp[(-1.250 * C_i^{-0.756} * H_i)]$
$K_d(\text{Tb})$	$= 0.0090 * (C_i^{-2.626}) * \exp[(-1.055 * C_i^{-0.673} * H_i)]$
$K_d(\text{Dy})$	$= 0.0137 * (C_i^{-2.608}) * \exp[(-0.895 * C_i^{-0.636} * H_i)]$
$K_d(\text{Y})$	$= 0.0236 * (C_i^{-2.535}) * \exp[(-0.713 * C_i^{-0.599} * H_i)]$

DISTRIBUTION OF AN INDIVIDUAL RARE EARTH ELEMENT FROM A MIXTURE OF RARE EARTHS

Following assumptions have been made to calculate the distribution of individual rare earth element from a mixture of Gd, Tb, Dy and Y. (1) The C_i of the individual rare earth is assumed to be equal to the C_i of the mixed rare earths. (2) By using the mathematical model of a particular element the D value can be calculated for this C_i , from which the concentration of the particular metal ion in the organic phase for this C_i can be evaluated. This concentration in the organic phase is then fractionated in the mole fraction of that individual rare earth as in the feed.

PROCESS OPTIMISATION

Dy concentrate obtained in the Y recovery process contains several impurities such as Gd, Tb, Y and other LRE (Table 3). The object of this investigation is to fractionate this concentrate into three components using partially saponified PC 88 A. (1) Gd and other LRE to be kept in raffinate in the

extraction process, (2) Tb which is better extracted than Gd but less than Dy to be scrubbed from the extract, (3) Dy, Y and other HRE which forms about 78% of total oxides and better extracted than Tb to be kept in the extract. In the extraction cascade by using the computer program in which the mathematical models have been incorporated the parameters such as number of extraction stages, phase ratio, metal concentration and acidity of feed were optimised and are shown in Fig 1. In the scrubbing cascade the scrubbing was done with 1.8 M HCl using different phase ratios and it was found that for $R = 6$, Tb is scrubbed out efficiently. However, the Tb solution was not very pure as it carried Dy and other HRE impurities to a considerable extent making Dy recovery less in the extract. The organic scrubbing was therefore considered inevitable to improve the recovery of Dy in the extract and purity of Tb in the scrubbed solution. The optimum parameters such as phase ratio and the number of scrubbing stages in the organic scrubbing cascade have been determined using 1.8 M HCl. The parameters optimised for scrubbing are shown in the flow sheet (Fig. 1) along with the purity of Tb obtained.

TABLE 3

Composition of different fractions in the purification process of Dy-concentrate

	Total REO (g/L)	LRE oxides(%)	Composition(%)			
			Gd ₂ O ₃	Tb ₄ O ₇	Dy ₂ O ₃	Y ₂ O ₃
Dy-concentrate (feed)	31.0	2.9	4.4	15.0	56.6	21.0
Raffinate	1.85	49.2	33.0	16.0	1.4	0.3
Tb rich solution	9.6	0.1	10.3	82.7	6.4	0.5
Dy rich solution	22.4	0.07	0.13	0.7	97.2	1.9
Y rich solution	5.8	< 0.1	< 0.1	< 0.1	12.5	85.0

The extract containing Dy and Y is further scrubbed with 1.8 M HCl to obtain the Dy in the scrubbed solution. The parameters in the scrubbing cascade were again optimised. However, it was realised that to recover Y to a considerable extent and hence ultimately to get the desired purity of Dy in the scrubbed

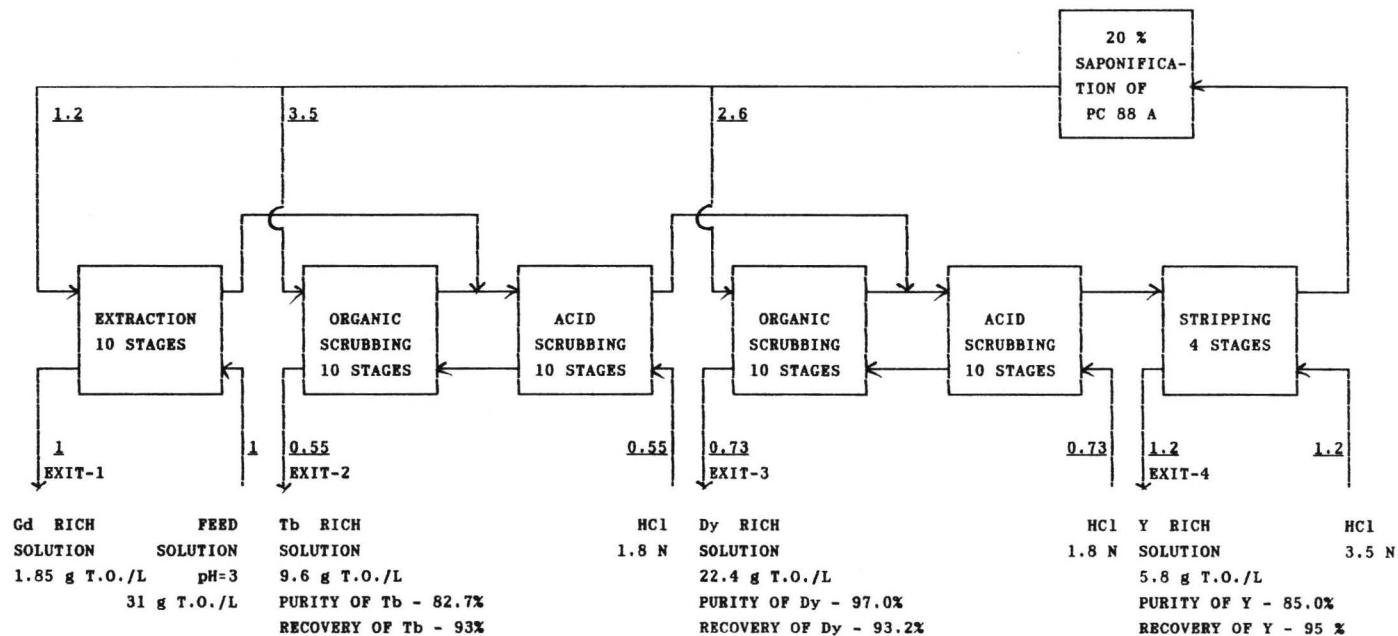


Fig.1 Flow-sheet for simultaneous purification of Dy and Tb by PC 88 A (a four-exit process)

solution it was essential to introduce the organic scrubbing for which the parameters were optimised (recorded in the flow sheet (Fig. 1)). The results shown in this flow sheet have been experimentally obtained using the parameters mentioned therein. This flow sheet (Fig. 1) indicates that the desired purity (97%) and recovery (93%) of Dy is obtained in this process. The process in addition yields Tb of 83% purity and 93% recovery as a Tb concentrate which can be further processed to obtain higher purity. Yttrium is obtained in the extract along with heavy rare earth impurities which is stripped using 3.5 M HCl in the stripping cascade and the raffinate retained Gd and other light rare earth impurities. This process appears to be suitable for industrial scale operation.

ACKNOWLEDGEMENTS

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NOMENCLATURE

SX Solvent extraction
 Kd Distribution coefficient
 H_i Initial acidity
 C_i Initial metal concentration
 B_i Separation factor
 R Organic to aqueous phase ratio
 A, B, A_1 , A_2 , B_1 , B_2 Arbitrary constants

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3.18

SEPARATION AND PURIFICATION OF RARE METALS BY COMBINATION OF SOLVENT EXTRACTION TECHNIQUES AND REDOX REACTIONS

T. HIRAI and I. KOMASAWA

Department of Chemical Engineering
Osaka University
Toyonaka, Osaka 560, Japan**ABSTRACT**

The separation and purification of rare metals by combination of solvent extraction and electrochemical or photochemical redox reactions was studied. Eu was reduced from trivalent to divalent form selectively by electroreduction using a Ti electrode or by photoreduction using a low pressure mercury lamp in H_2SO_4 – $(\text{NH}_4)_2\text{SO}_4$ aqueous solution, to give EuSO_4 precipitate. By using these methods, Eu was precipitated selectively from the alkyl phosphoric acid/xylene solution containing Sm, Eu and Gd. In the case of the separation of V and Mo, V(V) extracted by tri-*n*-octylmethylammonium chloride (TOMAC) was reduced to V(IV) or V(III) by photoreduction using the mercury lamp or a halogen lamp, and was stripped selectively, leaving Mo in the organic phase.

INTRODUCTION

Solvent extraction is one of the most effective methods for separation and purification of rare metals. The solvent extraction process consists of three stages: extraction, scrubbing and stripping. The selective stripping of the target metal can enhance separation efficiency. In previous work (Hirai and Komasawa, 1990, 1991, 1992 and 1993), the chemical- and electroreductive stripping of V in the solvent extraction process for separation of V and Mo using tri-*n*-octylmethylammonium chloride (TOMAN) as an extractant was investigated. The pentavalent vanadyl anion was reduced to tetra- and trivalent cations by contact with a stripping solution containing a reduction agent (L-ascorbic acid) or by electroreduction using a Pt electrode as cathode. The reduction enabled V to be stripped selectively, leaving Mo in the organic phase, to achieve an effective separation. In this work, the separation of Eu from Sm and Gd by combination of solvent extraction and electro- or photoreduction, and separation of V and Mo by photoreductive stripping were investigated.

EXPERIMENTAL

Alkyl phosphoric acid extractants, bis(2-ethylhexyl)phosphoric acid (D2EHPA) and di-5-methyl-2-(1-methylnonohexyl)nonadecanoyl phosphoric acid (DP-18) were supplied by

Daihachi Kagaku Kogyo Co., Ltd., and were diluted with xylene. TOMAC was supplied by Koei Kagaku Kogyo Co., Ltd. The rare-earth elements were extracted by shaking equal volumes of the organic solution (0.4 M DP-18 or 0.2 M D2EHPA) and pH 6 aqueous solution (containing ca. 0.02 M or 5 mM SmCl_3 , EuCl_3 and GdCl_3 for the DP-18 or D2EHPA systems, respectively). To determine the elements in the organic phase, the organic solution was stripped with 1 M HCl (for DP-18) or 6 M HCl (for D2EHPA). The concentrations of these elements were ca. 2.1 mM and ca. 4.3 mM in the DP-18 and D2EHPA solutions, respectively. Extraction of V and Mo was carried out by shaking equal volumes of the 0.015 M TOMAC/benzene and pH 7 aqueous solution containing ca. 0.01 M NaVO_3 , 0.01 M Na_2MoO_4 and 0.07 M NaCl. The extraction percentages of V and Mo were greater than 98% and less than 8%, respectively, and the resulting organic solution contained ca. 0.01 M V and ca. 0.9 mM Mo.

The electrolysis was performed with a potentiostat (Hokuto Denko HA-303). The photoreduction was carried out by using a 20 W low-pressure mercury lamp (Eikohsha), which had emission peaks of 184.9 nm and 253.7 nm. When only the 253.7 nm line was required, the 184.9 nm line was cut off with a filter. A 300 W halogen lamp (Eikohsha) was also used. The concentration of the elements in aqueous solutions was determined by use of an argon plasma emission spectrophotometer (Nippon Jarrell-Ash ICAP-575MarkII).

RESULTS AND DISCUSSION

Separation of Eu from Sm and Gd by Electrochemical Reduction

The electroreduction of Eu in aqueous solution containing Sm^{3+} , Eu^{3+} , Gd^{3+} and $(\text{NH}_4)_2\text{SO}_4$ was carried out first. A Ti plate (7.5 cm^2 area) was used as a cathode, which had a higher hydrogen overvoltage than a Pt electrode. Voltammetric analysis showed that the electrolysis voltage of -3 V was suitable. The relationship between electrolysis time and metal concentration in the aqueous solution is shown in Fig. 1. The concentration of Eu decreased by electrolysis, while those of Sm and Gd were almost constant, indicating that Eu precipitated selectively as EuSO_4 . Up to 35% of Eu was recovered as EuSO_4 precipitate. Since EuSO_4 precipitated mainly on the electrode surface, the active area of cathode may be reduced during the electrolysis, and therefore

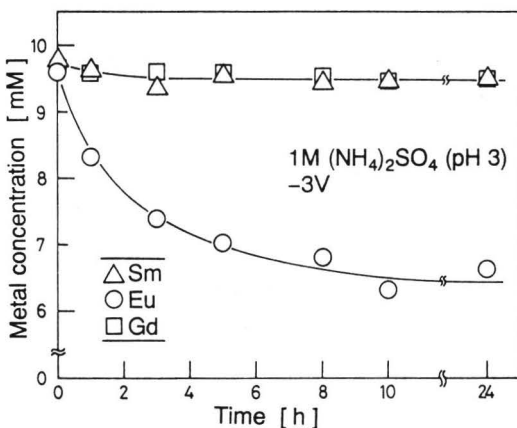


Fig. 1 Relationship between electrolysis time and metal concentrations in aqueous solution

complete precipitation was not achieved. The white precipitate contained Eu (97.1%), Sm (2.5%) and Gd (0.4%).

Electroreductive stripping of Eu was then carried out by using a two-compartment electrochemical cell shown in Fig. 2. Since the electrical conductivity of the metal-loaded organic solutions is extremely small, it is unlikely to reduce the extracted Eu at the organic phase/electrode interface. Thus, Eu^{3+} must be reduced at the aqueous phase/electrode interface after the mass transfer of Eu from the organic phase into aqueous phase, as in the case of electroreductive stripping of V (Hirai and Komazawa, 1991, 1992 and 1993). The sintered glass filter equipped in the cell could prevent the cathode from meeting with the organic solution. The aqueous solutions in the compartments were 1 M $(\text{NH}_4)_2\text{SO}_4$ of appropriate pH. The metal-loaded organic and aqueous solutions were agitated and electrolyzed in the cathodic compartment at room temperature.

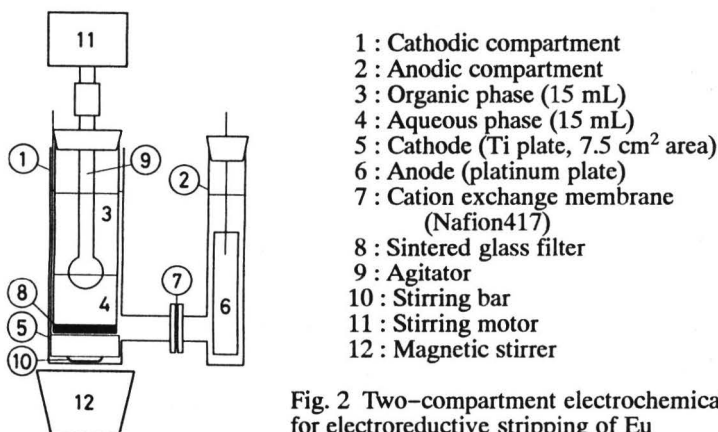


Fig. 2 Two-compartment electrochemical cell for electroreductive stripping of Eu

Figure 3 shows the relationship between aqueous phase final pH and relative mole fraction of Eu in the precipitate, the aqueous and organic phase after 48 hours electrolysis at -3V , where the feed amount of Eu in the organic phase is made as 100%. The fraction of Eu in the precipitate was calculated by mass-balance. In the range of pH greater than 3 in the DP-18 system and pH greater than 2.4 in the D2EHPA system, no precipitation of EuSO_4 occurred, since the mass transfer of Eu^{3+} from the organic into aqueous phase hardly occurred. At $\text{pH} < 2.9$, 40 ~ 60% of the feed Eu was precipitated in the DP-18 system. In this case, the amount of Eu remaining in the organic phase was smaller than that obtained without electrolysis as shown by the closed triangular keys. This indicates that the electrolysis can enhance the stripping of Eu. In the D2EHPA system, similar results were obtained, except for the pH condition. The precipitation of EuSO_4 occurred at $\text{pH} < 2.3$.

The relationship between electrolysis time and stripping yields of Sm and Gd and precipitation of EuSO_4 at various final pH conditions in the DP-18 system is shown in Fig. 4. The

recovery of Eu as EuSO_4 reached 83.2% at pH 1.8. The stripping of Sm and Gd decreases with increasing pH. The selective recovery of Eu as EuSO_4 is therefore feasible, Sm and Gd remaining in the organic phase. In the case of 72 hours electrolysis at pH 2.9, the fractions of EuSO_4 and Eu^{3+} in the aqueous phase were 38.7% and 17.6%, respectively, and the stripping percentage was the sum of them, 56.3%, while those of Sm and Gd were 40.3% and 25.6%, respectively. However, it seems to be difficult to retain all of the Sm and Gd in the organic phase because of the very similar stripping performances of the three elements.

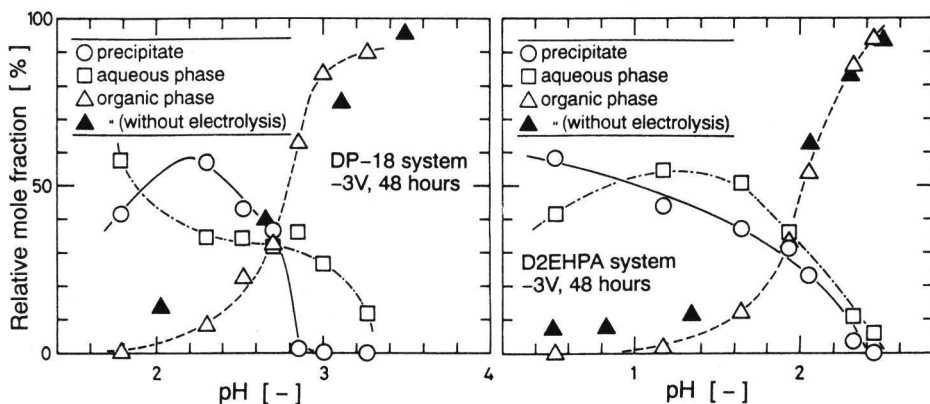


Fig. 3 Relationship between aqueous phase final pH and relative mole fraction of Eu in precipitate, aqueous and organic phase

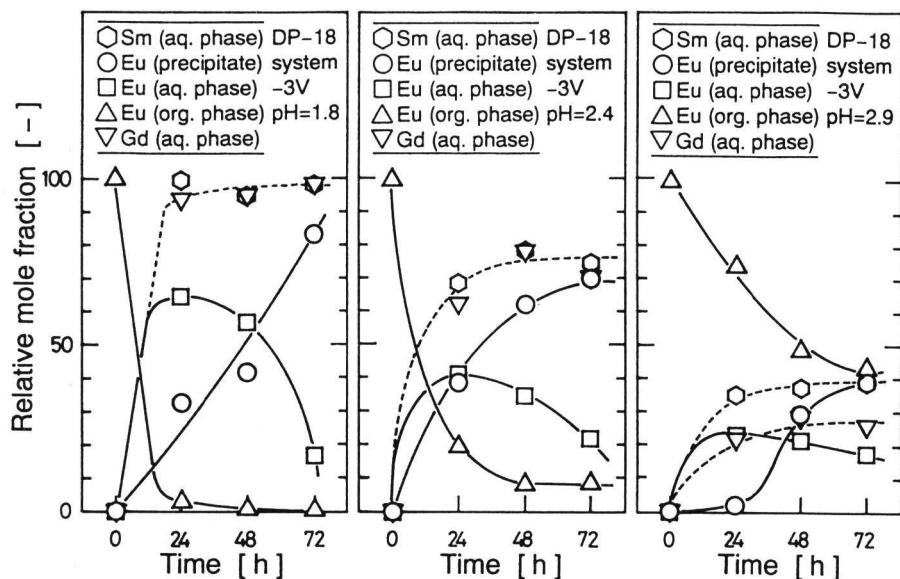
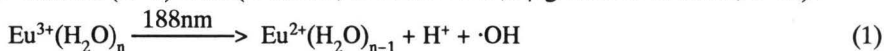


Fig. 4 Relationship between electrolysis time and stripping yield of Sm and Gd and precipitation of EuSO_4 at various final pH conditions in DP-18 system

Separation of Eu from Sm and Gd by Photochemical Reduction

Eu^{3+} is photoreduced by electron transfer from a binding ligand such as H_2O or SO_4^{2-} in its charge-transfer (C-T) band (Donohue, 1977 and 1979, Jørgensen and Brinen, 1963).



A radical must be scavenged to avoid a reverse reaction. Water is a poor radical scavenger, but alcohols such as 2-propanol and esters such as isopropyl formate are effective.

Figure 5 shows the absorption spectra of aqueous solutions containing EuCl_3 . The solution containing Eu^{3+} and SO_4^{2-} shows an absorption band at around 235 nm corresponding to the C-T band from SO_4^{2-} to Eu^{3+} (Donohue, 1977). This suggests that longer wavelength light as well as shorter wavelength light may be employed for the photoreduction. The solutions containing SO_4^{2-} and Cl^- also show the absorption in the deep UV region. These anions may be reduced by the 184.9 nm line ($\text{SO}_4^{2-} \rightarrow \text{SO}_4^{\cdot-} + \text{e}^-$, $2\text{Cl}^- \rightarrow \text{Cl}_2^{\cdot-} + \text{e}^-$) and the electron may reduce the Eu^{3+} ion.

The photoreduction of Eu in aqueous solution was carried out in a beaker type glass bottle with agitation by using a magnetic stirrer. The relationship between irradiation time and mole fractions of Sm, Eu and Gd in $(\text{NH}_4)_2\text{SO}_4$ aqueous solution (15 mL) are shown in Fig. 6, for the case using isopropyl formate as the scavenger (3 mL). The feed amounts of the elements are made as 100%.

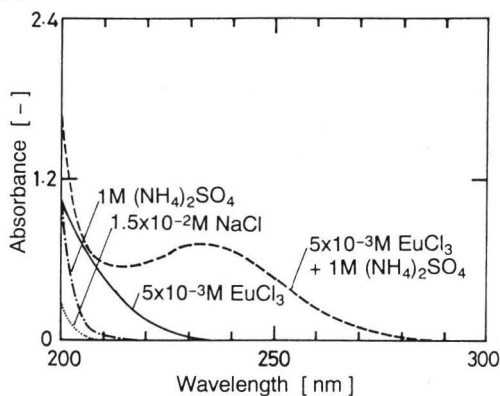


Fig. 5 Absorption spectra of aqueous solutions containing Eu^{3+}

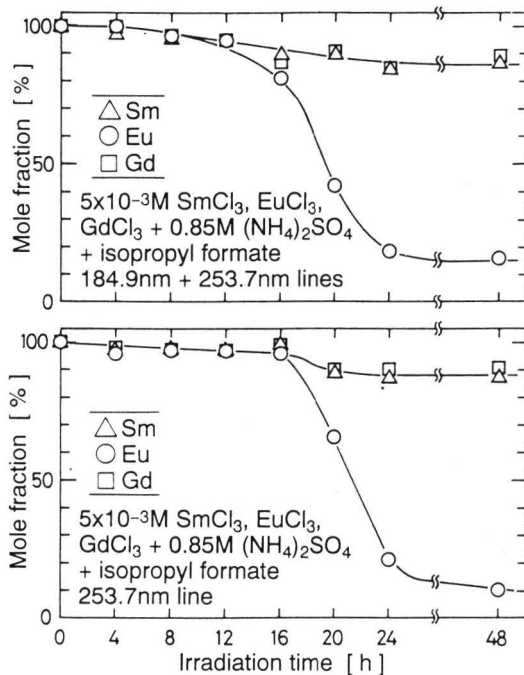


Fig. 6 Relationship between irradiation time and mole fractions of rare-earth elements in aqueous solution using isopropyl formate as scavenger

The concentration of Eu decreased by photolysis, while those of Sm and Gd were almost constant, indicating that Eu precipitated selectively as EuSO_4 . The precipitation did not occur when the scavenger was not added. The recovery of Eu as EuSO_4 precipitate attained up to 80–90%. The purity of Eu in the white precipitate was higher than 97%.

The absorption spectrum of the metal-loaded D2EHPA/xylene solution showed no absorption corresponding to the C–T band. The photoreduction of Eu seems to occur only when the coordinated water (or SO_4^{2-}) and scavenger are located near the Eu, and it does not occur in the D2EHPA/xylene solution. Therefore, Eu^{3+} must be reduced in the aqueous phase after the mass transfer of Eu from the organic into aqueous phase. The aqueous solution of pH < 2.5 must be used as in the case of electroreductive stripping in the D2EHPA system.

Figure 7 shows a two-compartment photochemical cell separated by a sintered glass filter. The metal-loaded organic solution, aqueous solution (1 M H_2SO_4 – $(\text{NH}_4)_2\text{SO}_4$) and isopropyl formate were agitated and photolyzed.

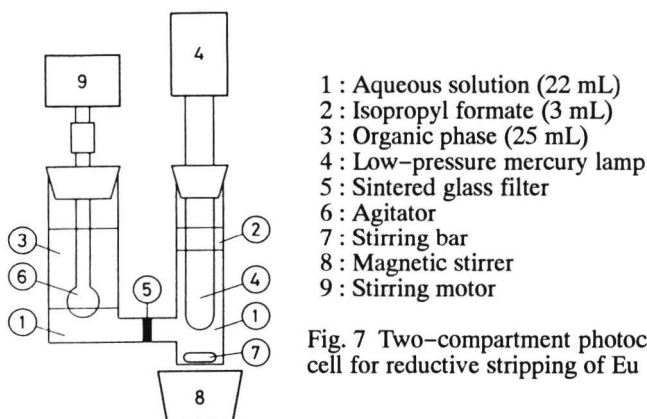


Fig. 7 Two-compartment photochemical cell for reductive stripping of Eu

The relationship between irradiation time and stripping yields of Sm and Gd and precipitation of EuSO_4 is shown in Fig. 8, where the feed amounts of the elements in the organic phase are made as 100%. The pH values in the figure show the aqueous phase final pH. The fraction of Eu in the precipitate was calculated by mass-balance. The purity of Eu in the precipitate was higher than 95% in all cases. The recovery of Eu as EuSO_4 reached 68% at pH 0.4. In the case of 24 hours irradiation at pH 1.8, the fractions of EuSO_4 and Eu^{3+} in the aqueous phase were 42.7% and 36.7%, respectively, and the stripping percentage was the sum of them, 79.4%. This is greater than the stripping percentage obtained by non-irradiation (72.9%). This indicates that the photoreduction can enhance the stripping of Eu.

Separation of V and Mo by Photoreductive Stripping

The absorption spectra of aqueous solutions containing V before and after the UV light irradiation by using the mercury lamp are shown in Fig. 9. The absorption at around 770 nm is

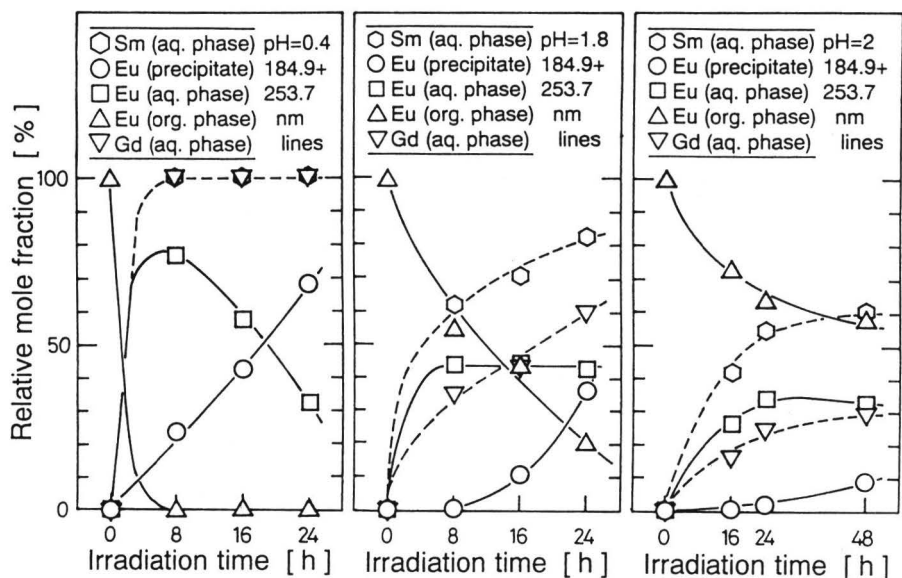


Fig. 8 Relationship between irradiation time and stripping yield of Sm and Gd and precipitation of EuSO_4 at various final pH conditions in D2EHPA system

attributed to V(IV) (VO^{2+}), and the absorption at around 400 and 610 nm are attributed to V(III) (V^{3+}). In the absence of the scavenger, V(V) was reduced to V(IV) slowly. In the presence of isopropyl formate, V(V) was reduced rapidly to V(IV), and then to V(III). When the 184.9 nm line was cut off, the reduction rate decreased. In the case of using the halogen lamp, V(V) was photoreduced to V(IV).

The absorption spectra of TOMAC/benzene solutions containing V and Mo after irradiation showed an absorption at around 870 nm, which was attributed to V(IV). V(V) could be photoreduced to V(IV) in the organic phase as well. In this system, H_2O has been found to be extracted with the molar ratio of H_2O : TOMAC = 4.7 : 1.

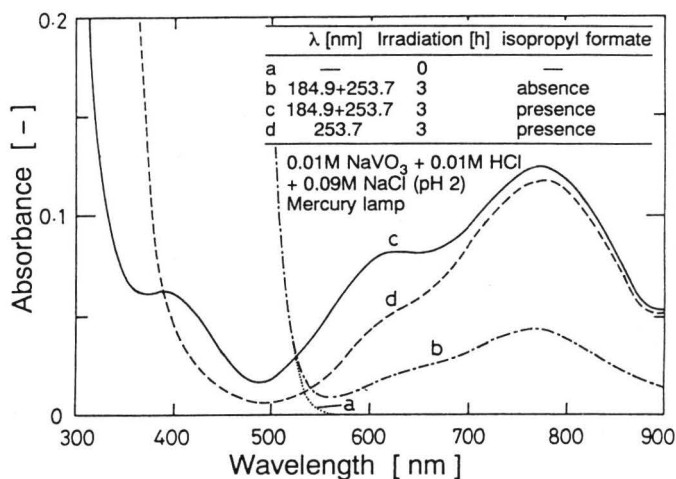


Fig. 9 Absorption spectra of aqueous solutions containing V before and after irradiation

The electron transfer from H_2O to V(V) may occur in the organic phase.

The organic phase (15 mL), aqueous phase (0.1 M HCl-NaCl , pH 2, 15 mL) and isopropyl formate (3 mL) were agitated at 800 min^{-1} in a beaker type glass bottle by using a magnetic stirrer. The relationship between irradiation time and stripping yields of V and Mo is shown in Fig. 10. The data at time = 0 show the stripping yields at equilibrium without irradiation. The stripping of V was remarkably enhanced (maximum 86%), especially when isopropyl formate was added, whereas that of molybdenum was insensitive to the irradiation. The resulting molar ratio of V to Mo in the stripping solution reached 400 ~ 1800 by single extraction followed by single photoreductive stripping. Almost no decomposition of the organic phase was observed by the irradiation, especially when using the halogen lamp. The organic phase was found to be re-usable for another extraction.

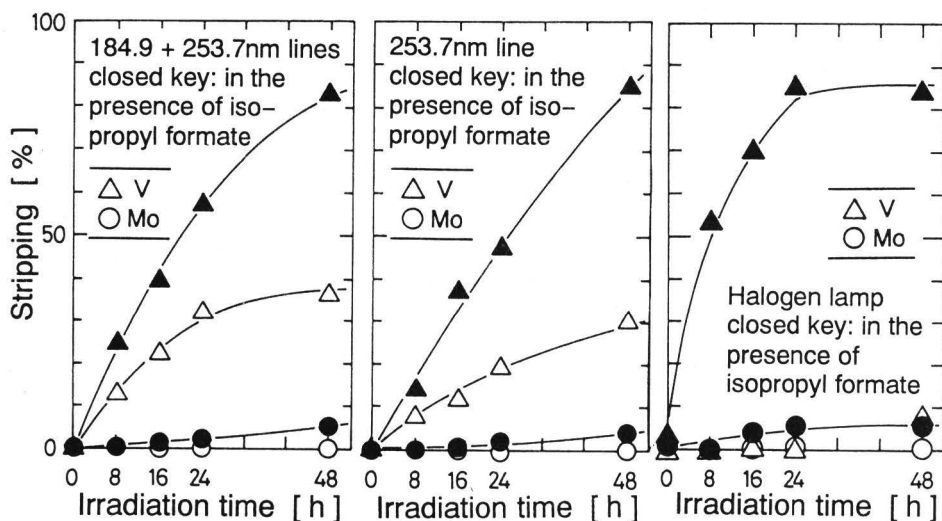


Fig. 10 Relationship between irradiation time and stripping yields of V and Mo

ACKNOWLEDGEMENTS

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EXTRACTION OF RARE EARTH METALS WITH NEW EXTRACTANTS OF CALIXARENE DERIVATIVES

Keisuke OHTO, Masayuki YANO, Katsutoshi INOUE
 Department of Applied Chemistry
 Saga University
 Honjyo 1, Saga 840, Japan
 Takehisa YAMAMOTO, Masahiro GOTO, Fumiyuki NAKASHIO,
 Takeshi NAGASAKI, Seiji SHINKAI
 Department of Chemical Science & Technology
 Kyushu University
 Hakozaki, Fukuoka 812, Japan

ABSTRACT

Hexa- and tetra-carboxylate derivatives of *p*-tert-octylcalix[6]arene and *p*-tert-octylcalix[4]arene as novel types of extractants for rare earths as well as *p*-tert-octylphenoxy acetic acid as the parent compound were synthesized to investigate extraction equilibria of rare earth metal ions, Ln^{3+} (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Ho, Er) from acidic aqueous solution. From the relation between $\text{pH}_{0.5}$ values and lanthanoid series for these extractants, it was found that calixarene derivatives offer much higher extractability and greater separation efficiency than the parent compound.

INTRODUCTION

Calixarene is a cyclic and phenolic oligomer and a novel type of attractive host compound (Gutsche, 1989; Vicens and Böhmer, 1991). The chemical modification of the phenolic hydroxide groups is relatively easy; consequently, the derivatives have potential as extractants for rare earths due to their chelate effect and rigid skeleton.

In this paper, we report the synthesis of hexa- and tetra-carboxylate derivatives of *p*-tert-octylcalix[6]arene (abbreviated as 'Oct[6] CH_2COOH) and *p*-tert-octylcalix[4]arene ('Oct[4] CH_2COOH) as new extractants for rare earth metals as well as *p*-tert-octylphenoxy acetic acid ('Oct[1] CH_2COOH) as their parent compound and their extraction behavior for rare earths.

EXPERIMENTAL

Synthesis of extractants

The chemical structure of the extractants used in the present work are shown in Fig. 1. The syntheses of the extractants were carried out according to the method mentioned in a

previous paper (Ohto et al.,1991).

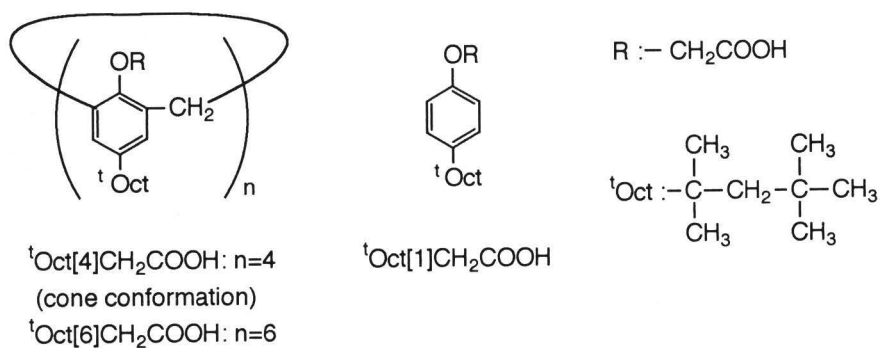


Fig.1 Structures of the extractants

TABLE 1
Experimental conditions

($\text{tert-Oct}[6]\text{CH}_2\text{COOH}=\text{H}_6\text{R}$, $\text{tert-Oct}[6]\text{CH}_2\text{COOH}=\text{H}_4\text{R}$, $\text{tert-Oct}[1]\text{CH}_2\text{COOH}=\text{HR}$)

1. HNO_3 - NaNO_3 ($\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$) system

Aqueous phase; $\text{H}_6\text{R}, \text{H}_4\text{R} : 0.1\text{mol/dm}^3 \text{ HNO}_3 - 0.1\text{mol/dm}^3 \text{ NaNO}_3$,

HR: $0.1\text{mol/dm}^3 \text{ CH}_3\text{COOH} - 0.1\text{mol/dm}^3 \text{ CH}_3\text{COONa}$

H_6R : 8 kinds of rare earths ($[\text{Ln}^{3+}]=0.05\text{mol/m}^3 \times 8$)

$\text{H}_4\text{R}, \text{HR}$: 3 kinds of rare earths ($[\text{Ln}^{3+}]=0.1\text{mol/m}^3 \times 3$) in one stock solution

Organic phase; diluent: toluene $[\text{H}_6\text{R}]=[\text{H}_4\text{R}]=5\text{mol/m}^3, [\text{HR}]=10\text{mol/m}^3$

2. HNO_3 -glycine system

Aqueous phase; $0.1\text{mol/dm}^3 - 0.1\text{mol/dm}^3$ glycine

3 kinds of rare earths ($[\text{Ln}^{3+}]=0.1\text{mol/m}^3 \times 3$) in one stock solution

Organic phase; diluent: CHCl_3 $[\text{H}_6\text{R}]=[\text{H}_4\text{R}]=5\text{mol/m}^3, [\text{HR}]=10\text{mol/m}^3$

Temperature: 303K

Measurement of metal concentration: ICP-AES

Reagents

The organic solution was prepared by dissolving each extractant into analytical grade toluene or chloroform to required concentrations. The aqueous solution was prepared by dissolving each rare earths chloride into an aqueous mixture of 0.1 mol/dm³ nitric acid and 0.1 mol/dm³ sodium nitrate or into 0.1 mol/dm³ glycine solution. The purity of each rare earth chloride used in this study was above 99.9 %. In the case of the experiment using ¹⁴⁷Oct[1]CH₂COOH, it was prepared by dissolving in an aqueous mixture of 0.1 mol/dm³ acetic acid and 0.1 mol/dm³ sodium acetate. Other inorganic reagents used were analytical grade and used without further purification.

Procedure

The distribution equilibria of rare earth metals with each extractant were investigated by the conventional method described in a previous paper (Nakashio et al.,1982). The quantitative analysis for metal ions was carried out by using a SEIKO model SPS-1200VR ICP-AES spectrophotometer.

The detailed experimental conditions are listed in Table 1.

RESULTS AND DISCUSSION

Figures 2(a) – (b) show the effect of equilibrium pH on the distribution ratio, *D*, for ¹⁴⁷Oct[6]CH₂COOH, ¹⁴⁷Oct[4]CH₂COOH and ¹⁴⁷Oct[1]CH₂COOH in the case of HNO₃ – NaNO₃ (or CH₃COOH–CH₃COONa) and HNO₃ – glycine systems as typical results, respectively.

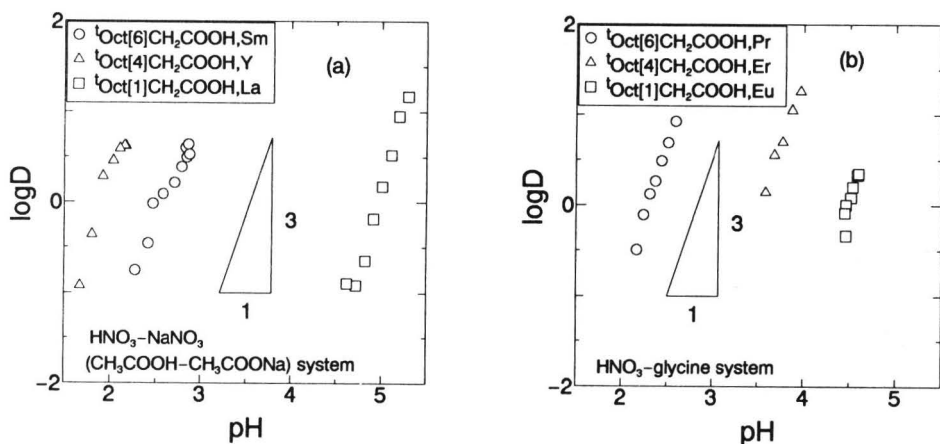


Fig.2 Effect on equilibrium pH on distribution ratio

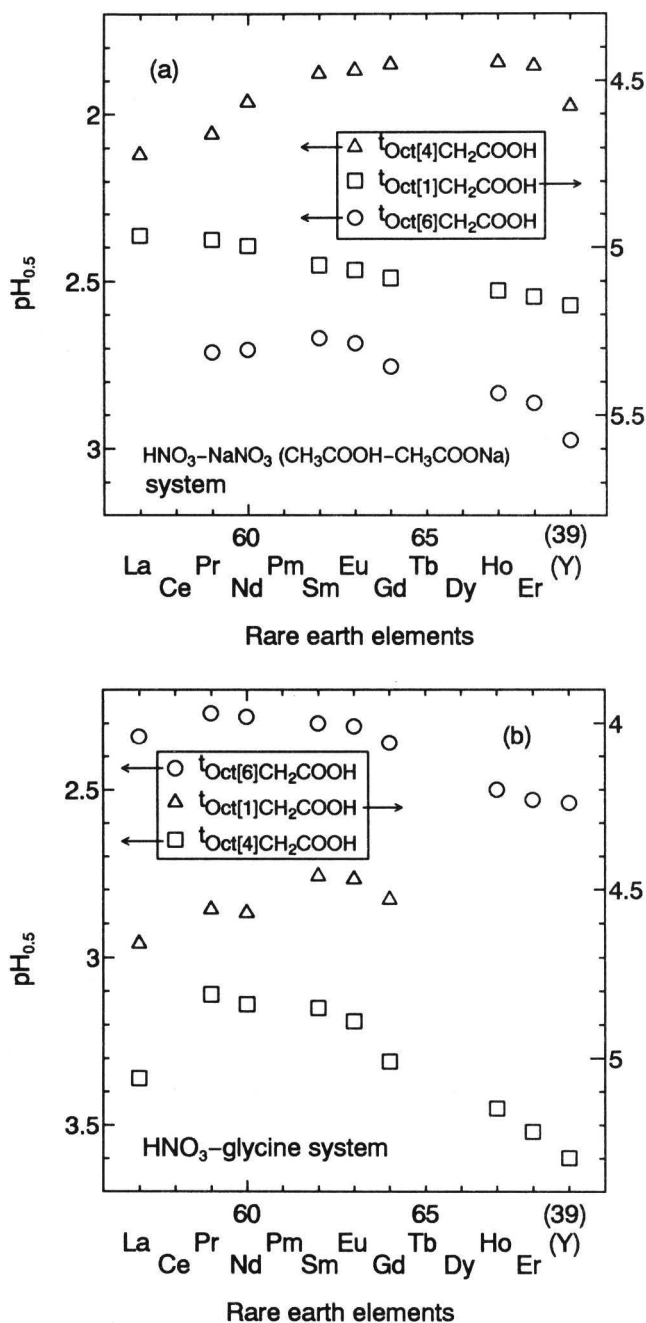


Fig.3 Relation between $\text{pH}_{0.5}$ vs. atomic number of rare earths

All of the plots (Fig.2(a)) in the pH region where metal ions were extracted considerably are straight lines with slope less than 3. This result may be attributable to sodium ions co-existing in the aqueous phase. The excess amount of sodium ion added forms complexes interacting with phenoxy oxygen atoms in the extractant molecules and impedes the extraction of rare earths. This hypothesis was supported by chemical shifts of ^1H -NMR spectroscopies (Arduini et al.,1986). All of the plots in Fig. 2(b) are straight lines with slope of 3. There is no retardation by co-existing species (i.e. glycine) in the extraction of rare earths.

These results show that the extraction reactions of rare earths with $^1\text{Oct}[6]\text{CH}_2\text{COOH}$, $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ and $^1\text{Oct}[1]\text{CH}_2\text{COOH}$ take place according to an ion exchange mechanism.

Figures 3(a) – (b) show the relation between $\text{pH}_{0.5}$ and lanthanoid series for three kinds of extractants in the case of $\text{HNO}_3 - \text{NaNO}_3$ (or $\text{CH}_3\text{COOH} - \text{CH}_3\text{COONa}$) and $\text{HNO}_3 - \text{glycine}$ systems respectively.

Obviously in both figures the extractability of $^1\text{Oct}[6]\text{CH}_2\text{COOH}$ and $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ as multi-functional extractants is higher than that of $^1\text{Oct}[1]\text{CH}_2\text{COOH}$ as single-functional extractant, though the experiments with each extractant were carried out under different conditions. Even if the total number of functional groups in the multi-functional extractants is the same as that in the single-functional extractant, the extractability of multi-functional extractants may be much higher than that of single-functional extractant. In the comparison of $^1\text{Oct}[6]\text{CH}_2\text{COOH}$ with $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ in the case of $\text{HNO}_3 - \text{glycine}$ system that were carried out under the same conditions, the extractability of $^1\text{Oct}[6]\text{CH}_2\text{COOH}$ with greater number of functional groups is greater than that of $^1\text{Oct}[4]\text{CH}_2\text{COOH}$. This is due to chelate effects.

The separation efficiencies of rare earths with these extractants are estimated by the differences for $\text{pH}_{0.5}$ of each metal. $^1\text{Oct}[6]\text{CH}_2\text{COOH}$ and $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ as cyclic extractants are larger in the differences of $\text{pH}_{0.5}$ than $^1\text{Oct}[1]\text{CH}_2\text{COOH}$ as an acyclic extractant. In the comparison of $^1\text{Oct}[6]\text{CH}_2\text{COOH}$ with $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ in both systems, the separation efficiency of $^1\text{Oct}[4]\text{CH}_2\text{COOH}$ with more rigid structure is higher than that of $^1\text{Oct}[6]\text{CH}_2\text{COOH}$. This is due to the rigid skeleton of the extractants.

All of the plots in both figures are convex curves, while $\text{pH}_{0.5}$ values of usual acidic extractants (e.g., D2EHPA, PC-88A, Versatic 10, etc.) tend to increase with the increase of atomic number of rare earths. This result may suggest that these extractants, calixarene derivatives, have the ability of ion recognition. Each extractant has a maximum point where the ring size (strictly speaking, size of functional groups) is suitable for the radii of metal ions.

These plots also exhibit the so-called "tetrad effect" (Peppard et al.,1969,1970).

CONCLUSION

Carboxylate derivatives based on calixarenes and their parent compound were synthesized to investigate distribution equilibria of nine kinds of rare earths from acidic nitrate media at 303 K. The following can be concluded;

- (1) The extractability of calixarene derivatives as multi-functional extractants is much higher than that of their parent compound. This is due to the chelate effect.
- (2) The separation efficiencies of calixarene derivatives as cyclic extractants were greater than that of an acyclic one. This is due to the effect of the rigid skeleton of calixarene.
- (3) In particular, calixarene derivatives exhibited the potential of ion recognition.
- (4) The relation between $\text{pH}_{0.5}$ and atomic number of rare earths exhibited the so-called "tetrad effect".

The application of calixarene derivatives as extractants for rare earths showed high potential in the enhancement of the extractability and separation efficiency.

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3.20

**SOLVENT EXTRACTION AND DETERMINATION OF EUROPIUM (III) IN
GEOLOGICAL MATRICES BY ATOMIC EMISSION SPECTROMETRY USING
THE REAGENT 1-PHENYL-3-METHYL-4-p-NITROBENZOYL-5-PYRAZOLONE**

G.N. RAO

Indian Institute of Technology
New Delhi-110 016, India

and

P.N. BANGROO and H.C. ARORA

Department of Atomic Energy
Atomic Minerals Division
West Block-7, R.K. Puram, New Delhi-110 066, India

ABSTRACT

A rapid method for the concentration of europium(III) present in geological materials has been developed. The extraction was carried out with 0.02 M solution of 1-phenyl-3-methyl-4-p-nitrobenzoyl-5-pyrazolone (HNMP) in butanol-methyl isobutyl ketone mixture. The estimation of europium was carried out in the organic phase by atomic absorption spectrometer in emission mode. The sensitivity of the method is 0.05 mg/L of europium in the organic phase.

INTRODUCTION

The rare earth elements serve as a group of indicator elements for the study of ore deposits, as well as in petrology for finding the genesis of the deposits. Amongst the rare earths, europium has a unique position as it is present in nature in two oxidation states, i.e. Eu(II) and Eu(III). This gives rise to the well known europium anomaly which is used to predict the genesis of some calcium bearing minerals and rocks.

A literature survey (Sen Gupta, 1976; Oeghe, Verb, 1974; Jaworowsky, 1967; Vanloon, 1971) for the estimation of europium (III) by atomic absorption spectrometry indicates that most of the methods make use of classical techniques, i.e. fluoride-oxalate-hydroxide precipitation for the concentration of europium. These methods are time-consuming and become unmanageable when one is compelled to take a large amount of sample containing a very low amount of europium. It was thought worthwhile to try an alternative procedure for the concentration of

europium. In our earlier work with β -diketones (Bangroo et al., 1989) it was observed that the reagent 1-phenyl-3-methyl-4-p-nitrobenzoyl-5-pyrazolone (HNMPP) shows promise as a good extractant for the rare earth elements. A procedure using HNMPP for the concentration of europium present in the geological samples has been tried, followed by estimation in the non-aqueous phase by AAS in the emission mode. The method is simple, rapid and sensitive.

EXPERIMENTAL

Apparatus and Reagents

A stock solution (1 g/L) of europium(III) was prepared from reagent grade Eu_2O_3 (99.9%, Fison, Philadelphia) in dilute HCl. Further dilutions were made from this stock solution. Solutions of other matrix elements (Y, La, Ce, Nd, Gd, Yb, U, Th, Fe, Al and Zr) studied were prepared by standard methods using reagent grade salts.

The reagent HNMPP was synthesised by the method of Jensen from methyl phenyl pyrazolone (BDH), p-nitrobenzoyl chloride (BDH), calcium hydroxide (BDH) and dioxan (Merck). A solution of the reagent HNMPP was prepared in a mixture of n-butanol-methyl isobutyl ketone (MIBK) in the ratio of 4:1.

A Varian model 634 spectrophotometer was used for spectrophotometric determinations. A Varian model AA-475 atomic absorption spectrometer with a single slot nitrous oxide-acetylene burner was used for estimation of europium under the parameters in Table 1.

TABLE 1

Instrumental conditions for determination of europium

Mode	: Emission
Wave length	: 459.4 nm
Slit width	: 0.2 nm
Fuel	: C_2H_2 (3 L/min)
Oxidant	: N_2O (7 L/min)
Flame condition	: Slightly reducing

An Omniscrite B-5000 strip chart recorder was used to record the emission spectrum of europium. The measurement of pH was carried out using an Elico pH meter. The shaking was carried out in stoppered glass vials.

Extraction Procedure

Preliminary studies of the extraction of europium(III) revealed that the time needed to attain equilibrium in extraction is two minutes. An aliquot of standard Eu(III) solution (0.1 mg) was extracted with 10 mL of 0.02 M HNMPP in n-butanol-MIBK (4:1 mixture) at different pH values (pH 1 to 6) for two minutes. The recovery of Eu(III) was checked in the extraction

raffinate by spectrophotometry using the Alizarin Red-S method. Due to incomplete recovery, extraction was repeated at pH 1 to 6 in the presence of sodium chloride (5 to 10%). It was found that europium (III) is quantitatively extracted at pH 3.5 to 4.5 in the presence of NaCl in a single extraction. But in this pH range, iron(III) which is present in natural samples becomes hydrolysed. To overcome this, citric acid was used to complex Fe(III) and extraction of Eu(III) was carried out at pH 5.5 to 6.5 in the presence of NaCl. A recovery of 92% of Eu(III) was observed under these conditions. Therefore, two extractions were carried out to quantitatively recover europium. All future experiments were carried out at pH 5.5 to 6.5 in the presence of citric acid (1 g) and NaCl (5 to 10%) with 0.02 M HNMPP in n-butanol-MIBK (4:1) mixture.

RESULTS AND DISCUSSION

As it is well known that organic solvents enhance the absorption/emission signal of metals in A.A.S. it was decided to use organic solvent for aspiration. Various solvents viz. n-butanol, ethylacetate, n-butylacetate and MIBK, suitable for aspiration in A.A.S., were tried for extracting Eu(III) with HNMPP. It was observed that among these solvents, n-butanol proved to be the best for the extraction of Eu(III). But the solubility of the ligand HNMPP was found to be poor in n-butanol and a mixture of n-butanol and MIBK was found to be the best compromise between solubility and extractability. This mixture also improves the physical characteristics of the solvent leading to more efficient nebulisation in A.A.S.

The emission spectrum of europium was recorded on a chart recorded by scanning the wavelength range 458 nm to 461 nm (Figures 1 and 2). It was observed that the minimum concentration of europium that could be detected is 0.05 mg/L in the organic phase.

In order to check the scope of the method for natural samples a study on the recovery of europium in the presence of various associated elements viz. yttrium, lanthanum, cerium, neodymium, gadolinium, ytterbium, zirconium, uranium, thorium, iron and aluminium was made by extracting the mixtures at the established parameters. It was observed that 1 mg each of Y, La, Ce, U and Th; 0.1 mg of Nd, Gd, Yb and Zr do not interfere.

Al(III) is partially extracted and seriously depresses the signal of europium. This problem was avoided by opening the sample with sodium peroxide fusion and leaching the melt with water. This also removes fluoride and phosphate ions which otherwise interfere in the extraction of europium.

To check the validity of the method of determination of europium in geological materials, two synthetic samples (silicate matrices) and also some geological samples were analysed. The recovery ranges from 92% to 98% and the results are shown in Tables 3 and 4.

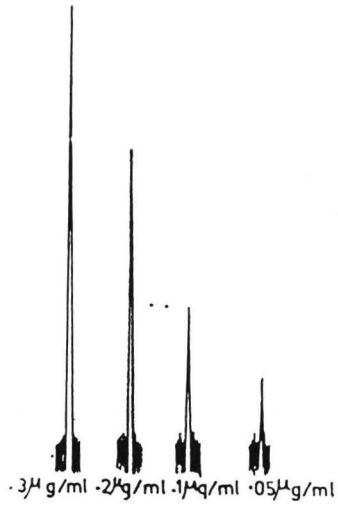


Fig. 1

PEAK HEIGHTS OF Eu(III)
STANDARDS IN ORGANIC PHASE

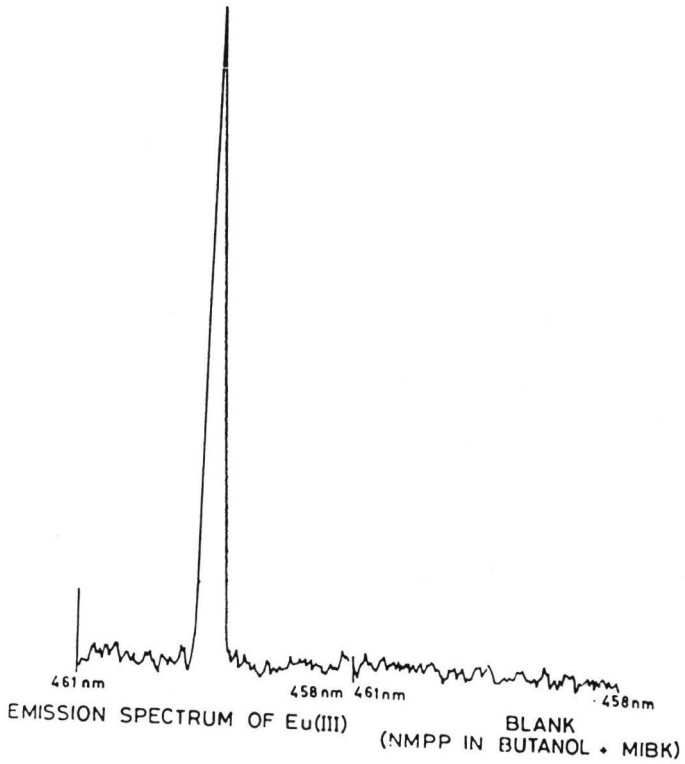


Fig. 2

TABLE 2

Recovery of Eu(III) with HNMPP (0.02 M) at pH 6.0
in the presence of foreign elements

Eu(III) = 0.0125 mg

Sodium Chloride = 1 g

Citric acid = 1 g

Organic Phase = 25 mL

Emission signal in absence of other elements = 0.350

Ion added	Quantity of the ion added	Europium signal in AAS (Org. phase)
Y	1 mg	0.347
La	1 mg	0.348
Ce	1 mg	0.351
Nd	0.1 mg	0.349
Gd	0.1 mg	0.345
Yb	0.1 mg	0.350
Zr	0.1 mg	0.351
U	1 mg	0.348
Th	1 mg	0.348
Al	100 mg	0.368

TABLE 3

Analysis of geological samples

Sample No.	Eu present in the sample mg/kg	Eu found [#] by the present method mg/kg	% Recovery
SYNTHETIC-1	500	491	98%
SYNTHETIC-2	1000	970	97%

Mean of two values

TABLE 4

Analysis of geological samples

Sample No.	Eu found by present method mg/kg	Eu added (μg)	Eu found by the present method (μg)	% Recovery
NC-23	nil	10.0	9.2	92%
NC-24	1.7	10.0	11.2	95%
NC-26	nil	10.0	9.4	94%

RECOMMENDED PROCEDURE

An accurately weighed approximately 1 g sample is fused with sodium peroxide flux in a nickel crucible. After cooling, the melt is leached in water and the mixture is thoroughly boiled and filtered through Whatman filter paper. The residue containing europium and other rare earths, iron etc., is washed with hot NaOH solution and the residue dissolved in HCl and the extraction and estimation of europium is carried out as discussed above.

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3.21

A NOVEL SOLVENT EXTRACTION SYSTEM FOR RHODIUM**E. BENGUEREL and G.P. DEMOPOULOS**

Department of Metallurgical Engineering
McGill University
Montreal, Quebec, Canada, H3A 2A7

ABSTRACT

The intricate aqueous chemistry of rhodium (Rh) in chloride-based solutions has in the past hindered the development of modern and efficient separation techniques for this element. By making use of SnCl_2 , however, the aqueous chemistry of Rh can be modified such that quantitative extraction of Rh from chloride-based solutions can be achieved in a single contact. A novel solvent extraction system based on this principle and using Kelex 100, a commercially available 7-alkylated 8-hydroxyquinoline extractant, has been developed and recently patented.

In this paper, some of the chemistry involved in this new solvent extraction scheme is reviewed. The effect of a number of parameters such as the Sn:Rh feed ratio, the acidity and age of the feed on Rh extraction are discussed and, in addition, the potential application of this Rh recovery scheme to typical PGM refining liquors is addressed.

INTRODUCTION

The separation/purification of rhodium (Rh) is a most difficult problem in platinum group metal refining. The recovery of Rh, as it is practised today, involves a number of successive chemical transformations of the Rh feed liquor such that impurities are removed by precipitation-dissolution steps (Edwards, 1976; Stern, 1981; Demopoulos, 1989). Because each of these transformation steps is associated with low yield and selectivity, some of the precipitations must be performed a number of times. The result is a very lengthy refining process which can take several months, due in part to long filtrations, for the final recovery of pure Rh. All of these considerations have led to dissatisfaction with this method and to the

need for a more efficient, modern separation process, such as solvent extraction.

Through the introduction of solvent extraction, precious metal refineries have improved their efficiency in refining most platinum group metals. However, this is not the case in the recovery of Rh. A number of studies have been performed on the solvent extraction of Rh but the systems proposed were not industrially viable since they were developed for analytical chemistry needs. It is generally agreed upon that the difficulties encountered in purifying Rh arise due to its complex chemistry in chloride solutions, where Rh forms a number of aquochloro complexes (Palmer and Harris, 1975; Robb and Harris, 1965). The poor response of Rh towards solvent extraction, from chloride solutions, can be understood by examining its relevant solution chemistry.

AQUEOUS CHEMISTRY OF RHODIUM

Rhodium in Chloride Solutions

As mentioned briefly above, Rh forms a number of aquochloro complexes in chloride solutions of the type $\text{RhCl}_{6-n}(\text{H}_2\text{O})_n^{(3-n)-}$ (where $0 \leq n \leq 6$). The total chloride content of the Rh solution governs the overall abundance of each complex present in solution. Figure 1 shows the speciation diagram for rhodium chloride complexes in pure HCl solutions as a function of the HCl concentration. This diagram is based on chloride and water activities for such solutions. A detailed description of this diagram can be found in Benguerel et al, 1993. In the region of chloride content typical of most refining liquors (4M chloride), the most abundant species (about 60%) is $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$.

This species, being a highly hydrophilic complex, does not usually respond well to direct solvent extraction. Only about 40% RhCl_6^{3-} is available for direct extraction. Assuming that all of the RhCl_6^{3-} can be extracted, adjusting the feed to chloride levels where the most abundant complex is $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ does not seem a very practical solution since about 8M total

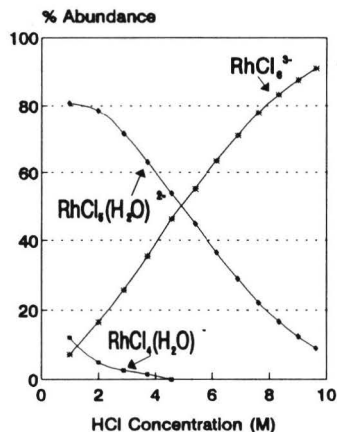


Figure 1: Rh-Cl speciation diagram based on chloride and water activities (taken from Benguerel et al, 1992)

chloride is required before 80% of the Rh is in the form of RhCl_6^{3-} , for pure HCl solutions. Considering therefore all of the problems encountered when dealing with Rh chloride solutions, it seems reasonable to suspect that some type of manipulation, probably chemical, on the Rh feed solution is necessary to achieve acceptable extraction and stripping levels.

Interaction of Rhodium with SnCl_2

The interaction of Rh with SnCl_2 has long been used by analytical chemists for the trace determination of Rh (Al-Bazi and Chow, 1984; Diamantatos, 1983; Uttawar and Joshi, 1981). Adding SnCl_2 to a Rh feed is one solution adjustment procedure which can be used to make Rh more prone to extraction. A number of studies have been performed on the aqueous complexes formed when Rh(III) and Sn(II) are allowed to react. Similarly to Rh in aqueous chloride solutions, a number of different complexes have been reported including $[\text{RhCl}_{6-n}(\text{SnCl}_3)_n]^{3-}$ (where $0 \leq n < 6$), $[\text{Rh}(\text{SnCl}_3)_5]^{4-}$ and $[\text{RhH}(\text{SnCl}_3)_5]^{3-}$ (Moriyama et al, 1981; Iwasaki et al, 1984; Yamakawa et al, 1985; Hall and Koch, 1991). The distribution of the various Rh-Sn complexes formed is a function of the Sn:Rh molar ratio in solution. When the Sn:Rh feed ratio is less than 6:1, Rh(III) complexes of the type $[\text{RhCl}_{6-n}(\text{SnCl}_3)_n]^{3-}$ dominate. When the Sn:Rh ratio is six or more, however, Rh(I) complexes are formed. The overall reaction believed to describe the formation of one of these complexes is:



where SnCl_3^- , one of the Sn(II) chlorocomplexes, acts both as ligand and as reductant and where the reduction of Rh(III) to Rh(I) is accompanied by the oxidation of Sn(II) to Sn(IV). This reduction occurs only when each of the six chloride (or water) ligands have been replaced by SnCl_3^- ligands (Iwasaki et al, 1984).

The advantage in producing Rh-Sn complexes is that compared to the aquochloro complexes, they tend to respond well to solvent extraction (Khattak and Magee, 1969) since they are non-aquated and therefore much less hydrophilic. In addition, the Rh-Sn complexes are considered to be quite reactive, or labile, and therefore likely to undergo chemical reactions.

The behaviour of Rh-Sn complexes with extractants such as 8-hydroxyquinoline derivatives has not been studied previously although these extractants have been studied for the separation and recovery of Pt and Pd (Pouskoupleli et al, 1987; Demopoulos et al, 1989, Côté and

Demopoulos, 1993a,b). Recently, a patent was granted for the recovery of Rh using SnCl_2 and Kelex 100 (Demopoulos et al, 1992) and some important features of this system are detailed below. An earlier announcement on the subject was made in a recent IPMI-sponsored symposium (Demopoulos and Benguerel, 1992).

EXPERIMENTAL

The organic solution was composed of 2 v% Kelex 100, 5 v% tridecanol and 93 v% Solvesso 150, corresponding to about a $5.6 \times 10^{-2} \text{M}$ extractant solution. The standard aqueous feed solution contained 1.5M HCl, 4M total chloride (adjusted with MgCl_2) and about 0.4 g/L Rh, except if otherwise stated. SnCl_2 was added to the Rh feed solution at the desired Rh/Sn ratio and the solution was heated to about 70°C for 15 minutes. The extraction/stripping tests were performed at room temperature using a Burrell automatic wrist action shaker. The aqueous to organic ratio (A/O) was 1 with the loading stage contact time fixed at 10 minutes and the stripping contacts at 15 minutes each. The Rh and Sn concentrations in all of the aqueous solutions were determined by atomic absorption.

RESULTS

The extraction of Rh from 0.7 to 8M HCl solutions, either treated with SnCl_2 or from similar solutions but not containing SnCl_2 , is shown in Figure 2. Enhanced extraction is observed for the feeds treated with SnCl_2 with quantitative extraction throughout the acidity range tested. For the pure Rh solutions, the extraction is always below 40%, and the tendency for increased extraction with increasing acidity may be due to the overall increase in abundance of RhCl_6^{3-} as the HCl content, and thereby the total chloride concentration, is increased.

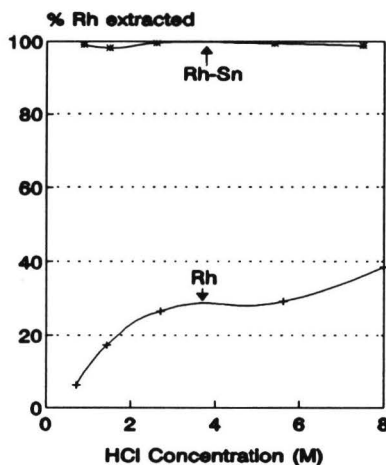


Figure 2: Extraction of Rh from HCl solutions (with or without SnCl_2)

As expected, the amount of Sn added to the Rh feed solution affects the degree of extraction.

It has been found that a molar ratio of 2:1 Sn:Rh is required for quantitative Rh extraction. Adding higher quantities of Sn does not hinder the extraction in any way since it remains quantitative at least up to a ratio of 20:1 Sn:Rh (maximum ratio tested).

The extraction isotherm for a feed having a Sn:Rh molar ratio of 12:1 is shown in Figure 3. Analysis of the fully loaded organic has shown that under fully loaded conditions, the molar ratio of Kelex 100:Sn:Rh is 3:4:1. The extraction isotherm shows a sharp incline to the maximum loading capacity for 2 v% Kelex 100 at about 2000 mg/L.

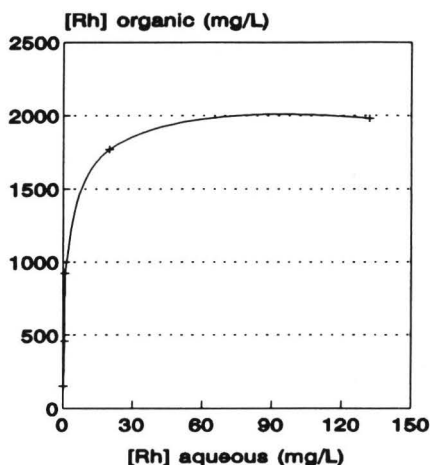


Figure 3: Extraction isotherm for a 12:1 Sn:Rh feed, 2 v% Kelex 100, A/O=1

The extraction is so powerful that it remains quantitative regardless of factors such as acidity (0.7-8M), total chloride content (1.5-

6M) and age (up to seven days) of the Rh feed as long as the Sn:Rh ratio is 2:1 or greater.

It is also important to mention that the extraction is extremely rapid, occurring in as little as 30 seconds mixing time, which could prove important when dealing with real liquors where very short contact times for extraction can help to reduce the level of impurity co-extraction.

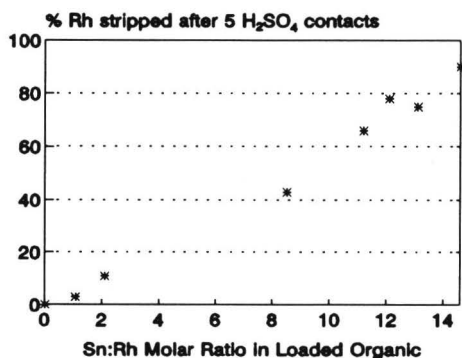
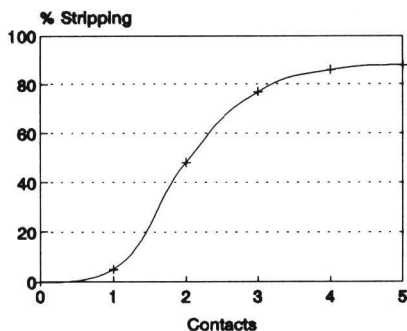


Figure 4: Rh stripping dependence on Sn:Rh feed ratio

Stripping of Rh from the loaded organic is achieved using a sulfate solution composed of 1.7M H₂SO₄ + 1M Na₂SO₄. Contrary to the extraction stage, a number of parameters directly affect the quantity of Rh which can be stripped. Figure 4 depicts the percent Rh stripped (for a cumulation of 5 consecutive contacts) versus the initial Sn:Rh feed molar ratio. It is clear that the extraction is reversible only at relatively high ratios

(about 12:1) with virtually no stripping occurring at feed ratios below 2:1.

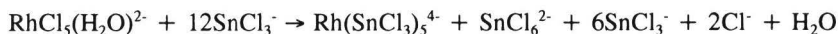
A typical Rh stripping curve for a 12:1 feed is shown in Figure 5. No stripping is observed during the first contact. Most of the Rh is recovered during the second and third contacts. Some stripping occurs in the fourth contact as well, and a plateau is reached by the fifth contact.



CHEMISTRY OF SYSTEM

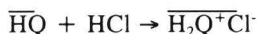
Much of the exact chemistry of this system remains uncertain but some of the most probable steps which occur during the course of the process

can be suggested. Only the high Sn:Rh (12:1) molar ratio will be examined since the extraction is reversible only in this case. During the feed pretreatment stage, when the Rh solution is allowed to interact with SnCl_2 , the governing chemical reaction could be as follows;



with the formation of the Rh(I) complex dominating.

During extraction, since the Rh-Sn feed solution contains a high level of acidity (1.5M HCl), Kelex 100 is immediately protonated on contact with the feed (Côté and Demopoulos, 1993a), giving rise to the following reaction;



The quantitative extraction of the Rh-Sn complex can then quickly occur via ion-pair formation. Although the exact complex in the organic phase has not been determined, it is speculated, from the results obtained to date, that Rh(I) is reoxidized to Rh(III) forming a complex of the type $\text{Rh}(\text{HQ})_2(\text{SnCl}_3)_4 \cdot \text{H}_2\text{Q}^+$. The Kelex:Sn:Rh ratio of 3:4:1 which has been found for the fully loaded organic agrees with this postulation.

Figure 5: Progression of Rh stripping with sulfate media

POTENTIAL APPLICATION TO PLATINUM GROUP METAL REFINING

The proposed system for the recovery of Rh using both SnCl_2 and Kelex 100 is envisaged to take place following Pt and Pd solvent extraction (Figure 6). As the extraction stage can be of very short duration, some impurity co-extraction can be avoided. However, some common impurity elements such as Cu, Ni and Pb are only slightly extracted with 8-hydroxyquinoline derivative extractants (Aprahamian et al, 1991). Any entrained impurities can be removed by scrubbing with dilute HCl since this solution does not strip the Rh-Sn extracted complex. The excess Sn coextracted and not stripped along with Rh is removed at the end of the flowsheet with a caustic scrub solution. Finally, the solvent is washed

with $\text{HCl}/\text{H}_2\text{O}$ prior to its return to the extraction stage. Rhodium may be recovered from the resultant Rh/Sn sulphate strip solution by various techniques.

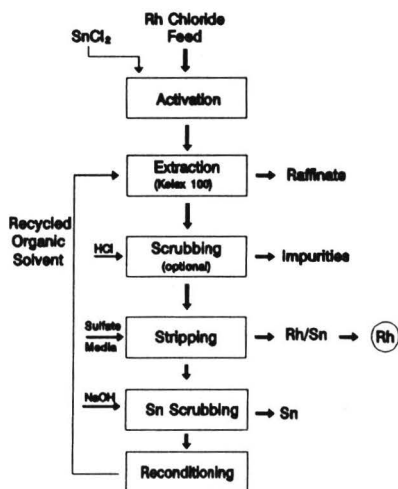


Figure 6: Simplified flowsheet of the activation solvent extraction scheme for Rh (applied after primary PGM recovery)

ACKNOWLEDGEMENTS

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3.22

SEPARATION OF SCANDIUM(III), YTTRIUM(III), LANTHANIDES(III) AND IRON(III) WITH ORGANOPHOSPHINIC MONO-ACIDIC ESTER AS EXTRACTANTS

Deqian LI, Genxiang MA, Xiaofeng ZHANG, Yunling ZHAO,
Lizhen XUE, Xiaohong ZHI

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

ABSTRACT

The extraction equilibrium of Sc(III), Y(III), Ln(III) (Ln=Ho, Er, Yb, Lu) and Fe(III) from HCl solutions with bis (2, 4, 4 - trimethylpentyl) phosphinic acid (HBTMPP) and di (2-ethylhexyl) phosphinic acid H(DEHP) has been investigated. It has been found that the order of extractability of the above elements is as follows: $\text{Sc} > \text{Fe} > \text{Lu} > \text{Yb} > \text{Er} > \text{Y} > \text{Ho}$. It is possible to separate Sc(III) from Fe(III) and Ln(III) and heavy lanthanides(III) from each other with H(DEHP) or HBTMPP. Stripping of Sc(III) with mineral acid (HCl, H_2SO_4) has been carried out systematically. By the methods of slope analysis, saturation capacity and IR, NMR spectra, the composition of extracted complex of Sc(III) with H(DEHP) or HBTMPP has been determined to be $\text{Sc}(\text{HA}_2)_3$. The equilibrium constants and thermodynamic functions of reaction have been calculated.

INTRODUCTION

Acidic organophosphorus extractants for extraction of rare earths have been studied and applied extensively with di (2-ethylhexyl) phosphoric acid (HDEHP) (Weaver, 1968) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP) (Li et al., 1980). By substituting a P-C bond for a P-O-C in the HEH/EHP molecule, the pKa value of the resulting compound di (2-ethylhexyl) - phosphinic acid (H(DEHP), HA) or bis (2, 4, 4 - trimethylpentyl) phosphinic acid (HBTMPP, HA) would be increased owing to the weakened effect of negativity of the alkoxy group. At the same time the distribution ratio (D) of rare earth by the above organophosphinic

mono — acidic esters would also be decreased. Besides, H(DEHP) or HBTMPP possesses notable properties in extracting and stripping in lower acidic solutions showing remarkable favorable behavior. However, so far only a few reports dealing with the extraction behavior of H(DEHP) (Xue and Li, 1991, Yue and Li, 1990) and HBTMPP (Li and Freiser, 1986; Komatsu and Freiser, 1989) containing double P—C bond for rare earths have appeared. The extraction separation of Sc(III), Y(III), Ln(III) and Fe(III) with H(DEHP) or HBTMPP from hydrochloric acid solutions has not been reported previously.

Scandium often co-exists with yttrium, lanthanide and iron and its separation from the elements by solvent extraction is of practical significance. The purpose of this paper is to report studies on the extraction behavior of Sc(III), Y(III), Ln(III) (Ln=Ho, Er, Yb, Lu) and Fe(III) from HCl solutions with H(DEHP) or HBTMPP in n-octane and the extraction mechanism of Sc(III).

EXPERIMENTAL

H(DEHP) and HBTMPP were supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences and American Cyanamid Co. respectively, and were purified with the conventional copper salt method, analytical grade n-octane was employed for diluent. The stock solutions of Sc(III), Y(III) and Ln(III) were prepared by dissolving their oxides (purity 99.9%) in concentrated hydrochloric acid. Fe(III) solutions were prepared by analytical reagent $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. All other chemicals were of analytical reagent grade.

The experimental apparatus and procedures for the extraction of metal ions were described by Li et al. (1988). The extraction experiments (except temperature effect) were carried out at $25 \pm 1^\circ\text{C}$. Concentrations of scandium, iron, yttrium and lanthanide in aqueous phase or organic phase (stripping with HCl or HNO_3) were determined as described by Xue and Li (1991); Islam et al. (1979); Ren et al. (1987) respectively.

RESULTS AND DISCUSSION

Effect of acidities of equilibrium aqueous phase on metal ions(III) extraction with H (DEHP) or HBTMPP

The extraction of Sc(III), Y(III), Ln(III) and Fe(III) from HCl solutions by H (DEHP) or HBTMPP was examined with the results shown in Fig. 1.

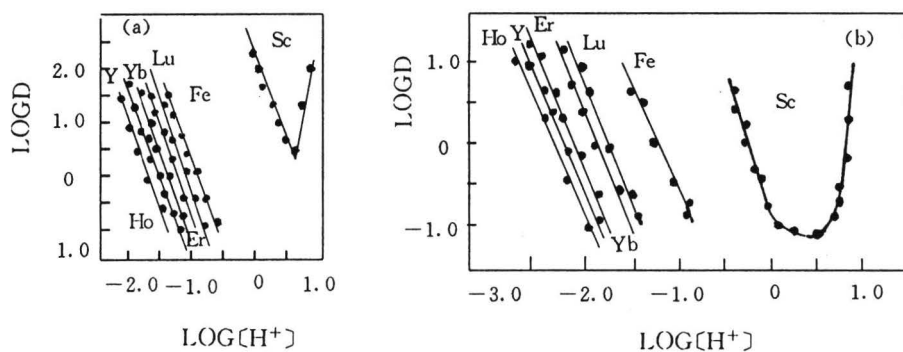


Fig. 1 Plots of logD vs log [H⁺]

(a) H(DEHP) system
 $[HA] = 0.16 \text{ M}$, $[Sc, Y, Ln] = 1.10 \text{ mM}$, $[Fe(III)] = 1.33 \text{ mM}$
 (b) HBTMPP system
 $[HA] = 20.0 \text{ mM}$, $[Sc, Y, Ln] = 0.4 \text{ mM}$, $[Fe(III)] = 0.42 \text{ mM}$

The equilibrium curves of logD vs log[H⁺] give straight lines having a slope of -3 at low aqueous acidities. It is indicated that Sc(III), Y(III), Ln(III) and Fe(III) can be extracted by ion exchange reaction. The shape of the equilibrium curve suggests the possibility of Sc(III) extraction by other reactions at high aqueous acidity. It has also been found that the order of extractability of the above elements is as follows: $Sc \gg Fe > Lu > Yb > Er > Y > Ho$. Y lies between Ho and Er. It is possible to separate Sc(III) from Y(III), Ln(III) and Fe(III), and heavy lanthanides(III) in sequence by H (DEHP) or HBTMPP. The separation factors (β) for extraction of Fe(III), Y(III) and Ln(III) with H(DEHP) or HBTMPP are illustrated in Table I. For comparison with HEH/EHP, Fig. 2 shows the results of extraction of Fe(III), Yb(III) and Lu(III) by HEH/EHP. The data of Figs. 1, 2 indicate that extractability of H(DEHP) for Sc(III), Y(III), Ln(III) and Fe(III) is lower than that of HEH/EHP, but for separation of

similar elements, the selectivity of the former is greater than that of the latter. Under similar conditions, $\beta_{\text{Fe/Lu}} = 4.3$ (H(DEHP)), $\beta_{\text{Fe/Lu}} = 2.3$ (HEH/EHP), $\beta_{\text{Lu/Yb}} = 2.2$ (DEHP), $\beta_{\text{Lu/Yb}} = 1.9$ (HEH/EHP), etc.. Fig. 1 also shows the extractability of HBTMPP for Sc(III), Y(III), Ln(III) and Fe(III) is lower than that of H(DEHP). It is thought that the steric hindrance effect of the substituent is the main factor determining their extractability.

TABLE 1

The β values for the extraction of Fe(III), Y(III) and Ln(III) with H(DEHP) or HBTMPP

Extractant	pH _{aq.}	$\beta_{\text{Fe/Lu}}$	$\beta_{\text{Lu/Yb}}$	$\beta_{\text{Yb/Er}}$	$\beta_{\text{Er/Y}}$	$\beta_{\text{Y/Ho}}$
H(DEHP)	1.60	4.26	2.16	4.57	1.48	2.24
HBTMPP	2.10	2.81	1.32	6.38	1.63	1.30

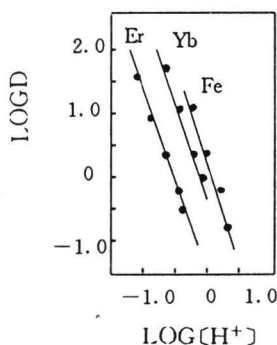
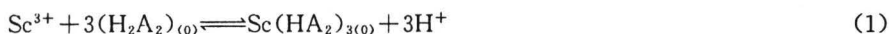


Fig. 2 Effect of acidities on extraction of metal ions with HEH/EHP

$[\text{HEH/EHP}] = 0.16 \text{ M}$;
 $[\text{Ln(III)}] = 1.1 \text{ mM}$
 $[\text{Fe(III)}] = 1.33 \text{ mM}$

Effect of H(DEHP) or HBTMPP concentration on extraction equilibrium of Sc(III)

Fig. 3 shows $\log D$ as a function of the equilibrium concentration of H (DEHP) or HBTMPP. The slopes of the plots of $\log D$ vs $\log [\text{H}_2\text{A}_2]_{(o)}$ are 3 for Sc(III) at low aqueous acidities. Thus the extraction mechanism of Sc(III) with H(DEHP) or HBTMPP could be written as follows:



The composition of extracted complex of Sc(III) with H(DEHP) or HBTMPP determined by the saturation method is $\text{Sc}(\text{HA}_2)_3$. The equilibrium constant for the reaction of Equation (1) is

$$\log K = \log D + 3 \log [\text{H}^+] + \log (1 + \sum_i \beta_i [\text{Cl}^-]^i) - 3 \log [\text{H}_2\text{A}_2]_{(o)} \quad (2)$$

In the experimental conditions, considering the overall stability constants of Sc(III) with Cl^- (Sillen, 1971), then the equilibrium constants ($\log K$) of reaction (1) according to Equation (2) have been calculated to be 5.80 for H(DEHP) and 4.82 for HBTMPP.

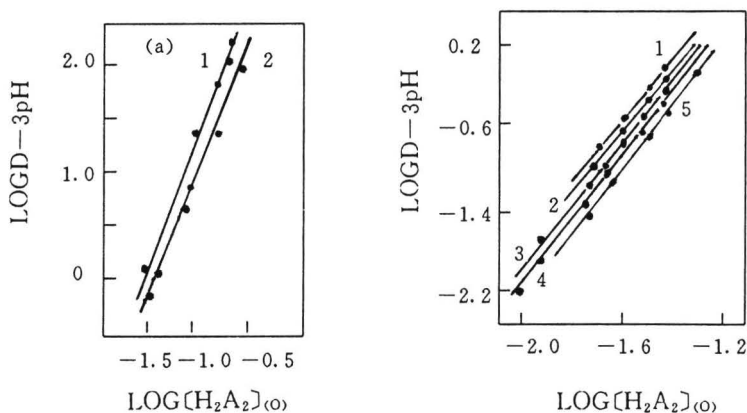


Fig. 3 Plots of $\log D$ vs $\log[\text{H}_2\text{A}_2]_{(O)}$

- (a) H(DEHP) system
 $[\text{Sc(III)}] = 1.10 \text{ mM}$, $[\text{Cl}^-] = 0.5 \text{ M}$, 1- $[\text{H}^+] = 0.46 \text{ M}$, 2- $[\text{H}^+] = 0.60 \text{ M}$
 (b) HBTMPP system
 1- $[\text{Cl}^-] = 1.7 \text{ M}$, $[\text{H}^+] = 0.70 \text{ M}$; 2- $[\text{Cl}^-] = 1.6 \text{ M}$, $[\text{H}^+] = 0.60 \text{ M}$
 3- $[\text{Cl}^-] = 1.5 \text{ M}$, $[\text{H}^+] = 0.50 \text{ M}$; 4- $[\text{Cl}^-] = 1.0 \text{ M}$, $[\text{H}^+] = 0.50 \text{ M}$
 5- $[\text{Cl}^-] = 1.0 \text{ M}$, $[\text{H}^+] = 0.60 \text{ M}$

Effect of temperature on extraction equilibrium of Sc(III)

The effect of temperature on extraction equilibrium of Sc(III) with H(DEHP) or HBTMPP was investigated. Results indicate that reaction (1) is exothermic and the values of enthalpy change (ΔH^0) were estimated to be $-46.44 \text{ kJ} \cdot \text{mol}^{-1}$ (H(DEHP) system) and $-32.13 \text{ kJ} \cdot \text{mol}^{-1}$ (HBTMPP system).

The values of the corresponding free energy (ΔG^0) and entropy change (ΔS^0) at 25°C can be calculated as $-33.33 \text{ kJ} \cdot \text{mol}^{-1}$ and $-0.04 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for H(DEHP); $-27.69 \text{ kJ} \cdot \text{mol}^{-1}$ and $-14.89 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for HBTMPP respectively.

IR and ^1H NMR spectra of extracted complexes of Sc(III)

In order to obtain the formation of the structure in extracted complexes, the IR and

^1H NMR spectra of extracted complexes of Sc(III) have been studied. Results suggest that H^+ of the OH group in HA is partially substituted by Sc(III) and H(DEHP) or HBTMPP coordinates with Sc(III) through the O atom of $\text{P}=\text{O}$ group. The data of the IR and ^1H NMR spectra are in good agreement with the obtained extraction mechanism of Sc(III) by H(DEHP) or HBTMPP.

Stripping of Sc(III) with mineral acid (HCl , H_2SO_4) from organic phase

As shown in Fig. 1 and Fig. 2, the extraction ability of H(DEHP) or HBTMPP is lower than that of HEH/EHP and HDEHP, and thus it can be expected that their stripping property should be superior to HEH/EHP and HDEHP. Fig. 4 shows that the percentage stripping of Sc(III) varies with the concentration of HCl or H_2SO_4 and the results indicate that when stripping of Sc(III) from 0.1 M extractant in *n*-octane is performed by using 3.0 M HCl or 2.5 M H_2SO_4 , with HEH/EHP or HDEHP, the percentage stripping is only 4–8% or 1–2%, while with H(DEHP) or HBTMPP, it is as high as 85–87% or 75–82% respectively

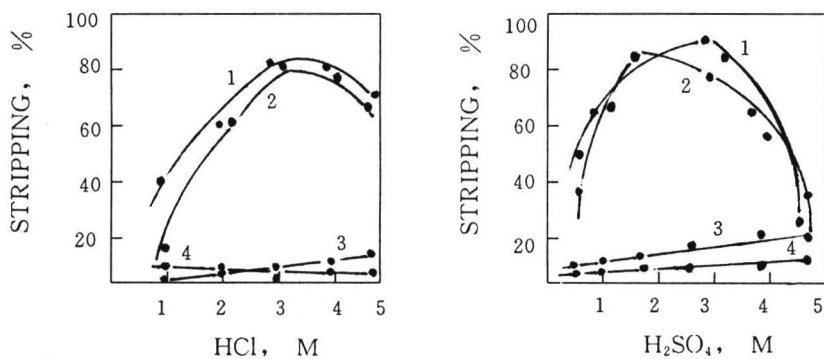


Fig. 4 Stripping of Sc(III) with mineral acid (HCl , H_2SO_4) from acid organophosphorus extractants

$$[\text{HA}]_{(0)} = 0.1 \text{ M}, [\text{Sc(III)}]_{(0)} = 12.0 \sim 14.0 \text{ mM}$$

1—H(DEHP), 2—HBTMPP, 3—HEH/EHP, 4—HDEHP; (a) HCl , (b) H_2SO_4

The shapes of stripping curves in Fig. 4 show two different extraction mechanisms of Sc(III) in good agreement with the equilibrium curves of Fig. 1.

CONCLUSIONS

The extraction equilibrium of Sc(III), Y(III), Ln(III) (Ln=Ho,Er,Yb,Lu) and Fe(III) from aqueous hydrochloric acid solution with H(DEHP) or HBTMPP in n-octane has been investigated. The results show that the order of extractability of the above elements is as follows: $\text{Sc} \gg \text{Fe} > \text{Lu} > \text{Yb} > \text{Er} > \text{Y} > \text{Ho}$. It is possible to separate Sc(III) from Fe(III) and Ln(III), and heavy lanthanides from each other with H(DEHP) or HBTMPP. Using the methods of slope analysis, saturation capacity and IR, HNMR spectra, the composition of the extracted complex of Sc(III) has been determined to be $\text{Sc}(\text{HA}_2)_3$. The equilibrium constants and thermodynamic functions of reaction have been obtained. Stripping of Sc(III) with mineral acid has also been carried out.

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3.23

INFLUENCE OF INORGANIC SALTS ON THE KINETICS OF ERBIUM(III) EXTRACTION FROM HYDROCHLORIC ACID SOLUTIONS WITH HEH/EHP

Ducheng SUN, Santang YUE and Deqian LI

Laboratory of Rare earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

ABSTRACT

The influence of inorganic salts (NaClO_4 , NaNO_3 , NaCl) on the kinetics of Er(III) extraction from hydrochloric acid media by HEH/EHP in n-heptane has been studied using the growing drop technique at 30°C. The rate of Er(III) extraction from HCl solutions by HEH/EHP is shown to be increased significantly when NaClO_4 or NaNO_3 is added to the aqueous phase. The activation energy for the extraction is calculated to be 23.4 kJ. mol⁻¹ for NaCl system, 19.5 kJ. mol⁻¹ for NaNO_3 system and 13.2 kJ. mol⁻¹ for NaClO_4 system. The extraction mechanisms of Er(III) for both systems are also discussed.

INTRODUCTION

2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP, HL) is an excellent extractant for the extraction separation of rare earths (Li et al., 1980). Recently we reported the kinetics of erbium(III) extraction from different mineral acid (HCl, H_2SO_4) solutions by HEH/EHP (Yue and Li 1992, 1990). Previous work (Li et al., 1985) has also studied the extraction equilibria of rare earth elements(III), and it indicates that the equilibrium time of rare earth extraction with HEH/EHP under the same conditions increases in the following order: $\text{HClO}_4 \sim \text{HNO}_3 < \text{HCl} < \text{H}_2\text{SO}_4$. However, the influence of mineral additives on the rate of rare earth extraction by HEH/EHP has not previously been reported. The present work reports studies of the influence of inorganic salts (NaClO_4 , NaNO_3 , NaCl) on the kinetics of Er(III) extraction from HCl solutions by HEH/EHP.

EXPERIMENTAL

HEH/EHP was supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, and was purified with the conventional copper salt method. Analytical grade n-heptane was employed for diluent. The stock solution of erbium(III) was prepared by dissolving its oxide (purity >99.9%) in concentrated hydrochloric acid. NaClO_4 , NaNO_3 , NaCl and other chemicals were of analytical reagent grade.

The concentration of erbium(III) in aqueous phase or organic phase (stripping with a solution of 5 M HCl) was determined by a Spectrophotometric method (Ren et al., 1987). The experimental apparatus and procedures for the studies of extraction kinetics of erbium(III) by the growing drop method were described by Hughes and Zhu (1985). The extraction experiments (except temperature effect) were carried out at $30 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

The rate of mass transfer of Er(III) from aqueous phase into organic phase exceeds significantly the rate of inverse reaction of Er(III) because the kinetic study is made under the conditions far from extraction equilibrium using the growing drop method. Under the conditions of the present experiment the effect of the mass transfer of inverse reaction on the extraction rate has been neglected. The forward initial rate (R_f) of this extraction process can be expressed as follows:

$$R_f = \Delta[\text{Er}^{3+}]_{(0)} \cdot V/S \cdot t \quad (1)$$

In the present work, R_f can be written as:

$$R_f = k_f[\text{Er}^{3+}]^a[\text{H}^+]^b[\text{Cl}^-]^c[\text{H}_2\text{L}_2]^d[\text{B}] \quad (2)$$

where H_2L_2 refers to the dimeric reagent, and B represents the additive (NaClO_4 or NaNO_3). According to Lambert—Beer Law,

$$A = \epsilon l [\text{Er}^{3+}]_{(0)} \quad (3)$$

at constant concentration of B. The following relationship must be held by using the equation (1)–(3)

$$\log(A/t) = \log k_f \cdot S/V \cdot \epsilon l \cdot [\text{B}] + a \log[\text{Er}^{3+}] + b \log[\text{H}^+]$$

$$+c\log[Cl^-]+d\log[H_2L_2]_{(0)} \quad (4)$$

In the present study, S/V is constant. Under the investigation of extraction mechanism we keep the $[B]$ constant and then equation (4) becomes

$$\log(A/t) = K + a\log[Er^{3+}] + b\log[H^+] + c\log[Cl^-] + d\log[H_2L_2]_{(0)} \quad (5)$$

Where $K = \log k_t \cdot \epsilon l \cdot S/V \cdot [B]$

Influence of inorganic salts on the rate of Er(III) extraction

The effect of $NaClO_4$ and $NaNO_3$ on the extraction rate of Er(III) from HCl solutions by HEH/EHP was examined with the result shown in Fig. 1. The data of Fig. 1 indicate that the rate of Er(III) extraction increases with increasing perchlorate or nitrate concentration. It shows the enhancement of the rate of phase transfer by addition of ClO_4^- or NO_3^- to the aqueous phase, and the acceleration of ClO_4^- is greater than that of NO_3^- . However, the chloride concentration has no effect on the rate of Er(III) extraction. This may be due to the addition of $NaClO_4$ or $NaNO_3$ resulting in a decrease of interfacial tension (Robert et al., 1988–1989) shows that the surface tension of inorganic solutions at the same concentration increases in the following order: $HClO_4 < HNO_3 < HCl$. The chemical analysis of the organic phase shows that perchlorate, nitrate or chloride ions are absent in the extracted species. The NO_3^- more easily forms the complex of species $Er(NO_3)_i^{3-i}$ with Er(III) (Li et al., 1988) in the aqueous phase and then $Er(NO_3)_i^{3-i}$ arrives at the liquid–liquid interface quickly, and forms the $Er(HL_2)_3$ with HEH/EHP adsorbed on the interface by ion exchange reaction. It ends up with the enhancement of the rate of Er(III) extraction. Therefore the NO_3^- has a catalytic effect as does thiocyanate ion (Sun and Li, 1991) in the extraction process of Er(III) by HEH/EHP.

Deduction of the extraction mechanism

The extraction mechanism of Er(III) by HEH/EHP has been discussed at constant concentrations of $NaClO_4$ or $NaNO_3$ of 0.10 M. According to the above data, the effect of the various factors on the rate of Er(III) extraction has been examined. The effect

of Er (III) concentration on the extraction rate has been studied (Fig. 2). These results show that $\log(A/t)$ increases with increase in Er(III) concentration, and the slopes of straight lines are 1.02 (NaClO_4 system) and 1.05 (NaNO_3 system), suggesting that the extraction rate is first order with respect to Er(III), viz. $a=1$.

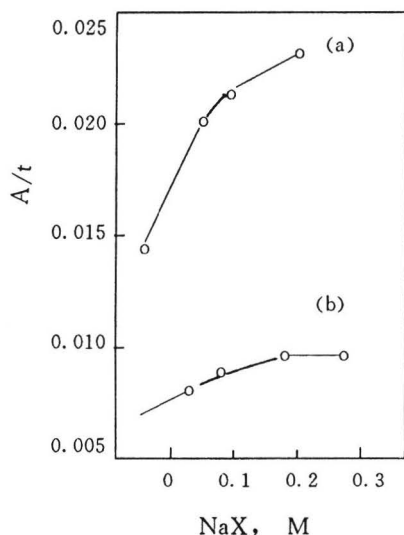


Fig. 1 Effect of NaClO_4 and NaNO_3 on the extraction rate

$[\text{Er}^{3+}] = 1.0 \text{ mM}$;
 $[\text{Cl}^-] = 0.20 \text{ M}$;
 $\text{pH} = 1.80$
 (a:) NaClO_4 , $[\text{H}_2\text{L}_2]_{(0)} = 21.0 \text{ mM}$
 (b:) NaNO_3 , $[\text{H}_2\text{L}_2]_{(0)} = 6.5 \text{ mM}$

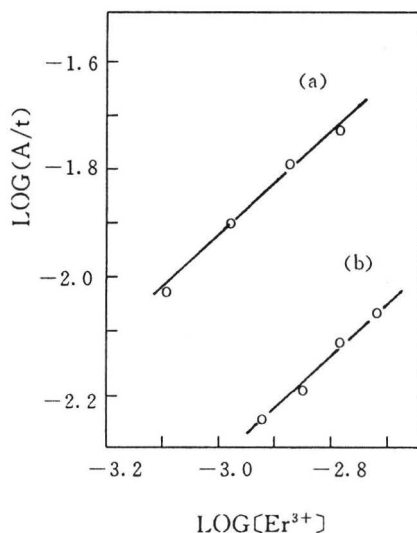
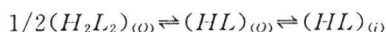


Fig. 2 Effect of Er(III) concentration on the extraction rate

$[\text{H}_2\text{L}_2]_{(0)} = 21.0 \text{ mM}$;
 $[\text{Cl}^-] = 0.21 \text{ M}$
 $\text{pH} = 1.80$
 (a:) NaClO_4 , 25°C (b:) NaNO_3

An inverse first order dependence of the extraction rate on the H^+ concentration was observed for NaClO_4 and NaNO_3 systems (Fig. 3)(b is -1). An apparent zero order dependence of the extraction rate on the Cl^- concentration was also observed for both systems ($c \approx 0$). Lastly, the effect of the concentration of HEH/EHP on the extraction rate has been studied. The slopes of those straight lines are 0.61 (NaClO_4 system) and 0.54 (NaNO_3 system)(Fig. 4), which suggests that the extraction rate is of half order with respect to $[\text{H}_2\text{L}_2]_{(0)}$, viz. $d=1/2$. Experiment by Shen et al. (1984) indicate that HEH/EHP is adsorbed at the interface in the form of a single molecule. Thus, the fol-

lowing equilibrium must hold:



This suggests that Er(III) in the aqueous phase reacts first with monomer of HEH/EHP at the interface, because the monomer is more interfacially active than the dimer (Vandegrift and Horwitz, 1980).

The kinetic equation determined experimentally can be represented as follows:

$$R_f = k_f [Er^{3+}] [H_2L_2]_{(o)}^{1/2} / [H^+] \quad (6)$$

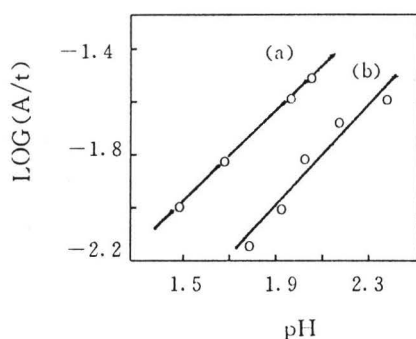


Fig. 3 Effect of H^+ concentration on the extraction rate

$[H_2L_2] = 21.0 \text{ mM}$
 $[Cl^-] = 0.20 \text{ M}$
 $[Er^{3+}] = 1.0 \text{ mM}$
 (a:) $NaClO_4$, $25^\circ C$
 (b:) $NaNO_3$

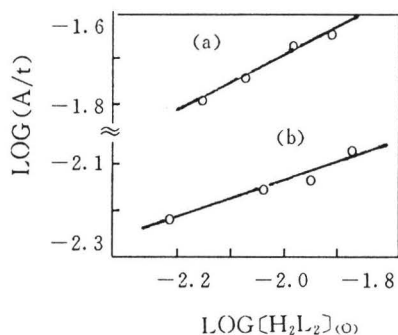
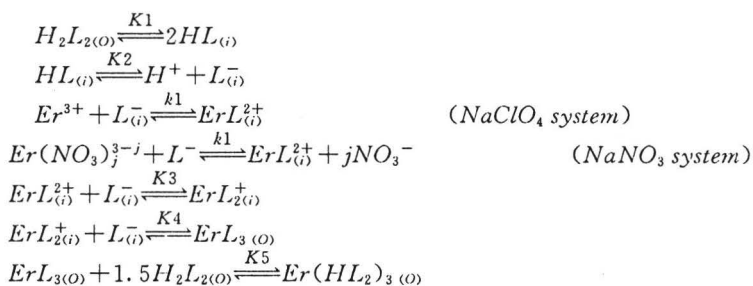


Fig. 4 Effect of concentration of HEH/EHP on the extraction rate

$[Er^{3+}] = 1.0 \text{ mM}$
 $[Cl^-] = 0.20 \text{ M}$
 $pH = 1.80$
 (a:) $NaClO_4$, $25^\circ C$
 (b:) $NaNO_3$

According to the results of kinetics and thermodynamics, the extraction mechanism of both systems can be deduced by the following reaction:



where the third or fourth step is the rate-determining step. The forward rate equation can be represented as follows:

$$R_f = k_1[Er^{3+}][L^-]_{(i)} = k_1K_1^{1/2}K_2[Er^{3+}][H_2L_2]_{(o)}^{1/2}/[H^+]$$

Under the conditions of the present experiment:

$$Er(NO_3)_3^{3-} \approx [Er^{3+}] \text{ for } NaNO_3 \text{ system. } K_f = k_1K_1^{1/2}K_2$$

$$\text{thus: } R_f = K_f[Er^{3+}][H_2L_2]_{(o)}^{1/2}/[H^+]$$

The forward rate equation deduced theoretically agrees with Eqn. 6.

Activation energy of the extraction

The effect of temperature on the extraction rate has been determined in the range of 20–40°C. The activation energy is 13.2 kJ · mol⁻¹ for ClO₄⁻ + Cl⁻ system and 19.5 kJ · mol⁻¹ for NO₃⁻ + Cl⁻ system. However, E_a = 23.4 kJ · mol⁻¹ for the chloride system. These differences in the activation energy agree with the enhancement of the extraction rate by addition of NaClO₄ and NaNO₃ in the aqueous phase.

ACKNOWLEDGMENT

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NOMENCLATURE

$\Delta[Er^{3+}]_{(o)}$	mole change of Er(III) concentration in drop of organic phase during initial time t(s)
(0)	organic phase
(i)	interface
S	surface area (cm ²)
V	volume of the drop (cm ³)
E _a	activation energy
R _f	forward initial rate
K _f	rate constant
a, b, c, d	order number of reactant
A	absorbancy
ε	molar absorbancy index
l	thickness of liquid (cm)

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3.24

SOLVENT EXTRACTION OF YTTRIUM(III) AND LANTHANOID(III) IONS WITH LONG-CHAIN ALKYL SUBSTITUTED N-PHENYLHYDROXAMIC ACIDS

Kensaku HARAGUCHI*, Toshio OGATA*, Koichi NAKAGAWA*,
Manabu OKUYAMA**, Tohoru SAITOH**, Tamio KAMIDATE**,
and Hiroto WATANABE**

*The Government Industrial Development Laboratory, Hokkaido
Tsukisamu-Higashi, Toyohira, Sapporo 062, Japan

**Faculty of Engineering, Hokkaido University
N13-W8, Kita, Sapporo 060, Japan

ABSTRACT

The extraction of scandium(II), yttrium(III) and lanthanoid(III) ions from aqueous solutions into carbon tetrachloride solutions containing various long-chain alkyl substituted N-phenylhydroxamic acids(R-PHA) has been studied at 298 K and ionic strength, 0.1(NaNO₃). The R-PHAs studied were N-octanoyl-N-phenylhydroxylamine(C8-PHA), N-(2-hexyldecanoyl)-N-phenylhydroxylamine(HD-PHA), N-(2,2-dimethylpentanoyl)-N-phenylhydroxylamine(DMP-PHA) and some other alkyl substituted R-PHAs. The metal ions were extracted with all the R-PHAs except DMP-PHA as self-adducts of the form $ML_3(HL)_2$, where L and HL represent the ligand anion and neutral ligand, respectively. The extracted species with DMP-PHA were $ML_3(HL)_3$. The extraction constants were evaluated. The introduction of additional alkyl groups at the α -position of the carbonyl group in the R-PHA significantly enhanced the selectivity in extraction of yttrium from heavy lanthanoids.

INTRODUCTION

The demand for high-purity lanthanoids, yttrium and scandium is growing recently in various advanced industries, such as electronics and new ceramics. Because of the similarity in chemical properties of these elements, their mutual separation is generally difficult. Solvent extraction is a simple and effective separation technique and widely employed in the separation of metal ions. For an industrial-scale separation of lanthanoids and yttrium, di(2-ethylhexyl)-phosphoric acid(D2EHPA) has mainly been employed as an extractant (Sherrington, 1983). However, the development of more selective extractants is desired in order to establish an effective separation process for the metal ions.

N-Benzoyl-N-phenylhydroxylamine(BPHA) and its analogues have been used as gravimetric, spectrophotometric and extracting reagents for a wide variety of metal ions (Majumdar, 1972). Since their complexation with metal ions occurs through the carbonyl and hydroxyl oxygens, they are likely to react with "hard" metal ions including lanthanoids(III). On the other hand,

attention has recently been paid to chelating reagents having long-chain alkyl substituents, because of their successful application in hydrometallurgical separation of metal ions (Flett, 1977). Previously, we reported the extraction of some lanthanoids(III) by the use of alkyl substituted N-phenylhydroxamic acids having primary and secondary alkyl substituents(R-PHAs) (Haraguchi, 1990). Among the R-PHAs employed, N-(2-hexyldecanoyl)-N-phenylhydroxylamine(HD-PHA) was a good choice for the intragroup separation of heavy lanthanoids, while N-octanoyl-N-phenylhydroxylamine(C8-PHA) was suitable for the separation of light lanthanoids. R-PHAs with tertiary alkyl substituents are also available, and their use in the extraction and separation of lanthanoids(III) would provide information of substituent effects on the selectivity of R-PHAs. The present study is thus extended to the extraction of scandium(III), yttrium(III) and lanthanoids(III) with R-PHAs having primary, secondary or tertiary alkyl substituents at the α -position of the carbonyl group in relation to the mutual separation of these metal ions.

EXPERIMENTAL

Reagents

All R-PHAs were prepared in a similar fashion to that described previously (Haraguchi, 1989). Confirmation of the white crystalline products was carried out by melting-point measurements and elemental analyses, as well as measurements of their H-NMR, IR and MS. Stock solutions of metal ions(10 mM) were prepared by dissolving the metal nitrates(>99.99 %, Rare Metallic Inc.) in 1 mM nitric acid. All other chemicals were of analytical grade. Distilled-deionized water was used throughout the experiments.

Apparatus

R-PHAs extracted into the organic phase were determined with a Hitachi 320 double-beam spectrophotometer. The concentration of the metal ions in the aqueous phase was measured with a Shimadzu GVM-1000P ICP atomic emission spectrometer. A Toa HM-15A pH meter was employed for measuring the pH of the aqueous phase. A Yamato SA-31 mechanical shaker was utilized for mixing the two phases. A Kokusan H-200 centrifuge was also used for rapid and complete separation of the two phases.

Procedure

A 30-cm³ aliquot of aqueous solution containing a specified metal ion(50 μ M), sodium nitrate(0.1 M), sodium tartrate(10 mM) and an appropriate buffer component(1 mM) was shaken with a 5.00-cm³ aliquot of carbon tetrachloride solution of a specified R-PHA, in which the R-PHA concentration was in the range from 1.6 mM to 16 mM, for 1 h for equilibration at 298 K. If necessary, 1 M sodium hydroxide was also added to the aqueous phase for controlling the pH. After centrifuging 10 min at 1,500 min⁻¹ the pH as well as the metal concentration in the aqueous phase were determined. The metal concentration in the organic phase was calculated on the basis of the material balance.

RESULTS AND DISCUSSION

Preparation of R-PHA

All the R-PHAs were prepared by the addition of appropriate acid chlorides to N-phenylhydroxylamine(PHA) in an ether solution in the presence of sodium hydrogen carbonate at a temperature below 273 K. The products were purified by recrystallization from an ether-hexane or an ethyl acetate-hexane solution. The R-PHAs thus obtained were C8-PHA, HD-PHA N-(2-propylpentanoyl)-PHA (PP-PHA), N-(2,2-dimethylpentanoyl)-PHA (DMP-PHA), N-octanoyl-N-(4-chlorophenyl)hydroxylamine(C8-PHACl), N-(2-propylpentanoyl)-N-(4-chlorophenyl)hydroxylamine(PP-PHACl) and N-(2,2-dimethylpentanoyl)-N-(4-chlorophenyl)hydroxylamine(DMP-PHACl). The acid dissociation constants, K_a , and distribution constants, K_d , of these R-PHAs between aqueous phase and carbon tetrachloride phase were determined spectrophotometrically at 298 K and ionic strength 0.1(NaNO_3). These values are summarized in Table 1.

TABLE 1
log K_d and pK_a values of R-PHAs

R-PHA	log K_d	pK_a	R-PHA	log K_d	pK_a
C8-PHA	2.88	8.76	C8-PHACl	3.45	8.71
PP-PHA	2.46	9.26	PP-PHACl	3.00	8.90
HD-PHA	4.00	9.74	DMP-PHACl	2.75	9.25
DMP-PHA	1.96	9.65			

Extraction equilibrium of metal ions

When free metal ion is predominant in the aqueous phase, the extraction of trivalent metal ion (M^{3+}) with R-PHA(HL) can be generally described according to



where the subscript, (O), refers to the species in the organic phase. The extraction constants, K_{ex} , is thus defined by

$$K_{ex} = [ML_n(HL)_m]_{(O)}[H^+]^n / [M^{3+}][HL]_{(O)}^{(n+m)} \quad (2)$$

Therefore, the distribution ratio of a metal ion, D_M , between the two phases can be given by

$$\log D_M = \log K_{ex} + (n+m) \log [HL]_{(O)} + npH \quad (3)$$

Accordingly, the stoichiometries of the extracted species and the extraction constants can be obtained by the slope analysis of the equilibrium data according to Eqn. (3). The relationships between $\log D_M$ and pH at a fixed R-PHA concentration were linear with slope of 3 within the experimental error for all the extraction systems studied. Similarly, the plots of $\log D_M$ against $\log [HL]_{(O)}$ at constant pH gave straight lines for all the extraction systems. The slope of 5 was obtained for the plots with C8-PHA, PP-PHA and HD-PHA for all the metals studied. A slope

of 6 was obtained with DMP-PHA for yttrium(III) and lanthanoids(III). These results indicate that scandium(III), yttrium(III) and lanthanoids(III) are extracted with R-PHAs except DMP-PHA as a self-adducted form, $ML_3(HL)_2$. Meanwhile, the extracted species of yttrium(III) and lanthanoids(III) with DMP-PHA were self-adducted chelates with a form of $ML_3(HL)_3$.

The extractant constants, K_{ex} , thus evaluated for the extraction systems are summarized in Tables 2 and 3. As shown in Table 2, the $\log K_{ex}$ values of C8-PHA are larger than those obtained for PP-PHA HD-PHA and DPM-PHA for all the metal ions studied except scandium(III). This indicates that the extractability of C8-PHA is the largest among the R-PHAs studied. The most likely reason for this observation is a steric hindrance of the alkyl substituent, because PP-PHA, HD-PHA and DMP-PHA have one or two additional alkyl groups neighboring to the chelating group.

TABLE 2

$\log K_{ex}$ values for the extraction with various R-PHAs

	C8-PHA	PP-PHA	HD-PHA	DMP-PHA
Sc	-5.86	-4.45	-5.50	-6.91
Y	-9.85	-11.35	-13.06	-13.52
Pr	-12.19	-14.44	-15.40	-15.68
Nd	-12.10	-14.20	-15.31	-15.80
Eu	-10.96	-13.30	-14.38	-14.78
Gd	-10.87		-14.29	-14.39
Tb	-10.15		-13.81	-13.76
Dy	-9.73		-13.27	-13.07
Ho	-9.58		-13.03	-12.89
Er	-9.49		-12.73	-12.26
Tm	-9.39		-12.34	-11.96
Yb	-9.29	-11.20	-11.50	-11.69
Lu	-9.13		-11.53	-11.45

TABLE 3

$\log K_{ex}$ values for the extraction with various RPHACl s

	C8-PHACl	PP-PHACl	DMP-PHACl
Y	-8.44	-10.42	-13.19
Yb	-7.98	-9.01	-11.24

In the extraction of heavy lanthanoids from Ho(III) to Lu(III) with HD-PHA or DMP-PHA, the differences in the $\log K_{ex}$ values between two adjacent lanthanoids(III) are greater than those of C8-PHA. This suggests that R-PHAs having a branched alkyl substituent are suitable for the mutual separation of heavy lanthanoids(III).

For a further elucidation of the selectivity of R-PHAs, separation factors (SF) for a pairs of metal ions were compared. The separation factor is defined as the ratio of extraction constants for the pair,

$$(\text{SF}) = K_{\text{ex(I)}} / K_{\text{ex(II)}} \quad (4)$$

where the subscripts, (I) and (II), refer to the different metal ions. In Table 4, the log (SF) values for R-PHAs are shown along with those values for other extractants reported (Freiser, 1988, Pierce, 1963, Mori, 1989).

TABLE 4
Logarithmic values of separation factor

	Eu / Pr	Yb / Eu	Y / Pr	Yb / Y	Sc / Y	Sc / Yb
C8-PHA	1.23	1.67	2.34	0.51	3.99	3.43
PP-PHA	1.14	2.10	3.09	1.50	6.90	6.75
HD-PHA	1.02	2.88	2.34	1.56	7.56	6.00
DMP-PHA	0.90	3.09	2.16	1.83	6.61	4.78
C8-PHACl				0.51		
PP-PHACl				1.41		
DMP-PHACl				1.95		
D2EHPA[1]	1.26	2.70	2.91	1.02		
Kelex 100[2]	1.58	2.10				
Aliquat336[3]			0.62	-0.06		
TBP[3]			0.65	-0.03		
Versatic10[3]			0.44	0.58		

[1] Pierce, 1963, [2] Freiser, 1988, [3] Mori, 1989

The log (SF) value of C8-PHA for Sc/Yb pair is considerably smaller than those of other R-PHAs having a branched alkyl substituent. However, the separation of scandium(III) from ytterbium(III), or lanthanoids(III), will be complete by the use of R-PHAs. Similarly, the separation between scandium(III) and yttrium(III) can be attained easily with these extractants. The log (SF) value of C8-PHA for the pair Eu/Pr is very close to that reported for D2EHPA which is currently employed for industrial-scale separation of lanthanoids. On the other hand, for the pair Yb/Eu, though the log (SF) value of C8-PHA is considerably smaller than that of D2EHPA, HD-PHA and DMP-PHA give larger log (SF) value than that of D2EHPA. Therefore, it can be concluded that HD-PHA and DMP-PHA are very promising extractants for the mutual separation of heavy lanthanoids, while C8-PHA is suitable for the separation of light lanthanoids. Furthermore, the log (SF) values obtained for the Yb/Y pair with PP-PHA, HD-PHA and DMP-PHA are much larger than that of D2EHPA. The result indicates that R-PHAs having a branched alkyl substituent are also useful for the separation of yttrium(III) from heavy lanthanoids(III).

As discussed above, appropriate branching at the α -position of the alkylcarbonyl group of

R-PHA can provide a good means for improving the selectivities. However, as shown in Table 2, the extraction constant decreases in the order C8-PHA > PP-PHA > HD-PHA > DMP-PHA for the metal ion studied except scandium(III). This is probably the effect of the steric hindrance of alkyl group in the extractants. As shown in Tables 2 and 3, the introduction of chlorine at the 4-position of phenyl group of C8-PHA, PP-PHA and DMP-PHA improves the extractability of yttrium(III) and ytterbium(III) without giving any effect on the selectivity for Yb/Y pair of these extractants (Table 4). This finding suggests that the introduction of proper substituents at the appropriate position of the phenyl group of R-PHA enhances the extractability of metal ions.

Thus, we can conclude that the steric factor of the alkyl substituent and probably the electronic property of substituents in the phenyl group of R-PHA are of great importance in connection with controlling the extractability and selectivity of R-PHAs.

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**SYNTHESIS AND CHARACTERISATION OF DIAMIDE EXTRACTANTS
FOR EXTRACTION OF NEODYMIUM**

Qinzhi TIAN

Beijing Research Institute of Chemical Engineering and Metallurgy,
Beijing, P.O. Box 234
China

M. A. HUGHES

Department of Chemical Engineering,
University of Bradford,
Bradford,
W. Yorks., BD7 1DP, UK

ABSTRACT

The aim of this study was to prepare a series of amide extractants and to assess their properties as potential metal extractants for the rare earth metal neodymium.

A number of diamides and a mono-amide were synthesized with different substituting groups including alkyl-chains, cyclohexyl-chains and aryl-chains. The general method for synthesizing the above extractants was to react relevant acyl chlorides with secondary amines in basic medium. The yields for diamides were in the range 32-50% and for mono-amide 90%.

A systematic investigation has been carried out on the extraction properties of the extractants synthesized using the neodymium ion Nd^{3+} to monitor the extraction of a typical three valent rare earth species. The effects of the variables (i) diluent type (ii) the structure of diamides (iii) aqueous acidity and (iv) salting-out agents, on the extraction of Nd^{3+} are discussed.

The effect of aqueous acidity on the distribution ratios proved that there was a competition between the metal ion and HNO_3 for the diamide coordination sites. When the nitric acid concentration in the aqueous phase was varied, a maximum extraction was observed in the region of 3M HNO_3 for all eight diamides investigated. From the results it can be concluded that the diamides are effective extractants for neodymium in the region of 3M HNO_3 . The neodymium can be stripped by dilute HNO_3 .

INTRODUCTION

During the past twenty years, bidentate ligands as extractants have come to occupy an important place in the solvent extraction of metals. The special features of these extractants are that they are more selective, kinetically faster and exhibit higher efficiency (Kordosky et al, 1985; Mackay, Rogier, 1988; Horwitz et al, 1981; Kalina et al, 1987); these

characteristics are partly due to their ability to form chelate complexes. These extractants are successfully applied in different areas, such as in the recovery of copper (Fisher, Notebaart, 1983) and in the disposal of nuclear waste (Horwitz, Schulz, 1985).

There is a particular class of bifunctional ligands namely β -diamides which have been the subject of several recent investigations and are expected to be effective extractants (Cuillierdier et al, 1990; Musikas, 1988; Musikas, 1987). Studies relating to the utilization of N,N' -dimethyl, N,N' -dioctylmalonamide as an alternative to TBP in the nuclear reprocessing industry have been carried out over a number of years (Musikas, 1988; Musikas, 1987; Musikas, Hubert, 1987; Thiollet, Musikas, 1989).

The objective in this study was to investigate the synthesis of a number of diamides with different structure and a mono-amide and to examine their extraction behaviour with respect to the rare earth element neodymium. Of particular interest was the selection of the diamides effective in the extraction of Nd^{3+} and finding the optimum conditions for the above process in order to obtain the maximum extraction.

In this paper the extraction conditions such as (1) diluent type (2) extractant type (3) acidity of the aqueous phase and (4) salting out agent have been studied in a more systematic manner than in the work of Musikas (1988) and Thiollet and Musikas (1989).

THE SYNTHESIS OF AMIDES

A number of routes were considered for the synthesis of the diamides --- N,N' -tetrasubstituted malonamides (Figure 1). These reactions include the reaction of secondary amines with acid esters (I), the reaction of secondary amines with acid anhydrides (II) and the reaction of secondary amines with acyl chlorides (III).

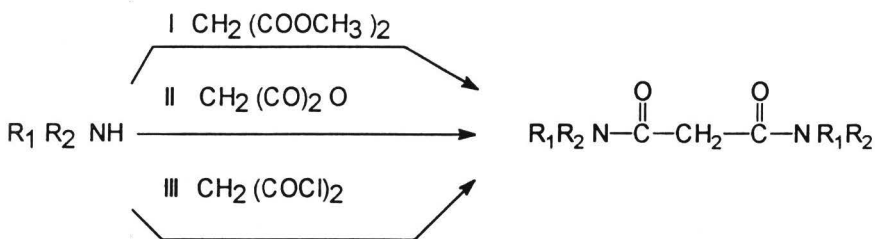


Fig. 1 Amidation routes

The reactivity of amidation increases in the order: $I < II < III$.

The product details and relevant data are shown in Table 1.

The amides in Table 1 were chosen to give an interesting range of structures. Only three of these amides i.e. DMDBMA, DMDOMA and TBMA have been reported on before. (Musikas, Hubert, 1987).

TABLE 1
Synthesis and Characteristics of Amides

Name	Acronym	Formula	M.W.	b.p.	Yield %
N,N'-dimethyl,N,N'-dibutylmalonamide	DMDBMA	$(\text{CH}_3\text{C}_4\text{H}_9\text{NCO})_2\text{CH}_2$	242	138-142°/0.2	40.0
N,N'-dimethyl,N,N'-dihexylmalonamide	DMDHMA	$(\text{CH}_3\text{C}_6\text{H}_{13}\text{NCO})_2\text{CH}_2$	298	175-180°/0.3	44.0
N,N'-dimethyl,N,N'-dicyclohexylmalonamide	DMDCHMA	$(\text{CH}_3\text{C}_6\text{H}_{11}\text{NCO})_2\text{CH}_2$	294	165-168°/0.2	35.0
N,N'-dimethyl,N,N'-dioctylmalonamide	DMDOMA	$(\text{CH}_3\text{C}_8\text{H}_{17}\text{NCO})_2\text{CH}_2$	354	*N/A	35.1
N,N'-diethyl,N,N'-dibutylmalonamide	DEDBMA	$(\text{C}_2\text{H}_5\text{C}_4\text{H}_9\text{NCO})_2\text{CH}_2$	270	144-148°/0.2	41.2
N,N'-diethyl,N,N'-dibenzylmalonamide	DEDBEMA	$(\text{C}_2\text{H}_5\text{CH}_2\text{C}_6\text{H}_5\text{NCO})_2\text{CH}_2$	338	170-175°/0.2	32.4
N,N'-tetrapropylmalonamide	TPMA	$[(\text{C}_3\text{H}_7)_2\text{NCO}]_2\text{CH}_2$	255	143-146°/0.2	38.2
N,N'-tetrabutylmalonamide	TBMA	$[(\text{C}_4\text{H}_9)_2\text{NCO}]_2\text{CH}_2$	270	168-172°/0.2	50.3
N,N-dibutyloctanamide	DBOA	$(\text{C}_4\text{H}_9)_2\text{NCOC}_7\text{H}_{15}$	326	117°/0.2	90.1

* not available, but very high b. p.

CHARACTERISATION OF AMIDES

All amide products were characterised by NMR, IR, elementary analysis and potentiometry.

Infrared (IR) spectra were recorded on a Nicolet 205 FT - IR spectrophotometer using 32 scans at 4 cm^{-1} resolution. Proton nuclear magnetic resonance spectra (NMR) were measured on a JNM-GX 270 FT NMR spectrometer.

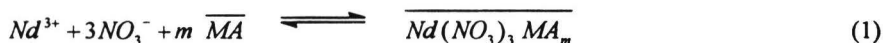
It was found that the purity, based on equivalent weight for all amides synthesized except DEDBeMA was in the range of 97 - 99%. The IR spectra and potentiometry data are shown in Table 2.

TABLE 2
Characteristic IR Bands and Analytical Data for Amide Products

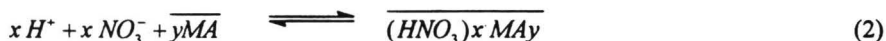
MA acronym	$\nu_{\text{C=O}}(\text{cm}^{-1})$	$\nu_{\text{C-N}}(\text{cm}^{-1})$	neutralization equivalent	Purity %
DMDBMA	1641	1463,1427	254	99
DMDHMA	1642	1463,1427	304	98
DMDCHMA	1637	1482,1427	302	98
DMDOMA	1647	1466,1401	364	98
DEDBMA	1640	1457,1426	280	97
DEDBeMA	1647	1453,1432	301	90
TPMA	1641	1464,1427	275	98
TBMA	1641	1464,1426	328	99
DBOA	1649	1466,1423	258	99

EXTRACTION OF NEODYMIUM BY DIAMIDES

The general equilibrium for Nd^{3+} extraction by N,N'-tetrasubstituted malonamides (MA) can be represented as in eq. (1).



It is also true that the amide can extract nitric acid according to



It was found that the nature of the diluents, the structure of the amides, the acidity of the aqueous and the salting out agents may strongly affect the distribution ratios of Nd^{3+} .

Effect of diluents on distribution ratios of Nd^{3+}

When Nd^{3+} was extracted from aqueous HNO_3 , the complexes formed have a limited solubility in non-polar diluents especially aliphatic hydrocarbons. However, optimum proportions of dodecane can be added to aromatic diluents and good distribution ratios were then obtained. The influence of diluent on Nd^{3+} distribution ratios is shown in Table 3.

It was clear from Table 3 that there is an order for DEDBMA and DMDOMA, i.e., the distribution ratios increase with the modification of the diluent associated with increasing aromaticity. But for DMDBMA, it seems there is no such order because of the poor solubility of the Nd-DMDBMA complex in the organic solvents.

Following the above results, the solvent mixture of 80% dodecane and 20% toluene was chosen as a diluent for the further investigation of the extraction properties.

TABLE 3

Diluent Effect on Nd^{3+} Distribution Ratios $D(\text{Nd}^{3+})$
between 1M MA and Nd^{3+} in 3M HNO_3 ($25 \pm 2^\circ\text{C}$)

Diluent	DMDBMA	DMDOMA	DEDBMA
Toluene	0.67	0.79	0.79
Xylene	0.53	0.83	0.92
t-Butylbenzene	0.15	1.35	1.44
Dodecane 90% Decanol 10%	0.15	1.65	1.70
Dodecane 80% Xylene 20%	0.10	2.23	2.51
Dodecane 80% Toluene 20%	0.13	2.33	2.75

Effect of structure of amides on distribution ratios of Nd^{3+}

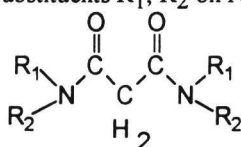
The nature of the N-substituents in the diamides has a great influence upon the distribution ratios of Nd^{3+} .

Three of these compounds were studied by Musikas and Hubert (1987) but for the extraction of Am^{3+} from nitric acid. It is noted that the extraction order measured by the D value is correct for the reagents DMDBMA (Am^{3+} 0.55, Nd^{3+} 0.67) and DMDOMA (Am^{3+} 1.18, Nd^{3+} 2.33) but TBMA is a much better extractant for Nd^{3+} (2.24) than was observed with Am^{3+} (0.18).

It can be seen from Table 4 that DEDBMA, DMDHMA and DMDOMA are the best extractants and DMDBMA is one of the poorest. The effect of carbon chain length on extraction is perhaps best seen in Figure 2. A reasonable explanation of the increase in the distribution ratios of Nd^{3+} in the case of extraction by higher diamides is a change in the solubility of the diamides and their metal complexes in the organic solution.

It is seen from Table 4 that the steric hindrance of the cyclohexyl groups in DMDCHMA and the benzene rings in DEDBeMA inhibits the carbonyl donor groups to attack the Nd^{3+} ion. These two chemicals appear to have poor ability in extracting Nd^{3+} .

TABLE 4
Influence of the Substituents R_1 , R_2 on Nd^{3+} Distribution Ratios



Acronym	R_1	R_2	$D(Nd^{3+})$
DEDBeMA	C_2H_5	 - CH_2	0.41
DMDBMA	CH_3	C_4H_9	0.67
DMDCHMA	CH_3		0.82
TPMA	C_3H_7	C_3H_7	2.14
TBMA	C_4H_9	C_4H_9	2.24
DMDOMA	CH_3	C_8H_{17}	2.33
DMDHMA	CH_3	C_6H_{13}	2.45
DEDBMA	C_2H_5	C_4H_9	2.75

Effect of concentration of nitric acid and diamides on the distribution ratios of Nd^{3+}

Figure 3 shows the variation of $D(Nd^{3+})$ as a function of the concentration of HNO_3 for the eight diamides synthesized. The data indicate that diamides are effective extractants for Nd^{3+} in 3M HNO_3 . It can be seen that from 0.05M to 3.0M HNO_3 , as acidity increases, the extraction of metal increases.

Very low values of distribution ratios were obtained at acidities lower than 0.05M HNO_3 , thus permitting easy stripping of Nd^{3+} with dilute acid solution.

Figure 4 shows the effect of DEDBMA concentration, [MA], in the organic phase. The $D(Nd^{3+})$ increase with an increase in [MA]. The maximum $D(Nd^{3+})$ was attained at 3M HNO_3 for different [MA] values.

Effect of salting-out agents on the distribution ratios for Nd^{3+}

The presence of salting-out agents may modify the extraction of Nd^{3+} by diamides. The salting-out agent effect for diamides is reported here for the first time.

Figure 5 shows the effect of the salting-out agents magnesium and sodium nitrates when Nd^{3+} was extracted by 0.5M DEDBMA, TBMA and TPMA. A salting-out agent with high water binding capacity will cause the neodymium to be less hydrated and will render the aqueous solution more deficient in freewater.

As shown in Figure 5, The Nd^{3+} distribution ratios increase as the charge on the cation increases. The effectiveness also increases when the concentration of the salting out agent increases.

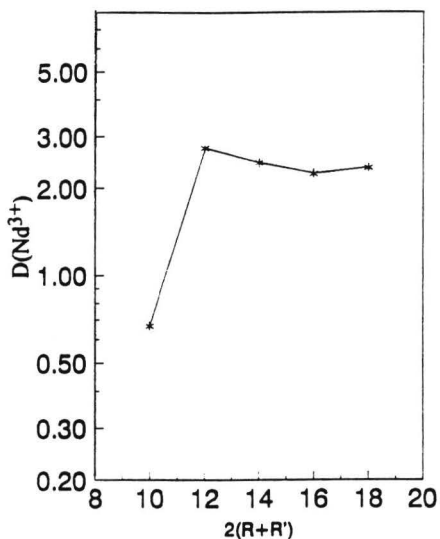


Fig.2 Effect of the chain length of MA on Nd^{3+} extraction ($25 \pm 2^\circ\text{C}$)

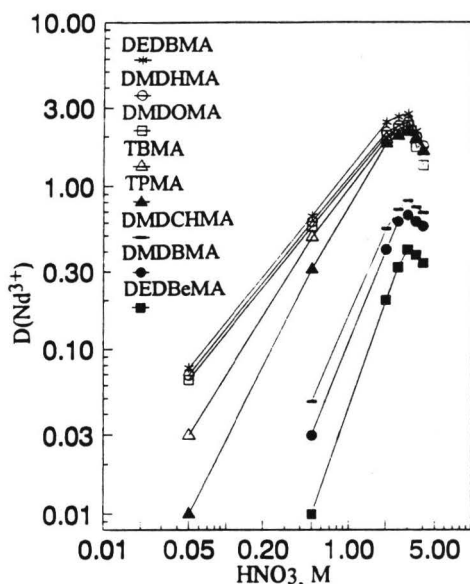


Fig.3 Effect of HNO_3 concentration on Nd^{3+} extraction ($25 \pm 2^\circ\text{C}$)

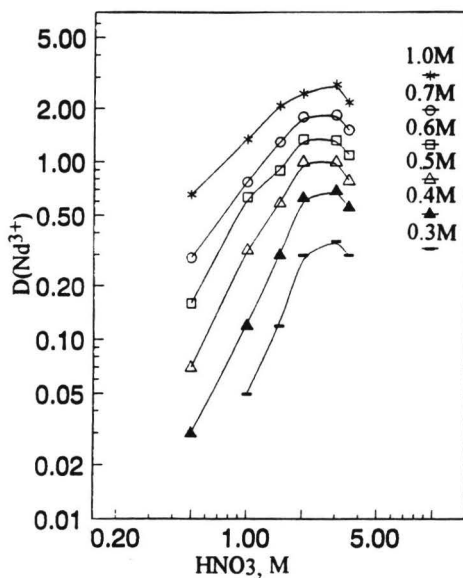


Fig.4 Effect of MA concentration on Nd^{3+} extraction ($25 \pm 2^\circ\text{C}$)

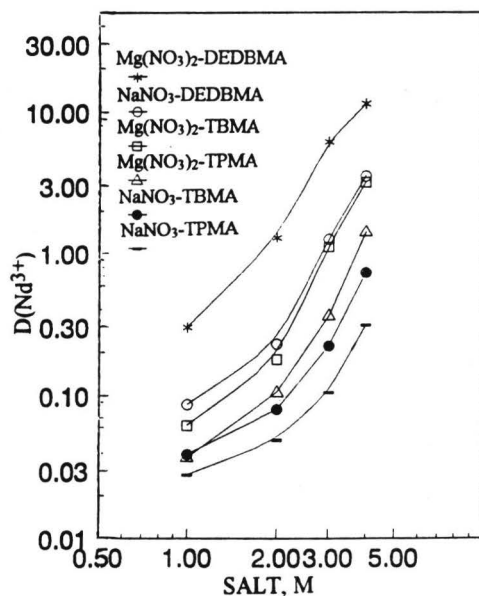


Fig.5 Effect of salting out agent on Nd^{3+} extraction ($25 \pm 2^\circ\text{C}$)

CONCLUSION

The interest in diamides for the extraction of rare earths is established. In the synthesis part of this work the yield is affected by solvent choice and reaction temperature.

In terms of the structures studied here, either different side chain structures or steric hindrance groups have been introduced, see Figure 4. When the best diluent choice was made, i.e. dodecane 80 %%, toluene 20 %%, and the D value for Nd^{3+} was measured with each diamide then some interesting observations can be made.

It is apparent that the steric hindrance introduced by the bulky cyclohexyl and benzene groups in DMDCHMA and DEDBeMA respectively inhibits the extraction of the neodymium.

According to equation 1 the extraction of neodymium increases with nitric acid concentration because the nitrate salts out the rare earth. Only at very high nitric acid concentrations, i.e. above 3M, will the nitric acid begin to be extracted. Then the diamide is competing for both the neodymium and the nitric acid.

Indeed, salting-out of neodymium is shown here to be possible using magnesium or sodium nitrate, this is also seen in the salting out of the uranyl ion from nitric acid media (Harrington, Ruehle, 1959).

It is shown that by alteration of diamide structure, choice of diluent, concentration of aqueous acid and salting-out agent then an optimum condition might be reached for the extraction of a typical trivalent rare earth element.

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SESSION 4

HYDRODYNAMICS AND MASS TRANSFER

4.1

THE EFFECT OF VISCOSITY ON DROP TRANSPORT AND BREAKUP IN PULSED AND STIRRED LIQUID-LIQUID EXTRACTION COLUMNS

G. WAGNER and E. BLASS
Lehrstuhl A für Verfahrenstechnik
Technische Universität München
Munich, Germany

ABSTRACT

The influence of the viscosity on the break-up of single drops in a pulsed sieve-plate column and a stirred column was compared. An apparatus was designed for establishing breakage laws for fluid two-phase systems with higher viscosities (up to 50 mPas). It consisted of two columns, a pulsed sieve-plate and a stirred column. Each of them had (i) a pilot-column compartment ($D=80\text{mm}$), (ii) a system to inject calibrated drops in the column, (iii) a collector of drops including a capillary tube, where drop sizes were measured by means of photoelectric cells, and (iv) a high-speed-camera to realize the effect of drop breakage. Drop injection, data acquisition and data processing were achieved by means of a personal computer. The experimental study led directly to a stable drop diameter and a drop diameter that would surely break. Both diameters depend on energy input of the pulsator and stirrer. The influence of the viscosity on the drop breakage is discussed.

INTRODUCTION

The major difficulty in the design and in the operation of any liquid-liquid extraction is the behaviour of the dispersed phase. There are three mechanisms which influence the work of an extraction column: transport, breakage and coalescence of drops.

In order to compare different column types it should be possible to compare only transport and breakage of the droplets with single drop experiments. Especially these two mechanisms depend on the type and the geometry of an extractor. In many cases, coalescence is considered to be of minor importance. Studies of the behaviour of single drops passing through short sections of columns have proved to be very useful in finding the influence of the physical properties of the test systems and the geometry of the extractor on the behaviour of the drops (Haverland (1988)). Therefore an automatic apparatus was designed in order to investigate the

drop-breakage in pulsed and stirred columns. The experimental study was carried out with the system: mineraloil/n-hexane and water/glycerol. The addition of n-hexane and glycerol was used to adjust viscosity. The viscosity of the continuous and dispersed phases was varied between 1 and 50 mPas. The phases were saturated before the experiments, no mass-transfer took place.

EXPERIMENTAL EQUIPMENT AND TEST SYSTEMS

The equipment consisted of two columns, a stirred and a pulsed sieve-plate column. Each column had only one stage, an injection system to create drops and a measuring system for the daughter-drop sizes. A personal computer was used to control the injection and for data acquisition and data processing (see Fig.1).

Column

The column stage was made of glass, 700mm high and with a diameter of 80mm. The bottom of the column and the top were stainless steel plates. The bottom held the injection unit (1), the top the daughter-drop size measurement system. A variable speed motor (M2) was fixed to the shaft under the base plate of the stirred column (K2). The agitation of the pulsed column (K1) was achieved with a lateral pulsator (M1). The amplitude and the frequency of the pulsation were both adjustable (Fig. 1).

In both columns a guide tube (2) led the drops up to the compartment. For the pulsed sieve plate column it consisted of two stainless steel plates (3). The free area of the sieve-plates was 26%, the hole diameter was 4mm. For the stirred column the compartment consisted of two stators and one stirrer with a rotor diameter of 42mm. In the experiments compartments of a rotating disc contactor and of a Kühni extractor were used. For the Kühni extractor the stator geometry was varied.

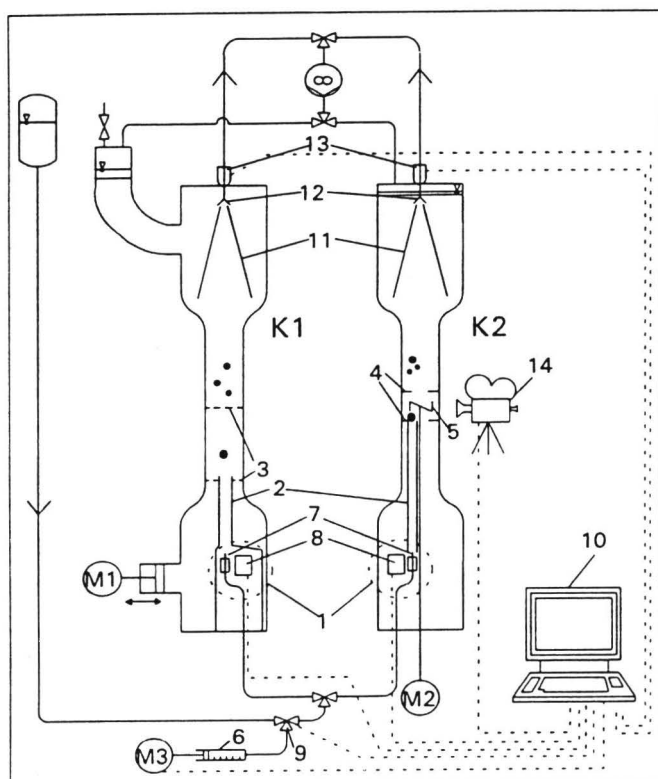


Fig.1 Diagram of the experimental equipment

Drop injection unit and measuring system

The drops were created by pushing a defined volume out of a microsyringe (6). For the motion of the axle of the syringe a step by step motor was used (M3). The drop was formed at the top of a needle inside the column. After a lateral movement of the needle forced by an electric magnet (8) the drop of lighter phase broke away and rose. Using a three-way micro valve (9) the syringe could be refilled. The step by step motor, the electric magnet and the valve were controlled by a personal computer (10). At the top of the column a funnel (11) was located which collected the daughter drops. The measuring system consisted of a capillary tube (12) with a small funnel as an inlet for the collected drops. In the tube the drops were formed into cylinders. A photoelectric cell (13) detected the passage of drops in the tube and a computer calculates the diameter of the drops. This measurement system has been often used for a large number of liquid-liquid systems (Blaß (1988)). A high speed camera was used to study the mechanism of break-up (14).

Test system

In all experiments the lighter phase was dispersed. The addition of n-hexan and glycerol was used to adjust viscosity. The properties of the solvent systems employed are listed in Table 1. The interfacial tension for all combinations was around 33 mN/m.

TABLE 1
Physical properties of the test systems:

	Density /kg/m ³	Viscosity /mPas
53% mineral oil(thin) 47% n-hexane	753	1,2
67,5% mineral oil(thin) 32,5% mineral oil(fluid)	854	50,0
100% water	1000	1,0
21,3% water 78,7% glycerol	1205	50,6

EXPERIMENTAL OBSERVATION

As did Haverland (1988) we found in pulsed sieve-plate columns four typical regions, as shown in Fig.2: one in which the drops are stable (Regime A), one in which break-up occurs with a probability of 100% (Regime B), one in which breakup sometimes occurs (AB) and one in which the drops stick at the sieve-plate (Regime C). A similiar behaviour we found in the Kühni-column, but here the region where the drops stuck at the sieve-plate is missing, as shown in Fig.3.

A higher viscosity gives larger stable diameters (d_{stab} -Line) and larger diameters which break with a probabiliy of 100% (d_{100} -Line). The comparison between Fig.2 and Fig.3 shows that the influence of a higher dispersed phase viscosity on a pulsed sieve plate column is more significant than on a Kühni-column. A rotating disc contactor was also investigated. In the case of viscous dispersed phase a RDC needs much more energy-input to break the drops. Viscosity has a significant influence on the drop diameter, therefore it has to be regarded in the calculation of drop break-up.

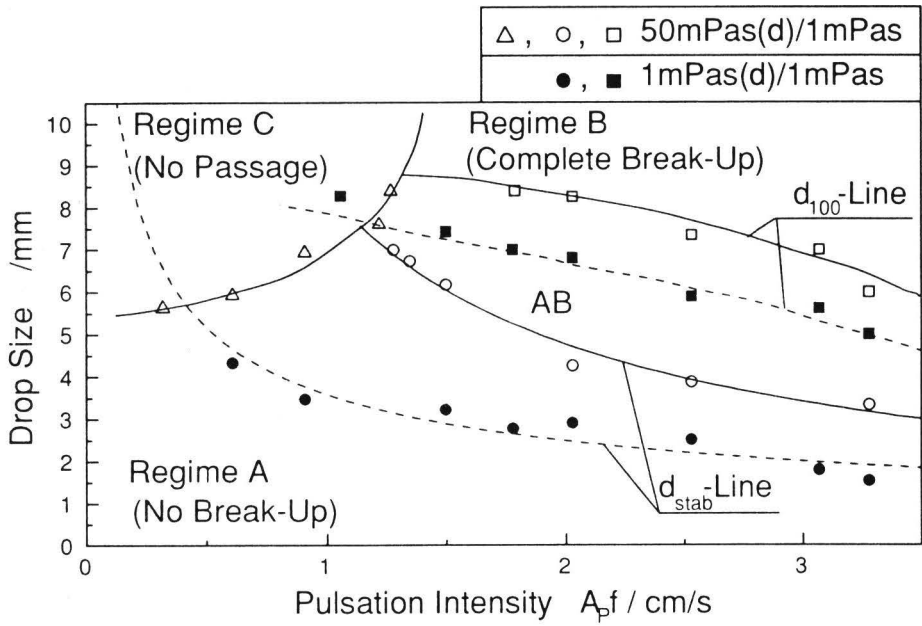


Fig.2 Influence of dispersed phase viscosity on a pulsed-sieve plate column

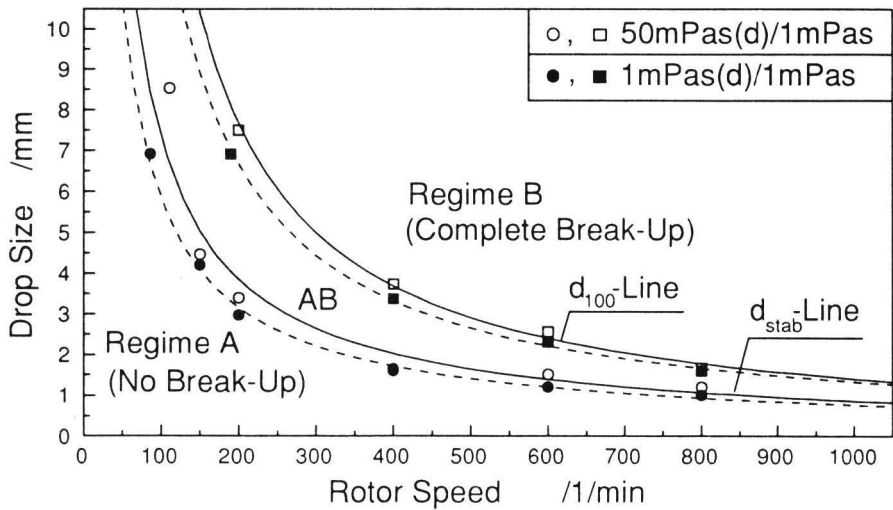


Fig.3 Influence of dispersed phase viscosity on a Kühni-column

ACKNOWLEDGMENTS

The financial support from the "Arbeitsgemeinschaft Industrieller Forschungsvereinigungen e. V." (AIF) is gratefully acknowledged.

NOMENCLATURE

The nomenclature used coincides with the standard nomenclature.

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4.2

THE BREAKAGE OF DROPS IN ROTATING DISC CONTACTORS

V.CAUWENBERG, P.VAN ROMPAY

Dept. of Chemical Engineering, Catholic University of Leuven, Heverlee (Leuven), Belgium

Z-Q. MAO, M.J.SLATER

Dept. of Chemical Engineering, University of Bradford, Bradford, W.Yorks. BD7 1DP, UK

ABSTRACT

Further studies have been made of the breakage probability of single drops in rotating disc contactors. Such information is required in estimating drop size distributions which are usually expected to change along the column. In this study drop coalescence effects are avoided. Results have been correlated using a ratio of the number of drops breaking to the number not breaking which is taken to be a function of a Weber number based on boundary layer theory. For very viscous continuous phase systems some corrections are required, presently thought to be associated with variations in drop shape and drop vibration as the drop passes the edge of the rotor.

INTRODUCTION

Our previous work on this topic (Bahmanyar, Slater, 1991; Bahmanyar, 1989) concerned a limited range of physical properties and only one column diameter. The accuracy of correlation was worse than the experimental uncertainty. The further work undertaken has covered a very wide range of physical properties and three column diameters have been used, 150, 300 and 600 mm, (Cauwenberg et al, 1990). More emphasis has been placed on continuous phase viscosity and some experiments were carried out with interfacial tension altered using a surfactant.

Experiments were made by observing 300 drops under specified conditions and counting the number of drops which broke. There is randomness associated with the breakage observations. The source of this randomness is considered to be

1. Fluctuations in position of arrival of drops near the rotor edge when the needle is placed in line with the edge.
2. Varying orientation of drops of non-spherical shape.
3. Oscillation of drops
4. Variations in drop surface local interfacial tension.

The statistical uncertainty based on the number of broken drops is no better than $\pm 11\%$ (for breakage of all 300 drops) and normally $\pm 16\%$ or worse for fewer than 50% drops broken. Empirical correlation of single drop breakage data is now possible within this accuracy but a

physically realistic explanation has been difficult to find. The problem of describing breakage behaviour in drop swarms has not yet been faced.

This paper describes our approach to better correlation of the data and discusses the general nature of the drop breaking process. A better understanding is needed if rotating disc contactor design is to be improved and scale-up procedures are to be more scientifically based. The hydrodynamics and the mass transfer process are affected by drop dynamics so such studies as this one are considered to be necessary for all types of column contactor.

EXPERIMENTAL WORK

Single drops of solvent were formed at glass needles of several different sizes; the equivalent spherical drop size could be calculated knowing the solvent flow rate and the number of drops formed in a given time. The non-flowing continuous phase was usually water but experiments were also done with sucrose added up to 60 wt% (viscosity up to 62 mPa s). The surfactant sodium dodecyl sulphate was added in some experiments to a water continuous phase through which toluene drops were passed. Drop sizes changed slightly but other properties remained nearly constant. Three columns were used, with 5 stages (152 mm diameter column), with 7 stages (300 mm diameter) and 23 stages (600 mm): Figure 1 shows the typical layout and Table 1 gives other details. Needles were positioned at the bottom of the column such that drops rising in the absence of agitation just missed the edge of the first rotor; breakage probability was measured only at the first rotor level. The needle tips were positioned 20 to 50 mm below a stator. Some work was done with needle tips placed at different radial positions and at different heights. The equipment was made of glass, stainless steel and Teflon.

For each solvent system and drop size 300 drops were observed and the number fraction which broke in the first stage was noted. This was done at various rotor speeds; at high speeds it was difficult to observe by eye clearly when most drops suffered breakage. In some cases a colour video camera was used to analyse drop behaviour. Typical data are shown in Fig.2.

TABLE 1
Column dimensions

Column diameter (mm)	152	300	600
Rotor diameter (mm)	101	180	360
Stator diameter (mm)	110	210	420
Compartment height (mm)	76	76	90
Rotor and stator thickness (mm)	3.2	3.2	3.2

OBSERVATIONS ON THE BREAKAGE PROCESS

1. Drops broke almost without exception at the edge of the rotor. Drops do not break in the body of liquid in a stage since in general conditions are not homogeneously turbulent in the stage (based on Misk's (1964) Reynolds number criterion).

2. Drops were not all spherical. Nearly all drops had terminal velocities less than the maximum value beyond which drop oscillation can occur.

3. If a rising drop approached the rotor and had to move radially to get around the disc

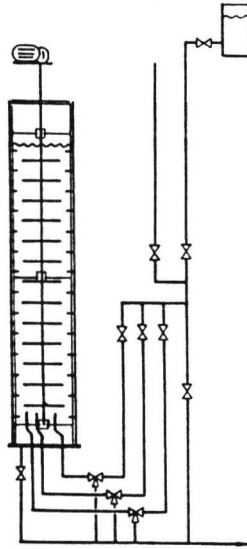
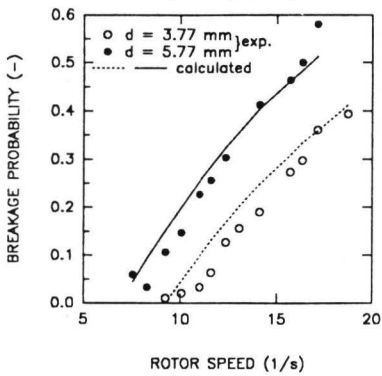


Figure 1: Experimental apparatus

300 mm RDC:
TOLUENE + OIL (33 vol%) (DISP.) - WATER (CONT.)



152 mm RDC:
TOLUENE (DISP.) - WATER + ETHYLENEGLYCOL (CONT.)

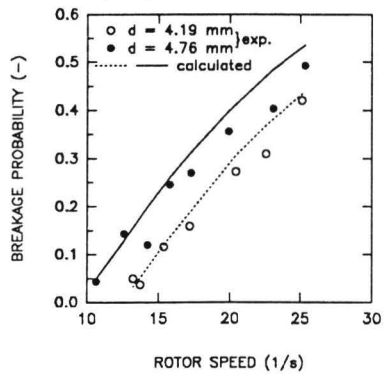


Figure 2: Typical data on the breakage probability

edge then sometimes it broke and sometimes did not.

4. If a drop missed the disc edge it usually did not break.

5. In viscous continuous phase systems a drop approaching the underside of the rotor could be swept radially well away from the rotor edge before rising again and it then usually did not break.

6. In a few experiments in a 600 mm RDC (not reported here) drop breakage fraction sometimes increased with rotor speed to a maximum then decreased.

7. Dye tracer experiments and other shadow techniques did not reveal strong turbulence at the disc edge under the conditions used. A thick (many mm) boundary layer under a disc could be clearly observed using a dye when a viscous liquid (ethylene glycol) was used. This observation is in agreement with calculated boundary layer thickness.

8. When a needle was positioned nearer the shaft of the rotor assembly drops rose in a path curving towards the edge of the disc, following the continuous phase flow pattern. Drops which approached the disc surface closely then moved outwards along the disc surface, and if they broke, it was always at the disc edge.

9. The orientation of large non-spherical drops at the rotor edge varied.

10. One run of 1000 observations supported the idea of the existence of a critical rotor speed below which no drops of a fixed size broke. However, in a few cases breakage fractions of up to about 0.02 persisted as rotor speed decreased towards zero.

11. At zero rotor speed drops falling vertically to hit the rotor edge were more easily broken as continuous phase viscosity decreased. The kinetic energy of drops was considered responsible. As speed increased drops tended to hit the underside of the rotor first and then did not break as they rolled around the edge.

A model of the breakage process was sought which was in accord with all these observations.

CORRELATION OF BREAKAGE PROBABILITY

Early work proposed that the number fraction of drops which broke relative to the number fraction which did not break was related to the ratio of breakage force to resisting force due to interfacial tension, i.e. a Weber number. It was suggested that

$$p / (1-p) = 0.0011 (\rho_c [N^2 - N_{cr}^2] D R^2 d / \gamma)^{1.2} \quad (1)$$

The scatter was large but individual data sets show a good correlation with this Weber number (Bahmanyar, Slater, 1991; Bahmanyar, 1989).

Using Schlichting's boundary layer results (Cauwenberg et al, 1990; Schlichting, 1955) for laminar and turbulent conditions on the disc face the shear force on a drop can be estimated and we obtain better correlations for a limited range of continuous phase viscosity

$$p / (1-p) = 0.258 \{ \rho_c^{0.5} \mu_c^{0.5} [N^{1.5} - N_{cr}^{1.5}] D R d / \gamma \}^{1.16} \quad (2a)$$

for $Re_D < 6 \cdot 10^4$ (143 points, 152 mm diameter column, $\pm 6\%$ on p) (Figure 3) and for turbulent conditions, i.e. $Re_D > 6 \cdot 10^4$, (59 points for 152 mm column; 244 points, 300 mm diameter column, $\pm 6\%$ on p)

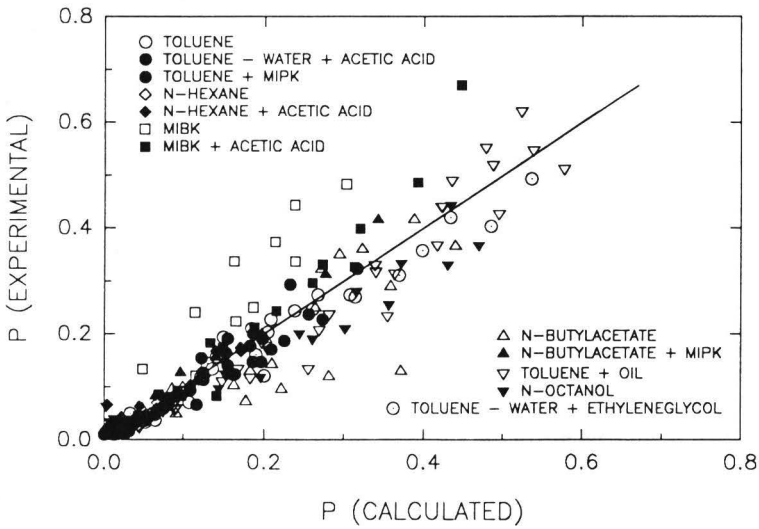


Figure 3: Correlation of data for laminar conditions (152 mm RDC)

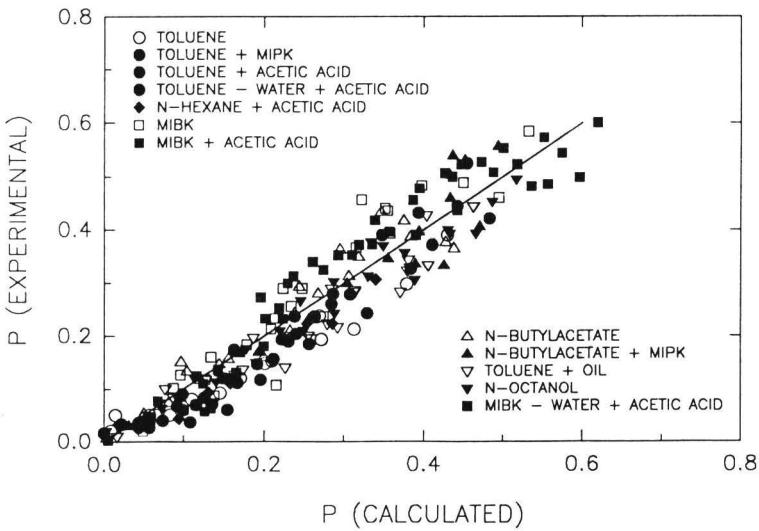


Figure 4: Correlation of data for turbulent conditions (300 mm RDC)

$$p/(1-p) = 0.00312 \{ \rho_c^{0.8} \mu_c^{0.2} D_R^{1.6} [N^{1.8} - N_{cr}^{1.8}] d / \gamma \}^{1.01} \quad (152 \text{ mm}) \quad (2b)$$

$$p/(1-p) = 0.00624 \{ \rho_c^{0.8} \mu_c^{0.2} D_R^{1.6} [N^{1.8} - N_{cr}^{1.8}] d / \gamma \}^{0.99} \quad (300 \text{ mm}) \quad (2c)$$

Figure 4 shows the correlation for the 300 mm column. The ranges of the physical properties are; $995 < \rho_c < 1010 \text{ kg/m}^3$, $650 < \rho_d < 890 \text{ kg/m}^3$, $0.83 < \mu_c < 2.4 \text{ mPa s}$,

$$0.31 < \mu_d < 8.8 \text{ mPa s}, 1.55 < \gamma < 42.3 \text{ mN/m}.$$

The preconstants in eqs (2b) and (2c) appear to be in proportion to the ratio of column diameter to compartment height. We have examined a very large number of possible dimensionless variables employed in various ways to obtain some improvement.

DROP SHAPE AND OSCILLATION

Eccentricity is a function of $E\ddot{o}$ under conditions of unhindered non-oscillating vertical motion (Wellek et al, 1966);

$$e = (1 + 0.13 E\ddot{o}) \quad (4)$$

but with agitation, additional use of the viscosity group $Vi = \mu_c / (\rho_c d \gamma)^{0.5}$ was found to be required to correlate data. Lihou (1972) shows that Vi is associated with vibration of a drop in a viscous medium. These groups were used in following correlations.

EFFECT OF CONTINUOUS PHASE VISCOSITY

Experiments with aqueous sucrose solutions were used to explore the effect of high continuous phase viscosity; these results were not so well modelled by eqs(2) and modified correlations were sought.

Using the Eötvös and viscosity groups leads to correlations for laminar and turbulent conditions respectively;

$$p/(1-p) = 0.012 (\rho_c^{0.5} \mu_c^{0.5} [N^{1.5} - N_{cr}^{1.5}] D_R d / \gamma) \cdot (1 + 0.13 E\ddot{o})^{0.67} \cdot (1 + 3173 [\mu_c^2 / \rho_c d \gamma]^{0.5})^{0.90} \quad (5)$$

$$p/(1-p) = 0.0011 (\rho_c^{0.8} \mu_c^{0.2} [N^{1.8} - N_{cr}^{1.8}] D_R^{1.6} d / \gamma) \cdot (1 + 0.13 E\ddot{o})^{0.67} \cdot (1 + 640 [\mu_c^2 / \rho_c d \gamma]^{0.5})^{1.03} \quad (6)$$

The regression coefficients are 0.9 and the standard errors ± 16 to 21% on p . The correlations are within the experimental error. The viscosity range is 0.83 to 62 mPa s . These equations do not have the same preconstants as eqs(2) obtained for low viscosity data and the data fit is not so good.

CRITICAL CONDITIONS

The critical rotor speed N_{cr} was first estimated from plots of p versus N then a best linear fit was made for $p/(1-p)$ against the modified Weber number optimizing N_{cr} . Empirical fits for N_{cr} were made first to establish the exponents on the major variables (d , γ , $\Delta\rho$ and μ_c for the

152mm column, laminar conditions, and d , γ and DR for the 300 and 600mm columns, turbulent conditions). Hence for laminar conditions

$$N_{Cr} = 0.445 d^{-1.0} \gamma^{0.8} \mu_c^{-0.1} \Delta p^{-0.3} \quad (R=0.908, \pm 17\%) \quad (7)$$

and for turbulent conditions

$$N_{Cr} = 0.378 d^{-0.29} DR^{-1.47} \gamma^{0.72} \quad (R=0.912, \pm 17\%) \quad (8)$$

We propose that for turbulent conditions the critical Weber number is a function of a disc Reynolds number and the viscosity group in the form

$$We_{Cr} = c Re_D^m Vi^n \quad (9)$$

and we match exponents on important variables to find m and n . To obtain a better match on all three important variables for turbulent conditions we have used a modified Reynolds number based on circulating flow in a compartment, $Re_{Dm} = \rho_c N_{Cr} DR^3 / H_c \mu_c$ and so find

$$(\rho_c^{0.8} \mu_c^{0.2} N_{Cr}^{1.8} DR^{1.6} d / \gamma) = 0.929 Re_{Dm}^{-0.7} Vi^{-1.5} \quad (10)$$

which can be written as

$$N_{Cr} = 0.96 d^{-0.1} DR^{-1.5} H_c^{0.28} \gamma^{0.7} \mu_c^{-0.40} \rho_c^{-0.30} \quad (11)$$

for turbulent conditions, correlation coefficient 0.901, absolute error $\pm 17\%$ on N_{Cr} , 39 data points for 300 and 600 mm columns (Figure 5). As Re_{Dm} increases it is thought that the increased circulating flow pushes drops nearer the column axis and drops remain longer under a disc; enhanced shape changes dependent on the viscosity group then could make breakage easier.

For laminar conditions a similar procedure was tried but consistency with eq(7) could not be obtained using eq(9); good agreement could be obtained with

$$(\rho_c^{0.5} \mu_c^{0.5} N_{Cr}^{1.5} DR d / \gamma) = 0.0322 Vi^{0.26} E\ddot{o}^{-0.18} \quad (12)$$

which can be written as (cf eq(7))

$$N_{Cr} \propto d^{-0.99} DR^{-0.67} \gamma^{0.70} \mu_c^{-0.16} \rho_c^{-0.42} \Delta p^{-0.12} \quad (13)$$

with a correlation coefficient of 0.883, an absolute error of $\pm 22\%$ on N_{Cr} , 59 data points for the 152mm column, one third being for high continuous phase viscosity (Figure 5). The lack of influence of Re_{Dm} may suggest that drops are not much diverted from vertical (spiral) motion. As Vi becomes larger drops can stretch or vibrate more; as $E\ddot{o}$ increases drop shape changes from spherical. These seem to act in opposition.

Any further influence of viscosity ratio is not easy with present data to distinguish for either laminar or turbulent conditions so these equations cannot be considered as final.

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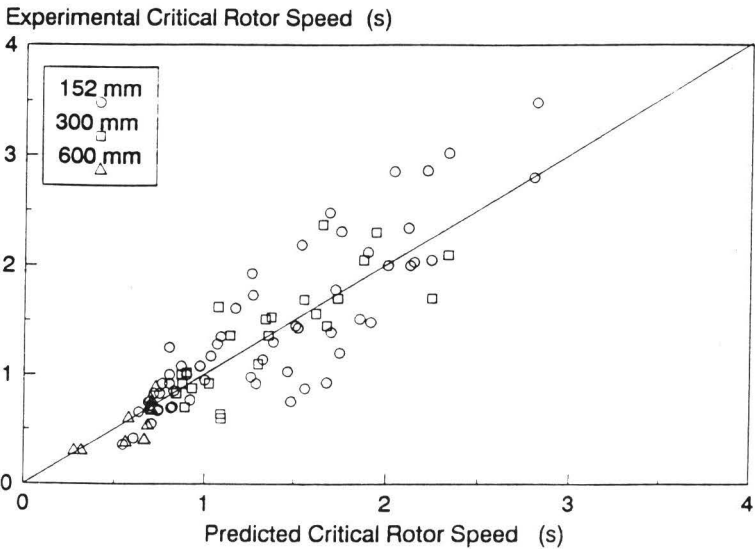


Fig. 5 Correlation of critical rotor speed

NOMENCLATURE

Standard Nomenclature is used except for

e eccentricity of drop

$Eö$ $g d^2 \Delta \rho / \gamma$

H_c compartment height m

N_{cr} critical rotor speed s^{-1}

p number breakage fraction

Re_D $\rho_c N_{cr} D R^2 / \mu_c$

Re_{Dm} $\rho_c N_{cr} D R^3 / H_c \mu_c$

Vi $\mu_c / (\rho_c d \gamma)^{0.5}$

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4.3

**HOLD-UP PROFILES OF THE DISPERSE PHASE IN A RECIPROCATING-PLATE
EXTRACTION COLUMN****E. STIEBING, S. LEUTHOLD, S. WEISS**

Department of Chemical Engineering
Martin-Luther-University of Halle-Wittenberg
0-4200 Merseburg, Geusaer Str., Germany

ABSTRACT

Dependence of the the hold-up profiles on operational, material and constructional parameters are systematically investigated and represented. Experiments for determining the axial hold-up profiles and axial drop size distribution and mean drop diameter were performed in a reciprocating-plate extraction column (0.1 m diameter and 5 m operating height) with plates with rectangular openings.

INTRODUCTION

In recent years, inhomogeneities in fluid dynamics have increasingly been observed in extraction columns with additional mechanical energy, Jiricny (1979). Axial hold-up profiles have been found both in systems with mass transfer in which a change of hold-up along the column can be attributed to a change in physical properties of the materials, and in systems without mass transfer. By equalization of the hold-up profiles which can be achieved by a calculated change of the geometry of the extractor and thus of flow conditions, the mode of operation can be optimized.

EXPERIMENTAL

Figure 1 shows the technological schme of the pilot plant. The core is the extraction column of glass with a diameter of 0.1 m and an operating height of 5 m, equipped along the height with sampling valves. Plates with rectangular openings are mounted which have a circular segment section as downcomer for the continuous phase. The specific free area of the 16 openings is 17% and the specific free area of the downcomer is 23.5%, compared to the cross section area of the column. The plates are attached to an axis in a central position, with plate spacing of 0.05 m. For reciprocating drive an eccentric connected with an electric motor is used. The arrangement of the equipment on different operating floors permits an improved production by

utilizing the geodetic difference in level. The volume flow rates are determined by a rotameter and are recycled.

The testing system toluene and water recommended by EFCE was used. The liquids used were of technical grade. Density and viscosity for toluene as dispersed phase are:

867.4 kg/m^3 and 0.6894 mPa s and for water as a continuous phase 999.5 kg/m^3 and 1.0248 mPa s . The interfacial tension of the system is 0.035 N/m . The continuous phase is fed to the head of the column and the dispersed phase is fed to the bottom of the column by a finger distributor ($D_N = 3 \text{ mm}$; $N_N = 25$).

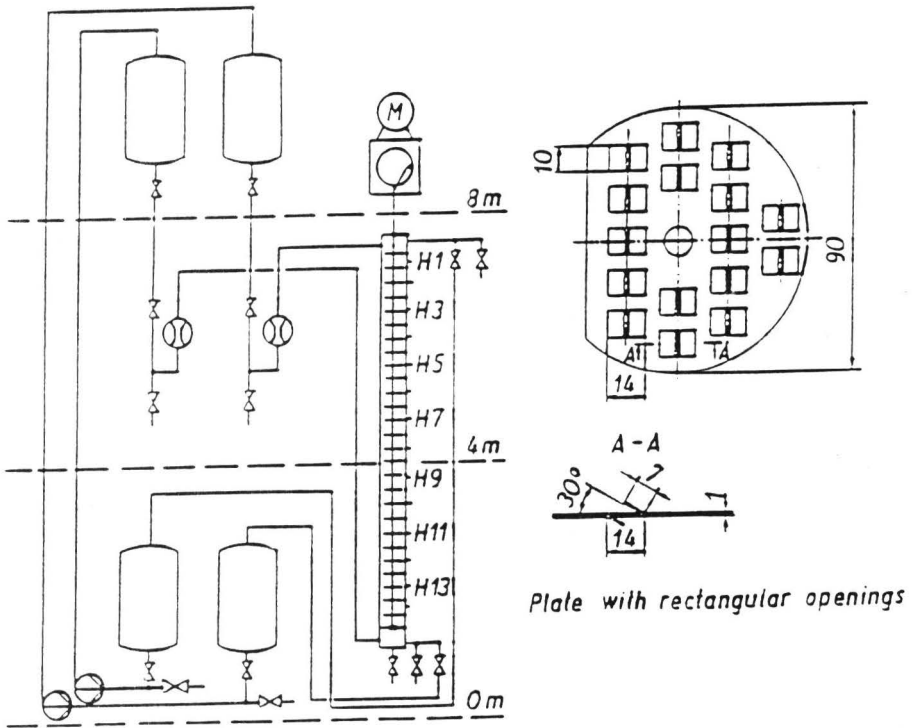


Fig. 1 Experimental arrangement and plate with rectangular openings

The axial hold-up profile was determined by sampling from 14 side valves, a radial equipartition of the hold-up being assumed. The sample was 10 mL. Total hold-up was determined by the rapid closing of all inlet and outlet valves. The drop diameter was determined photographically; 400 to 1000 drops were counted and classified per experimental point.

In selecting the operating conditions, one of the parameters was varied at a time whereas the others remained constant: ratio of dispersed and continuous phase, superficial phase velocity of

dispersed and continuous phase, frequency and amplitude of vibration and total throughput (Table 1). Some experiments on initial distribution of the dispersed phase were also made.

TABLE 1
Experimental conditions

$V_d, \text{mm/s}$	$V_c, \text{mm/s}$	R	$V_d + V_c, \text{mm/s}$	A_p, mm	f, s^{-1}	$I, \text{mm/s}$
1.77	5.30	0.33	7.07	5.0	1.80	18.0
2.65	5.30	0.50	7.95	5.0	1.80	18.0
3.53	5.30	0.66	8.83	5.0	1.80	18.0
5.30	5.30	1.00	10.60	5.0	1.80	18.0
3.53	3.53	1.00	7.06	5.0	1.80	18.0
3.53	7.07	0.50	10.60	5.0	1.80	18.0
3.53	3.53	1.00	7.06	5.0	2.15	21.5
3.53	3.53	1.00	7.06	5.0	2.37	23.7
3.53	3.53	1.00	7.06	4.0	2.37	18.9
3.53	3.53	1.00	7.06	2.0	2.37	9.5
3.53	10.61	0.33	14.14	4.0	1.80	18.0

DEPENDENCE OF HOLD-UP PROFILE ON OPERATING PARAMETERS

The hold-up profiles experimentally determined to about 85% of the flooding show a uniform shape. All profiles have two maxima, one occurring at the introduction of the dispersed phase, the other near the exit of the dispersed phase. The maximum near the exit of the dispersed phase may be assumed to have been caused by the axial dispersion of the dispersed phase and by the effect of the settler. The maximum at the disperse phase inlet may be accounted for by the entrainment of small drops of the dispersed phase by the continuous phase and their accumulation in the upper part of the column.

Influence of throughput

For a small total throughput and a small flow rate of dispersed phase no definite hold-up profile occurred. There is no significant dependence of the phase ratio on hold-up profile. An increasing flow rate of disperse phase with a small total throughput causes a hold-up profile increasing in the flow direction of the dispersed phase. On varying flow rate of continuous phase, a maximum forms, the position of which shifts with increasing flow rate of continuous phase in the flow direction of this phase. With increasing total throughput and a large flow rate of dispersed phase another maximum forms at the introduction of dispersed phase. A fine droplet fraction accumulates in the upper part of the column and the amount is increased by

increasing the flow rate of the dispersed phase (Fig. 2), Milot (1990). The same effect will be reached if the flow rate of the continuous phase is increased (Fig. 3), Bensalem (1985).

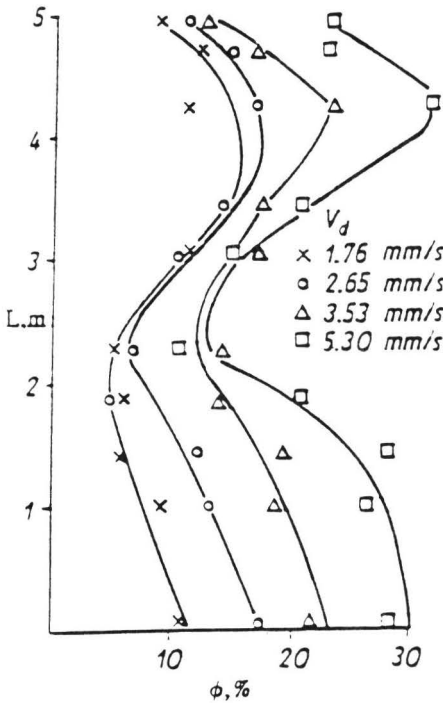


Fig. 2 Dependence of axial hold-up profile on superficial velocity of disperse phase V_d ($A_p = 5$ mm, $f = 1.8$ s $^{-1}$, $V_c = 5.3$ mm/s)

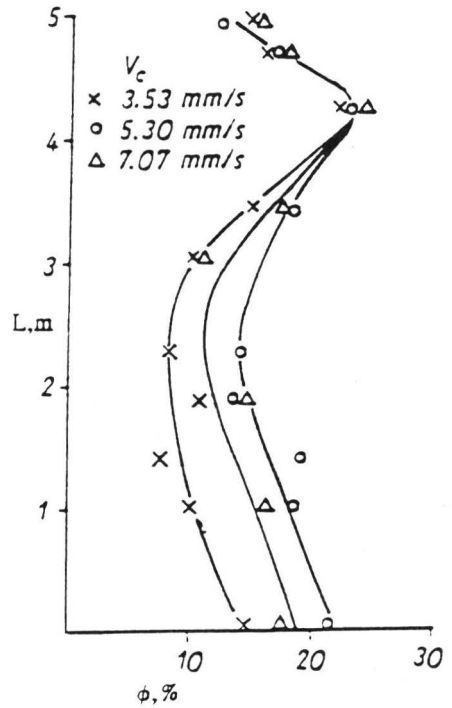


Fig. 3 Dependence of axial hold-up profile on superficial velocity of continuous phase V_c ($A_p = 5$ mm, $f = 1.8$ s $^{-1}$, $V_d = 3.53$ mm/s)

Influence of frequency

Increasing the frequency or vibration results in a higher motion of the plates which increases the dissipation energy and intensifies the size reduction of the drops. This increases the number of small drops and the hold-up. These small drops considerably influence a definite maximum at the point of introduction of dispersed phase (Fig. 4).

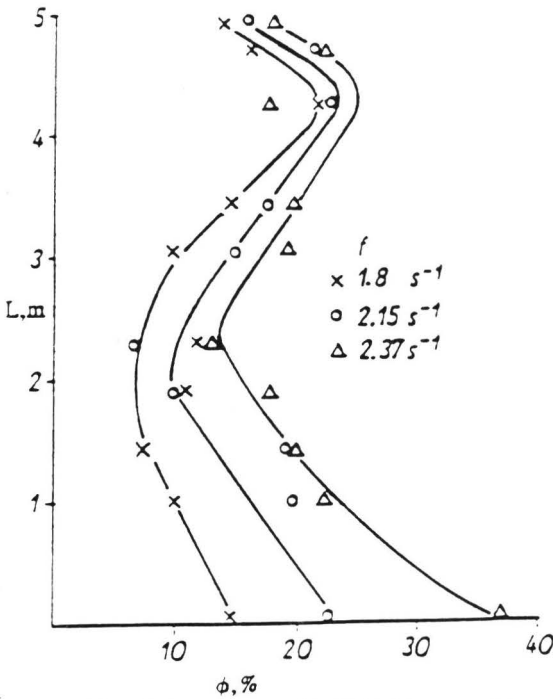


Fig. 4 Dependence of axial hold-up profile on frequency f
 $(A_p = 5 \text{ mm}, V_d = 3.53 \text{ mm/s}, V_c = 3.53 \text{ mm/s})$

Influence of amplitude

Increasing the amplitude results in increasing the vibrational intensity and thus an increased drop size reduction. In general the shape of the hold-up profile is maintained. Nowhere is an excessive increase in the hold-up found (Fig. 5). With constant vibration intensity, a frequency change more strongly influences the hold-up and the shape of the profile than does the amplitude.

Influence of initial distribution

In a comparison of the hold-up profiles without a distributor and two finger distributors (hole diameter 2 mm and 3 mm) a more unfavourable hold-up profile could be observed because of missing initial distribution. Without a distributor, a lower hold-up is obtained because of larger drops (Fig. 6). As these differences are not too influential, it may be concluded that the initial distribution in columns with diameter up to 0.1 m is of little importance.

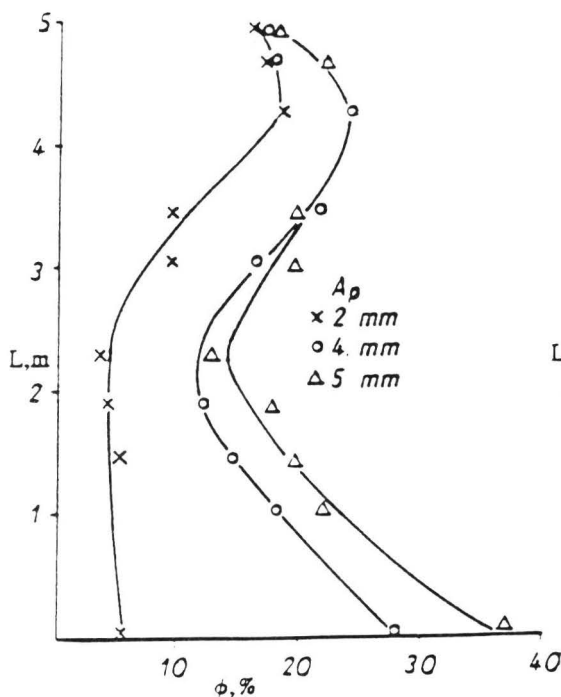


Fig. 5 Dependence of axial hold-up profile on amplitude A_p ($f = 2.37 \text{ s}^{-1}$, $V_d = 3.53 \text{ mm/s}$, $V_c = 3.53 \text{ mm/s}$)

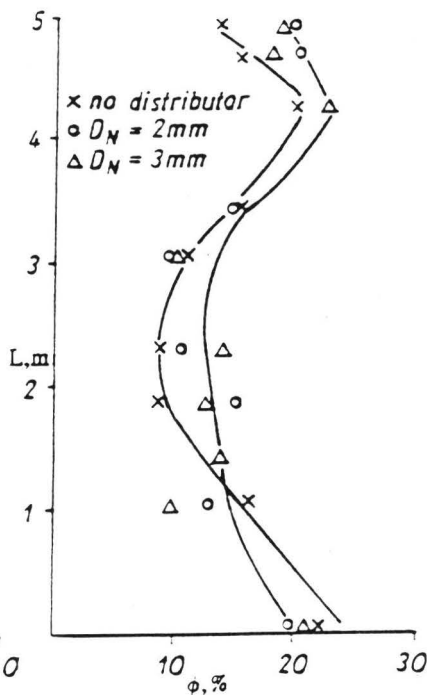


Fig. 6 Dependence of axial hold-up profile on initial distribution ($A_p = 4 \text{ mm}$, $f = 1.8 \text{ s}^{-1}$, $V_d = 3.53 \text{ mm/s}$, $V_c = 10.6 \text{ mm/s}$)

PHENOMENOLOGICAL DETERMINATION OF HOLD-UP PROFILES

A first attempt failed to determine the hold-up profiles by a change in mean drop diameter along the column height (Fig. 7). It becomes evident that the drop diameter continuously decreases along the height in the flow direction of the dispersed phase. The largest decrease is to be found in the lower part of the column. If the hold-up profile could be determined by the Sauter diameter, the respective hold-up profile would monotonously increase in the flow direction of the dispersed phase. This is not the case. The wide range of drop size is inadequately determined by the Sauter diameter. It becomes necessary therefore, to examine the drop size distribution (Fig. 8). At the inlet of the dispersed phase into the column two distinctly different types of drops appear. The first type are large drops produced by the distributor, the second type are small drops entrained by the continuous phase on its way through the column and accumulating in the lower part of the column. This gives a bimodal distribution. Other reasons for the development of a bimodal distribution may possibly be an unfavourable initial distribution or an asymmetric break-up of large drops, Sovova (1983). The large number of

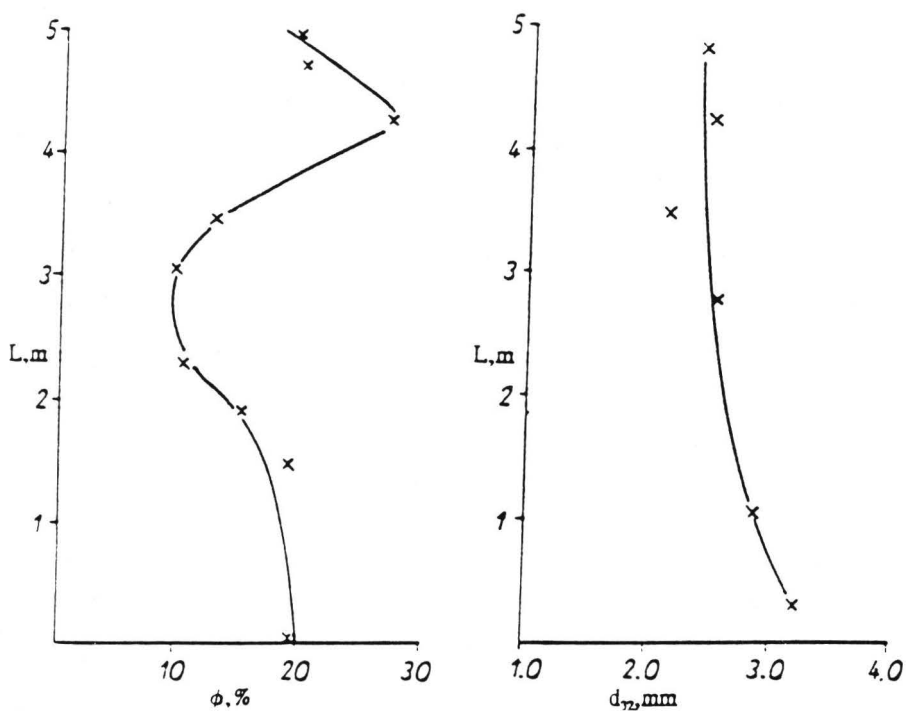


Fig. 7 Dependence of axial hold-up profile on mean drop diameter

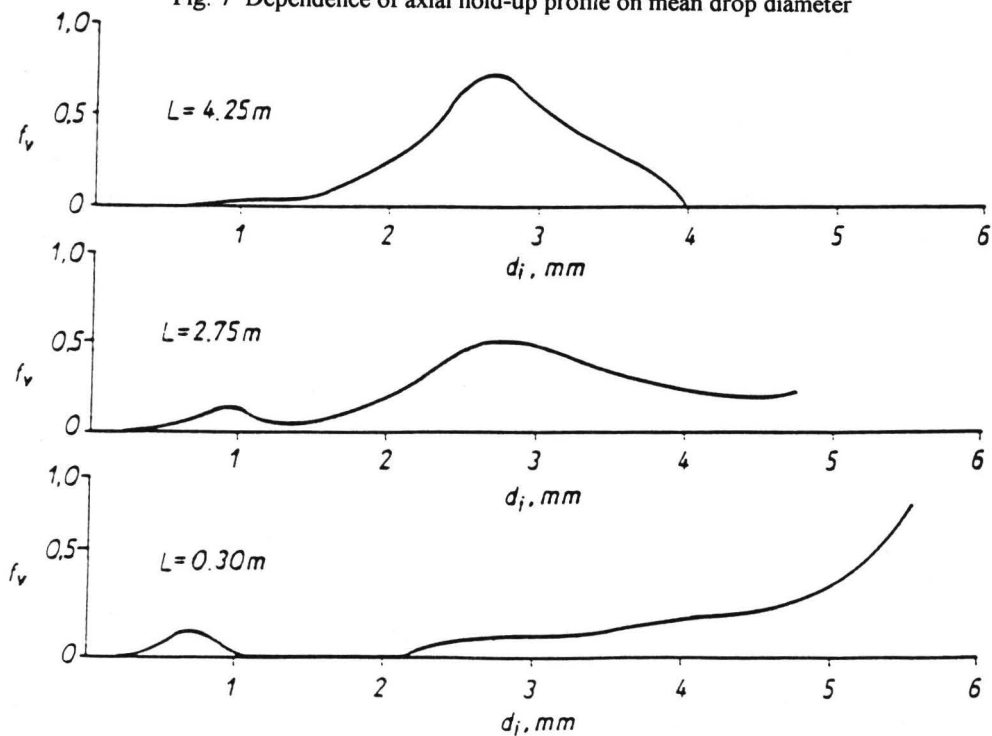


Fig. 8 Dependence of the volume density distribution on column height

drops with a size below 1 mm by their low terminal velocity result in an increase of the hold-up to a maximum. At the middle of the column (Fig. 8; $L = 2.75$ m) the distribution has already changed so much that the two peaks of distribution are not distinguishable. The number of very small drops has decreased considerably and the large ones produced by the distribution have been dispersed. The mean residence time of the drops is essentially determined here by the large number of drops with a diameter of 2.8 mm, which results in a hold-up minimum. At $L = 4.25$ m, the volume density distribution is nearly unimodal. The decrease of the drop diameter by dispersion results in an increase of the hold-up in the flow direction of the dispersed phase. The hold-up decrease at the top of the column results from the enlargement of the settler. The motion of the drops is no longer impeded by the flow of the continuous phase and the plates. It becomes evident that knowledge of the change in drop size distribution along the column height makes it possible to determine the developing hold-up profile.

The processes that result in a local and axial drop size distribution must be determined and specified. It is necessary to determine the processes of drop dispersion and coalescence. Drop dispersion, on the one hand, results from direct contact of the drops with the plates and, on the other, from turbulent eddies caused by the motion of the plate. It seems to be a characteristic of the plates with rectangular openings that the geometry of the plates develops more strongly the contact of the drops with the perforation and the dispersion of the drops by turbulence. The result is a very fine drop fraction, Jares (1987). As a process which is in direct interaction with drop dispersion, coalescence must be taken into account. The transport of the drops through the column is of great importance for the development of an axial drop size profile. The drops move through the column at different velocities. Plate spacing limits the free rise of the drops. Small plate spacing results in a stronger back mixing of the phases between the plates, Baird (1992). For mathematical modelling the following partial processes have to be taken into account, according to the phenomenological determination.

1. Modelling of drop size distribution dependence on material, operating and geometrical parameters.
2. Consideration of the initial distribution of the drops by the distributor and its effect on the hold-up.
3. Consideration of the change in drop size distribution by the motion of the drops in two-phase flow and the effect of the extension of the settlers.

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4.4

**AQUEOUS PHASE ENTRAINMENT IN LIQUID-LIQUID EXTRACTION
CONTACTORS**

S. T. ARM and J. A. JENKINS

AEA Fuel Services
AEA Technology
Harwell Laboratory
Didcot, OX11 0RA, UNITED KINGDOM

ABSTRACT

The phenomenon of aqueous phase entrainment and associated carry-over of impurities of low extractability such as caesium has been investigated in a pulsed perforated plate column, a gravity mixer-settler and an annular centrifugal contactor. The experiments have shown that entrained drops are produced by the dispersive processes of coalescence and breakage, and as a result of the precipitation of water. Precipitation in the present study occurs as the water solubility of the organic phase is reduced due to uranium extraction and produces drops ($\sim 1 \mu\text{m}$ in diameter) in all studied contactor types. The interactions of the dispersive and precipitated drops are important when considering the scrubbing of impurities.

In a pulsed column, the precipitated drops are very much smaller than the smallest observed dispersive drops and so are unable to participate fully in the hydrodynamic mixing processes. The behaviour of the precipitated drops therefore becomes the determining factor in the mechanism of impurity scrubbing. By contrast, in the annular centrifugal contactor, the secondary dispersive drops are also $\sim 1 \mu\text{m}$ in diameter and so the precipitated drops rapidly become assimilated with the former to maintain the steady state haze concentration. Impurities associated with entrained material are, therefore, successively diluted as the haze drops are coalesced and re-dispersed within each stage. As a result of the wide distribution of turbulent energy, the interactions of the different drops and the mechanism of impurity carry-over associated with the gravity mixer-settler are a combination of those observed in the pulsed column and centrifugal contactor.

INTRODUCTION

Operation of liquid-liquid extraction contactors can give rise to entrainment of very small drops of aqueous phase in the organic product. Such entrainment results in carry-over of impurities, originally dissolved in the aqueous feed, with the product stream and can place an undesirable burden on downstream purification and waste treatment processes. It is

important, therefore, to understand the mechanisms which cause aqueous phase entrainment and to determine how it can be minimised.

For uranium extraction into 20% tri-n-butyl phosphate / odourless kerosene (TBP/OK), Jenkins et al (1988) identified two mechanisms which determined the drop size distribution in a pulsed perforated plate column,

- hydrodynamic mixing (dispersive processes)
- water precipitation from the organic phase which occurs when the major solutes are extracted into the organic phase.

The latter mechanism produced 'haze' drops approximately 1 μm in diameter which compared with approximately 1 mm for the diameter of the primary drops. Jenkins et al (1989) explained the persistence of the precipitated haze drops into the solvent product in the pulsed column experiments by considering the effects associated with the large difference in drop size.

Caesium was introduced into the pulsed column experiments in order to study the effect of aqueous phase entrainment on the behaviour of impurities of low extractability (distribution coefficient $\sim 10^{-6}$). From analysis of the initial results, Jenkins et al (1990) reported a preliminary model which described the behaviour of precipitated drops and associated impurity carry-over.

This paper describes the results of recent experiments on a pulsed column, a batch operated gravity mixer-settler and annular centrifugal contactors (originally developed at the Oak Ridge and Argonne National Laboratories and Savannah River Laboratory in the USA). Mathematical models of the aqueous phase entrainment and caesium carry-over have been developed for the centrifugal contactor and that for the pulsed column reported by Jenkins et al (1990) has been modified in the light of the recent results.

EXPERIMENT

The mixing process in a gravity mixer-settler was simulated by means of a 200 mL capacity beaker (60 mm diameter) fitted with four baffles (of 5 mm diameter). A Rushton type impeller (20 mm diameter) was used to provide agitation with the speed measured by an optical tachometer. The centrifugal contactor pilot plant consisted of 8 extraction and 4 scrub stages operated in counter-current mode (Jenkins et al (1993)). The earlier pulsed column experiments in which the columns consisted of extraction and scrub sections of lengths 6 m and 4 m, respectively, have been described by Jenkins et al (1988). In all experiments, an organic phase consisting of 20% TBP/OK was contacted with 3M nitric acid containing various concentrations of uranyl nitrate. Caesium was dissolved in the aqueous phase at a concentration of up to 2.6 g/L.

Entrained drop size distributions were measured with a laser spectrometer (a Malvern 'Mastersizer') which was capable of measuring drop sizes down to 0.1 μm .

RESULTS FROM PULSED COLUMN

In the light of subsequent work, the results from the pulsed column pilot plant at Harwell were re-assessed. The dissolved and entrained water concentration profiles from the 100 mm diameter extract/scrub column are illustrated in Fig. 1.

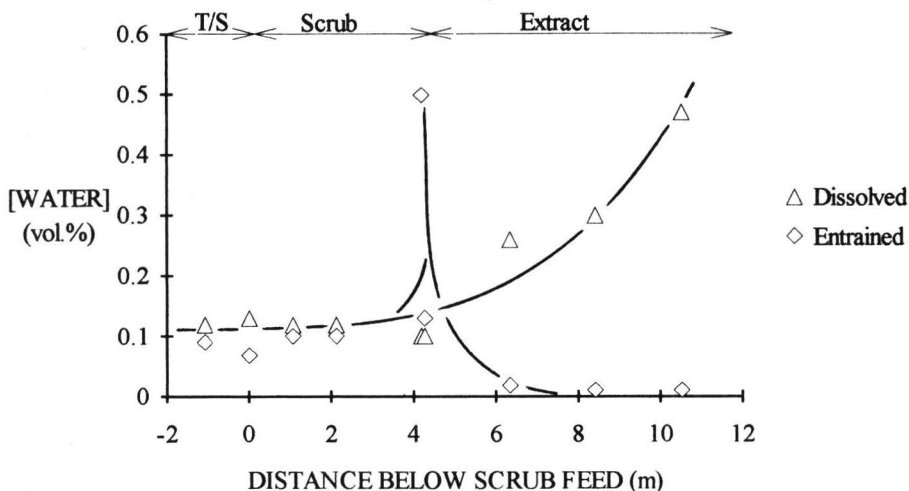


Fig. 1: Water concentration profiles in the pulsed column pilot plant

Note: T/S - top settler.

The data show that there was no significant reduction in the entrained water concentration within the scrub section (the average concentration was 0.125 vol.%). The precipitated drop size of $\sim 1 \mu\text{m}$ was very much smaller than the size of the smallest observed dispersive drops ($\sim 0.5 \text{ mm}$) and so the former would not be expected to participate fully in the hydrodynamic mixing processes.

Below the uranium feed point, towards the raffinate end of the extraction section where very little uranium is present, the organic phase becomes loaded with caesium so that chemical equilibrium is achieved between the two liquid phases. The caesium distribution coefficient decreases with increasing uranium concentration and so as uranium is extracted, caesium is displaced from the organic phase. Theoretical calculations indicated that, on account of the very large interfacial area, the precipitated drops were expected to strip the displaced caesium. The average concentration of caesium in the solvent in the extract section on the basis of chemical equilibrium with the 2.6 gCs/L in the uranium feed, is 20 $\mu\text{g/L}$. Assuming that 0.125 vol.% of haze was precipitated and all of the caesium in the solvent was stripped then the concentration in the haze would have been expected to be 0.016 g/L and this compares with an observed value of 0.038 g/L. Considering that the experimental values are subject to errors associated with both the water and caesium analyses, the agreement with the theoretical values gives support to the theory.

Further calculations indicated that, as a result of the lower interfacial area of the primary drops in the scrub section and low distribution coefficient, there was expected to be negligible mass transfer of caesium to the scrub acid from the organic phase. Hence, at steady state, the concentration of caesium in the haze drops should have remained practically constant throughout the mixing operation and this was also verified in the experiments.

RESULTS FROM THE GRAVITY MIXER-SETTLER

The concentration of entrained haze is illustrated in Fig. 2 as a function of mixing time at an impeller speed of 1500 min^{-1} .

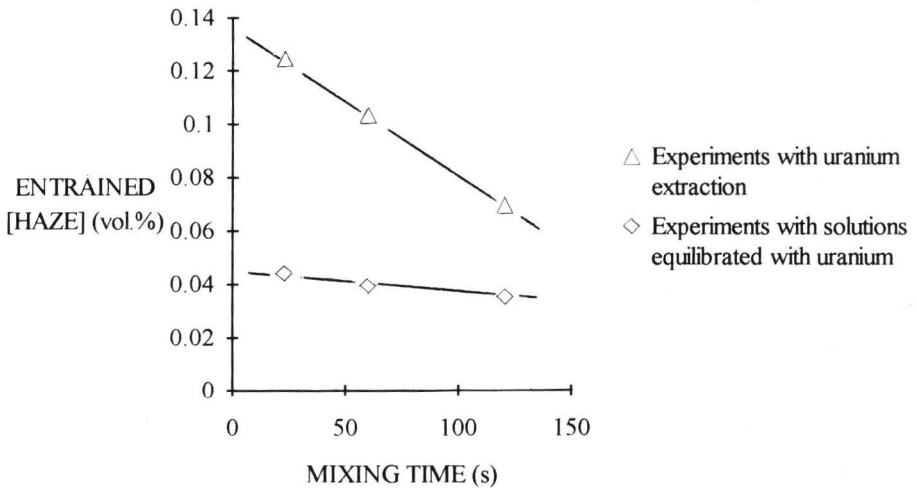


Fig. 2: Effect of mixing time on haze entrainment

The trend shown in this figure may be explained on the basis that the precipitated haze drops were gradually assimilated with the dispersive drops so that the concentration of haze decreased to approach its equilibrium value after $\sim 180 \text{ s}$. Drop size analysis indicated that the secondary drops were of the same size as the precipitated drops and so constituted a 'dispersive' haze.

There tends to be a wide distribution of turbulent energy in a mixer as recently pointed out by Godfrey et al (1989) who, drawing on the work of Park and Blair (1975), found that drop breakage occurred mainly in the impeller region where turbulence is most intense and coalescence occurred in the remainder of the vessel where turbulence is relatively quiescent. In the experiments reported here it is therefore proposed that in the impeller region the turbulent energy was sufficient to produce dispersive haze drops and that the dispersive and precipitated drops then underwent coalescence in the region away from the impeller. Presumably, the disparity between the turbulent energies and residence times in the two regions was such that the precipitated drops persisted for a significant period of mixing.

In the gravity mixer-settler, there are two significant mechanisms by which caesium is dissolved in entrained aqueous phase.

- A proportion of the entrained drops will be derived from the dispersive processes occurring in the contactor and will consist of both primary and secondary drops. The concentration of caesium in these drops will be the same as that in the bulk aqueous phase.
- In addition, as a result of the uranium extraction, drops of aqueous phase will be precipitated. Caesium will be stripped into the precipitated drops from the organic phase as uranium extraction reduces the solubility of the solute. The mass of caesium dissolved in these drops will be approximately that dissolved in the organic phase (at chemical equilibrium with the aqueous phase) prior to uranium extraction.

Therefore, in considering the carry-over of impurities in a gravity mixer-settler it is necessary to consider the precipitated and dispersive haze drops separately since their respective concentrations will be different.

RESULTS FROM THE CENTRIFUGAL CONTACTOR

The profile of entrained aqueous phase (aqueous uranium feed into stage 4) is illustrated in Fig. 3.

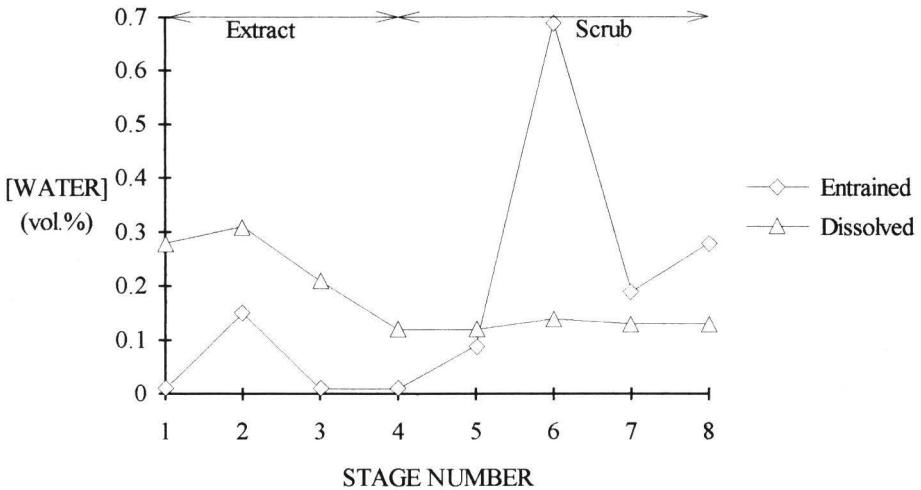


Fig. 3: Profiles of entrained and dissolved water

The concentration of dissolved water decreased in the extract stages as a result of uranium extraction. However, there was no corresponding increase in the concentration of entrained aqueous phase which indicated that the precipitated haze had been totally assimilated with the dispersive drops. Analysis of the entrained drop size distribution showed that, in the absence of uranium extraction, the secondary dispersive drops were approximately the same size as the precipitated haze drops. i.e. $1\ \mu\text{m}$ in diameter.

A qualitative analysis indicated that the turbulent energy was distributed with greater spatial homogeneity than in the mixer-settler. Hence, the precipitated drops were able to fully participate in the hydrodynamic mixing processes to maintain the steady state haze concentration. By considering this phenomenon a mathematical model was developed to describe the scrubbing of impurities of low extractability such as caesium.

Consider a scrub stage with a solvent feed containing entrained haze drops in which is dissolved caesium at a concentration $[Cs]_{hin}$. The caesium concentration of the haze produced in the contactor will be the same as that in the scrub acid from which it is derived, $[Cs]_{aout}$ (assuming perfect mixing). The steady state haze concentration is then maintained by the coalescence of drops from both sets of hazes (i.e. the hazes produced in the contactor and present in the solvent feed) with the primary drops. The probability of capture of a drop from a particular set is the ratio of the volume of haze in that set to the total volume of haze in both sets so that the final caesium concentration in the haze, $[Cs]_{hout}$, is;

$$[Cs]_{hout} = \frac{v_{hin}}{v_{hi} + v_{hin}} [Cs]_{hin} + \frac{v_{hi}}{v_{hi} + v_{hin}} [Cs]_{aout} \quad (1)$$

where v_{hi} , v_{hin} = haze concentration produced in stage i and entering the stage respectively (vol. %)

A model of the scrub process (consisting of 4 stages) incorporating the above mechanism has been set up on a spreadsheet. The set of simultaneous equations was solved with the total mass balance as the constraint and using the experimental entrained aqueous phase concentrations. A comparison of the experimental and predicted data is illustrated in Fig. 4.

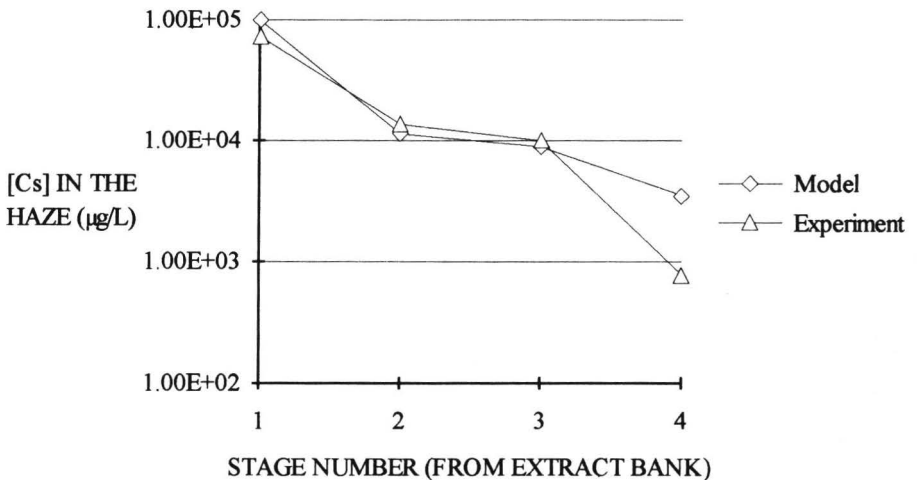


Fig. 4: Comparison of experimental and model $[Cs]$ profile data

The fit of the predicted data is very good considering that the raw analytical data were in terms of solvent volume and therefore subject to errors associated with both water and caesium analyses.

CONCLUSIONS

As well as the drops formed by the dispersive processes, drops of $\sim 1 \mu\text{m}$ in diameter can also be precipitated when the water solubility of the organic phase is reduced by uranium extraction. Both types of drop can be entrained with the organic phase to provide a mechanism whereby impurities of low extractability can be carried into the solvent product. Impurities are stripped into the precipitated drops from the organic phase and mass transfer from these drops is negligible on account of the low distribution coefficient of the impurity species. In the pulsed column, the precipitated drops are very much smaller than the smallest observed dispersive drops and cannot fully participate in the dispersive processes. Impurities are, therefore, only removed into the scrub acid as a result of the slow process of direct capture of the precipitated drops by the dispersive drops. In the gravity mixer-settler, the turbulent energy in the region swept by the impeller is sufficient to produce a significant dispersive haze. However, it appears that the relatively quiescent conditions in the remainder of the vessel ensure that the precipitated haze persists for a significant period of mixing before becoming assimilated within the equilibrium dispersion. In a continuous process there is evidence to suggest that in considering the carry-over of impurities, it is necessary to consider the precipitated and dispersive haze drops separately since their respective concentrations will be different. In the centrifugal contactor, the secondary dispersive drops are also the same size as the precipitated drops but the turbulent energy is more spatially homogeneous so that the latter drops become rapidly assimilated within the steady state dispersion. Impurities associated with entrained drops are successively diluted in each stage as the drops coalesce and re-disperse.

ACKNOWLEDGEMENTS

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NOMENCLATURE

v - haze concentration (vol. %)

Subscripts on concentrations:

a_{out} - product aqueous phase

h_i - haze produced in stage i

h_{in} - haze entrained in feed solvent

h_{out} - haze entrained in product solvent

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MASS TRANSFER DIRECTION AND SURFACTANT INFLUENCES ON THE SELECTION OF THE DISPERSED PHASE IN AGITATED VESSELS

JEFFREY S. KANEL

Chemical Process Engineering Research Laboratory
Eastman Chemical Company
Kingsport, TN 37662 USA

A. H. P. SKELLAND

Department of Chemical Engineering
The Georgia Institute of Technology
Atlanta, GA 30332 USA

ABSTRACT

Criteria are identified for selecting the dispersed phase in an agitated liquid-liquid dispersion as related to extractors. The choice of the dispersed phase was found to have a significant effect on the mass transfer characteristics of the extraction. Factors that can influence the decision include: the volume fraction of the dispersed phase, the direction of mass transfer, the interaction between the solute and the raffinate phase, the occurrence of Marangoni type instabilities, and the presence of surfactants. Concerning the latter factor, minima were observed in plots of surfactant concentration versus mass-transfer coefficients when solute was transferred from one phase. However, when solute was transferred from the opposite phase, increasing surfactant concentration corresponded to enhanced coefficients. These phenomena are identified as being important in the selection of the dispersed phase.

INTRODUCTION

Dispersed phase selection is commonly performed industrially, but has been rather neglected in the literature. Heuristics are currently used when extreme solvent to feed ratios are not encountered, and they include dispersing the phase which alternatively: a) is present in larger volume for greater interfacial area; b) offers less resistance to mass transfer, as trace amounts of surfactants (that reduce internal drop circulation) have a less serious effect on the transfer rate when the dominant resistance resides in the continuous phase (Skelland, 1974); c) promotes interfacial turbulence (Bailes, 1988, Hanson and Hughes, 1983); d) reduces the coalescence time (Bailes, 1988, Hanson and Hughes, 1983); e) minimizes solvent entrainment in the raffinate (which could result in solvent loss and possible effluent problems) (Hanson and Hughes, 1983); or f) promotes a dispersion that will not undergo phase inversion (Bailes, 1988).

Skelland and Chadha (1981) formulated a criterion for evaluating dispersed phase selection in spray and plate extraction columns, with or without surfactants, when one phase offered the dominant resistance to mass transfer. Application of their criterion to both high and low interfacial tension systems indicated that a critical height between plates existed beyond

which the fractional extraction was greater when the controlling phase was continuous. Surfactants were found to decrease this critical distance for both high and low interfacial tension systems. This analysis was extended by Skelland (1992) for extreme phase ratio systems.

Generally, the chosen dispersed phase should minimize extractor volume (mass transfer and settling sections). Focusing here on the former, the rate of solute transfer is proportional to the interfacial area and the overall mass-transfer coefficient. Thus, selection criteria can be formulated based on maximizing both of these quantities. Dispersed phase selection influences the interfacial area via: the mean drop size [see Skelland and Kanel (1992c)], which in turn depends on the breakage and coalescence rates; volume fraction of the dispersed phase; and wetting characteristics of the drops. The choice of dispersed phase affects the overall mass-transfer coefficient by: changing physical properties that impact individual coefficients; influencing the effect of surfactants on the rate of solute transfer; and causing or preventing Marangoni instabilities. Other external factors that guide dispersed phase selection include: extreme phase ratios; dispersion stability against phase inversion; and undesired entrainment.

Thus, the object of this work was to determine the effect of dispersed phase selection on the overall mass-transfer coefficient in batch agitated liquid-liquid dispersions. Major experimental variables included the dispersed phase selected, direction of solute transfer, presence of surfactant, and volume fraction of the dispersed phase.

EXPERIMENTAL

System and properties

Tetrabutylammonium bromide, TBAB, was the chosen solute since its concentration in both aqueous and some organic phases (chlorobenzene here) was directly proportional to the phase's electrical conductivity [Kanel (1990)] at the concentrations used in this study. Thus, its concentration in the continuous phase was monitored both continuously and instantaneously. Conductance of the dispersed phase was shown by Skelland and Kanel (1992a) to have a negligible effect on the continuous phase measurements of TBAB concentration at the dispersed phase volume fractions here encountered. Triton X-100, a non-ionic surfactant ($\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{9-10}\text{OH}$), was selected to eliminate electrical effects at the interface. Physical and transport properties were measured and are given in Table 1.

TABLE 1
Measured physical and transport properties of water and chlorobenzene at 25°C.

Fluid	Density (kg/m^3)	Viscosity (Ns/m^2)	Diffusivity of TBAB (m^2/s)
Chlorobenzene	1083	7.3×10^{-4}	2.62×10^{-10}
Water	997.1	8.7×10^{-4}	6.24×10^{-10}

Interfacial tension was determined by the du Nouy ring method, and the resulting interfacial tension versus Triton X-100 concentration curve was given by Kanel (1990). The effect of TBAB concentration on interfacial tension in the presence of Triton X-100 was found to be negligible in the concentration range used here.

Apparatus

The equipment was previously described by Skelland and Kanel (1992b). Briefly, a Model ELB experimental agitator kit made by Chemineer Kenics was used. The impellers were 316 stainless steel six-flat-blade turbines, with diameters of 0.063 and 0.102 m. The cylindrical, flat bottomed glass vessel was 0.213 m in diameter and was filled to a height equal to its diameter. The impeller was centrally located, and four radial baffles, of width equal to 9% of the vessel diameter, were used. The agitated vessel was immersed in a plane glass aquarium filled with water maintained at 25°C, and photographs of the dispersion were taken during each run. A Nikon F3 camera with a Micro-Nikkor 55mm *f*/2.8 lens was used, together with Kodak Technical pan film for black and white prints. One Hedler Halogen-U lamp placed beside the vessel provided lighting.

The solute concentration in the continuous phase was measured by an electrical conductivity cell constructed from two 7-mm-diameter glass capillary tubes 21 cm in length, both parallel and side by side with 15 mm of 20 gauge platinum wire exposed at one end. A glass bead was placed at the tip of the platinum wires to prevent them from moving in the turbulent flow field. The cell was connected to either a Yellow Springs Instrument Conductivity Meter Model 32 or a Hewlett-Packard 4329A High Resistance Meter.

Procedure and design

Both solvents were mutually presaturated, and the solute and surfactant concentrations established (Triton X-100 in the aqueous phase, TBAB in the appropriate phase). The camera was located with the focal plane 0.7 cm inside the vessel [axial position chosen to give an "average" drop size, see Weinstein and Treybal (1973)] that initially contained the continuous phase. It was sufficiently agitated to establish steady flow patterns before the dispersed phase was rapidly poured from two beakers into opposite sides of the vessel at a radial position equidistant between the impeller shaft and the vessel wall. Photographs of the dispersion were taken at 3-s intervals for the first 15 s and then at 10-s increments for the next 40 s. About 500 drops were sized from each photograph with a Carl-Zeiss Particle Size Analyzer.

The factorial experimental program utilized: four surfactant concentrations (0.00, 0.038, 0.10, and 2.00 g surfactant/L water with interfacial tensions of 33.5, 27.1, 21.0, and 16.0 dynes/cm, respectively), two impeller diameters, four impeller speeds (above the minimum impeller speed for complete dispersion [Skelland and Ramsay (1987)]), and two volume fractions of the dispersed phase (3 and 7 v%). Solute transfer direction was varied as was the phase dispersed.

ANALYSIS OF DATA

In the water/TBAB/chlorobenzene system, the distribution coefficient defined as

$$m = \frac{[\text{TBAB}]_{\text{organic}}}{[\text{TBAB}]_{\text{aqueous}}} \quad (1)$$

has the value 0.0213 (concentration units g/l) at low solute concentrations. A mass balance can be written as

$$v_c dc_{Ac} = K_c A (c_{Ac}^* - c_{Ac}) dt \quad (2)$$

and the overall continuous-phase mass-transfer coefficient is formulated in terms of the individual mass-transfer coefficients in the usual fashion (Skelland, 1974, p. 93). Separating the variables, assuming v_c , m , and c_{Ac}^* are constant, integrating, and factorizing a mean mass-transfer coefficient, $\langle K_c \rangle$, gives

$$\ln \left(\frac{c_{Ac}^* - c_{Ac}}{c_{Ac}^* - c_{Ac1}} \right) = - \left(\frac{\langle K_c \rangle A}{v_c} \right) (t - t_1) \quad (3)$$

Plotting the left hand side versus $(t - t_1)$ yields a straight line of slope $\langle K_c \rangle A / v_c$ for evaluating $\langle K_c \rangle$. The adequacy of this approach was demonstrated by the essential linearity of the plots shown by Kanel (1990). Interfacial area was determined from photographs of the dispersion (via the Sauter-mean drop diameter). The mean coefficient corresponds to the interfacial area at a specific fractional extraction. This coefficient was then used to compare mass-transfer rates when transfer was to or from the drops and when water or chlorobenzene was dispersed.

RESULTS AND DISCUSSION

The effect of surfactant concentration on the mass-transfer coefficient when TBAB transferred from the chlorobenzene phase is shown in Figure 1a and 1b. The aqueous phase was continuous or dispersed, respectively. In both cases the coefficient dropped significantly at low surfactant concentration, but remained constant or increased slightly at the highest surfactant level. Coefficients decreased nearly an order of magnitude upon surfactant addition when water was continuous, in contrast to the case where water was dispersed. Minima in this type of curve have been reported previously, but in different extraction equipment [Garner and Hale (1953), Skelland and Caenepeel (1972), and Skelland and Chadha (1981)]. Some of these references speculate on the reasons for such minima, but definitive explanations have not yet emerged. Interestingly, the substantial influence that the surfactant may have upon the solute distribution ratio (e.g., Teramoto et al., 1983), and the large change that may therefore occur in the concentration driving force with increasing surfactant concentration, have not been recognized as a possible explanation for this effect. Surprisingly, the mass-transfer coefficients increased with added surfactant when TBAB transferred from the dispersed aqueous phase, Figure 1c. A hypothesis to explain this

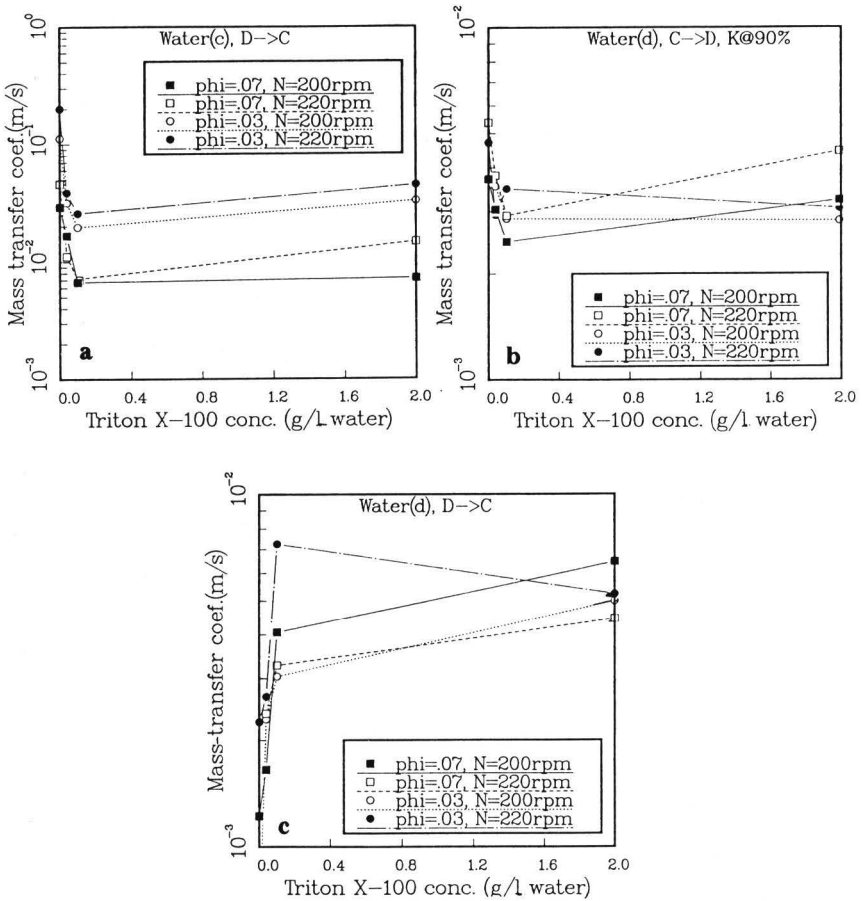


Figure 1. Effect of Triton X-100 concentration on mass-transfer coefficients based on an interfacial area corresponding to: a) 50% fractional extraction when water was the continuous phase receiving TBAB, b) 90% fractional extraction when water was the dispersed phase receiving TBAB, c) 90% fractional extraction when TBAB was extracted from water drops by chlorobenzene. The larger impeller was used here. Phi stands for the volume fraction of the dispersed phase and N is the impeller speed.

behavior was proposed by Liotta (1989) in terms of increased mobility of solute molecules in the aqueous phase near the interface due to loss of solvated H_2O molecules to the surfactant with which they are also solvated.

The pendant droplet technique was used to visually observe whether gross Marangoni type instabilities occurred at the chlorobenzene/water interface with TBAB transferring to/from the drop and with either phase dispersed. Only when TBAB transferred to the aqueous drop were mild Marangoni instabilities observed, in the form of a slightly rocking droplet.

The results of dispersed phase selection and switching the direction of diffusion are summarized in Table 2. Here, five phenomena (a to e) associated with higher transfer rates are listed, and their occurrence in various cases (α to δ) identified. The relative magnitude of the measured overall continuous-phase mass-transfer coefficients for various surfactant concentrations are also given. The five phenomena include: **a**) absence of hydrogen bonding between the solute and the raffinate [Licht and Conway (1950) and Garner et al. (1955)]; **b**) presence of interfacial turbulence or Marangoni effects [Davies (1972)]; **c**) transfer of solute from the dispersed phase and its promotion of coalescence [Groothuis and Zuiderweg (1960) and Smith et al. (1963)] which in turn would mix the droplet internals and enhance the mass-transfer coefficient when the dispersed phase controls; **d**) dispersion of the controlling phase, together with the transfer enhancing effects of repeated drop breakup [Skelland and Xien (1990)], thus in dispersed phase controlled systems, breakage may mix the drop interior on the one hand, while on the other hand create fresh interface for which the mass-transfer coefficient will be initially very high according to the penetration theory; and **e**) less adverse response to surface-active agents as demonstrated (Figure 1c). Analysis of Table 2 can elucidate the relative importance of these phenomena in selecting the dispersed phase.

Table 2 shows that the two highest mass-transfer coefficients (ranks 1 and 2) occurred in cases α and δ , regardless of surfactant concentration. Although both cases corresponded to the absence of hydrogen bonding between solute and raffinate phase, the added transfer-enhancing effects **c** and **d** for case α evidently outweighed that due to effect **b** in case δ . Perhaps this is due to the mild Marangoni effects observed in the system studied. Turning attention to the two lowest magnitude mass-transfer coefficients (ranks 3 and 4) in the absence of surfactant, Table 2 shows that the enhancing influence of effect **d** was clearly significant when compared to no enhancement factors in case γ . When surfactants were present, case γ was the one for which the coefficient actually increased with increasing surfactant concentration as shown in Figure 1c. Indeed, at the highest surfactant level the coefficients for cases γ and δ became comparable.

TABLE 2
Effect of dispersed phase selection, solute transfer direction, and surfactant concentration on the overall mass-transfer coefficient for the chlorobenzene/TBAB/water/Triton X-100 system.

			mass transfer enhanced by these factors:					ranking of mass-transfer coefficient magnitude: 1 = highest 4 = lowest			
Case	continuous phase	transfer direction	no H ₂ bonding between solute and raffinate solvent	gross Marangoni effects occur	coalesced promoted via transfer direction and dispersed phase controlled transfer	dispersed phase controlled mass transfer with breakage mixing and giving fresh surface	surfactant enhanced mass transfer	no surfactant present	0.038g of surfactant per liter of water	0.100g of surfactant per liter of water	2.000g of surfactant per liter of water
			a	b	c	d	e				
α	water	D $\rightarrow$ C	yes	no	yes	yes	no	1	1	1	1
β	water	C $\rightarrow$ D	no	no	no	yes	no	3	*	*	*
γ	chloro-benzene	D $\rightarrow$ C	no	no	no	no	yes**	4	3	3	2
δ	chloro-benzene	C $\rightarrow$ D	yes	yes#	no	no	no	2	2	2	2

* mass transfer data could not be obtained for this direction of dispersion and mass transfer

** surfactant enhanced the mass transfer to an increasing extent with higher concentration

gross Marangoni effect experimentally observed was weak

CONCLUSIONS

This study focused only on mass transfer effects for selecting the dispersed phase, since area-free coefficients were reported. The presence of hydrogen bonding between the solute and raffinate phase had a significant effect on the magnitude of the mass-transfer coefficients. Marangoni effects had a minimal impact on the coefficients in this study, possibly due to the low solute concentrations used specifically to minimize Marangoni instabilities. However, they should be considered in dispersed phase selection, as order of magnitude enhancement of mass-transfer coefficients have been reported by Davies (1972). Coalescence- and breakage-enhanced drop mixing (when the dispersed phase controls) significantly enhanced the coefficients at all surfactant levels in this system. However, surfactants affect each of these factors differently: effect **c** would only be important at lower surfactant concentrations, since surfactants tend to reduce coalescence rates; while effect **d** would be enhanced at higher surfactant concentrations due to decreased interfacial tension. This combination of enhancement effects may account for the minimum in Figure 1a. The absence of factor **d** in case δ could explain why this coefficient is approximately constant at the higher surfactant concentrations (Figure 1b). Thus, one should consider this criterion when selecting the dispersed phase. The mass transfer enhancing effect of added surfactant should also be considered when selecting the phase to disperse, according to these data.

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4.6

**DETERMINATION OF SINGLE DROP MASS TRANSFER COEFFICIENTS IN A
LABORATORY-SCALE STANDARD APPARATUS**

B. HOTING, M. QI and A. VOGELPOHL

Institut für Thermische Verfahrenstechnik
Technische Universität Clausthal
Leibnizstr. 15, 3392 Clausthal-Zellerfeld, Germany

ABSTRACT

Single drop mass transfer coefficients were determined in a standard apparatus as a function of drop size, mass transfer direction and pulsation intensity. Additionally, the influence of a sieve plate on the mass transfer was investigated. Based on the overall mass transfer coefficients obtained, the mass transfer performance of spray or pulsed sieve-plate extraction columns on a pilot scale may be predicted with a simplified drop population balance model.

INTRODUCTION

The design of solvent extraction columns is still based on expensive pilot tests. The main reason is the complex mechanism of mass transfer between the two liquid phases and the intricate interaction between mass transfer and fluid dynamics. The information obtained from simple single drop experiments in a laboratory-scale standard apparatus supply the fundamental data required for modelling and may be used to predict the behaviour of extraction columns. The effects of impurities or surfactants etc on fluid dynamics and mass transfer may be taken into account by drop experiments carried out with the original substances used in the process. Such an apparatus for the determination of break-up rates and daughter drop size distributions was proposed by Eid (1984) and developed by Haverland (1988). The suitability of this scale-up method for the prediction of the fluid dynamic behaviour of sieve plate extraction columns was shown by Haverland (1988) and Lorenz (1990) and for columns with structured packings by Leu and Vogelpohl (1993). A similar standard apparatus was used to determine single drop mass transfer coefficients as a function of drop size and energy input by liquid pulsation with and without the presence of a sieve plate. Overall mass transfer coefficients obtained in these experiments are suitable modelling parameters to predict mass transfer behaviour of spray and sieve plate extraction columns with a simplified drop population balance model.

SINGLE DROP MASS TRANSFER

According to the Maxwell-Stefan-equation, the mass flux of each component in a multi-component system depends in a complicated way on the molar concentrations of all other components and their diffusivities. Thus for practical reasons, the Maxwell-Stefan-equation is not suitable for modelling mass transfer in extraction columns. Therefore, the mass transfer often is described in the simplified form

$$\dot{w} = K_{od} a_p v_p \rho_d (y^*(x) - y) \quad (1)$$

With a given solute concentration in the continuous phase x and the droplet concentration y at the time t the mass balance for a spherical drop is given by

$$\frac{\pi}{6} d^3 \rho_d \frac{dy}{dt} = K_{od} \pi d^2 \rho_d (y^*(x) - y) \quad (2)$$

Assuming a constant continuous phase concentration x , the average mass transfer coefficient K_{od} , as defined in eq. (1), may be determined by integration of eq. (2) from y_1 to y_2 over the time step Δt

$$K_{od} = \frac{d}{6\Delta t} \cdot \ln \frac{y^*(x) - y_1}{y^*(x) - y_2} \quad (3)$$

Mass transfer also affects drop behaviour and drop size by interfacial effects and changes in system properties, especially in interfacial tension. Drop coalescence and break-up also depends on the direction and intensity of mass transfer.

EXPERIMENTAL WORK

Single drop experiments for determining mass transfer coefficients were carried out in a laboratory-scale standard apparatus with the standard test systems toluene(d)/water/acetone, butyl acetate(d)/water/acetone and butanol(d)/water/succinic acid, as recommended by Misek, Berger and Schröter (1985). The basic set-up of the standard apparatus is shown in Fig. 1. A sequence of monodispersed drops is formed at the needle of the nozzle. The drop size was varied in the range from 1.5 to 4.5 mm by adjusting the continuous phase flow rate in the outer tube of the nozzle. For drop sampling, two collecting funnels are installed in the column. The distance between the sampling-devices is 400 mm. The distance between the forming nozzle and the first sampling point is chosen sufficiently large, so that the influence of the formation process on drop motion and mass transfer may be neglected. The analysis of the concentration in the drops was carried out by gas chromatography for the systems toluene(d)/water/acetone and butyl acetate(d)/water/acetone and for the system butanol(d)/water/succinic acid by UV/VIS spectroscopy. Drop size was measured by a photoelectric

suction probe or by photography (system butanol/water/succinic acid). Suitable column internals may be inserted in the apparatus. The dependency of the mass transfer coefficient on drop size, direction of mass transfer and pulsation intensity was determined for freely rising droplets with and without the presence of a sieve plate.

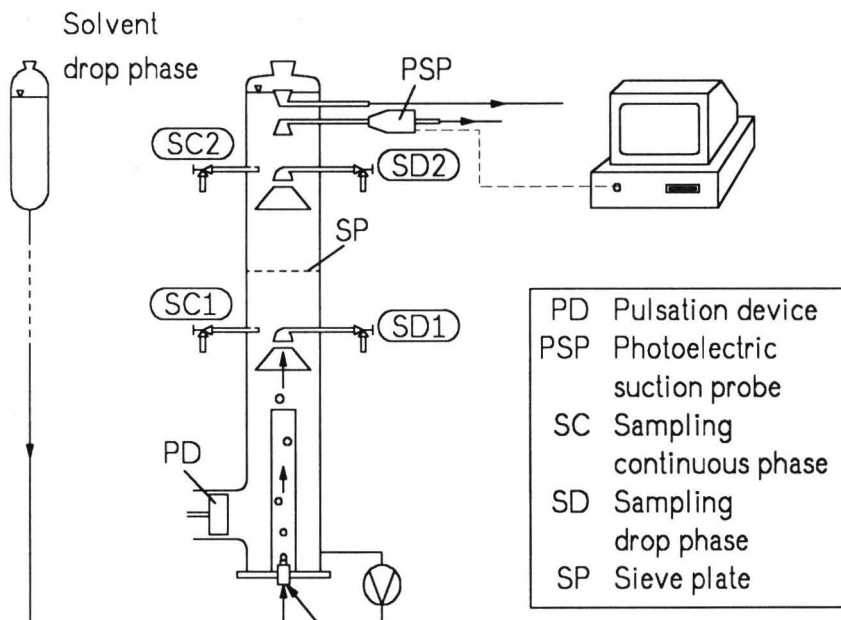


Fig. 1: Laboratory-scale standard apparatus

The standard apparatus developed by Haverland (1988) was used to investigate the influence of mass transfer on the break-up behaviour at a sieve plate. The system used was toluene(d)/water/acetone. Experiments were carried out to determine the maximum stable drop diameter, the break-up probability and the daughter drop distribution under conditions with mass transfer from the continuous into the dispersed phase.

EXPERIMENTAL RESULTS

Figs. 2 and 3 show the dependence of the average mass transfer coefficient K_{od} on drop size, direction of mass transfer and pulsation intensity for the system toluene(d)/water/acetone. Two obvious regions were found corresponding to the region of drop circulation or oscillation. In both regions the mass transfer rate increases with increasing drop diameter. The coefficients for a mass transfer direction from the dispersed into the continuous phase (d→c) are higher than for a mass transfer from the continuous phase into the drop (c→d). The mass transfer coefficient is also affected by pulsation. Because of disturbances caused by the pulsa-

tion, the change from circulating to oscillating drops is shifted to smaller drop diameters. These disturbances also increase the mass transfer coefficient. Fig. 3 also shows the influence of a sieve plate for the system toluene(d)/water/acetone. In these experiments a plate with an orifice diameter of 2 mm and a free area of 23 % was used. As expected, the mass transfer coefficient in the presence of a sieve plate is higher than without a plate. The distortion of the drop by direct contact with the edge of the plate holes during the plate passage disturbs the concentration profile inside the droplet and increases the mass transfer coefficient. In contrast to the experiments without a sieve plate, the mass transfer coefficient does not depend on pulsation. The experimental results for the system butyl acetate(d)/water/acetone show a similar dependency for the mass transfer coefficient on the drop diameter as for the system toluene(d)/water/acetone. In the experiments carried out without a sieve plate, no dependency on pulsation intensity was found. As expected, the influence of the sieve plate increases the mass transfer coefficient.

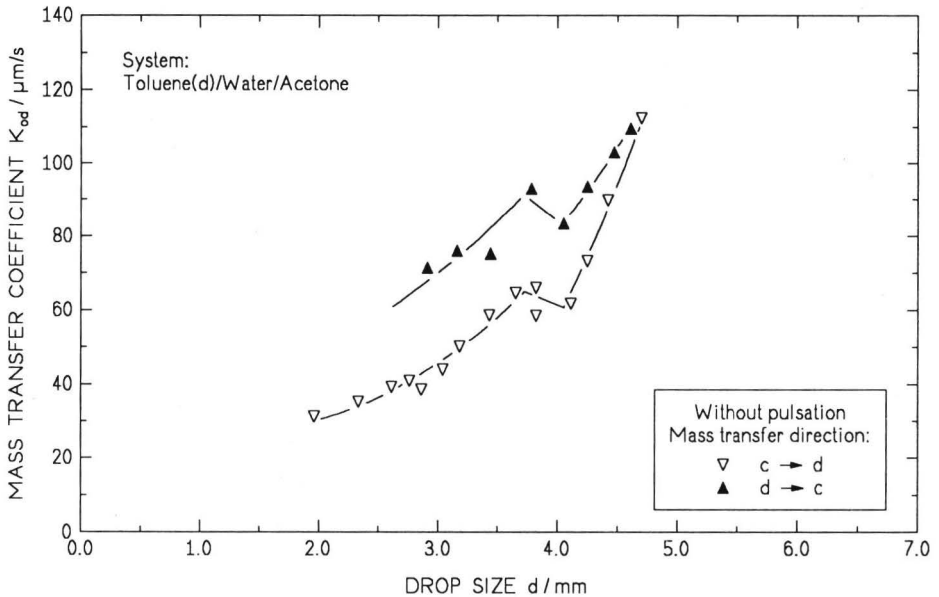


Fig.2: Dependency of the mass transfer coefficient on the drop size and the mass transfer direction

The mass transfer coefficients for the butanol(d)/water/succinic acid system show the same dependencies, but with lower values in the range from 5 for 1 mm to 15 $\mu\text{m/s}$ for 2.0 mm drops. Lower mass transfer coefficients are caused by lower diffusivities D_c and D_d in this system.

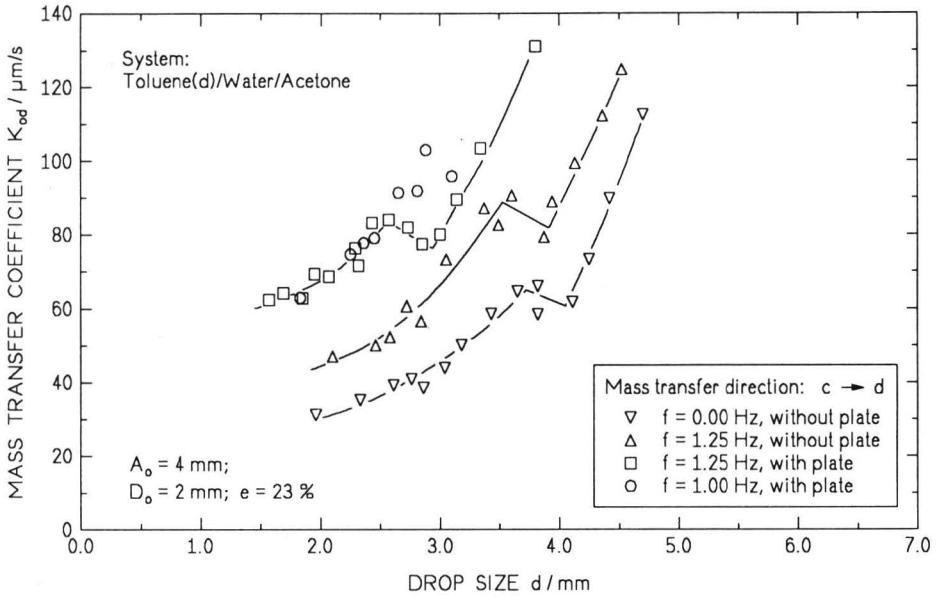


Fig. 3: Dependency of the mass transfer coefficient on the pulsation and the influence of a sieve plate

In systems with a negative gradient $d\sigma/dx$, as toluene(d)/water/acetone, mass transfer decreases drop stability. The maximum stable drop diameters are lower than without mass transfer. An influence on break-up probability and daughter drop distribution was also found in the experiments.

MODELLING

A simplified drop population balance model, as presented by Haverland (1988), was used for modelling of the fluid dynamics and the mass transfer behaviour of spray and sieve plate extraction columns. With known break-up probabilities $p(d)$ and the resulting daughter drop size distribution $q_{3,dd}(d)$, the drop size distribution $q_{3,n}(d)$ above a sieve plate n may be calculated from the distribution below the plate $q_{3,n-1}(d)$

$$q_{3,n}(d) = q_{3,n-1}(d) - p(d) \cdot q_{3,n-1}(d) + \int_d^{d_{\max}} p(d^*) \cdot q_{3,n-1}(d^*) \cdot q_{3,dd}(d^*, d) \delta d^* \quad (4)$$

Starting with a measured or calculated inlet distribution, the drop size profile may be determined. Using the relationship between slip velocity, hold-up and phase velocity, as given by eq. (5) for a polydispersed drop size distribution

$$\frac{V_c}{1-\Phi} + \frac{V_d}{\Phi} = \sum v_{slip,i} \cdot q_3(d_i) \cdot \Delta d \quad (5)$$

and the slip velocity between the drop class i (class width Δd) and the continuous phase

$$v_{slip,i} = \frac{V_{d,i}}{\Phi_i} + \frac{V_c}{1-\Phi} \quad , \quad (6)$$

with

$$V_{d,i} = V_d \cdot q_3(d_i) \cdot \Delta d \quad ,$$

the cross-sectional hold-up Φ and the hold-up of each class Φ_i may be computed by iteration with a given relation for the slip velocity.

The calculation of concentration profiles is based on mass balances according to Fig. 4, using the axial dispersion model to describe mixing in the continuous phase:

$$\dot{w}_{d,i} \frac{dy_i}{dh} = K_{od,i} A \frac{6\Phi_i}{d_i} \rho_d (y^*(x) - y) \quad , \quad (7)$$

$$\dot{w}_c \frac{d}{dh} \left[x + \frac{A(1-\Phi)D_{ax,c}\rho_c}{\dot{w}_c} \frac{dx}{dh} \right] = \sum \dot{w}_{d,i} \frac{dy_i}{dh} \quad (8)$$

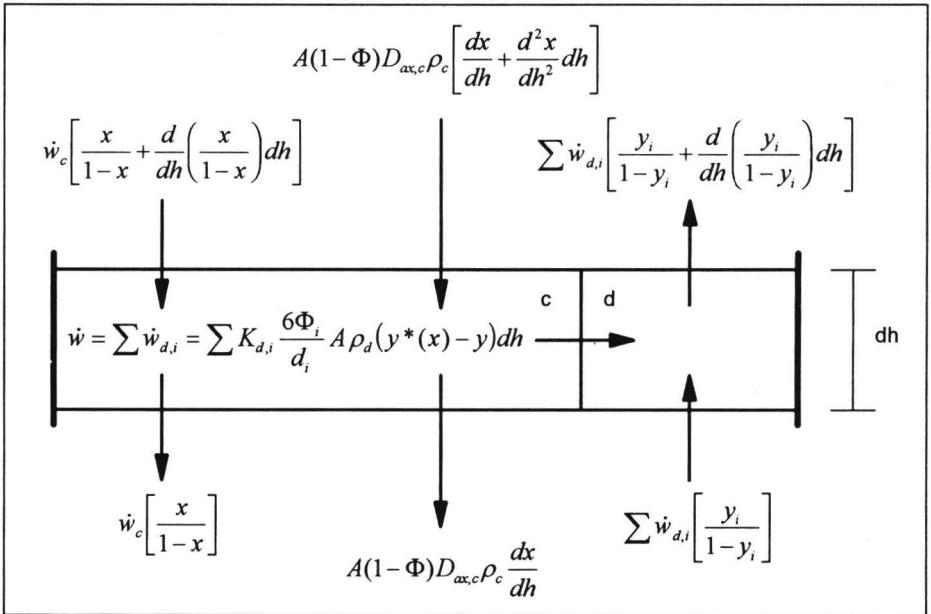


Fig. 4: Mass balance for a differential column cross section

With

$$X = \left[x + \frac{A(1-\Phi)D_{ax,c}\rho_c}{\dot{w}_c} \frac{dx}{dh} \right] \quad (9)$$

the eqs. (7) and (8) give the system of differential equations

$$\frac{dy_i}{dh} = \frac{A}{\dot{w}_{d,i}} \frac{6\Phi_i}{d_i} K_{od,i} \rho_d (y^*(x) - y_i) \quad , \quad (10)$$

$$\frac{dX}{dh} = \frac{\dot{w}_d}{\dot{w}_c} \sum q_3(d_i) \Delta d \frac{dy_i}{dh} \quad , \quad (11)$$

$$\frac{dx}{dh} = (X - x) \cdot \frac{\dot{w}_c}{A(1-\Phi)D_{ax,c}\rho_c} \quad (12)$$

It is assumed that the inlets of the continuous and the dispersed phase with the concentrations x_I and y_I are at the ends of the column and no mixing occurs into these inlets. At the inlet of the continuous phase the mixing between the incoming phase and the phase in the column causes a change in concentration. With the assumption that the concentration gradient at the outlet of the continuous phase approaches zero, the following boundary conditions hold for steady state

$$h = 0 : \quad \frac{dx}{dh} = 0 \quad , \quad y_i = y_0 \quad ,$$

$$h = H : \quad x_0 = x + \frac{A(1-\Phi)D_{ax,c}\rho_c}{\dot{w}_c} \frac{dx}{dh}$$

Starting with an estimated continuous phase outlet concentration x_0 , the concentration profiles of both phases may be calculated from the eqs. (10) to (12) using the Runge-Kutta-procedure. The estimated outlet concentration must be varied until the computed continuous phase concentration profile agrees with the given inlet value x_I . The required axial dispersion coefficient of the continuous phase is calculated with a correlation given by Kumar and Hartland (1989).

Fig. 5 (a,b) show computed concentration profiles compared with experimental data from pilot columns taken from the literature (Reissinger (1985)) and our own experiments. The concentration profiles in Fig. 5a are calculated with a measured drop size, hold-up and a dispersion coefficient as given by Reissinger and with a mass transfer coefficient determined in our own single drop experiments. The concentration profiles shown in Fig. 5b are computed as explained above. The results show that single drop parameters obtained in simple experiments in a laboratory-scale standard apparatus may be used to predict the behaviour of pulsed sieve plate extraction columns adequately. The same experimental and modelling procedure

may also be used for columns with structured packings. The influence of structured packings on the single drop mass transfer coefficient will be investigated in further experiments.

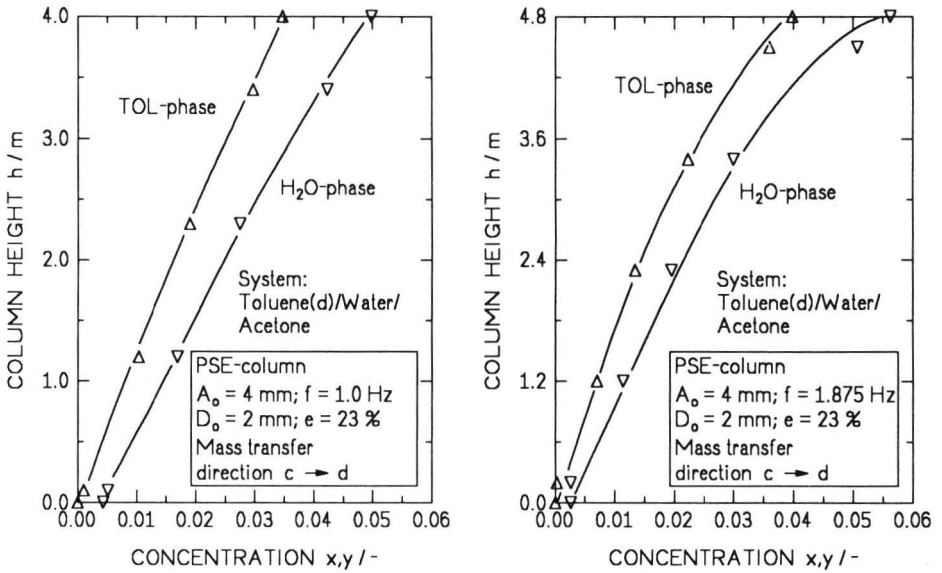


Fig. 5: Comparison of computed concentration profiles with experimental data

CONCLUSION

This investigation shows that the scale-up method based on information obtained from suitable single drop experiments may be used to predict fluid dynamics as well as the mass transfer behaviour of extraction columns.

NON-STANDARD NOMENCLATURE

Δd	class width (m)
D_{ax}	axial dispersion coefficient (m^2/s)
$q_{3,dd}$	daughter drop size volume distribution (1/m)
q_3	drop size volume distribution (1/m)
$\dot{w}$	mass flow rate (kg/s)

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4.7

AXIAL MIXING IN A LIQUID-LIQUID EXTRACTION COLUMN IN PRESENCE OF UNSTABLE DENSITY GRADIENT

M.H.I. BAIRD and K. ARAVAMUDAN

Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT

Axial dispersion coefficients have been measured in the continuous (aqueous) phase in a 5 cm diameter Karr reciprocating plate column by means of steady tracer injection. The dispersed phase was a kerosene (Isopar M) and the tracer was an aqueous sodium chloride solution injected at the top of the column. Energy dissipation in the continuous phase was therefore due to three effects: mechanical energy of plate agitation, buoyant energy from the dispersed phase, and buoyant energy due to the unstable density gradient in the aqueous phase. Although the third contribution to the total dissipation was relatively small (in the order of 1 mW per kg) it had a significant effect. A correlation equation has been developed taking all three factors into account.

INTRODUCTION

Axial dispersion in liquid-liquid extraction columns tends to reduce the number of ideal stages or transfer units. Therefore it must be taken account of in column design. Mathematical procedures for calculating concentration profiles with axial dispersion were developed about 30 years ago but accurate values are needed for the axial dispersion parameters. Axial dispersion is known to occur by several different mechanisms which include turbulence, circulation and transport in drop wakes (Pratt and Baird, 1983). Unpublished observations of mixing in industrial columns led Holmes et al. (1991) and Baird and Rama Rao (1991) to study systematically the effects of unstable axial density gradients on axial dispersion. They correlated their data for single phase operation without and with plate agitation on the basis of the isotropic turbulence model (Kolmogoroff, 1941).

$$E = \ell^{4/3} \varepsilon_m^{1/3} \quad (1)$$

The total specific energy dissipation rate per unit mass ϵ_m under single phase conditions consists of a buoyancy term and a mechanical agitation term.

$$\epsilon_m = \epsilon_{mb} + \epsilon_{mm} \quad (2)$$

The buoyant energy dissipation is given by

$$\epsilon_{mb} = V_c g \Delta \rho / \rho_0 \quad (3)$$

where $\Delta \rho$ is the difference between the liquid density at any point in the column, and the liquid density entering the base of the column. The mechanical energy dissipation is given for reciprocating plate columns (Hafez and Baird, 1978) as:

$$\epsilon_{mm} = [16\pi^2(1 - A^2)(A_p \hat{f})^3] / [3(C_0^2 A^2 H)] \quad (4)$$

The coefficient C_0 is normally taken as 0.6. The mixing length ℓ in Equation (1) represents approximately the largest eddy size, and the results of Baird and Rama Rao (1991) were correlated by:

$$\ell = \ell_m + (\ell_b - \ell_m)(\epsilon_{mb}/\epsilon_m)^{0.34} \quad (5)$$

The limiting mixing length ℓ_b in the absence of agitation was found to be 3.5 cm or about 70% of the column diameter. The limiting value ℓ_m was 0.3 cm.

The previous work (Holmes et al., 1991; Baird and Rama Rao 1991) was under single phase flow conditions. The present study examines the additional effect of the flow of an immiscible dispersed phase.

EXPERIMENTAL

The column (Fig. 1) was a 5.08 cm internal diameter reciprocating plate (Karr) column with overall height 2.3 m and active height 1.15 m. It was constructed of 15 and 30 cm flanged glass sections interspersed with stainless steel collars containing sample ports SP. The oscillation amplitude was set at 1.65 cm and the frequency was varied up to 3.33 Hz. The central shaft supported stainless steel plates perforated with 12.7 mm holes (fractional open area $S = 0.56$) and mounted at intervals H of either 2.55 or 5.1 cm. The dispersed (organic) phase was Isopar M, an odorless kerosene with density 810 kg/m³ and viscosity 2.5 mPa.s, fed to the base of the column at a superficial velocity of up to 0.39 cm/s. Fresh water was also fed to the base of the column as the continuous phase at a superficial velocity of 0.4 cm/s. Aqueous sodium chloride solution entered the column just above the plate stack where it mixed with the continuous aqueous phase. The density of the continuous phase at the top of the column was 35 to 39 kg/m³ greater than that of the water entering at the bottom, providing the potential for enhanced backmixing due to natural convection.

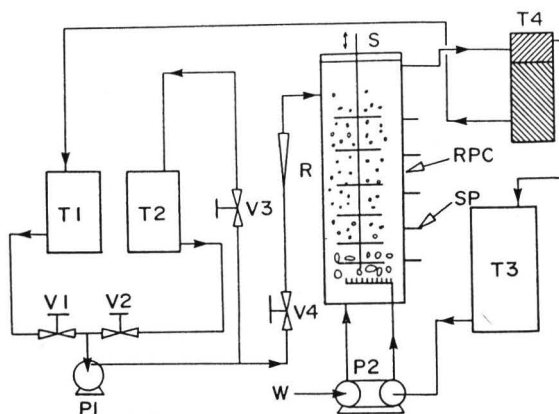


Fig. 1.

Extraction column and flow arrangements

D Organic phase distributor

T3 Organic phase tank

P1 Salt solution feed pump

T4 Overflow tank and phase

P2 Metering pump (water and organic phase feeds)

separator

T1 Salt solution recycle tank

R Salt solution rotameter

T2 Salt solution feed tank

S Reciprocating drive shaft

V1, V2, V3, V4 Salt solution flow valves

The three flows (water, Isopar, aqueous salt solution) were started and the column was run steadily for at least 20 minutes. Then, 25 to 30 mL samples were taken from each of the sample ports SP, allowing an interval of 10 to 15 s between each sample. The aqueous phase was analysed for dissolved salt by a calibrated electrical conductivity meter. Some tests were also carried out with neutrally buoyant tracer solution, prepared by adding methanol to a 3% salt solution until its measured density became the same as that of water (130 mL methanol per L of salt solution). A separate calibration curve of conductivity versus salt concentration was obtained for the water-methanol mixture.

RESULTS AND DISCUSSION

Concentration Profiles

Typical concentration profiles (Fig. 2) show that the backmixing in the absence of agitation is significantly reduced at a moderate agitation frequency (1.03 Hz) and then increases at the highest frequency (3.13 Hz). Steady state tracer profiles can be used to estimate axial dispersion coefficients (Mar and Babb, 1959). The tracer material balance is given by:

$$V_{cc} - E \, dc/dz = 0 \quad (6)$$

The axial dispersion coefficient can be evaluated directly from the local slope of the concentration profile:

$$E = V_c c / (dc/dz) \quad (7)$$

If E can be assumed constant as in the classical studies of back-mixing, Equation (6) can be integrated to show that:

$$c = c_0 \exp(V_c z / E) \text{ where } z \leq 0 \quad (8)$$

Measured salt concentration profiles are plotted in Fig. 2(a) on a semi-logarithmic scale, according to which they should be linear if E is constant.

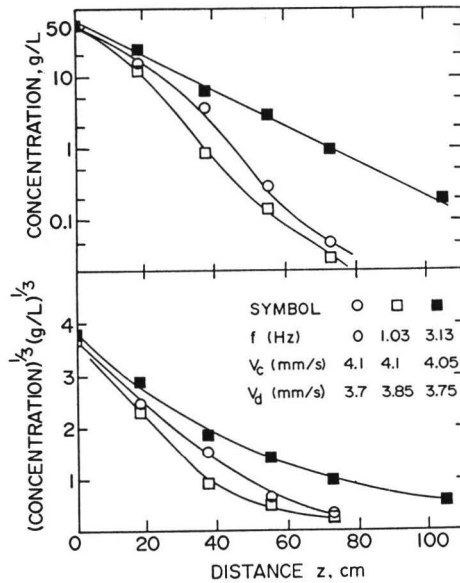


Fig. 2. Salt concentration profiles at plate spacing 2.55 cm
(a) Semi-logarithmic scale (b) $1/3$ power scale

Linearity was observed at the highest rates of agitation as shown by the black square points. However at moderate or zero rates of agitation the semi-logarithmic plots were curved, indicating that E was not constant.

For the special case where backmixing is predominantly controlled by natural convection, the steady state material balance is given by Equation (6), with E obtained from Equations (1) and (3):

$$V_c c - \ell_b^{4/3} (V_c g \Delta \rho / \rho_0)^{1/3} \cdot dc/dz = 0 \quad (9)$$

For linear density variation with concentration ($\Delta \rho = kc$) this equation can be simplified and integrated to give:

$$c^{1/3} = c_0^{1/3} + \{V_c^2 \rho_0 / (\ell_b^4 g k)\}^{1/3} z/3 \text{ where } z \leq 0 \quad (10)$$

The data are plotted as $c^{1/3}$ versus upstream distance ($-z$) in Fig. 2(b) and it is seen that the initial parts of the profile at moderate or zero mechanical agitation are linear as expected from Equation (10). The data at high rates of mechanical agitation which had given straight line semi-logarithmic plots on Fig. 2(a) are non-linear when plotted on the $c^{1/3}$ scale.

In many of the cases studied in this work, neither Equations (8) or (10) fully described the concentration profiles and therefore local values of E were obtained from Equation (7) by slope analysis. Because of the sensitivity of E to the slope and the difficulty of accurately estimating each experimental slope, the concentration profile was fitted by a 6th degree polynomial. The local slopes were obtained by differentiating the fitted polynomials.

Axial Dispersion Coefficients

The ranges of variables employed are given in Table 1. Table 1 shows that 7 types of data can be considered, depending on which combinations of energy dissipation are present. The total energy dissipation rate per unit mass may contain three terms as follows:

$$\varepsilon_m = \varepsilon_{mb} + \varepsilon_{mm} + \varepsilon_{md} \quad (11)$$

TABLE 1
Ranges of Specific Energy Dissipation Rate

Energy dissipation rate: given by Equation number:	ε_{mb} (3)	ε_{mm} (4)	ε_{md} (12)	
Ranges employed(mW/kg):	0-1.5	0-2600	0-650	Symbol
Combinations studied, and symbols in Figure 3:	-	-	>0	Δ
	-	>0	-	+
	>0	-	-	x
	-	>0	>0	o
	>0	>0	-	$\blacktriangle$
	>0	-	>0	$\bullet$
	>0	>0	>0	$\blacktriangledown$

The buoyancy and mechanical terms have been defined in Equations (3) and (4) respectively. The additional term ε_{md} refers to energy dissipation due to the rising dispersed phase:

$$\varepsilon_{md} = V_d g (\rho_c - \rho_d)/\rho_c \quad (12)$$

A multiple regression analysis was carried out on 55 data points to fit the measured values of E with Equation (1). The mixing length was expressed in terms of 3 energy-weighted contributions, compared with only 2 in Equation (5). The best-fit value of the mixing length is:

$$\ell = \ell_m + (\ell_b - \ell_m)(\varepsilon_{mb}/\varepsilon_m)^{0.486} + (\ell_d - \ell_m)(\varepsilon_{md}/\varepsilon_m)^{0.614} \quad (13)$$

where $\ell_m = 0.318$ cm; $\ell_b = 3.241$ cm; $\ell_d = 0.961$ cm.

The values of ℓ_m and ℓ_b are quite close to those reported by Baird and Rama Rao (1991) for single phase flow, but the exponent in the buoyancy term is significantly larger than the previous value of 0.34. The ℓ_d term is a new mixing length associated with the dispersed phase. The drop diameters were only in the order of 0.1 to 0.2 cm and the mixing length 0.961 cm is probably due to the drop wakes and also the interactions of drops with the 1.27 cm holes in the plates.

The fit between the data and the prediction from Equations (1) and (13) is shown in Fig. 3, with the symbols denoting the forms of energy dissipation present (see Table 1). The root mean square deviation between predicted and measured values was $1.35 \text{ cm}^2/\text{s}$, while for 95% confidence limits the deviation was $0.92 \text{ cm}^2/\text{s}$. Part of this deviation was due to some outlying points at low values of E . These corresponded to the "tails" of the profiles where the concentrations and gradients were extremely small and therefore hard to measure accurately. Another factor was a tendency to form trains of drops at low dispersed phase flow rates and low levels of agitation.

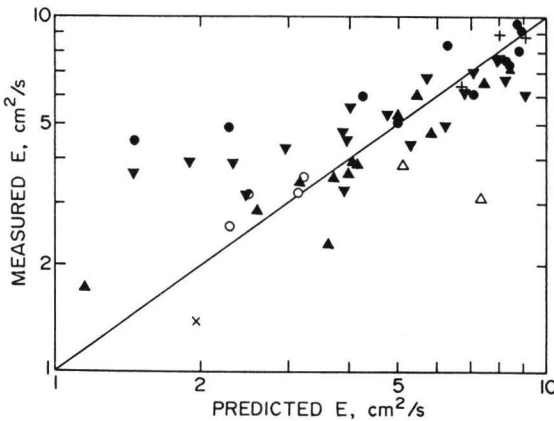


Fig. 3. Measured values of E compared with prediction from Equation (13). For symbols, see Table 1.

Although energy dissipation due to density gradients is relatively small (Table 1), its effect upon E is considerable because it is coupled with a large mixing length. This is illustrated in Fig. 4 in which calculated values of E at different agitation frequencies are plotted against buoyant energy dissipation, ϵ_{mb} .

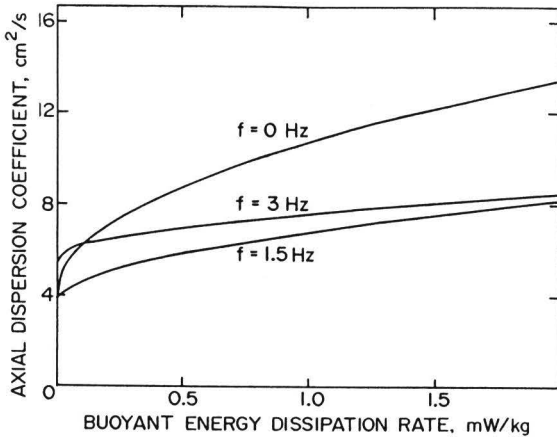


Fig. 4. Effect of buoyant energy dissipation upon E . Plate spacing 2.55 cm, $V_c = 4.0 \text{ mm/s}$, $V_d = 4.0 \text{ mm/s}$. Continuous lines are based on Equations (1) and (13).

ϵ_{mb} . The effect of ϵ_{mb} is greatest in the absence of agitation, but it is significant in well-agitated conditions. Axial dispersion is generally minimized at moderate levels of agitation.

CONCLUSIONS AND RECOMMENDATIONS

Unstable density gradients have been identified as a partial cause of axial mixing under two phase flow conditions, without and with mechanical agitation. Under mass transfer conditions the effect can be expected to be greatest when a continuous phase containing a dense solute is fed to the top of a column, or when a continuous phase containing a light solute is fed to the bottom. In such cases the locally high buoyant energy dissipation rate will enhance axial dispersion leading to reduced column performance near the continuous phase feed. Further research on this effect in the presence of mass transfer is recommended. Until this effect is more fully elucidated, designers may consider choosing the continuous and dispersed phases in such a way that unstable continuous phase density gradients are avoided.

ACKNOWLEDGEMENT

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NON-STANDARD NOMENCLATURE

c_0	concentration at $z=0$, kg/m^3
k	density coefficient of salt solutions, dp/dc
ℓ	mixing length, m

Greek symbols

$\Delta\rho$	density difference ($\rho-\rho_0$), kg/m^3
ρ	local density of salt solution, kg/m^3
ρ_0	density of pure water, kg/m^3

Subscripts

c	continuous phase
d	dispersed phase
mb	buoyancy
md	dispersed phase
mm	mechanical

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STUDY ON THE EFFECT OF ANNULAR SPACE DIMENSION ON THE AXIAL MIXING IN ANNULAR PULSED-SIEVE-PLATE EXTRACTION COLUMN

W.QIN, Y.DAI and J.WANG

Department of Chemical Engineering
Tsinghua University
Beijing, 100084, China

ABSTRACT

The axial mixing coefficient of continuous phase (E_c) is studied in an annular pulsed-sieve-plate extraction column of 0.1m i.d. with four different annular widths of 0.0125m, 0.0205m, 0.0265m and 0.0350m. 30%TBP(in kerosene)- H_2O is used as experimental system (water used as continuous phase). RTD curves are measured with stimulus-response technique. The axial mixing coefficient of continuous phase is evaluated based on the diffusion model and factors of influence are discussed. Results show that E_c increases with the increase of energy input and the increase of the ratio of annular width to column diameter. A correlation equation is suggested and the deviation between evaluated and calculated values is within the error of $\pm 20\%$.

INTRODUCTION

The annular pulsed-sieve-plate extraction column is a unique extraction equipment that can be used to ensure critical safety in reprocessing of irradiated nuclear fuel. The study of this kind of extraction column has been carried out and some results have been published in recent years (Benedict, 1980, Schmidt, 1986, Dai, 1987, Qin, 1988, 1989, 1990, 1992).

It is known that axial mixing is one of most important parameters affecting column behavior. Axial mixing of continuous phase in a small annular extraction column of 0.05m i. d. with annular width of 0.01m has been studied previously by the authors (Qin, 1988,1990). This work is to study the influence of the ratio of annular width to diameter on axial mixing of continuous phase to obtain information for design purposes.

EXPERIMENTAL WORK

The experiments were carried out for four different annular widths in a pulsed-sieve-plate extraction column of 0.10m i.d.. The geometric factors of each annular column cartridge are shown in Table 1. H_2O -30%TBP in kerosene was used as

experimental system (water as continuous phase). Air pulsation gives a practically sinusoidal wave. The physical properties of the system used in experiment are listed in Table 2.

The stimulus-response technique is applied with an imperfect pulse of tracer (saturated KCl solution). Two measuring points are set up downstream, samples of continuous phase free from dispersed phase are taken continuously by special designed sampler, and concentration signals are detected by the attached conductometer. An on-line computer (AT 286) is used for data collection and processing. The column and associated equipment are shown in Fig. 1.

TABLE 1
Geometric factors of column, m

Items	Case I	Case II	Case III	Case IV
Column diameter D			0.1	
Annular Space δ	0.0125	0.0205	0.0265	0.0350
Height of column H			1.02	
Plate space h			0.05	
Diameter of holes d_0			0.003	
Free area ϵ			23%	
Thickness of plates δ_p			0.001	

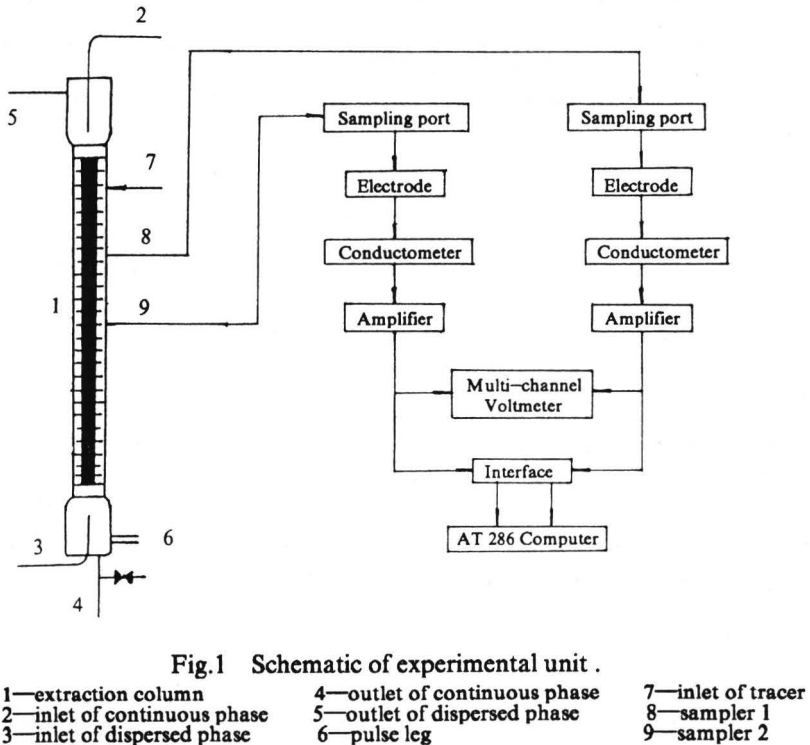


TABLE 2
Physical properties of system used in experiment

Dispersed phase	Continuous phase	Viscosity (mPa · s)		Density (kg / m ³)		Interfacial Tension σ (mN / m)
		μ_d	μ_c	ρ_d	ρ_c	
30%TBP (in kerosene)	H ₂ O	2.06	1.15	849.5	996.0	9.95

53 sets of RTD curves (Residence Time Distribution) and the fractional hold-up of dispersed phase of four annular widths were measured for various operating conditions, as listed in Table 3 .

TABLE 3
Operating conditions

Pulse frequency f (s ⁻¹)	Pulse amplitude A (m)	Velocity of continuous phase U_c (m / s)	Velocity of dispersed phase U_d (m / s)
1.33~2.50	0.0054~0.0170	0.0040~0.0065	0.0000~0.0042

In data processing, the axial mixing coefficient E_c is evaluated by fitting the measured RTD curves with the least-square method in the time domain based on a diffusion model (Yang, 1982).

The differential equation of material balance for tracer based on the diffusion model can be expressed in dimensionless form as follows:

$$\frac{\partial^2 C}{\partial Z^2} - Pe_c \frac{\partial C}{\partial Z} = Pe_c \frac{\partial C}{\partial \theta} \quad (1)$$

Where $Pe_c = \frac{U_c L}{E_c}$, $Z = \frac{l}{L}$, $\theta = \frac{t}{\tau}$. L is designated as the distance between two measuring points and τ as the mean residence time .

The output signal of the first measuring point $C_1(t)$ and the second $C_2(t)$ (or the concentration of tracer varying with time) in the extraction column should satisfy the convolution relationship as follows:

$$C_2(t) = \int_0^t f(\xi) C_1(t - \xi) d\xi \quad (2)$$

where $f(\xi)$ is called the response function of the system which can be written as :

$$f(\xi) = \frac{1}{\tau} \left(\frac{Pe_c \tau^3}{4\pi \xi^3} \right)^{\frac{1}{2}} \exp \left[-\frac{Pe_c}{4\xi} \left(1 - \frac{\xi}{\tau} \right)^2 \right] \quad (3)$$

Thus the response curve $C_2(t)$ can be calculated from $C_1(t)$ by equations (2) and (3). The least square fitting method in the time domain is applied to obtain the model parameters by minimizing the objective function. With discrete data the objective function can be expressed as:

$$J = \sum_{i=1}^n [C_2^*(t_i) - C_2(t_i)]^2 \rightarrow \min$$

Where $C_2^*(t)$ is measured response curve, n is the number of measuring points. The result of fitting curves is shown in Fig. 2.

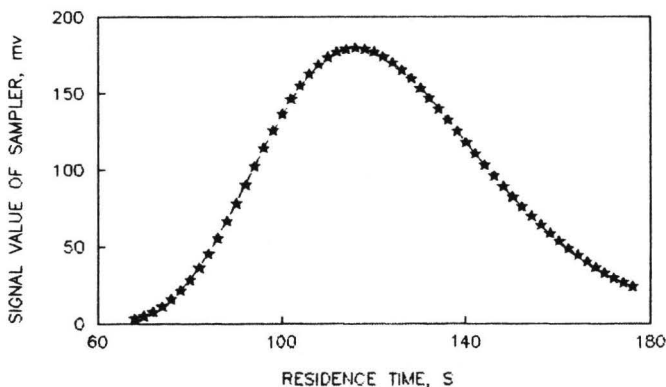


Fig.2 The result of fitting with least-square method in time domain.

— measured value of the second point

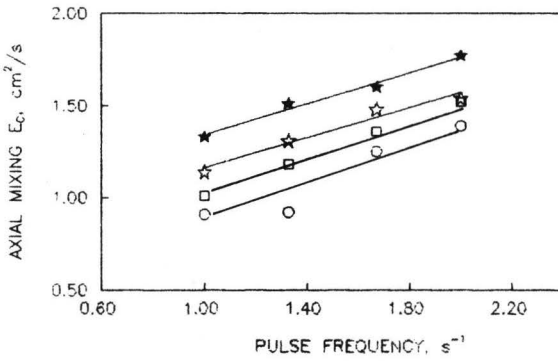
★ Fitting value of the second point

RESULTS AND DISCUSSION

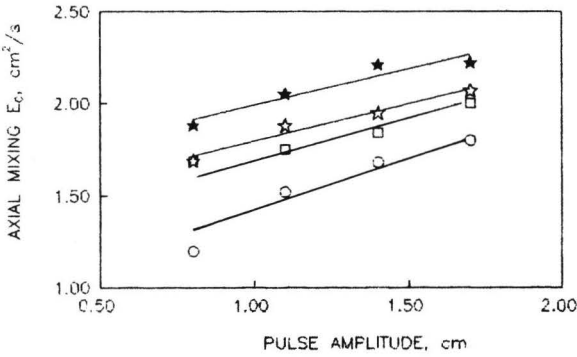
The influence of pulse frequency, pulse amplitude and superficial velocity of two phases on axial mixing of continuous phase for single phase flow and two phase flow in the extraction column with four different annular widths are shown in Fig. 3(a), 3(b), 3(c). Results show that axial mixing coefficient E_c increases with the increase of frequency f , amplitude A and superficial velocity of two phases U_c and U_d . U_d increases to a maximum value and decreases with further increase of U_d . It also can be seen that E_c increases with the increase of the ratio of annular space width to column diameter (δ/D) in Fig. 3(a), 3(b).

It was pointed out (Ingham, 1971) that entrainment of drops of dispersed phase in continuous phase is one cause of the axial mixing. It is assumed that the entrainment effect could be reasonably accounted for by the slip velocity, which in turn is expressed by $U_0(1-\Phi)^n(1+\Phi)^m$ where U_0 is a function of pulse intensity, Af , for a given working system (Lei, 1982).

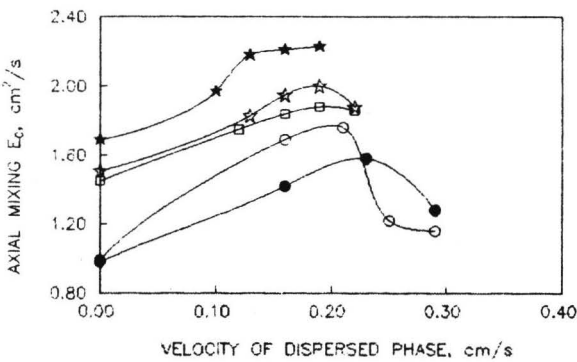
Summarizing these factors, the axial mixing coefficient in the annular column could be expressed by an equation of dimensionless groups:



(a) The influence of f
 $A = 1.4$ (cm)
 $U_c = 0.65$ (cm / s)
 $U_d = 0$ (cm / s)



(b) The influence of A
 $f = 1.3334$ (1 / s)
 $U_c = 0.65$ (cm / s)
 $U_d = 0.16$ (cm / s)



(c) The influence of the dispersed
 phase velocity
 $f = 1.333$ (1 / s)
 $A = 1.4$ (cm)
 $U_c = 0.65$ (cm / s)

Fig.3 The influence of operating conditions on E_c .

○ Case I ● Case I ($U_c = 0.4$ cm / s) □ Case II ☆ Case III ★ Case IV

$$\frac{E_c}{U_c L} = k \left(\frac{\delta}{D}\right)^p \left(\frac{fA}{U_c}\right)^q (1-\Phi)^n (1+\Phi)^m$$

When L , the distance between two measuring points, is a constant, then the equation could be written as:

$$E_c = K \left(\frac{\delta}{D}\right)^p \left(\frac{fA}{U_c}\right)^q (1-\Phi)^n (1+\Phi)^m U_c$$

By regression with 53 sets of experimental data, K , p , q , n and m are determined and the equation obtained is:

$$E_c = 0.027 \left(\frac{\delta}{D}\right)^{0.3} \left(\frac{fA}{U_c}\right)^{0.25} (1-\Phi) (1+\Phi)^{3.5} U_c \quad (4)$$

Fig. 4 shows that the calculated values of E_c fit well with the experimental value within an error of $\pm 20\%$.

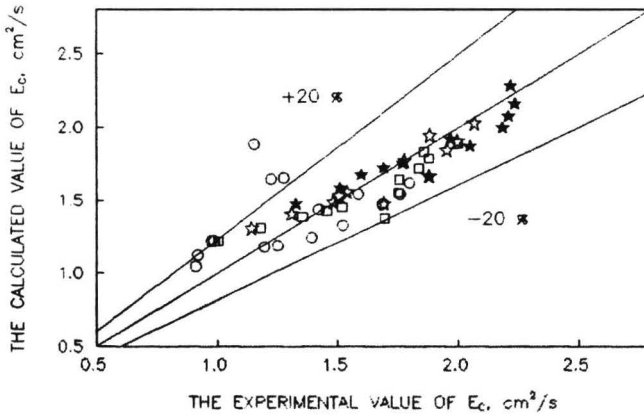


Fig.4 The fitting result of E_c .

○ Case I □ Case II ☆ Case III ★ Case IV

As indicated by Hussain et al. (1988) the behavior of droplets of dispersed phase is different in different operation regions, therefore it must be pointed out that equation (4) covers only the operating range of low energy input (fA up to $0.018 \text{ m}^2/\text{s}$) in the emulsion region, while the value of E_c increases with the increase of superficial velocity of two phases. In the range of high energy input in the emulsion region (fA above $0.02 \text{ m}^2/\text{s}$), entrained volume is smaller because of the smaller drop size and the rapid increase of the value of $U_c/(1-\Phi)$ resulting from the rapid increase of fractional hold-up with increase of superficial velocity of two phases U_c and U_d . E_c decreases with increase of U_c and U_d , as shown in literature (Schmidt, 1986, Qin, 1990, Shen, 1983).

CONCLUSION

The experimental results for different annular widths show that the values of E_c increase with increase of energy input and increase of the ratio of annular width to column diameter. E_c also increases with increase of superficial velocity of two phase in the range of low energy input in the emulsion region.

A correlation equation is suggested to express axial mixing coefficients in continuous phase for the annular extraction column with different annular widths by regression of 53 sets of experimental data.

$$E_c = 0.027 \left(\frac{\delta}{D} \right)^{0.3} \left(\frac{fA}{U_c} \right)^{0.25} (1 - \Phi) (1 + \Phi)^{3.5} U_c$$

The deviation between evaluated and calculated values is within $\pm 20\%$.

NOMENCLATURE

- A pulse amplitude (peak to peak) (m)
- C_1 measured concentration of the first measuring point (mv)
- C_2 calculated concentration of the second measuring point (mv)
- C_2 measured concentration of the second measuring point (mv)
- D column diameter (m)
- E_c axial mixing coefficient of continuous phase (m^2/s)
- f pulse frequency (s^{-1})
- l axial coordinate
- L distance between two measuring points (m)
- Pe Peclet number
- t time (s)
- U_c superficial velocity of continuous phase (m/s)
- U_d superficial velocity of dispersed phase (m/s)
- Z dimensionless height of column.

Greek

- δ annular space width (m)
- θ dimensionless time
- δ_p thickness of plates (m)
- τ mean resident time (s)
- Φ fractional hold-up of dispersed phase

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STUDIES ON HOLDUP, BACKMIXING AND CONVERSION OF CO-CURRENT FLOW LIQUID-LIQUID REACTION IN MULTISTAGE MIXER COLUMN

B.SIMANDI, ZS. SZILAGYI, K. FADGYAS

Department of Chemical Engineering
Technical University of Budapest, H-1521 Budapest, Hungary

ABSTRACT

Experimental investigations were carried out in four-stage mixer columns of the type RDC and Oldshue-Rushton. The geometry of the reactors was similar to that of the extractors. The holdup of the dispersed phase was measured experimentally in the continuous co-current two-phase liquid systems. The ratio of the feed rates and the mixing speed were varied. Minimum impeller speeds were sought where the feed ratio and the holdup were equal and a satisfactory dispersion was ensured. The residence time distribution was obtained in a limited range of flow rates and rotor speeds in single-phase and in the continuous phase of the liquid-liquid two-phase system. For describing the response curves obtained the stagewise model with backmixing was chosen. The method of weighted moments was used for the determination of model parameters. For conversion studies the saponification reaction between n-butyl acetate and sodium hydroxide was chosen. Under the conditions investigated the system conforms to a very slow reaction in two-phase. The measured conversion values were compared with data calculated on the basis of the mathematical model.

INTRODUCTION

Multistage agitated contactors are well known in liquid-liquid extraction (Lo et al., 1983). They have potential use as homogeneous as well as two-phase co-current flow liquid-liquid reactors if the interstage baffles are designed properly to minimize interstage mixing. Accurate experimental results concerning the behaviour of co-current flow liquid-liquid systems are scanty in the literature.

In the design of agitated contactors the main parameter to be evaluated is the volume of reactor required for the specified level of conversion. Depending on the circumstances the design of liquid-liquid reactors is complicated since there are a large number of cases. In continuous operation additional complexities arise due to the variation in holdup and the effects of backmixing. The aim of this study to consider some aspects of process design of a co-current reactor in which a very simple reaction takes place.

THEORY

Mixing models

One of the most frequently used models to simulate reactor performance is that of completely mixed cells in series or stagewise model (Levenspiel, 1972). Taking into consideration longitudinal dispersion, another well known model is the stagewise model with backmixing, which is also used to describe the more common types of multistage mixer columns (Ingham, 1971; Haug, 1971; Lelli et al., 1967). An analytical treatment of the model is given by Roemer and Durbin, 1976. The main assumption in these models is that each stage behaves as an ideally mixed vessel.

Determination of model parameters

The method of ordinary moments has been widely accepted for the determination of parameters from tracer response curves. However the moment method has the shortcoming that the tail of the signal is overweighted in the evaluation of moments. The method of weighted moments was chosen to overcome this disadvantage. It has been shown by many authors that this method gives better estimation than the ordinary moments one (Anderssen and White, 1971; Hunek et al., 1975; Wolff et al., 1979; Simandi et al., 1986). A review of the weighted moment method, its application and the estimation of errors has been published by Simandi et al., 1988.

According to the definition of the k -th ordinary moment:

$$M_k = \int_0^{\infty} t^k f(t) dt \quad (1)$$

in which the density function is multiplied by a weighting factor t^k . If t is large, the weighting factor t^k is seen to be particularly large, thereby increasing the weight placed on the attenuating portion of the density function. A better weighting which tends to zero for large values of t is

$$W_k(t) = t^k e^{-st} \quad (2)$$

wherein the weighting factor s is a real, positive value. With the above process of weighting, the weighted moment can be defined as follows:

$$M_k(s) = \int_0^{\infty} t^k e^{-st} f(t) dt \quad (3)$$

The 0-th weighted moment of the density function is

$$M_0(s) = \int_0^{\infty} e^{-st} f(t) dt \quad (4)$$

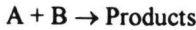
which is the Laplace transform of the density function, in which s is the variable of the Laplace transform. From the nature of the Laplace transform:

$$M_k(s) = (-1)^k \frac{d^k}{ds^k} [M_0(s)] \quad (5)$$

Using the above relationships, the interrelationship of the weighted moments and the parameters of the model is readily determined. For this purpose, the transfer function of the system must be known.

Solution of model equations

The reaction considered here is irreversible and kinetically of second-order. The chemical equation may be written as



For the very slow reaction, the rate of reaction between A and B is very much slower than the rate of mass transfer of A. Consequently, the aqueous phase in which the reaction occurs will be saturated with the solute A at any moment and the rate of formation of product is determined by the kinetics of the pseudo first-order chemical reaction:

$$r = k_2 c_A \cdot c_B = k_1 c_B \quad (6)$$

The stepwise fashion analysis of stirred tank reactors in series is well documented in the literature (Levenspiel, 1972).

In the case of stagewise model with backmixing the dimensionless form of the material balance equation for the species B around the i -th stage is:

$$(1 + \alpha) x_{B,i-1} - \left(1 + 2\alpha + \frac{Da_i}{n_p} \right) x_{B,i} + \alpha x_{B,i+1} = 0 \quad (7)$$

Expressions for the first and last stages deviate slightly from that of the general i -th stage. Equations are usually to be solved numerically. If the saturation concentration of species A can be substituted with an average value it is possible to obtain closed form solution of fractional conversion:

$$X = 1 - \frac{(1 + \alpha)^{n_p - 1}}{\prod_{i=1}^{n_p} \left(\frac{Da_i}{n_p} - \beta_i \right)} \quad (8)$$

Where β_i is the i -th eigenvalue of the state-coefficient matrix obtained from the material balance equations. The eigenvalues for the special cases $n_p=2,3,4$ can be determined easily

because exists a simple analytical solution. When $n_p > 4$, for the calculation of the eigenvalues numerical methods can be used (Simandi et al., 1986).

EXPERIMENTAL

Equipment

The reactors were similar to mixer columns used in extraction processes. The column consisted of a 93 mm diameter 250 mm long glass tube divided into 4 compartments. The diameters of disks and six-bladed standard disk turbines were 65 mm and 46.5 mm respectively. The inner diameter of stator rings was 25 mm. The effective volume of the column was 1.44 dm^3 . The rotor shaft was driven by a variable drive controlled by a variable frequency transformer. The stirring speed range was $0\text{--}800 \text{ min}^{-1}$. The heavy and light phases were supplied to the column from two storage tanks. The flow rates of both phases were measured by rotameters.

Holdup studies

The column was first filled with water. At the same time the rotation was started. The organic phase was then gradually introduced. After steady state was attained, the liquid inlets of both phases were shut off simultaneously. When the two liquid phases had separated the interface position was read.

Residence time distribution (RTD) studies

The RTD was obtained by determining the response curve to a near-pulse concentrated sodium chloride solution tracer input at the reactor inlet. The output signal of the conductivity meter was read and recorded automatically. The chosen time interval depended on the flow rate and could be adjusted between 0.1 s and 10 s. A few hundred points were recorded for each runs.

Conversion studies

For conversion studies the saponification reaction between n-butyl acetate and sodium hydroxide was chosen since the kinetics, rate constant and solubility data were known accurately (Parasanu et al., 1960; Sharma and Nanda, 1968; Sorensen, 1983). The butyl acetate itself constituted a pure phase and diffusion into an aqueous solution of sodium hydroxide was followed by chemical reaction in that phase. All concentrations were determined by titration techniques.

RESULTS AND DISCUSSION

Holdup measurements

Water and three organic chemicals (toluene, carbon tetrachloride and butyl acetate) were used in the RDC. In all cases organic was the dispersed phase at the start. The flow rates (F_c, F_d), flow ratio (R), agitator speed (N) and direction of flow (upward, downward) were varied. The holdup values obtained are shown in Figure 1 and Figure 2. It seems that the measured holdup

values are very different from those calculated using the feed flow ratio. When the liquids flowed upwards then the lighter phase ran out of the column, and when the liquids flowed downwards the heavier phase did the same. Due to the extremely high change of organic/water ratio inside the column, phase inversion was observed before steady state was attained (in spite of that fact, holdup was based on organic/water ratio). In conclusion RDC columns can not be applied generally to co-current liquid-liquid reactions since the mixing in columns is not efficient.

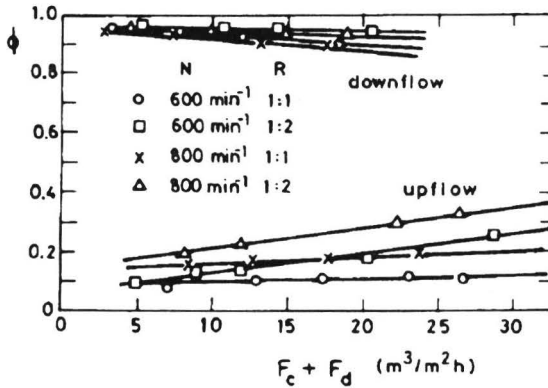


Fig. 1 Effect of rotor speed and total flow rate on holdup for toluene-water system

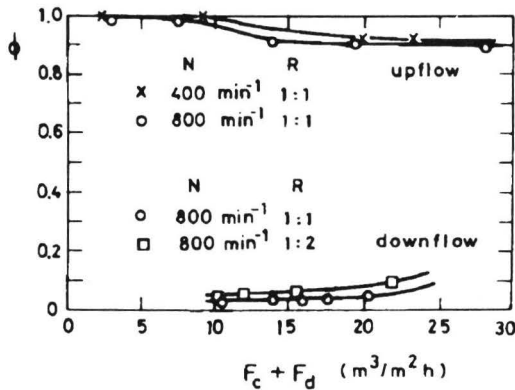


Fig. 2 Effect of rotor speed and total flow rate on holdup for carbon tetrachloride-water system

The mixing elements were changed to six-bladed standard turbines and experiments were repeated with the same liquid systems. The results for the butyl acetate-water system are shown in Figure 3. They show that a minimum mixing speed is needed for complete dispersion of one liquid in the other. Increasing mixing speed beyond the minimum value the holdup is

stable and steady. The minimum mixing speed is slightly dependent on the relative volume fractions of the mixture and very strongly dependent upon the system properties. Development of a general design correlation will require additional testing for various liquid-liquid systems.

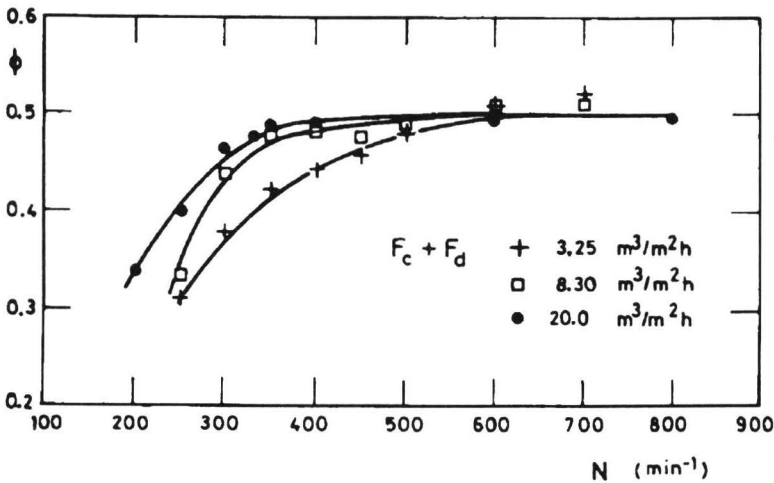


Fig. 3 Effect of flow rate on minimum mixing speed for butyl acetate-water system

Parameter estimation from RTD

For evaluating the tracer response curves the method of moments and weighted moments were used. The relationships between the model parameters and the weighted moments were determined by equation (5) from the transfer function, given by Roemer and Durbin (1967). After evaluating the RTD curves by different weighting factors the square deviations between the measured and calculated responses were determined. Optimal weighting factors were obtained at the minimum values of square deviations. From our experience the equation proposed by Anderssen and White (1971) gives a relatively good approximation of the optimum value of weighting factor. Using the k -th weighted moment the following equation satisfies the above requirements $s=(k+1)/t_m$.

The stagewise model with backmixing was chosen for the interpretation of RTD measured in six-bladed standard mixer column. Reliability of assumption on uniformity of mixing in each stage and the procedure adopted for the evaluation of α were checked by comparing experimental and theoretical curves. There have been many attempts to correlate the backflow ratio data obtained from various Oldshue-Rushton type extraction columns. A summary of reported experimental investigations for the continuous phase is given by Sawinsky (1978). Most of the correlations may be brought into a common form

$$\alpha = C \frac{D_R N}{U} \left[\frac{D_s}{D} \right]^2 \quad (9)$$

where C is the appropriate geometry group proposed by different investigators.

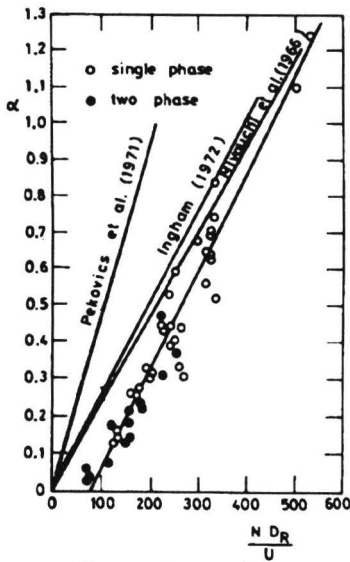


Fig. 4 Comparison of measured backflow ratio with literature correlations

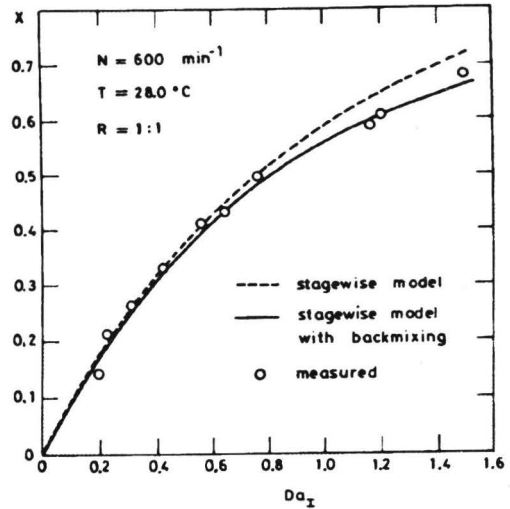


Fig. 5 Comparison between computed and experimental values of conversion

Figure 4 shows plots of experimentally obtained backflow ratio against the $D_R \cdot N/U$ dimensionless group. Comparing experimental α values with α predicted by various correlations it can be seen that the various empirical relations given in the literature can not be adapted to a column with such an extreme geometry that our reactor has. Because of not investigating reactors of different geometries we can not describe the effect of geometry on α with universal validity.

Conversion studies

Since the reaction is very slow the aqueous phase is saturated with butyl acetate at any moment and the rate of formation of product is determined by the kinetics of the chemical reaction. Determination of the saturation concentration of a substance in ionic solutions is described by Van Krevelen and Hofizer (1948). The measured conversion values have been plotted against the Damkohler number (Da_I) in Figure 5. The experimentally obtained values can be compared with conversion data calculated by the mixing models. It can be seen that there is no significant difference between the calculated values at low Da_I numbers. When $Da_I > 0.8$ the reactor performance can well be estimated by stagewise model with backmixing.

Non-standard nomenclature

c_A	saturation concentration of butyl acetate ($\text{mol} \cdot \text{dm}^{-3}$)
c_B	concentration of sodium hydroxide ($\text{mol} \cdot \text{dm}^{-3}$)
$f(t)$	RTD density function (s^{-1})
$k_1 = k_2 \cdot c_A$	rate coefficient (first order) (s^{-1})
k_2	rate coefficient (second order) ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)
M_k	k -th initial moment (s^k)
$M_k(s)$	k -th weighted initial moment (s^k)
r	rate of reaction ($\text{mol dm}^{-3} \cdot \text{s}^{-1}$)
$W_k(t)$	weighting factor (s^k)
X	fractional conversion (-)
$Da_1 = k_1 \cdot t_m$	Damkoehler number (-)
β_i	i -th eigenvalue of the state-coefficient matrix (-)

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4.10

**MASS TRANSFER CHARACTERISTICS AND MOTION OF
SINGLE DROPS IN A SHORT ROTATING DISC COLUMN**

WANG Dianxia and FAN Zheng

Institute of Chemical Metallurgy, Chinese Academy of Sciences
Beijing, 100080, China**ABSTRACT**

In this paper the terminal velocity, characteristic velocity and superficial velocity, as well as the mass transfer coefficient of drops in a rotating disc column (0.3 m in diameter and 0.54 m in height) have been studied. By regression analysis, the correlation of the overall mass transfer coefficient various influencing factors has been obtained. Correlating with our experimental data to the published equations offers satisfactory results.

INTRODUCTION

The rotating disc column (RDC) is a type of liquid-liquid extraction equipment widely used in industry. Much work on the hydrodynamic and mass transfer characteristics has been published. However, a complete pilot plant for this study needs not only large amounts of investment and reagents, but also a long operating time. To study the performance of an RDC with a short column may avoid the above-mentioned drawbacks. The authors of this paper give a brief survey of short column research.

This paper aims at a study of motion and mass transfer characteristics of drops in a short RDC with a relatively large diameter and a further inspection of the validity of the design data obtained from the short column investigated.

EXPERIMENTAL

The main equipment is a glass RDC. The column is 0.54 m in height and 0.30 m in diameter with 5 rotating discs 0.154 m in diameter made of aluminium plate with a

coat of paint baked on the surface. The spacing between the two baffles is 0.075 m. The organic phase contained in a head tank is injected into the column through a hypodermic needle. Once the organic phase drops reach the top of the column, they could be sucked immediately into the collecting tube by vacuum. The drop-collecting apparatus is made by fixing 37 special glass funnels (the inner diameter of neck is 0.0015 m) to an aluminium plate.

The dispersed phase is D2EHPA/n-heptane solution (D2EHPA concentration: 0.2 mol/L) and the continuous phase is an aqueous solution of ZnSO_4 . The reagents n-heptane, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 used are of A.R. grade, and D2EHPA is of industrial grade. The zinc concentrations in the continuous phase are 0.001, 0.0046, 0.0087 and 0.0276 (mol/L), and the initial zinc concentrations in the dispersed phase are 0, 0.001, 0.0054, 0.01 and 0.015 (mol/L) respectively. The values of distribution coefficient of the experimental system are listed in Table 1. The interfacial tension is measured by the drop weight method.

TABLE 1

Distribution Coefficients of the Experimental System		
Concn. in aq. phase	Concn. in org. phase	Distribution
(mol/L)	(mol/L)	coefficient
0.001	0.076	74.0
0.0046	0.078	17.0
0.0087	0.082	9.40
0.0276	0.091	3.30

The single drops method is applied to determine the terminal velocity, characteristic velocity and superficial moving velocity of drops, as well as the residence time distribution of drops and overall mass transfer coefficients. The drop size is measured by averaging the volumes of 50 drops.

The organic phase sample is stripped with 2M H_2SO_4 solution two times and the zinc concentration is analyzed with a Perkin-Elmer atomic absorption spectrophotometer. All of the experiments were carried out at a temperature of $18.5 \pm 0.5^\circ\text{C}$ and an aqueous phase acidity of pH 2.95 is adjusted with sulfuric acid.

EXPERIMENTAL DATA ACQUISITION AND DISCUSSION

Terminal Velocity

The dispersed phase drops rise up in the stationary continuous phase at accelerated velocity at first and then at constant speed. Due to the very small drop diameters, the time of acceleration is less than 0.1 seconds and could be neglected within our experimental range. Therefore the use of a short column for the determination of terminal velocity is feasible. Fig.1 shows the experimental values of terminal velocity and the calculated results obtained from Mišek(1970) and Grace(1976) correlations. The calculated values given by the Mišek model deviate greatly from our data, while those of Grace agree with well, especially for larger drops ($d=3-4$ mm) with an error less than 4.6%. Experimental results show that mass transfer does not much affect V_T .

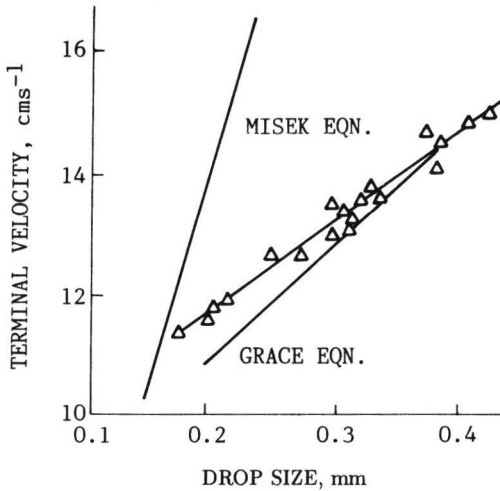


Fig.1 Terminal velocity of drops

Characteristic velocity

The characteristic velocity V_K expresses the terminal velocity of dispersed phase drops under the operating conditions when the continuous phase and dispersed phase flow rate tend to zero. Based on the definition of V_K , it is possible to find the value directly from the data of single drops in short column experiments. The dependence of V_K on variation of rotor speed is plotted in Fig.2. Many workers have correlated the characteristics

velocity of drops in the RDC, however, these correlations seem to be inappropriate for low rotor speed conditions. Under our experimental conditions, the Logsdail(1957) correlation gives high values of V_K (50% higher than the experimental data). Kung(1961) has noticed that the rotor speed affects V_K differently for different speed ranges, and suggested that the corresponding critical rotor speed, rather than the real rotor speed, should be substituted into the equation for V_K when the real rotor speed is lower than the critical rotor speed. Laddha(1978) and Zhang(1981) have proposed that the rotor speed would affect V_K within the whole speed range. However, their correlations still give low values of V_K compared with our experiments. Therefore, it is necessary to study the drop motion in the short RDC by further improving the observation and measuring devices.

Strand(1962) proposed $V_K = C_R V_T$. In our experiments, we have $C_R=0.39$. Only at higher rotor speeds, does V_K/V_T tend to C_R . When the rotor speed equals zero, $V_K/V_T = 1$. The values of V_K/V_T calculated by using Bahmanyar's(1990) correlation are close to our experimental data with deviation less than 2.7%.

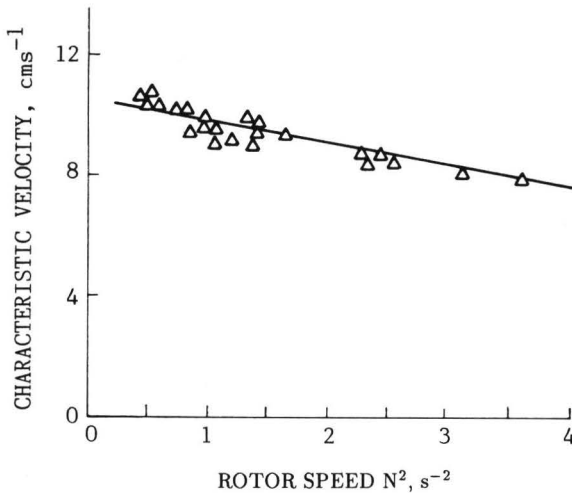


Fig.2 Characteristic velocity

Superficial Velocity

In the RDC, the turbulent motion of the liquid, which increases with increasing rotor speed, results in an increase in the rotational velocity of drops. However, the character-

istic velocity will decrease as rotor speed increases. In this paper the superficial velocity is calculated according to the following method: suppose the moving locus of drops is a spiral with a diameter $(D_S + D_R)/2$, the superficial velocity V_P will be:

$$V_P = \frac{1}{2t} [4z^2 + n^2 \pi^2 (D_S + D_R)^2]^{0.5} \quad (1)$$

V_P increases with increasing rotor speed. By multiple regression of the experimental data, equation (2) is obtained:

$$V_P = 3.375 N^{0.19} d^{0.35} \quad (2)$$

Calculation of overall mass transfer coefficient of drops

The overall mass transfer coefficient of drops can be calculated by using the following equation. In our experimental range, K_{od} of drops increases with increasing rotor speed, and decreases with increasing drop size.

$$K_{od} = \frac{d}{6t} \ln \left(\frac{C_{de} - C_{d0}}{C_{de} - C_{df}} \right) \quad (3)$$

The internal circulation becomes vigorous as the rotor speed increases, which would cause the mass transfer coefficient to increase. However, the calculated values decrease with increasing rotor speed when the characteristic velocity is substituted into the film mass transfer coefficient equations. In this work V_P is used to calculate Reynolds number, k_c , k_d and K_{od} . The Handlos-Baron(1957) model is used to calculate the drop mass transfer coefficient k_d , while Garner's(1960) internal circulation model, oscillating drop model and Higbie's(1935) non-rigid sphere model are used for the calculation of the continuous phase mass transfer coefficient k_c . The results obtained with the Garner model are close to the experimental data, while those with the Higbie model show larger deviation.

Correlation of Overall mass transfer

By taking Reynolds number, rotor disk Froude number and the properties of the system into account, the following overall mass transfer coefficient correlation is obtained. The error is within 11.5% (Fig.3).

$$K_{od} = 63.5 \left(\frac{N^2 D_R}{g} \right)^{0.40} \left(\frac{d \rho_c V_P}{\mu_c} \right)^{-0.44} \left(\frac{g^3 \Delta \rho^3}{\gamma \rho_c^2} \right)^{0.12} \quad (4)$$

To test whether the mass transfer coefficient data from the short column experiments coincide with the published correlations, the Logsdail(1957) and Laddha(1978) models are used for comparison. The correlation results indicate (Fig. 3) that the experimental data show large deviation from values given by the Laddha model, but agree well with the Logsdail model, giving an error less than 15%.

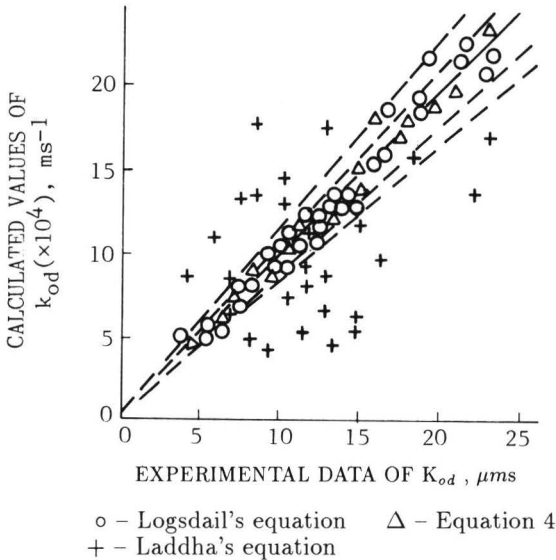


Fig.3 Correlation of overall mass transfer coefficient

CONCLUSIONS

Based on the definition of terminal velocity V_T and characteristic velocity V_K , it is convenient to measure V_T and V_K in the short RDC. The experimental values V_T agree with that given by the Grace model.

With a short RDC, it is possible to measure the moving velocity V_P which may allow better reflection of the state of drop motion. In this work, V_P is used to calculate mass transfer coefficients of the two phase film and overall mass transfer coefficient. The experimental data fit well the calculated results from the Handlos-Baron model for the drop mass transfer coefficient combined with the Garner-Tayeban model for the continuous phase mass transfer coefficient.

The correlation of overall mass transfer coefficient with Reynolds number, Froude num

ber and properties of the system gives satisfactory results. Agreement between the measured values and those given by the Logsdail model means that it is feasible to do the investigation of the mass transfer by the single drop method in a short RDC.

Owing to the superiority of the RDC both in structure and experimental method, development of research in this field is very attractive.

NOMENCLATURE

C_{do}	initial concentration in drop (kmol m^{-3})
C_{df}	final concentration in drop (kmol m^{-3})
C_{de}	equilibrium concentration of organic phase (kmol m^{-3})
C_R	constriction factor
D_R	rotor diameter (m)
D_S	stator inner diameter (m)
d	drop diameter (m)
k_c, k_d	film mass transfer coefficient of continuous and dispersed phase (m s^{-1})
K_{od}	overall mass transfer coefficient (m s^{-1})
N	rotor speed (s^{-1})
n	number of rotations of rising drop in column
V_K	characteristic velocity (m s^{-1})
V_P	drop superficial velocity (m s^{-1})
V_T	terminal velocity (m s^{-1})
z	effective height of column (m)

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4.11

EXTRACTION AND DROP SIZE IN A TANK AGITATED BY THE DELTA IMPELLER

N.V. RAMA RAO, M.H.I. BAIRD

Department of Chemical Engineering
McMaster University
Hamilton, Ontario L8S 4L7, Canada

Z.J. SHEN

Lightnin China
504/534 Hengshan Road
Shanghai 200030, China

ABSTRACT

The triangular paddle Delta Impeller was developed in China and has been applied in mixer-settler extractors. This performance study in a 27 L tank shows that under well-agitated conditions, the area-based mass transfer coefficients are close to those calculated for rigid drops. The optimum power inputs for three different systems are consistent with previous results.

INTRODUCTION

The delta impeller developed by Shen et al. (1982, 1983) has been applied in a cascade of hundreds of mixer-settler units for rare earth extraction (Shen et al., 1989). Shen and Baird (1991) observed that liquid flowed downwards and across the centre of the impeller to form a fast "jet stream" close behind the blade, moving typically at 1.5 times the tip velocity. This flow pattern distinguishes the delta impeller from conventional 4-blade and 6-blade turbines. Recently the delta impeller has been used to promote gas-liquid mass transfer (Baird et al., 1993).

EXPERIMENTAL

The apparatus (Fig. 1) consisted of a 30 cm square-sectioned tank agitated by a 20 cm diameter delta impeller mounted with a clearance H of 9 cm or 5.7 cm above the base of the tank. Baffling was provided as described by Shen and Baird (1991) to prevent the formation of a free vortex at the gas-liquid interface. Experiments were conducted batchwise with 13.5 L of aqueous phase and a layer of 15 cm depth (13.5 L) of organic phase resting on the aqueous phase in the absence of agitation. The systems used are listed in Table 1.

Hold-up of organic phase, ϕ , was measured by rapidly taking 60 mL samples. The samples were drawn from near the wall and midway between the corners, at different vertical positions using a 6 mm internal diameter tube. Power consumption was obtained from the measured torque τ and the impeller speed N .

$$P_s = 2\pi \tau N \quad (1)$$

The drop diameters were measured from close-up video frames (exposure time of 1/10,000 s) 6 cm above the tank base. Several frames (about 800 drops) were analysed to obtain the Sauter mean diameter d_m .

TABLE 1
System Properties and Drop Diameters

System	Continuous phase	Dispersed phase	σ (mN/m)	N (min ⁻¹)	ϕ	d_m (mm)	K
1.	Water $\rho = 997 \text{ kg/m}^3$ $\mu = 1.0 \text{ mPa.s}$	Isopar M* $\rho = 786 \text{ kg/m}^3$ $\mu = 2.48 \text{ mPa.s}$	53.0	50 60 70 80 100	<.01 .01 .02 .03 .46	1.64 1.19 0.89 0.74 0.77	.0288 .0263 .0273 .0299 .0438
2.	Water $\rho = 997 \text{ kg/m}^3$ $\mu = 1.0 \text{ mPa.s}$	Isopar M + 3% TBP $\rho = 792 \text{ kg/m}^3$ $\mu = 2.31 \text{ mPa.s}$	22.5	50 60 70 80	.01 .02 .13 .20	0.92 0.80 0.62 0.51	.0270 .0300 .0317 .0345
3.	Water + NaCl $\rho = 1200 \text{ kg/m}^3$ $\mu = 1.02 \text{ mPa.s}$	Isopar M $\rho = 786 \text{ kg/m}^3$ $\mu = 2.48 \text{ mPa.s}$	50.7	80 90 100	.02 .15 .5(2)	0.87 0.79 0.77	.0320 .0356 .0414
4.	Water + NaCl $\rho = 1200 \text{ kg/m}^3$ $\mu = 1.02 \text{ mPa.s}$	Isopar M + 3% TBP $\rho = 792 \text{ kg/m}^3$ $\mu = 2.31 \text{ mPa.s}$	18.8	(d _m not measured for this system)			

*Esso Canada Ltd. (kerosene).

Mass transfer was studied with benzoic acid as the transferring solute, using an indicator colour change technique. The apparatus was charged with each phase and a known amount of benzoic acid was gradually added under conditions of rapid agitation, until the two phases attained equilibrium. Agitation was shut off, and each phase was sampled and analysed to check the concentrations c_{o1} and c_{a1} . Phenolphthalein indicator (5 mL of 0.05% solution) was added to the aqueous phase, then agitation was started at a set rate N and an aliquot of 1 mol/L NaOH was rapidly added. The amount was sufficient to bring the aqueous phase to alkalinity, resulting in a red colour. The mass transfer of acid from the organic phase neutralized the remaining aqueous sodium hydroxide and eventually eliminated the red colour. The neutralization time (t_N) was noted.

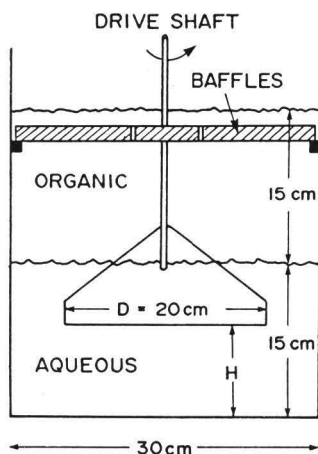


Fig. 1 Apparatus for liquid-liquid contact and hydrodynamics.

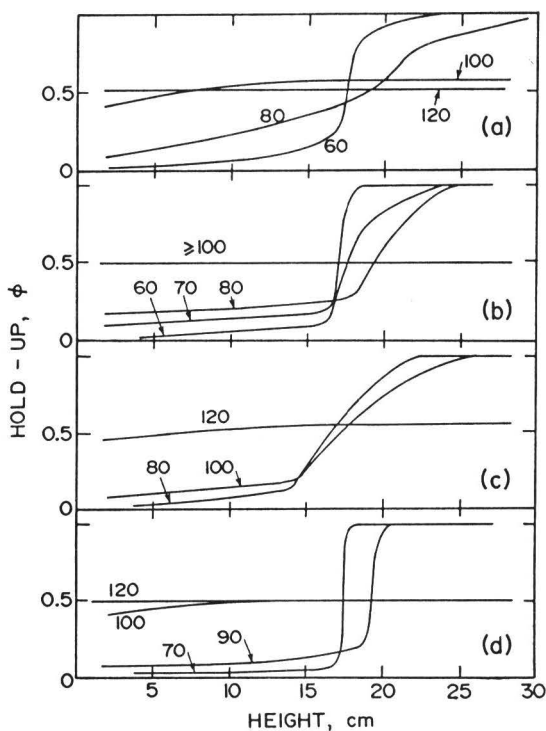


Fig. 2 Effect of system properties impeller speed (shown as min^{-1}) and clearance on vertical profiles of hold-up. (a) System 1, $H = 9.0$ cm; (b) System 2, $H = 9.0$ cm; (c) System 3, $H = 9.0$ cm; (d) System 1; $H = 5.7$ cm.

RESULTS AND DISCUSSION

Hold-up

Fig. 2(a) shows a typical set of hold-up profiles for system 1 (water-Isopar M), at different agitation speeds. At the lowest speed, 50 min^{-1} , the two phases are essentially stratified. As the impeller speed is increased, there is an increasing tendency for the organic phase to be drawn down at the axis of the impeller and dispersed radially into the aqueous phase. Relatively little dispersion of aqueous into organic phase occurred. As more drops are dispersed into the aqueous phase, the amount of organic phase remaining in a discrete layer gradually diminishes. At an impeller speed of 120 min^{-1} the mixture is uniformly dispersed. Similar curves in Figs. 2(b) to 2(d) show that dispersion is affected by system properties and impeller position, as well as impeller speed. The 5.7 cm impeller height was

used in the mass transfer work, since higher positions tended to cause phase inversion (Shen et al., 1982).

Power Consumption

The measured power consumption can be expressed as a power number as follows (Fig. 3):

$$N_p = P_s / (\rho_m N^3 D^5) \quad (2)$$

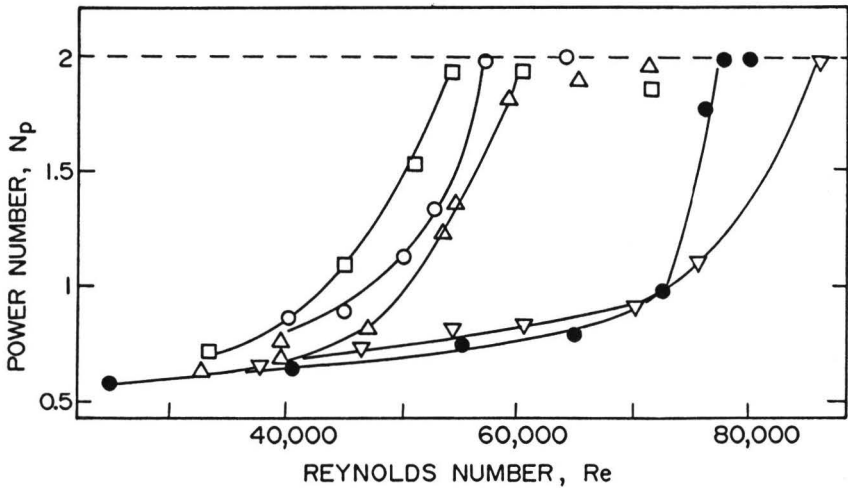


Fig. 3 Effect of impeller Reynolds number, system and impeller clearance on power number. $\square$ System 1, $H = 9$ cm; Δ System 1, $H = 5.7$ cm; $\circ$ System 2, $H = 9$ cm; ∇ System 3, $H = 9$ cm; $\bullet$ System 4, $H = 9$ cm

The lower N_p values correspond to the completely stratified regime. Once stratification has been eliminated, normal circulatory flow is possible and the power number reaches the value of 2 observed under single-phase conditions by Baird and Shen (1993). The effects of system properties are shown as a ranking, with the easiest dispersed system first.

$$2 > 1 > 4 > 3$$

The interphase density difference is a major factor, while interfacial tension has a smaller effect on ease of dispersion.

Drop Diameter

The measured size distributions were rather irregular at low speed, but as the speed was increased the sizes decreased and the distribution curve became more

regular. At 100 min^{-1} with system 1, the hold-up at the viewing point was 46% (Fig. 2(d)) and it became difficult to identify individual drops from the video frames. The Sauter mean drop diameters in agitated tanks and columns can be correlated as:

$$d_m = K Y^{0.6} / \rho_m^{0.2} \varepsilon^{0.4} \quad (3)$$

The specific power dissipation ε is taken as P_g/v , where v is the total liquid volume. Results are given in Table 1 and are well represented by Equation (3) with:

$$K = 0.028(1 + \phi) \quad (4)$$

The hold-up ϕ refers to the average value. Data on drop sizes in turbine-agitated stirred tanks are often correlated in terms of impeller Weber number $\rho_c N^2 D^3 / \gamma$ in the form

$$d_{32} / D \cdot \text{We}^{-0.6} = f(\phi) \quad (5)$$

The diameters at high levels of agitation (high hold-up) are comparable to values for turbine impellers (Davies, 1992), but our data as a whole are poorly represented by Equation (5) because N_p is not constant.

Mass Transfer

The agitated dispersion containing concentrations c_{a1} and c_{o1} of benzoic acid is treated with a solution containing M_1 mol of NaOH at time $t=0$. This mixes and reacts very rapidly with the benzoic acid in the aqueous continuous phase. The mols of free NaOH remaining are:

$$m = M_1 - v c_{a1} / 2 \quad (6)$$

Benzoic acid then transfers from the organic to the aqueous phase where it reacts with the unconsumed NaOH. Mass transfer is controlled primarily by diffusion in the organic phase. The rate equation is

$$k_o a c_o v = -(v/2) dc_o / dt \quad (7)$$

By integration,

$$c_o = c_{o1} \exp(-2k_o a t) \quad (8)$$

The mols of acid transferred in time t are:

$$M' = (v/2)(c_{o1} - c_o) = (v/2)c_{o1}(1 - \exp(-2k_o a t)) \quad (9)$$

Neutralization occurs when $M' = M$. If t_N is the time elapsed for neutralization to occur, it follows from Equations (6) and (9) that

$$t_N = - \frac{1}{2 k_o a} \ln \left[1 - \frac{2M_1 / v - c_{a1}}{c_{o1}} \right] \quad (10)$$

For t_N to be real and positive, M_1 must be between $c_{a1} v/2$ and $(c_{a1} + c_{o1}) v/2$. The measured values of t_N plotted for different values of M_1 according to

Equation (10) showed good linearity, which confirms the equation and its underlying assumptions.

The effect of impeller speed on k_0a is illustrated in Fig. 4, for systems 1 to 3. The mass transfer rate ranking between systems at the same value of N is $2 > 1 > 3$ which is similar to that noted for ease of dispersion. Interfacial area is provided mainly by the dispersed drops at higher agitation rates and mainly by the flat interface at very low agitation rates. The two contributions can be approximately combined by considering the mean hold-up ϕ in the aqueous phase, based on the profiles in Fig. 2. For volume $v/2$ of each phase, the aqueous dispersion volume is $v/2(1 - \phi)$. The specific interfacial area within that volume is $6\phi/d_m$. Therefore the specific interfacial area based on total liquid volume v is:

$$a = 3\phi/(d_m(1 - \phi)) + 3.33 \quad (11)$$

The second term represents the contribution of the flat surface with area 0.09 m^2 divided by the total volume $v = 0.027 \text{ m}^3$. The flat surface term predominates in the stratified regime with $\phi \rightarrow 0$.

Values of the area-based mass transfer coefficient k_0 have been obtained from the data on k_0a by means of Equation (11) using values of d_m from Table 1 or Equations (3) and (4).

For non-circulating (interfacially immobile) drops, k_0 can be calculated from the simplified form of the Newman equation (Treybal, 1963):

$$k_0 = 6.58 D_m / d \quad (12)$$

The molecular diffusivity D_m is estimated from the Wilke and Chang (1955) correlation, taking Isopar M to have molecular weight 170, as $6.56 \times 10^{-10} \text{ m}^2/\text{s}$. The values of k_0 from Equation (12), with d set arbitrarily as 0.5 mm , agree with data under well-agitated conditions.

Optimum Power Input

It is clear from Fig. 4 that the mass transfer rates increase sharply with agitation until complete phase dispersion is reached, with little further increase beyond that point. Thus the optimum power input corresponds to the minimum power required for uniform dispersion. Shen et al. (1983) proposed the following empirical equation for the optimum power input per unit volume for the delta impeller:

$$\epsilon_{\text{opt}} = 0.016 \gamma^{0.24} \Delta \rho^{0.50} \quad (13)$$

In this equation, the units of ϵ are W/L , γ is expressed in N/m and $\Delta \rho$ is in kg/m^3 . Table 2 shows results. Agreement is reasonable in view of the sensitivity of the values of ϵ to N , and the different conditions employed by Shen et al. (1983).

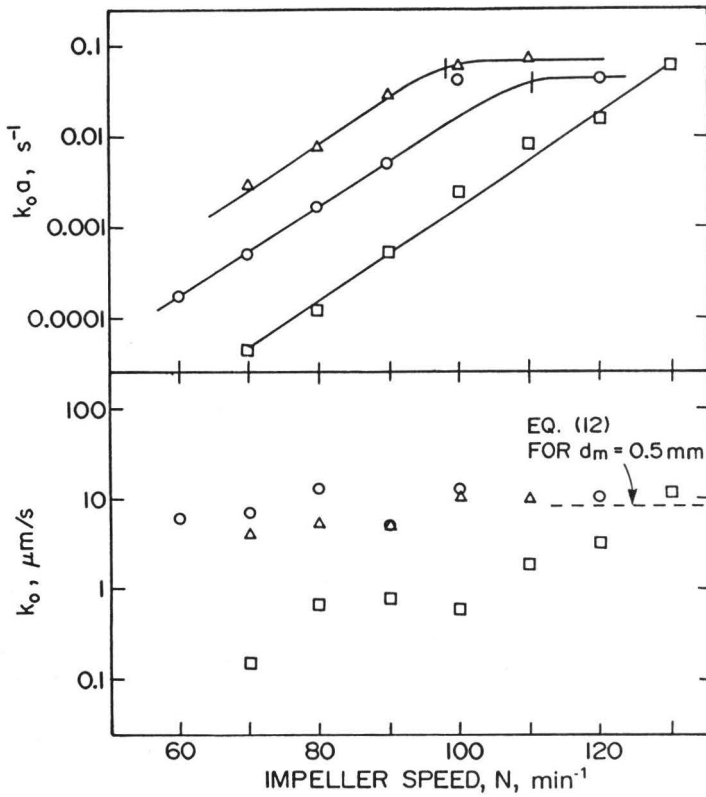


Fig. 4. Effect of impeller speed on (k_0a) and k_0 for systems 1 (O), 2 (Δ) and 3 ($\square$).

TABLE 2
Optimum Power Input for Different Systems

System (Table 1):	1	2	3
Optimum N (r.p.m.)	110	95	130
Optimum ϵ (W/L) (this work)	0.130	0.084	0.239
Optimum ϵ (W/L) (Shen et al., 1983)	0.115	0.092	0.159

ACKNOWLEDGEMENT

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Non-Standard Nomenclature

D	impeller diameter (m)
H	clearance between impeller and tank bottom (m)
K	constant in Equation (3)
M	mols sodium hydroxide
M'	mols benzoic acid transferred in time t
N_p	power number
Re	impeller Reynolds number, $\rho_m ND^2/\mu_c$
t_N	neutralization time (s)

Greek symbols

ρ_m	density of liquid-liquid dispersion (kg/m^3)
τ	torque on shaft ($\text{N}\cdot\text{m}$)

Subscripts

o	organic phase
1	initial value

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4.12

REQUIREMENTS FOR LIQUID-LIQUID DISPERSION STUDIES
WITH A MATCHED REFRACTIVE INDEX SYSTEM

K. H. ABID and J. C. GODFREY

Department of Chemical Engineering
University of Bradford
Bradford, W. Yorks., BD7 1DP, UK

ABSTRACT

Experimental studies with two liquid phases with matched or nearly matched refractive indices have received wide attention in recent years. These techniques allow flow visualisation experiments to be conducted which would not otherwise be possible. Liquid-liquid systems complying with safety and satisfying a range of experimental requirements are reported here. Continuous and representative measurements of dynamic dispersed phase hold-up in an environment free of hydrodynamic disturbance are discussed. Considerations of physical parameters and their measurement in a two phase liquid mixture with a matched refractive index are reported.

INTRODUCTION

Liquid-liquid dispersion studies suffer from visibility difficulties because of light scattering. A better understanding of the drop phase characteristics require visibility far from the contactor walls and regardless of the quantity of the dispersed phase. A possible answer is to modify the refractive index of one phase to use a system which has more or less similar refractive indices in the two phases (partial matching) or to use a system where their two indices are effectively the same. For convenience, the abbreviations PMRIT (Partial Matched Refractive Index Technique) and MRIT (Matched Refractive Index Technique) are used. Whereas, the former provides visible system the latter provides visibility as well as light free scattering system. The PMRIT was used by Allak and Jeffreys (1974) to study the coalescence characteristic of drops in a dispersion band and by Ramlochan (1990) and Mao (1993) to study the breakage of liquid drops in RDCs. The MRIT was used to measure dispersed phase hold-up by Burdett et al. (1981) (in packed column contactor) and by Abid and Godfrey (1990) (in agitated mixer). The PMRIT was used by Kubo et al. (1978) to study liquid

flow patterns and Al-Sharbaty (1990) reported the application of the MRIT to study the flow behaviour of the dispersed phase in a packed column. At Bradford University, applying both the PMRIT and the MRIT, experimental work in laboratory pilot scale mixers/column contactors uses large volumes of organic solvent. Therefore, the hazardous aspects of the chemical have to be considered. This paper considers different liquid-liquid systems which comply with the safety requirements and satisfy the experimental requirements for the PMRIT and the MRIT. The preferred optical arrangements for the MRIT application and physical measurement procedures for experiments with two liquid phases are discussed as well as the general considerations for selecting the liquid-liquid systems.

CRITERIA FOR SOLVENT-AQUEOUS SYSTEM SELECTION

There is at present a wide range of solvents available for industrial and research purposes. The criteria of solvent selection suggested in this paper was based on the comments made by Bailes et al. (1983) and the recommendations published by the European Federation of Chemical Engineering (EFCE) Working Party on Distillation, Absorption and Extraction; Misek (1978). However, the liquid-liquid systems discussed are limited since ternary systems are required for liquid-liquid extraction studies, whereas, binary systems are sufficient for studies with the PMRIT and the MRIT.

Based on the recommendations given by EFCE and the new COSHH (Control Of Substances Hazardous to Health) Regulations issued in 1988 in UK, the following features are regarded desirable for the PMRIT and MRIT studies:

- (a) flash point above 32⁰ C, closed cup.
- (b) no toxicity problem.
- (c) moderate viscosity and density.
- (d) availability and moderate cost.
- (e) water preferably as one of the liquid phases.
- (f) the difference in refractive index between both phases must be reasonably low to allow matching by adding a further component.
- (g) noncorrosive refractive index matching agent.
- (h) a dye tracer which is soluble in one of the two phases.
- (i) moderate separation time after dispersion.
- (j) no special requirements for material of construction.

It is clear that the fulfillment of all of the above criteria is virtually

impossible. A survey was carried out in an attempt to find a group of organic solvents which met the requirements listed above. In brief, the survey revealed two possible solvents which complied with of the necessary requirements and one other which could be used with some precautions. These solvents and their physical properties are shown in Table 1 below.

TABLE 1
Physical Properties of Suitable Solvents in Contact
with Water for PMRIT and MRIT Applications.

Solvent	ρ kg/m ³ 25.5°C	μ mPa.s 25.5°C	σ mN/m 25.5°C	R.I. (-) 25.5°C	F.P. °C	Soly W%	Hazard Rating†
n-Octanol	824.99	7.40	7.50	1.4275	112.0	0.05	1
Di-n-Butyl ether	764.10	0.60	26.50	1.3968	37.7	0.03	1-2
n-Butyl acetate	876.36	0.70	14.20	1.3827	22.2	0.68	1-2
water	997.89	0.882	—	1.3332	—	—	1

† the toxic hazard rating is based on the classification given by Sax (1984): 1 = slight, 2 = moderate. It is worthwhile mentioning that any substance with hazard rating of 3 is considered to be dangerous. The solvents shown in the Table 1 cover a wide range of physical properties, a range of interfacial tensions and show negligible solubility in the water phase.

MATCHED REFRACTIVE INDEX AGENTS

Matching refractive index agents are used in order to reduce the light scattering properties of the two phase liquid mixture and therefore producing a system giving good visibility and light transmission. Previous workers, Allak and Jeffreys (1974) and Burdett et al. (1980), used glycerine as a matching agent. Glycerine is soluble in alcoholic solvents as well as water and this limits its application. Sucrose is a good alternative and has advantages since it is not soluble in any common organic solvent. However, adding glycerine or sucrose as the matching refractive index purposes produces a considerable increase in the viscosity of the water phase.

Aqueous phase	R. I. (-)	μ mPa.s	Temp. °C	reference
67% glycerin-water	1.422	19.3	18.0	Burdett (1981)
53% sucrose-water	1.4251	17.4	25.5	this work
water	1.3332	0.88	25.5	this work

As a precaution, in order to prevent bacterial growth in the water-sucrose solution a biocide (Phylatol, BDH) could be used at 0.001% w/v. This biocide is colourless, only soluble in water, stable, safe in dilute solution and not surface active. Experience showed that covering the sucrose solution with a thin layer of organic phase prevents bacterial growth. Other matching refractive index agents such as metal salts give much lower water phase viscosity and density but are corrosive, since more than 50% w/w of salt may need to be added and therefore require special materials of construction.

CRITERIA FOR CHOOSING LIGHT SOURCE

In the continuous measurements of local/average volume fraction of the drop phase using the MRIT, the objective is to transmit light through a dispersion mixture where one of the liquid phases has been coloured by addition of a dye tracer. However, when the light is to be transmitted through a pilot scale liquid-liquid contactor, an additional characteristic of the light beam is its focussing potential. These features were necessary in the present work which involved light transmission through two glass walls of 0.0125 m in thickness and a 0.3 m path length. The transmitted light was to be focussed on a photo detector 6.9 mm in diameter and 15 cm from the mixer wall.

LASER CHOICE

The characteristics of a laser beam, such as coherence, brightness, monochromaticity and unidirectionality are all potentially useful in achieving the experimental objectives discussed above. A 10 mW He/Ne laser was used in this work, the beam width was 0.69 mm which with a beam expander of 10x magnification gave an average beam width 6.9 mm. This arrangement was suitable for the local measurements of the dispersed phase hold-up since the expanded beam was much larger than the expected drop size, thus minimizing experimental measurement errors.

OTHER REQUIREMENTS

- (i) Visual observations showed that the system temperature is the controlling parameter of visibility in applying the PMRIT and the MRIT.
- (ii) Water was filtered and purified in order to minimize light scattering. Filtration with a reverse osmosis cartridge is effective.
- (iii) The solvent dye tracer should not be surface active, e.g., Oil soluble green (used with red lasers) and O-red Oil (used with green lasers).

MEASUREMENTS

Refractive Index

Good temperature control of the sample is required for precise measurement of the refractive index. A suitable device is a Sodium-D line 518 refractometer. This provides good measurements but only the third decimal place can be precisely obtained. Previously, (Abid and Godfrey (1990), we had shown that mixing of two liquid phases with refractive indices matched up to the third decimal could still exhibit light scattering and a procedure to ensure having a free scattering liquid-liquid mixture. The connection of the mixer and the refractometer in series gave adequate control of the measurement of the refractive indices; all pipes and tubes were well-insulated. A refrigerated circulating system with automatic temperature control was used to ensure good temperature control under near ambient conditions. Measurements showed that adding the dye tracer to the organic solvent had no effect on the refractive index.

Rheology

The highest refractive index of the three organic solvents suggested is that of octanol. Experiments showed that the refractive index of the water phase becomes almost identical to that of organic phase when the sucrose content in the water phase is about 53% w/w. This water-sucrose solution is viscous and it was necessary to investigate the rheology since the viscosity of the aqueous solution might vary as the impeller/rotor speed changed. The viscosity was measured using the Haake RVII viscometer and it was found that the aqueous sucrose solution exhibits Newtonian behavior, i.e., viscosity does not change with changing the impeller speed. Data obtained at 25.5 °C are shown in Fig. 1.

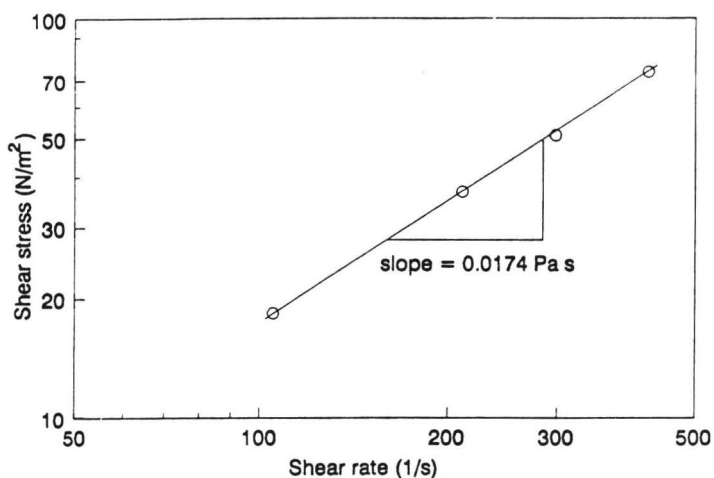


Fig. 1: Shear stress versus shear rates for the water-sucrose solution at 53% w/w.

Interfacial Tension

Measurements were carried out to establish the influence of sucrose on interfacial tension. The drop method Harkins and Brown (1919) was used. For matched refractive index systems, the drop formed from the capillary tube was invisible and therefore the heavier phase (aqueous) was coloured with a non surface active substance, e.g., methylene blue dye. Measurements of the octanol-water system was 7.5 mN/m^2 while that of octanol-water-sucrose system was 7.8 mN/m^2 . The effect of dye concentration in the aqueous media was also investigated and an amount just enough to make the drop visible has shown an interfacial tension value of 7.6 mN/m^2 . When the dye concentration was doubled no change in interfacial tension was observed.

CONCLUSION

Three liquid-liquid systems are suggested for matched refractive index measurement techniques. These systems show Newtonian behaviour and comply with safety requirements; they also cover a wide range of physical properties. A laser beam combined with a beam expander is considered a suitable choice to measure the local hold-up distribution in a mixer. Interfacial tension measurements showed that the effect of sucrose was small. As refractive index is temperature sensitive, precise temperature control is necessary when light transmission is used to measure local dispersed phase volume fraction.

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4.13

**THE INFLUENCE OF MASS TRANSFER
ON COALESCENCE IN LIQUID-LIQUID SYSTEMS**

A. SABONI, C. GOURDON and A. CHESTERS
Ecole Nationale Supérieure D'Ingénieurs de Génie Chimique
Chemin de la loge-31078 Toulouse Cedex France

ABSTRACT

This study concerns the influence of mass transfer on the coalescence process in liquid-liquid dispersions. The hydrodynamics of the film drainage and the mass transfer are coupled via a gradient of the interfacial tension associated with the variation of the solute concentration over the interface. The partial differential equations that describe the flow field (Navier-Stokes' equations) and the mass transport (diffusion-convection equations) are presented in the film and inside the drop according to some simplifying assumptions, which are discussed.

INTRODUCTION

The aim of this investigation is to take into account the influence of the mass transfer on coalescence phenomena in liquid-liquid dispersions. This problem has been evident for many years, but the modelling success has been always limited because of the complexity of the physico-chemical mechanisms involved.

Many authors have previously studied the coalescence of two bubbles or two drops without mass transfer, and this paper presents the first attempt to include mass transfer. This work is an extension of the previous investigations (Yiantsios and Davis, 1990 ; Chesters, 1991), that have been carried out for the prediction of the film drainage during coalescence in liquid-liquid dispersions. The state of the art has been detailed in a recent paper of Chesters (1991). The model of Yiantsios and Davis can be considered as the starting point of this work. The objective of this work is to couple the hydrodynamic description of the film drainage to the mass transfer process. Precisely, the diffusion- convection equation has to be solved in the film and in the bulk phase, in order to predict the gradient of solute concentration, which is responsible for the interfacial tension gradient. This work is devoted to the presentation of the model of film drainage including the mass transfer effect.

BASIC ASSUMPTIONS OF MODELLING

The basic assumptions of the modelling are the following (Fig.1):

i) The liquids are incompressible and Newtonian, ii) All gravitational and inertial effects are of negligible influence, consequently the flow inside the drops and in the film is considered as creeping flow, iii) The interaction force F between the drops is constant and is related to the film diameter by : $F = \pi a^2 2 \gamma_0 R$ where γ_0 is the interfacial tension relative to the reference concentration c_0 at the interface, iv) The film radius a is much smaller than the drop radius R , v) The distance separating the two drops is much smaller than the film radius, vi) No chemical reaction in the two phases, vii) Small variation of the solute concentration within each phase, viii) Constant molecular diffusivity D , viscosity μ and density ρ within each phase, ix) Viewed in the cylindrical coordinate system, fluid motion and concentration distribution are axisymmetric; and x) The film drainage (axisymmetric) governing equations between unequal particles are the same as those between equal particles of equivalent radius (Chesters and Hoffman, 1982) as follows : $2/R = 1/R_1 + 1/R_2$

THE FLOW MODELLING

In the film :

a) Velocity :

The radial component U_r can be approximated as equal to the interface velocity and the normal or axial component U_z then derives from the continuity equation, as follows:

$$U_r = U \quad (1)$$

$$\frac{\partial U_z}{\partial z} = \frac{1}{r} \frac{\partial r U_r}{\partial r} \quad (2)$$

b) Film thickness evolution :

The continuity (volume balance over surfaces at r and $r+dr$) requires :

$$\frac{\partial h}{\partial t} + \frac{1}{r} \frac{\partial (r h U)}{\partial r} = 0 \quad (3)$$

h is the local thickness and t is time

c) The interface condition for tangential stresses :

The variation of species concentration over the interface causes a corresponding variation of the interfacial tension. The variation of interfacial tension produces a net tangential force per unit area, therefore an additional term in the tangential stress balance appears, so that :

$$\mu_d \left(\frac{\partial U_r}{\partial z} \right)_d - \frac{h}{2} \frac{\partial p}{\partial r} + \frac{d\gamma}{dC} \frac{\partial C}{\partial r} = 0 \quad (4)$$

d) The interface condition for normal stresses :

Since the viscous terms are expected to be negligible in the validity range of the modelling, the normal stress condition is then restricted to :

$$p = p_d - \gamma \left(\frac{1}{R_a} + \frac{1}{R_b} \right)$$

where R_a and R_b are respectively the radii of curvature of the surface in the r - z plane, and in the perpendicular plane containing the normal. p_d is the pressure inside the drop. R_a and R_b (Chesters and Hoffman, 1982) are given by :

$$R_a = \frac{1}{2} \frac{\partial^2 h}{\partial r^2} \quad \text{and} \quad R_b = \frac{1}{2r} \frac{\partial h}{\partial r}$$

Finally we obtain a relationship between the pressure in the film and the film thickness:

$$p = \frac{2\gamma}{R} - \frac{\gamma}{2} \left(\frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) \quad (5)$$

e) Integral force balance :

At every time, the constant interaction force is related to the pressure by the next balance :

$$2\pi \int p r dr = F \quad (6)$$

2) Inside the Drop

a) Velocity

Provided that $\delta \ll a$, where δ is the thickness of the diffusion boundary layer. U_r can be approximated as equal to the interface velocity and U_z is then derived from the continuity equation :

$$U_r = U \quad (7)$$

$$\frac{\partial U_z}{\partial z} = \frac{1}{r} \frac{\partial r}{\partial r} U_r \quad (8)$$

b) Boundary Integral Theory

The boundary integral method is applied to the determination of the stress condition. The tangential stress is related to the film velocity (Davis et al, 1989) by :

$$\tau_d = 4 \int \phi(r', r) \left(\frac{U}{r'^2} - \frac{dU}{r' dr'} - \frac{d^2 U}{dr'^2} \right) dr' \quad (9)$$

$$\text{Where} \quad \phi(r', r) = \frac{1}{2\pi} \frac{r'}{(r^2 + r'^2)^{\frac{1}{2}}} \int \frac{\cos \theta d\theta}{1 - k^2 \cos \theta} \quad \text{and} \quad k^2 = 2rr'/(r^2 + r'^2)$$

MASS TRANSFER MODELING

The diffusion equation

The time dependent convective diffusion equation is classically given by :

$$\frac{\partial C}{\partial t} + U \cdot \nabla = D \nabla^2 C \quad (10)$$

we consider the general case for which the resistance to diffusion lies in the two phases, so that the convective diffusion equation must be resolved inside and outside the drops. In cylindrical coordinates the equation becomes :

$$\frac{\partial C}{\partial t} + U_r \frac{\partial C}{\partial r} + U_z \frac{\partial C}{\partial z} = D \left\{ \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} + \frac{\partial^2 C}{\partial z^2} \right\} \quad (11)$$

Interface condition :

The drop surface is assumed always to be in local equilibrium with the continuous phase concentration. The coupling boundary conditions are obtained from flux conservation across the interface.

$$C_d = K C \quad (12)$$

$$\rho_d D'_d \left(\frac{\partial C}{\partial z} \right)_d = \rho D' \frac{\partial C}{\partial z} \quad (13)$$

$$\text{where } D' = D/(1-C_0); \quad D'_d = D_d/(1-K C_0)$$

D is the molecular diffusivity and K is the distribution coefficient. C_0 is the reference solute concentration at the interface.

THE GOVERNING EQUATIONS

Non-dimensionalisation :

The first step is to make the variables dimensionless with the help of R, μ and σ_0 (the interfacial tension corresponding to C_0 :

$$r' = \frac{r}{R}; \quad z' = \frac{z}{R}; \quad h' = \frac{h}{R}; \quad U' = \frac{U}{(\gamma_0/\mu_d)}; \quad t' = \frac{t}{(R \mu_d/\gamma_0)}; \quad p' = \frac{p}{(\gamma_0/R)}; \quad C' = C; \quad C'_d = \frac{C_d}{K}$$

The governing equations relative to the dimensionless quantities finally become :

$$\left(\frac{\partial U'_r}{\partial z'} \right)_d - \frac{h'}{2} \frac{\partial p'}{\partial r'} + \frac{1}{\gamma_0} \frac{d\gamma}{dC'} \frac{\partial C'}{\partial r'} = 0 \quad (4')$$

$$\frac{\partial U'_z}{\partial z'} = \frac{1}{r'} \frac{\partial r' U'_r}{\partial r'} \quad (8')$$

$$\frac{\partial C'}{\partial t'} + U'_r \frac{\partial C'}{\partial r'} + U'_z \frac{\partial C'}{\partial z'} = \frac{1}{Pe} \left\{ \frac{1}{r'} \frac{\partial C'}{\partial r'} + \frac{\partial^2 C'}{\partial r'^2} + \frac{\partial^2 C'}{\partial z'^2} \right\} \quad (11')$$

$$\left(\frac{\partial C}{\partial z'} \right)_d = \frac{\rho D'}{K \rho_d D_d} \frac{\partial C}{\partial z'} \quad (13')$$

where Pe is the Peclet number is defined as : $Pe = R \gamma / \mu D$

2) Transformation of variables :

The next step is to carry out the transformation of variables in powers of $a'=a/R$ which leads to universal flow equations in the absence of mass transfer

$$\begin{aligned} r^* &= \frac{r'}{a'}; & z^* &= \frac{z'}{a'^2}; & z_d^* &= \frac{z'_d}{a'}; & t^* &= t'a'; & p^* &= p'; & U_r^* &= \frac{U_r'}{a'^2}; \\ U_z^* &= \frac{U_z'}{a'^3}; & (U_z^*)_d &= \frac{(U_z')_d}{a'^2}; & C^* &= \frac{C' - C_\infty}{\Delta C'}; & C_d^* &= \frac{C'_d - C_\infty}{\Delta C'} \text{ and } \Delta C' = C'_{d\infty} - C_\infty \end{aligned}$$

The governing equations for the dimensionless quantities become :

$$\left(\frac{\partial U_r^*}{\partial z^*} \right)_d - \frac{h^*}{2} \frac{\partial p^*}{\partial r^*} + \frac{\Delta C'}{\gamma_0 a'^2} \frac{d\gamma}{dc} \frac{\partial C^*}{\partial r^*} = 0 \quad (4^*)$$

$$\frac{\partial U_z^*}{\partial z^*} = - \frac{1}{r^*} \frac{\partial r^* U_r^*}{\partial r^*} \quad (8^*)$$

$$\frac{\partial C_d^*}{\partial t^*} + U_r^* \frac{\partial C_d^*}{\partial r^*} + U_z^* \frac{\partial C_d^*}{\partial z^*} = \frac{1}{a'^3 Pe_d} \left\{ \frac{1}{r^*} \frac{\partial C_d^*}{\partial r^*} + \frac{\partial^2 C_d^*}{\partial r^{*2}} + \frac{\partial^2 C_d^*}{\partial z^{*2}} \right\} \quad (11^*d)$$

$$\frac{\partial C^*}{\partial t^*} + U_r^* \frac{\partial C^*}{\partial r^*} + U_z^* \frac{\partial C^*}{\partial z^*} = \frac{1}{a'^3 Pe} \left\{ \frac{1}{r^*} \frac{\partial C^*}{\partial r^*} + \frac{\partial^2 C^*}{\partial r^{*2}} + \frac{1}{a'^2} \frac{\partial^2 C^*}{\partial z^{*2}} \right\} \quad (11^*)$$

$$\left(\frac{\partial C^*}{\partial z^*} \right)_d = \frac{\rho D'}{a' K \rho_d D_d} \frac{\partial C^*}{\partial z^*} \quad (13^*)$$

The final equations contain 4 dimensionless parameters :

$$\begin{aligned} N_1 &= \frac{\Delta C'}{\gamma_0 a'^2} \frac{d\gamma}{dc} & N_2 &= (a')^5 Pe = \frac{(a')^5 R \gamma_0}{\mu_d D} \\ N_3 &= (a')^3 Pe_d = \frac{D}{(a')^2 D_d} N_2 & \text{and} & N_4 &= \frac{\rho D'}{\rho_d D_d a' K} \end{aligned}$$

In the following, the calculations are made for $N_1 = 10^2 \Delta C'$, $N_2 = 250$, $N_3 = 25 \cdot 10^3$ and $N_4 = 10$, corresponding to $R = 10^{-3}$, $\gamma = 25 \cdot 10^{-3}$, $\mu_d = 10^{-3}$, $a' = 10^{-1}$, $D_d = D = 10^{-9}$, $K = 1$, $\rho/\rho_d = 1$, $1/\gamma d\gamma/dc = 1$.

NUMERICAL METHODS

Concerning the flow fields, the set of equations and boundary conditions are solved using the same algorithm as Yiantsios and Davis, 1990. A simple grid in the physical plane is not appropriate. New coordinate lines ξ and η are defined such that the drop surface becomes a coordinate line, in the physical space, the grid is not rectangular and not uniformly spaced. As a consequence the conventional difference quotients are difficult to use. The physical plane was changed into a simple rectangular region (Numerical plane) by transforming the independent

variable ζ to η and η' (inside and outside the drop). In the film, the independent variables r and z are transformed according to: $\zeta=r$; $\eta = 2 z / h(r)$. Outside the drop, where the gradients are steep, a finer mesh near the drop surface is preferable. For this, an exponential grid spacing is generated using the following transformation: $\Phi = \text{Log} (A+1-\eta)$, where A is a constant (in this work $A = 2$). Inside the drop the independent variable r and z are transformed as: $\zeta=r$; $\eta' = z - a'h(r) / 2$. The equations have been written in the ζ, η, η' coordinate systems. After discretization of all derivatives, the resulting system of equations were solved numerically. The transport equation is strongly influenced by the large value of the Peclet number, which confers on it a marked hyperbolic nature linked to the predominance of the convective term. For this reason, we have adopted a MacCormack (1981) scheme which is well adapted to solve this kind of problem.

RESULTS

As a first result, the interface concentration as a function of time during film drainage without taking account of the Marangoni effect (i. e the interfacial tension gradient) is shown on Figure 2. One can see that the concentration gradient is nearly zero near the center of the film. It is increasing with time far from the center of the film. When the mass transfer occurs, the solute concentration gradient generates a gradient of interfacial tension. In Figure 3 we can see the influence of the mass transfer on the evolution of the minimum film thickness as a function of time. When the mass transfer occurs from the continuous phase to the dispersed phase (C->D), we can observe that the coalescence time will be increased. This result agrees with many experimental observations (K/ourio,1989, Gourdon and Casamatta,1991) and : with C->D, coalescence is not the prevailing mechanism and the drop population is centered around smaller sizes. In contrast, for the opposite mass transfer direction (D->C), it is shown that the coalescence time will be decreased and consequently, coalescence is expected to be enhanced. Besides, for a given mass transfer direction (C->D), the influence of the mass transfer intensity is also clearly exhibited. When ΔC is increasing, the effect on the drainage time evolution is sensitive : a slower decrease of the film thickness is found.

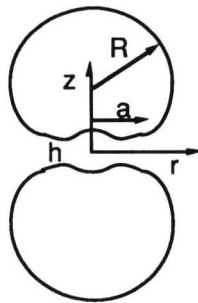


Figure 1 : Geometrical Parameters of the film

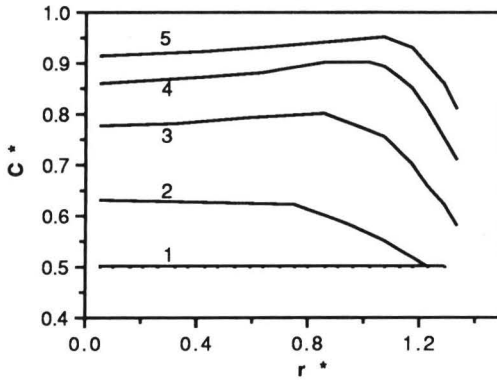


Figure 2 : Interface concentration as function of time during film drainage ($d\sigma = 0$). $t^* = 0; 20; 24; 29; 38$

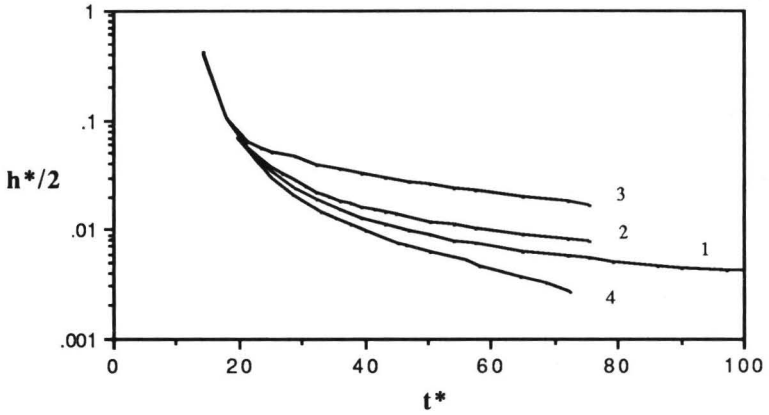


Figure 3 : Minimum film thickness as function of time

1 : without mass transfer. 2 : $\Delta C = 10^{-3}$ (C $\rightarrow$ D)

3 : $\Delta C = 5 \cdot 10^{-3}$ (C $\rightarrow$ D) 4 : $\Delta C = 10^{-3}$ (D $\rightarrow$ C)

ACKNOWLEDGEMENT

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NOMENCLATURE

a	film radius
c	dimensionless concentration
c_0	surface concentration of drop
d	particle diameter
D_μ	molecular diffusivity
F	interaction force exerted by one particle on another
h	film thickness
p	film pressure
Pe	Peclet number
r	radial coordinate
$R_{1,2}$	particle radius
R	equivalent radius
t	time
U	interface velocity
U_r	radial velocity
U_z	axial velocity
z	axial coordinate
μ, μ_d	continuous and dispersed viscosities
ρ, ρ_d	continuous and dispersed density
γ	interfacial tension
τ_d	shear stress exerted on the film by the dispersed phase

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SESSION 5

METALS (REAGENTS AND MODIFIERS)

5.1

LIQUID-LIQUID EXTRACTION AND MOLECULAR MODELLING

C. SELLA*, F. FOURCOT** and D. BAUER*

*Laboratoire de Chimie Analytique, 10 rue Vauquelin, 75005 PARIS, FRANCE

**Rhône Poulenc S.A., 52 rue la Haie Le Coq, 93308 Aubervilliers

ABSTRACT

The purpose of the present work is to show if molecular modelling can be used as a novel aid to account for the results of solvent extraction. Molecular modelling is a means of visualizing extracted complexes in their most stable conformation but it can also help to calculate the atomic charge distribution and to quantify the steric and electrostatic effects of these species by the energy minimization procedure. This quantification allows us to consider structure-activity relationships based on the assumption that correlations exist between the energy of modelled complexes and the ability to be extracted. The molecular modelling software used is SYBYL. The chosen examples are taken from the literature. We have investigated, firstly, the differences of extractibilities of various dianions by diphosphonium extractants in which the length of bridging methylene chain connecting the two phosphonium centers varies and offers an effective molecular recognition field. Secondly, we have modelled metal complexes that are formed in the extraction of rare earths with dialkyl phosphoric acids and in the extraction of zinc(II) with 8-quinolinols in presence of various pyridinic adducts

INTRODUCTION

The purpose of this work is to show if molecular modelling can also be used as a novel aid to account for the results of solvent extraction, and in the longer term to be a helpful tool in extractant design. The first steps have been made by Dalton and Price [1982] and by Gatrone and Horwitz [1988]. Molecular modelling is a means of providing an optimization for the geometry and for visualizing extractable species, extractants and extracted complexes but it can also help to calculate the atomic charge distribution and to quantify the steric and electrostatic effects of these species by the energy minimization procedure. This quantification allows us to consider structure-activity relationships based on the assumption that correlations exist between the energy of modelled complexes and the stability of extracted complexes or the ability to be extracted (Fourcot [1991], Sella and Bauer [1992]). The experimental extraction percentage or the stability constant of complexes quantifies this ability. The molecular modelling software used is SYBYL, developed by Tripos Associates [1988].

In this work, the chosen examples, from the literature (Ohki et al [1989,1990]; Fourcot [1991] Freiser et al [1968]), are those of extraction reactions based firstly on ion exchange mechanism and secondly on complexes formation. The modelled ion-pair species are those which occur by the extraction of organic dianionic species such as dibenzoyltartrate, phthalate isomers and dianionic metal complexes (ZnCl_4^{2-} , $\text{Zn}(\text{CN})_4^{2-}$, $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$) by dicationic extractants such as polymethylenebis-(trioctylphosphonium), C_nBP^{2+} where n is the number of methylene group connecting the two phosphonium cationic centers ($n=2$ to 12) and which offers an effective molecular recognition field. The modelled extractable metal complexes are those which occur by the extraction of rare earths with organophosphorus compounds and by the extraction of zinc with substituted 8-quinolinols in presence of various pyridinic adducts. In our treatment, we do not include the effect of the diluent molecules. We compare the energies of a series of modelled complexes with their experimental extraction abilities determined in the same diluent and we assume that the solvent effect is the same in all the cases.

PROCEDURE

While good geometries can be obtained by rules based methods, the most common method of molecular modelling being used presently is that of energy minimization, using a molecular mechanics force field. The Tripos force field has been shown to produce molecular geometries close to those of crystal structures for a diverse selection of molecules (Clark et al [1989]). It allows the modelling of any organic species. Unfortunately, this is not the case for metallic complexes : there is a lack of molecular mechanics force field for metal-ligand bonds (except for few metallic atoms such as Zn, Al). Nevertheless, SYBYL software allows the introduction of new atoms (here metallic atoms) and of the parameters required to define their bondings (bond type, bond length, bond angle and their corresponding force constants). The energy minimization procedure consists of moving the atoms of a molecule in such a way as to always reduce the total energy of the system based on an empirical representation of the interaction energy of the molecule by means of several potential functions which can modify bond length, bond angle, torsion angle. The value of the minimization energy E_t is only a measure of intramolecular strain relative to a hypothetical situation for which this energy would be equal to zero. The energy E_t can be divided into two terms, E_s a steric one and E_e an electrostatic one. The various dianions, dications and ligands are first separately modelled in their most stable conformations, this being obtained by successive minimizations. Then, the ion-pair species are built from the dianion and dication by approaching them on the screen and taking into account the size of the species (Van der Waals radii of atoms), the localization of the ionic centers and a good adjustment of the anionic and cationic parts of the species (atoms carrying the highest positive charge for the dicationic extractants and atoms carrying the highest negative charge for the dianionic species) in order to obtain the best electrostatic contacts. The metal complexes are built by arranging the modelled ligands around metal atom and binding them with suitable

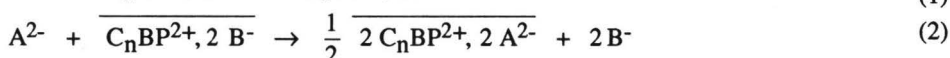
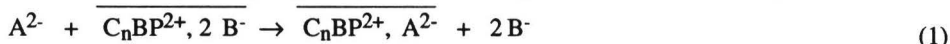
bonds, with respect to the coordination properties of the metal. All these complexes are minimized by taking into account the atomic charge distribution calculated by a semi-empirical molecular orbital method. The most stable conformations (with the lowest value of the minimized energy) are obtained from systematic conformational searches which systematically explore the different viable conformations. The comparison of the ion pairs or complexes energy is not obvious. For example, these energies increase (by their steric term) with the number of involved atoms as it appears by comparison of the energies of various species in homologous series. This comparison is even more difficult when the species have atoms that differ in number and in nature. To avoid this difficulty, we chose to compare the association energy calculated as follows : the sum of total energies of separated species involved in the complex is subtracted from the total energy of the ion pair or of the complex. This association energy is independent of the number and the weight of the involved species. The value of this difference is divided by 2 in the case of 2:2 ion-pair species, to reduce it to a double ionic center comparable to 1:1 ion-pair species and to allow comparison between 2:2 and 1:1 ion-pair species. So, the association energy of the various extracted species can be compared. We will try to check if the assumption that the smallest association energy value which corresponds to the more stable species, corresponds also to the more extracted species.

RESULTS AND DISCUSSION

Ion-pair species

The chosen example is taken from the recent works of Ohki et al [1989, 1990]. The experimental extractibilities of various dianions by diphosponium extractants (Fig. 1) depend on the number n of methylene group in C_nBP^{2+} extractant. The results for diphosponium extractants have shown clearly that the positive charge of phosphorus atoms is delocalized, particularly on the hydrogen atoms carried by the first carbon atoms close to the phosphorus atom. Even more, if these extractants are placed in a plane, two approaches of the ionic center can be considered, one on each side of this plane. For the conjugated dianions, analysis of the atomic charge distribution shows that the negative charges are distributed on oxygen, chlorine or nitrogen atoms, respectively.

The solvent extraction reactions involved are anion-exchange reactions, and we considered that the extraction of a dianion A^{2-} by dicationic C_nBP^{2+} extractants may occur by the formation of 1:1 ion-pair complexes (C_nBP^{2+} , A^{2-}) as described in the literature but also by the formation of 2:2 ion-pair complexes ($2 C_nBP^{2+}$, $2 A^{2-}$) following reactions (1) and (2) respectively.



The bar notation indicates a species in an organic phase

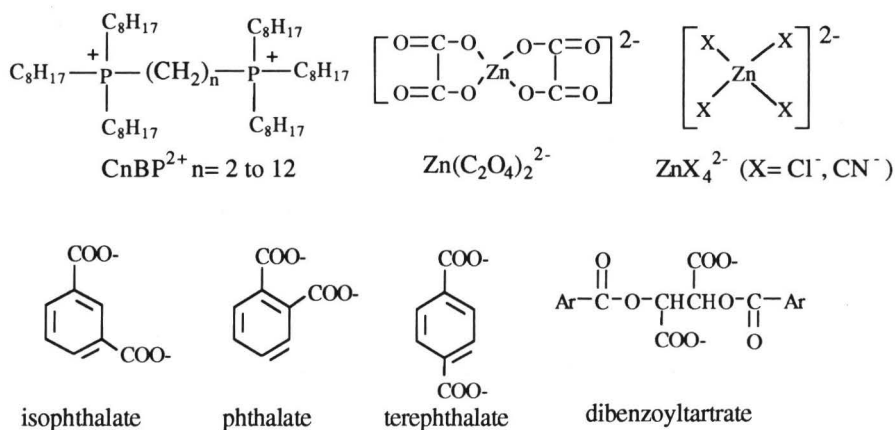


Fig. 1 : Formulas of the studied dianions and dications.

For each dianion, the series of 1:1 and 2:2 ion-pair species are modelled with C_nBP^{2+} , n varying from 2 to 12. The modelled ion-pair species (C_6BP^{2+} , IPH^{2-}) and ($2 \text{C}_6\text{BP}^{2+}$, 2IPH^{2-}) are represented in Fig. 2. The atoms carrying the highest charges are represented on a dot surface (corresponding to Van der Waals radii) and the rest of the molecule is simply represented by lines corresponding to the bonds between atoms. The electrostatic interactions may be an important factor in the formation of these complexes and the electrostatic energy is an important component of the total energy which vary both in the same way versus n . To determine the association type which is the most favorable in each case, we compare the association energy values of 1:1 and 2:2 ion-pair species. It results that 2:2 association is the most suitable, except for phthalate isomers with C_nBP^{2+} $n = 2, 4$ and for $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$ with C_nBP^{2+} $n \leq 6$ for which it is 1:1 association

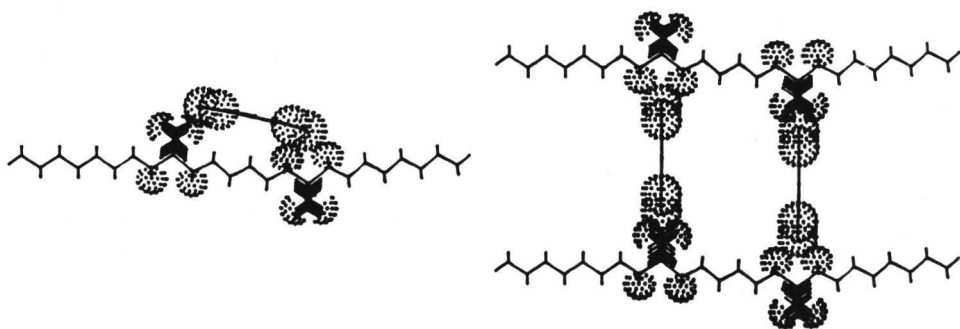


Fig. 2 : Modelled 1:1 and 2:2 ion-pair species (C_6BP^{2+} , IPH^{2-}), ($2 \text{C}_6\text{BP}^{2+}$, 2IPH^{2-}).

Fig. 3 shows the plot of the association energy of the modelled 2:2 ion-pair species with dicarboxylate compounds (phthalate PH^{2-} , terephthalate TPH^{2-} , isophthalate IPH^{2-} , dibenzoyltartrate DBZ^{2-}) and zinc oxalate complex versus the extraction percentage.

Correlations are obtained for each series except for those of terephthalate which presents a dispersion. According to our assumption, the association energy values decrease whereas the extraction percentages increase.

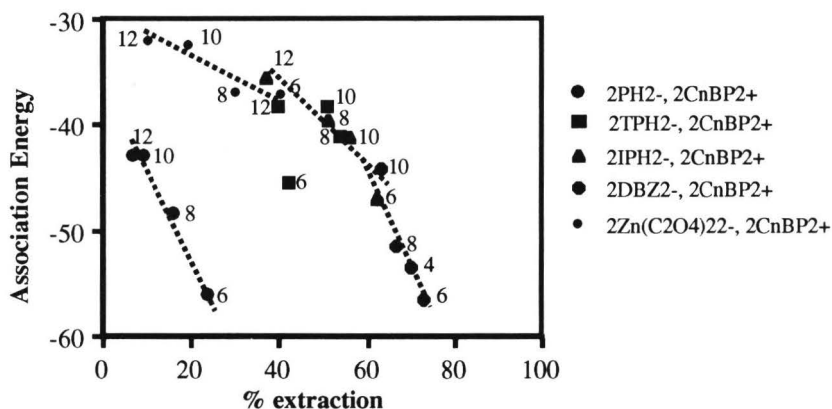


Fig. 3 : Association energy (in kJ/4.18.mol) of 2:2 ion-pair species versus the experimental extraction percentage. The values of n of C_nBP^{2+} are indicated in the figure.

Rare earths (RE) extraction by dialkyl phosphoric acids (Fourcot [1991])

Rare earths extraction has been widely studied, especially by organophosphoric species. Our purpose in this study was to check if the energy of the extracted complex (one extractant and the series of the RE) can be correlated with the extraction constants.

From literature, 6 or 9 are possible coordination numbers. We have limited our study to an extracted complex $\text{RE}(\text{HL}_2)_3$ with an octahedral geometry. By taking advantage of the symmetry of this structure, we have minimized firstly the third part of the complex before the minimization of the complete structure. The formation of this third part of the complex ($\text{RE}_{1/3}\text{HL}_2$) is obtained by replacing one of the hydrogen atoms of the dimeric form H_2L_2 of the extractant by the RE atom. From the literature, we have obtained the extraction constants of each RE by diethylhexylphosphoric acid (DEHPA), denoted here HL. For the modelling of species involving RE, we have introduced in the software the bond type, bond length, bond angle and corresponding force constants. The software then creates a suitable force field, as described in Fourcot [1991].

In the first part of the work, we try to verify if a relation between the extraction constant and the energy of the formed complex exists. We plot the logarithm of the extraction constant of RE

with the DEHPA versus the energy of the complex (Fig. 4). DEHPA has been chosen for a large number and a good accuracy of the experimental results but the molecule is too large (56 atoms for monomeric form, 334 atoms for the complex) to allow reasonable (less than one week) duration for the calculations. So, the calculated energies are those obtained for a sister molecule of DEHPA, 2-methyl-butyl phosphoric acid (MBPA). Both MBPA and DEHPA, are singly branched in position 2. A good correlation appears. An optimistic person can even see the tetrad effect (Nugent [1970]).

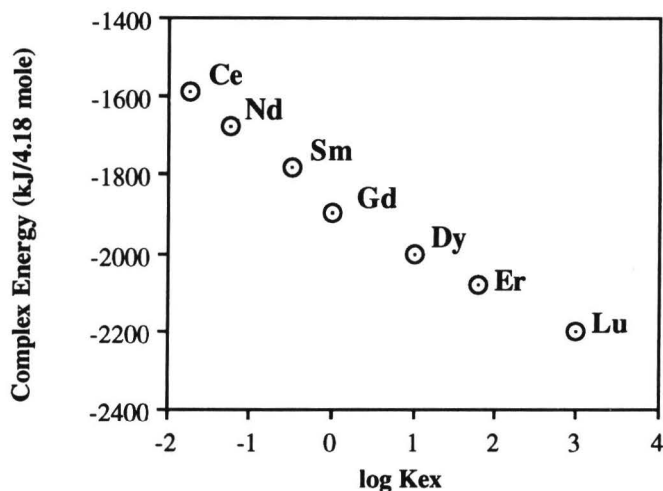


Fig. 4 : Correlation between the extraction constant (log) of DEHPA and the total energy of complexes with a sister molecule of DEHPA, 2-methyl-butyl phosphoric acid (MBPA).

In the second part of this work, we compare the energy of the formed complexes, in relation to the branching of the extractant which undergoes the steric hindrance in the complex formation. The calculations have been made for the following extractants, according to the increase of steric hindrance: linear chains, singly branched chains in position 2, doubly branched chains in position 2 and doubly branched chains in position 1.

The overall energy of the complex of the various RE is plotted for the 4 types of extractants in Fig. 5. We see that the energy is always low for the complexes obtained with the extractant having linear chains (n-propyl chains). On the contrary, the energy is always very high for the complexes obtained with the extractant having doubly branched chains in position 1 (1,1-dimethyl-propyl chain). The steric hindrance is then a very effective factor. The complexes obtained with the extractant having singly branched chains in position 2 (2-methyl-butyl chains) have intermediate behavior between the first two. An interesting case concerns the extractant with doubly branched chains in position 2 (2,2-dimethyl-propyl chains). A break appears for

atomic number 60 (Nd). For the RE of higher atomic number, the complexes formed with this extractant exhibit low energies (close to those obtained with linear chains), for lower atomic number, the complexes formed with this extractant exhibit a rapid increase.

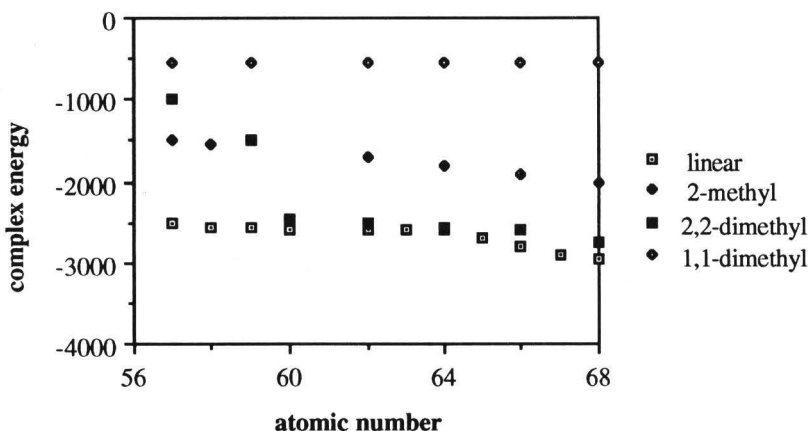
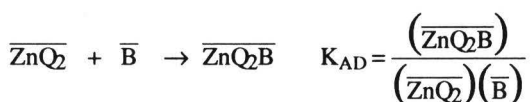


Fig. 5 : Variation of total energies of complexes of RE (represented by their atomic number) for several dialkylphosphoric acids undergoing increasing steric hindrances.

Extraction of zinc by substituted 8-quinolinols in presence of various pyridinic adducts

We have modelled adduct species which are formed in the extraction of zinc(II) by substituted 8-quinolinols in the presence of various adducts. The considered reaction of adduct formation in the organic phase and its equilibrium constant K_{AD} is such that :



The only adduct species of importance in the organic phase is ZnQ_2B where Q^- represents an 8-quinolinolate anion and B an adduct molecule. The values of adduct formation constants for various adducts (pyridine, 2-methylpyridine, 4-methylpyridine, 2,4,6-trimethylpyridine, 1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline) of three zinc 8-quinolinates (8-quinolinolate, 2-methyl-8-quinolinolate, 4-methyl-8-quinolinolate) are reported in the literature [1968].

There is a competition between the steric effect produced by the methyl groups and the synergistic effect produced by the increase in basicity due to the methyl groups. The adduct formation constant is the resultant of these two effects. Fig. 6 shows the plots of the association energy of modelled adduct complexes versus the adduct formation constant.

The association energy accounts for the steric hindrance. Correlations are obtained for each 8-quinolinolate between the association energy and the adduct formation constant. According to our assumption, the association energy decreases as the adduct formation constant increases.

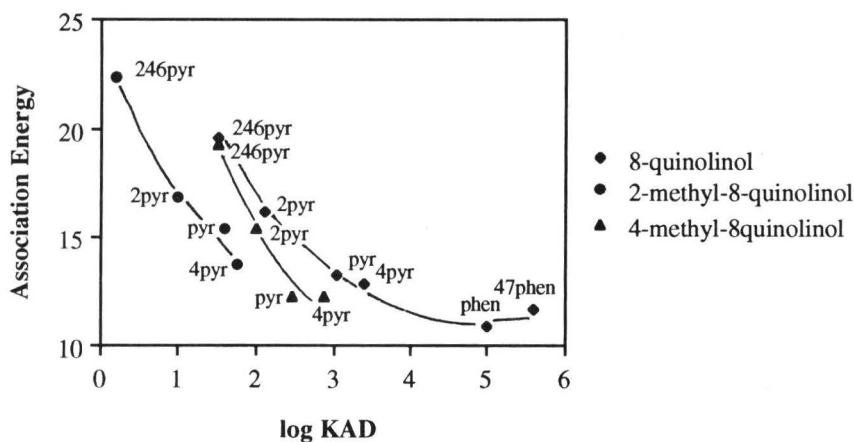


Fig. 6 : Plots of association energy (in kJ/4.18.mol) of zinc adduct complexes with three 8-quinolinols versus log K_{AD} . The nature of adducts is indicated in the figure.

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5.2

**SYNERGISM IN THE EXTRACTION OF Cu(II) BY POLYDENTATE THIA LIGANDS
COMBINED WITH DIDODECYLNAPHTHALENE SULFONIC ACID****BRUCE A. MOYER, R. A. SACHLEBEN, AND G. N. CASE**Chemistry Division, Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6119, U.S.A.**ABSTRACT**

Tetradentate alkyl thia ethers strongly enhance the extraction of Cu(II) from aqueous sulfuric acid solution by the strong-acid cation exchanger didodecyl-naphthalene sulfonic acid (HDDNS). Among the 12-, 14-, and 16-membered macrocyclic tetradentate thia ethers, the strongest enhancement was found with the 14-membered ring. Weak enhancement was observed for one monodentate and two bidentate alkyl thia ethers. Two acyclic tetradentate thia ethers exhibited stronger enhancement than expected from the aqueous-phase macrocyclic effect. An equilibrium scheme is proposed to rationalize the results for the tetradentate ligands.

INTRODUCTION

Thia macrocycles present a remarkable contrast to oxa crown ethers as extraction synergists for the separation of divalent first-row transition metals. Our recent work with oxa crown ethers combined with the strong-acid cation exchanger didodecyl-naphthalene sulfonic acid (HDDNS) has revealed selective synergism for the extraction of Mn(II) and, to a lesser extent, Zn(II) by *t*-butylcyclohexano-15-crown-5 (McDowell et al., 1986; Lumetta and Moyer, 1991). The importance of ligand-field effects led us to test thia macrocycles, where the strong-field sulfur donor atoms were expected to favor the central metals in the series Mn(II) - Zn(II). In fact, strong, selective synergism in the extraction of hydrometallurgically important Cu(II) has been observed for certain macrocyclic thia ethers (Moyer et al., 1988).

The synergistic systems under study provide a means for "tuning" extraction properties based on variation of either neutral synergist or cation exchanger (McDowell, 1988). In particular, the use of a cation exchanger obviates the co-extraction of aqueous anions with the attendant dependence of extraction strength on anion concentration and type, affording extraction from mineral acids (or their salts) by pH swing. The weak selectivity of HDDNS allows control of resultant selectivity according to the coordination properties of the added synergist.

In an effort to build an understanding of the relationship between thia-ligand structure and extraction efficiency in synergistic systems, the extraction of Cu(II) from sulfuric acid by

HDDNS combined with a series of thia ethers (Fig. 1) in toluene has been surveyed for low loading conditions. We report herein results concerning the macrocyclic effect and the effects of variation of the number of thia donor atoms and variation of the number of bridging carbons.

EXPERIMENTAL SECTION

The macrocycles were purchased from Aldrich Chemical Co.; 14-ane-S₄ and 16-ane-S₄ were recrystallized from ethyl acetate-petroleum ether, and 12-ane-S₄ was used as received (97%). Hx₂S (Aldrich) was washed with aqueous NaOH and distilled. Et₂-2-S₂ (bp 102-105 °C @ 25 Torr) and Et₂-3-S₂ (bp 99 - 100 °C @ 15 Torr) were prepared by alkylation (NaOEt/EtOH/EtBr) of the corresponding dithiols (Aldrich, used as received). Me₂-2,3,2-S₄ was prepared by the method of Rosen and Busch (1969). Et₂-2,3,2-S₄ (bp 171 - 174 °C @ 0.04 Torr) was prepared by alkylation (NaOEt/EtOH/EtBr) of tetrathiaundecane (Rosen and Busch, 1969). All four linear sulfides were purified by distillation, and the purities were verified by GC.

HDDNS was obtained from King Industries and was purified by anion-exchange as described previously (Danesi et al., 1973). Stock solutions of HDDNS were standardized by acid-base titrations in ethanol-water. Toluene was of spectrophotometric-grade (Burdick and Jackson). ⁶⁴Cu and ⁶⁷Cu tracers (NEN Research Products) were received as the nitrate salts and converted to the sulfate form by adding the received solutions to dilute sulfuric acid and evaporating to dryness. Water was doubly distilled. All other chemicals were of reagent quality and were used as received.

Distribution measurements were carried out by ⁶⁴Cu or ⁶⁷Cu tracer techniques described earlier (Moyer et al, 1993). Aqueous solutions containing CuSO₄ (0.1 - 760 μM), H₂SO₄ (0.03 - 6.0 M), and tracer were contacted nondispersively with equal volumes of toluene solutions containing 0.01 M HDDNS plus 0.02 M Hx₂S, 0.01 M bidentate ligand, or 0.005 M tetradentate ligand by gently rocking the vials at 25.0 ± 0.1 °C for 18 - 142 h. Distribution coefficients (*D*_{Cu}) were calculated as $D_{Cu} = [Cu]_{org}/[Cu]_{aq}$. The maximum loading ratios $[Cu]_{org}/[HDDNS]_{initial}$ and $[Cu]_{org}/[thia\ ligand]_{initial}$ attained

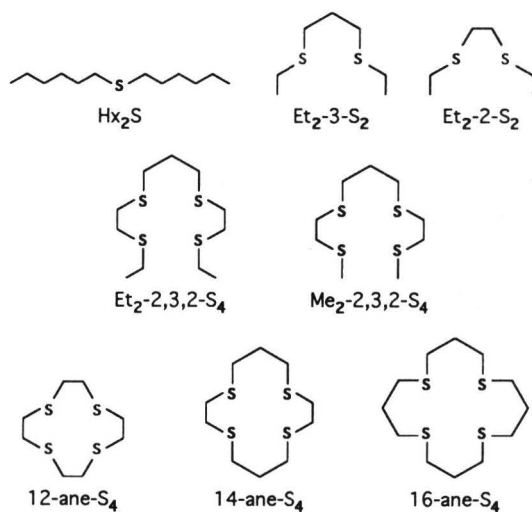


Fig. 1. Alkyl thia ethers studied.

were respectively less than 0.008 and 0.016. Within this regime of low loading, tests of HDDNS alone or together with Hx_2S , 12-ane- S_4 , 14-ane- S_4 , or 16-ane- S_4 indicated no variation of D_{Cu} within experimental error (generally less than $\pm 10\%$). Examples of the experimental data for two of the thia compounds are shown in Fig. 2.

To test the reversibility of extraction, equilibrations were performed in which the direction of mass transfer was reversed (Fig. 2).

Stock solutions of 0.01 M HDDNS and thia ligand at an appropriate molarity in toluene were loaded with a small quantity of Cu(II) by contacting with 0.03 or 0.1 M H_2SO_4 containing 76 μM CuSO_4 plus added tracer. The resulting organic phases were separated from the original aqueous phases and used in extraction tests with aqueous phases containing only H_2SO_4 . Values of

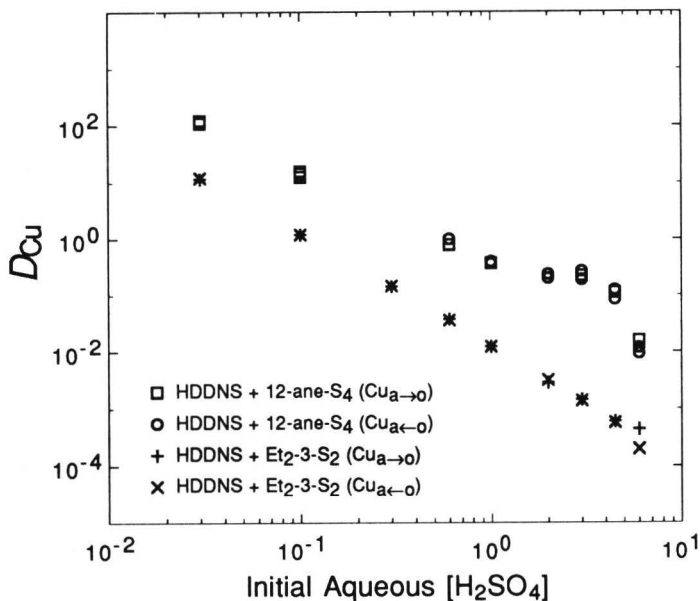


Fig. 2. Sample data: extraction of Cu(II) under low-loading conditions from 0.03 - 6.0 M H_2SO_4 by 0.01 M HDDNS in toluene combined with 0.01 M $\text{Et}_2\text{-3-S}_2$ or 0.005 M 12-ane- S_4 . The Cu(II) was initially either in the aqueous phase (+, $\square$) or in the organic phase ($\times$, $\circ$) as indicated.

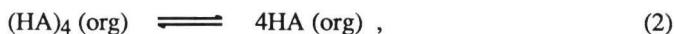
D_{Cu} were found to be independent of the direction of equilibration (Fig. 2), proving the reversibility of extraction and attainment of equilibrium for each of the thia ethers over the full range 0.03 - 6 M H_2SO_4 . Moreover, this result also indicates the negligible partitioning of HDDNS or any of the thia ligands to dilute aqueous H_2SO_4 (0.03 or 0.1 M). Negligible partitioning of 14-ane- S_4 and 16-ane- S_4 to water from toluene ($< 0.1\%$) was demonstrated previously (Moyer et al., 1988) and would by extension be expected for the other ligands, which have comparable or more favorable C/S atom ratios. Although work in progress indicates that 14-ane- S_4 partitions slightly to aqueous solutions containing Cu(II) (Moyer et al., 1992), this effect may be neglected at the low Cu(II) molarities employed here.

It was noted in the course of the experiments that the times required to achieve equilibrium varied over the range of thia ethers and aqueous acidities tested. Whereas 14-ane- S_4 reached

equilibrium within 18 h in all cases, the other tetradentate and bidentate thia ethers required times exceeding 100 h. The equilibration times were generally rapid (less than 24 h) when the aqueous molarity of H_2SO_4 was less than 1 M but increased in the higher range of acidities.

RESULTS AND DISCUSSION

As shown by the smoothed extraction curves in Fig. 3, the solvent containing only 0.01 M HDDNS in toluene exhibits decreasing Cu(II) extraction with increasing H_2SO_4 concentration. The behavior of D_{Cu} as a function of aqueous-phase H_2SO_4 and CuSO_4 concentrations and organic-phase HDDNS concentration has recently been modeled by the program SXLSQA in terms of cation exchange and deaggregation:



where $(\text{HA})_4$ is a hydrated organic-phase aggregate containing four HDDNS molecules (Moyer et al., 1993); the water molecules associated with the organic-phase species are not shown.

Comparison of extraction curves shows that combination of HDDNS with various alkyl thia ethers produces an enhancement in D_{Cu} over that obtained with HDDNS alone (Fig. 3). The observed behavior strongly depends on thia ether structure and on the aqueous acidity. Three approximate regions of behavior may be identified. The first region encompasses aqueous

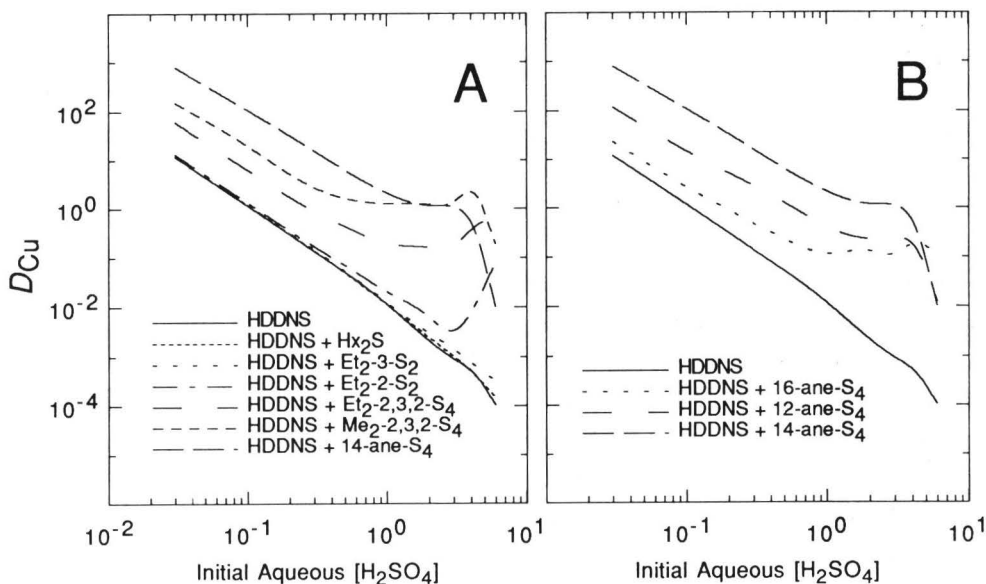


Fig. 3. The macrocyclic effect (A) and ring-size effect (B) in Cu(II) extraction by HDDNS combined with thia ethers. Smoothed curves are spline fits of data (see, for example, Fig. 2).

H₂SO₄ concentrations up to 0.3 M and is characterized by regular behavior, wherein all curves nearly parallel the HDDNS curve. The second and third regions exhibit irregular, though reproducible, behavior. In the second region, extending from 0.3 to 3.0 M H₂SO₄, the curves tend to level off, and in the third region, extending from 3.0 to 6.0 M H₂SO₄, most of the curves descend steeply. Reversible extraction was observed in each region.

Among the macrocycles tested, enhancement of D_{Cu} in the first region follows the order 12-ane-S₄ < 14-ane-S₄ > 16-ane-S₄ (Fig. 3B). The fact that this is the same order observed for the complexation of Cu(II) in aqueous solution (Sokol et al., 1981) suggests that the extraction involves similar coordination chemistry. Mononuclear 1:1 complexes of the macrocycles with Cu(II) have been characterized by X-ray diffraction, showing 14-ane-S₄ to be best suited for optimal coordination of Cu(II) about its equatorial plane (Glick et al., 1976; Pett et al., 1983).

Comparison of the enhancement of Cu(II) extraction by an increasingly pre-organized series of thia ethers (Fig. 3A) demonstrates a macrocyclic effect in the first region. Hx₂S exhibits essentially no discernible enhancement. The bidentate ligands Et₂-3-S₂ and Et₂-2-S₂ also exhibit little enhancement. An X-ray structure of the compound [Cu(Me₂-2-S₂)₂(BF₄)₂] has shown the Cu²⁺ ion to be equatorially bound by a coplanar rectangular array of S atoms and two approximately axial BF₄⁻ anions (Baker and Norris, 1977). Moderate enhancement of D_{Cu} is obtained from the tetradentate thia ethers Me₂-2,3,2-S₄ and Et₂-2,3,2-S₄. An X-ray structure of [Cu(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄) again indicates the disposition of Cu(II) to be bound equatorially by four S atoms, though steric interactions force one of the S atoms to move out of the plane containing the Cu²⁺ ion and the other three S atoms; water and perchlorate ion occupy the axial sites (Diaddario et al., 1985). The greatest enhancement occurs with the tetradentate macrocycle 14-ane-S₄, indicating an operative macrocyclic effect. In the model compound [Cu(14-ane-S₄)(OCIO₃)₂], the cation lies in the center of the square-planar set of four S atoms with O atoms from the anions coordinating axially (Glick et al., 1976).

In quantitative terms, the macrocyclic effect in the Cu(II) extraction is weaker than observed for the complexation of Cu(II) by the same thia ethers in homogeneous aqueous solution. We denote the Cu(II) distribution coefficient as $D_{\text{Cu,HDDNS}}$, $D_{\text{Cu,mac}}$, or $D_{\text{Cu,acy}}$, according to whether HDDNS is respectively used alone, combined with a macrocycle, or combined with the acyclic tetradentate analog. The magnitude of the extractive macrocyclic effect $E_{\text{mac,acy}}$ may then be expressed by the difference $E_{\text{mac,acy}} = \log(D_{\text{Cu,mac}} - D_{\text{Cu,HDDNS}}) - \log(D_{\text{Cu,acy}} - D_{\text{Cu,HDDNS}})$; here, subtraction of $D_{\text{Cu,HDDNS}}$ inside the parentheses corrects for the extracted Cu(II) that is not bound by a thia ligand. Evaluated at 0.3 M H₂SO₄, $E_{14\text{-ane-S}_4, \text{Me}_2\text{-2,3,2-S}_4} = 0.75$ and $E_{14\text{-ane-S}_4, \text{Et}_2\text{-2,3,2-S}_4} = 1.32$. By comparison, for the complexation of Cu(II) by the same compounds in 0.1 M HClO₄ at 25 °C, $\log K_{14\text{-ane-S}_4} - \log K_{\text{acy}} = 2.37$ and 2.16 for respectively Me₂-2,3,2-S₄ and Et₂-2,3,2-S₄ (Sokol et al., 1981).

In probing the equilibria of these systems, our work in progress (Moyer et al., 1992) has focused on the 14-ane-S₄ system as a model. Results from computer modeling have

demonstrated that the extraction behavior in the first region is consistent with 1:1 complexation of Cu(II) by 14-ane-S₄ (B) according to the equilibrium



where x is 3 or 4. The visible spectrum of the organic phase (Moyer et al., 1992) matches that of the 1:1 Cu(II) complex with 14-ane-S₄ (Jones et al., 1975; Glick et al., 1976).

Since the extraction of Cu(II) when 14-ane-S₄ or 16-ane-S₄ is used alone has been shown to be negligible (Moyer et al., 1988), the enhancement in D_{Cu} over that found with HDDNS alone is *definitely synergistic* for these two macrocycles in the first region. As shown by eq. 3, the synergism for 14-ane S₄ is based on a coupling of metal-ion coordination and a net exchange of two protons per Cu²⁺ ion. The parallel dependence of D_{Cu} on the initial H₂SO₄ concentration observed for all curves in the first region (Fig. 3) suggests synergistic 2-equivalent cation exchange for the other thia ethers tested. We further note that the independence of D_{Cu} with respect to the Cu(II) molarity at low loading seen for the three macrocycles indicates the mononuclearity of their organic-phase species. Although the stoichiometries of the organic-phase complexes have not been further elucidated, our extraction results together with the reported results on complexation in solution (Jones et al., 1975; Sokol et al., 1981) and in the solid state in the presence of weakly coordinating ClO₄⁻ or BF₄⁻ anions (Glick et al., 1976; Pett et al., 1983; Diaddario et al., 1985) suggest the applicability of eq. 3 in the first region for all of the tetradentate ligands tested.

The fact that the order 12-ane-S₄ < 14-ane-S₄ > 16-ane-S₄ found for the extraction of Cu(II) in the first region (Fig. 3)

is the same order found for the Cu(II) complexation constants K_{cpx} in homogeneous solution (Jones et al., 1975; Sokol et al., 1981) suggests that D_{Cu} and K_{cpx} are correlated for these ligands. Why this result may be

expected is illustrated by Fig. 4. This scheme leads to eq. 3 as a resultant reaction and yields the relationship,

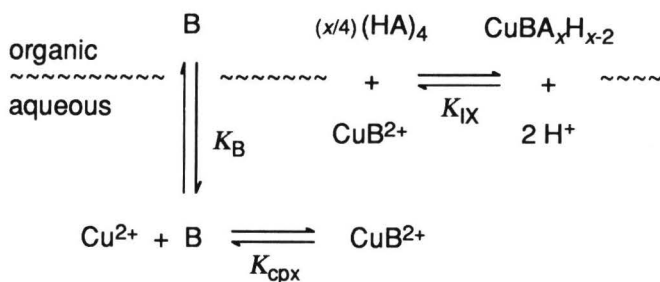


Fig. 4. Equilibrium scheme.

$$\log(D_{\text{Cu}} - D_{\text{Cu,HDDNS}}) = -\log K_B + \log K_{\text{cpx}} + \log K_{\text{IX}} + C. \quad (4)$$

At constant acidity and low loading, the term C , containing activity coefficients and the concentration ratio $[\text{H}^+]^2/[(\text{HA})_4]^{x/4}[\text{B}]$, is constant. The terms $-\log K_B$ (partitioning of B)

and $\log K_{IX}$ (ion exchange of aqueous CuB^{2+} complex) are essentially solvation controlled and thus may give a constant difference in a regular series of ligands. The expected linear plot of $\log(D_{Cu} - D_{Cu,HDDNS})$ vs. $\log K_{cpx}$ having approximately unit slope (actual slope is 0.86) is obtained for the macrocycles (Fig. 5).

In accord with the weaker macrocyclic effect in the extraction of $Cu(II)$ compared with the

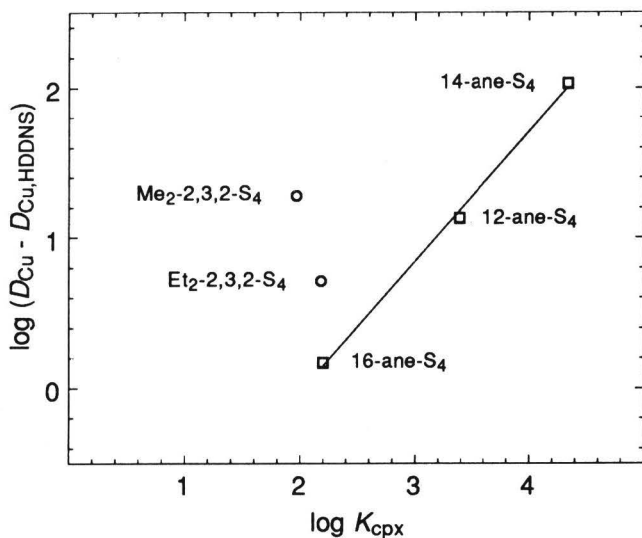


Fig. 5. Correlation of distribution coefficients at 0.3 M H_2SO_4 (Fig. 3) with aqueous complexation constants (Sokol et al., 1981).

aqueous complexation of $Cu(II)$, points for $Me_2-2,3,2-S_4$ and $Et_2-2,3,2-S_4$ in Fig. 5 lie above the macrocycle line. From Fig. 4, it may be concluded that the term $(-\log K_B + \log K_{IX})$ opposes the overall macrocyclic effect. No macrocyclic effect is expected in the ion-exchange term ($\log K_{IX}$) according to the structural evidence (Baker and Norris, 1977; Diaddario et al., 1985; Glick et al., 1976), which shows similar structures for both linear and macrocyclic ligands. In view of the weak coordinating ability of sulfonate anions, the structural integrity of the CuB^{2+} complexes is expected to be preserved upon ion exchange (K_{IX}); this is supported by solution evidence (Sokol et al., 1981) that shows the effect of ClO_4^- anion coordination to be structurally unperturbing to the thia-ligand coordination and to be thermodynamically similar for all of the tetradentate ligands. Thus, from this reasoning it may be concluded that it is primarily the remaining term $(-\log K_B)$ in eq. 4 that opposes the overall extractive macrocyclic effect; that is, the transference of ligand from the toluene phase to the aqueous medium will be more favorable for the linear tetradentate thia ethers than for the thia macrocycles. Indeed, this conclusion agrees with the conclusion from kinetic studies of $Cu(II)$ complexation that the linear thia ethers are slightly better solvated than their macrocyclic analog in aqueous solution (Diaddario et al., 1979).

As mentioned above, the second and third acid regions give rise to irregular behavior (Fig. 3). Although we have not further studied the leveling-off seen in the second region, it would be difficult to understand this behavior except in terms of co-extraction of sulfate or bisulfate anions. Possibly useful for stripping, the precipitous drop in D_{Cu} that some of the curves

exhibit at the highest aqueous acidities studied (third region) must involve a competing process, perhaps acid extraction. Since both the ring-size and macrocyclic effects disappear in the third region, the role of the thia ligands obviously shifts from the simple picture in the first region to a role in which the macrocyclic cavity appears unimportant in the third region. Whether the systems remain synergistic in the second and third regions has not yet been definitely confirmed.

CONCLUSIONS

Addition of linear and macrocyclic thia ethers to HDDNS leads to the enhancement of D_{Cu} over the range of aqueous H_2SO_4 concentrations 0.03 - 6.0 M. Extraction curves in all cases approximately parallel the HDDNS curve up to 0.3 M H_2SO_4 but become irregular at higher H_2SO_4 molarities. In the parallel region, the effect of increasing ring size on D_{Cu} is given by the order 12-ane- S_4 < 14-ane- S_4 > 16-ane- S_4 , and the effect of increasing pre-organization on D_{Cu} is given by the order Hx_2S < Et_2-3-S_2 < Et_2-2-S_2 < $Et_2-2,3,2-S_4$ < $Me_2-2,3,2-S_4$ < 14-ane- S_4 . These orders have been rationalized according to a proposed set of equilibria (Fig. 4) based on a detailed equilibrium analysis of the case of 14-ane- S_4 , published X-ray crystal structures, and published homogeneous-solution complexation data.

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5.3

PHOSPHINE OXIDE PHASE MODIFIERS IN THE RECOVERY OF INDIUM

W.A. RICKELTON
Cyanamid Canada Inc.
Phosphine Technical Centre
P.O. Box 240
Niagara Falls, Ontario, Canada L2E 6T4

ABSTRACT

Indium is usually recovered by solvent extraction from sulphate solutions with di(2-ethylhexyl)phosphoric acid (D2EHPA). However, the extracted complex is very stable and requires the use of high concentrations of hydrochloric or sulphuric acid for stripping before pure indium is recovered. It has been found that using various phosphine oxides to modify the solvents allows stripping to be accomplished with relatively weak acids. Benefits are in reduced corrosion and waste-acid disposal problems. An added advantage is that the presence of the phase modifiers prevents the accumulation of ferric iron in the solvent. Accumulation can lead to increased viscosity, poor phase disengagement properties and, eventually, solvent poisoning.

INTRODUCTION

The most important source of indium is as a by-product from primary zinc production. Processing involves the recovery of indium by solvent extraction with D2EHPA from acidic sulphate leach liquors derived, for example, from flue dusts. However, indium, like ferric iron, is strongly extracted by D2EHPA and excessive quantities of strong mineral acids are required for stripping. For example Keishi (1981) used 8-9M HCl. Handling such volumes of acid on an industrial scale poses difficult problems in terms of safety, waste disposal, corrosion and cost.

It has been found that modifying D2EHPA solvents with phosphine oxides allows stripping to be accomplished with relatively weak acids, e.g. 2M H_2SO_4 . An added advantage is that the presence of the phosphine oxides prevents the accumulation of a difficult-to-strip ferric iron complex in the solvent (Rickelton 1983). This complex is thought to be an Fe^{3+} -D2EHPA polymer having a molecular weight of approximately 100,000.

The two phosphine oxides in question are CYANEX®923 and 925 extractants. Both compounds are liquids. CYANEX 923 is a mixture of four, straight-chained phosphine oxides and CYANEX 925 contains branched chains. Detailed information on their properties is available elsewhere, (American Cyanamid Company 1987, 1988).

EXPERIMENTAL

CYANEX 923 and 925 extractants (Cyanamid Canada Inc.), D2EHPA (Albright and Wilson) and Exxsol D-80 diluent (Exxon Corporation) were used without purification. All other reagents were A.R. grade.

Batch shake-out tests were conducted in stirred, water jacketed, baffled glass beakers. Metal analysis was carried out by atomic absorption spectrophotometry and acid analysis by potentiometric titration. Equilibrium concentrations of metals in the organic phase were determined by mass balance.

RESULTS AND DISCUSSION

Indium Extraction

The synergy exhibited by acidic extractants such as D2EHPA and solvating reagents such as trialkylphosphine oxides has most recently been exploited commercially in the extraction of uranium (6+) from wet process phosphoric acid. This followed the pioneering work of Hurst (1972) and his colleagues at the Oak Ridge National Laboratories. During an investigation into the synergic extraction of other metals with mixtures of D2EHPA and phosphine oxides, it became apparent that, in the case of indium, an antagonistic rather than a synergic effect existed. This is illustrated by the results of some batch, shake-out tests using D2EHPA and CYANEX 923 given in Table 1 and Fig. 1.

The unmodified solvent, containing only D2EHPA, yielded a high degree of indium extraction over the tested range of sulphuric acid concentration; approximately 20 to 200 g/L. The addition of 5 v/o CYANEX 923 to the solvent depressed indium extraction markedly at high acidities (> 50 g/L H_2SO_4). The magnitude of the effect was further increased when the concentration of CYANEX 923 was raised to 10 v/o. No addition displacement of the curves shown in Figure 1 was observed at a modifier concentration of 15 v/o.

Replacing the straight chained phosphine oxide, CYANEX 923, with a branched chain phosphine oxide, CYANEX 925, had a similar effect but at a lower concentration in the solvent (5 v/o versus 10 v/o). This is illustrated in Fig. 2 which was plotted using the results in Table 1.

The inferences to be drawn from the data are that the presence of the phosphine oxides will allow quantitative indium extraction at low acidities, approximately <50 g/L, and that the phase modifiers will facilitate indium stripping with lower-than-normal concentrations of sulphuric acid. While the mechanism of the interaction between the acidic and solvating extractants is not understood, it should be noted that Blake (1955) has reported analogous results for the extraction of uranium using D2EHPA combined with straight and branched chain phosphine oxides, i.e. trioctyl and tri(2-ethylhexyl)phosphine oxides.

TABLE 1

Effect of CYANEX 923 and 925 Extractants on Indium Recovery With D2EHPA

Solvents : See below
 Aqueous : 1 g/L In (3+) as sulphate. Various H₂SO₄ concentrations
 Phase Contact : A/0=1 for 5 minutes at 24° C

	% Indium Extraction	Equilibrium H ₂ SO ₄ Concentration (g/L)
5 v/o D2EHPA	81.9	188
	88.6	143
	97.1	102
	98.9	70.9
	99.8	44.9
	100	28.0
	100	18.7
5 v/o D2EHPA 5 v/o CYANEX 923	15.0	184
	27.5	136
	47.5	95.1
	64.0	66.1
	91.2	42.8
	96.1	24.4
	98.5	16.2
5 v/o D2EHPA 10 v/o CYANEX 923	2.5	181
	8.7	134
	22.5	95.9
	40.0	64.7
	59.0	44.1
	82.5	26.6
	93.5	17.5
5 v/o D2EHPA 5 v/o CYANEX 925	0	157
	7.5	113
	24.0	79.9
	45.0	55.7
	73.5	36.7
	89.5	21.9
	95.0	14.1

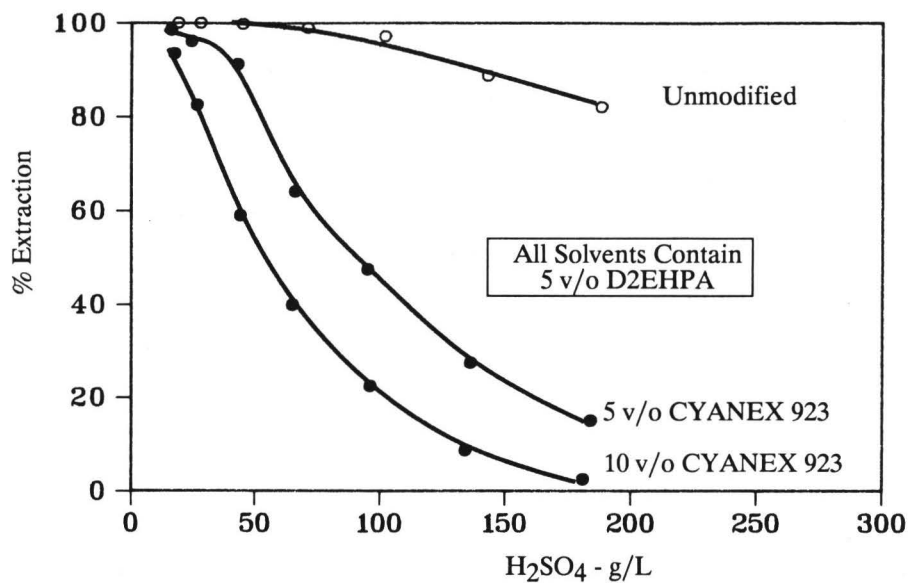


Fig. 1: Effect of Phase Modifiers on Indium Extraction

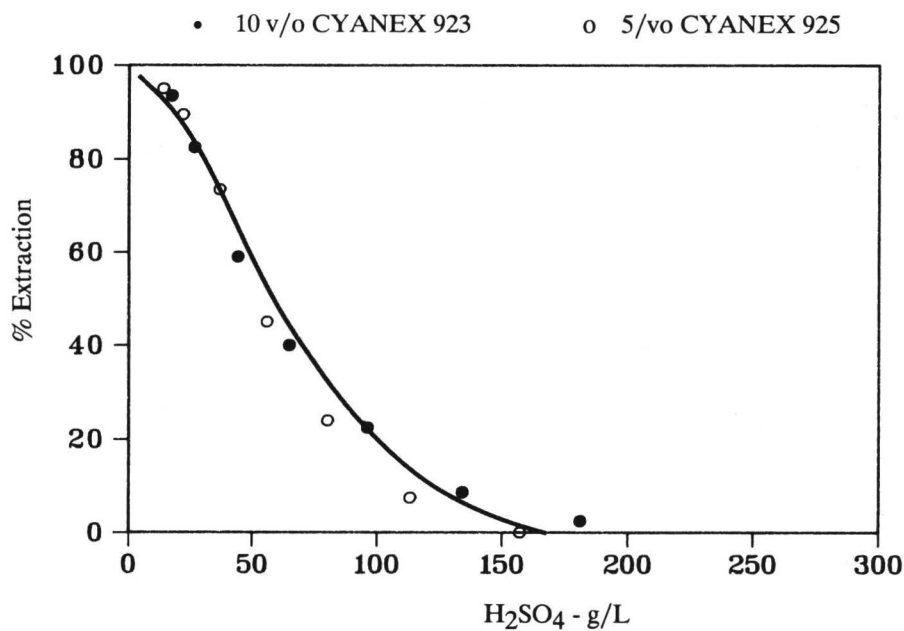


Fig. 2: Effect of Chain Branching on Indium Extraction

Indium Stripping

Two stripping isotherms were generated to confirm the suspected effect of the phosphine oxides. One isotherm was obtained with D2EHPA alone and the second with a solvent also containing CYANEX 925. Experimental conditions and results are given in Table 2. The isotherms are plotted in Fig. 3.

TABLE 2

Indium Stripping Isotherms

Solvents	:	1) 5 v/o D2EHPA in Exxsol D-80 diluent loaded to 1.98 g/L In (3+) 2) 5 v/o D2EHPA, 5 v/o CYANEX 925 extractant in Exxsol D-80 diluent loaded to 1.62 g/L In (3+)
Strip Feed	:	200 g/L H ₂ SO ₄
Phase Contact	:	24° C at various A/O ratios

A/O	Equilibrium In (3+) Concentration - g/L			
	5 v/o D2EHPA		5 v/o D2EHPA + 5 v/o CYANEX 925	
	Organic	Aqueous	Organic	Aqueous
0.2	-	-	0.94	3.90
0.5	1.23	1.49	0.42	2.60
1	1.03	0.95	0.24	1.48
2	0.76	0.61	0.18	0.77
5	0.54	0.29	0.09	0.33

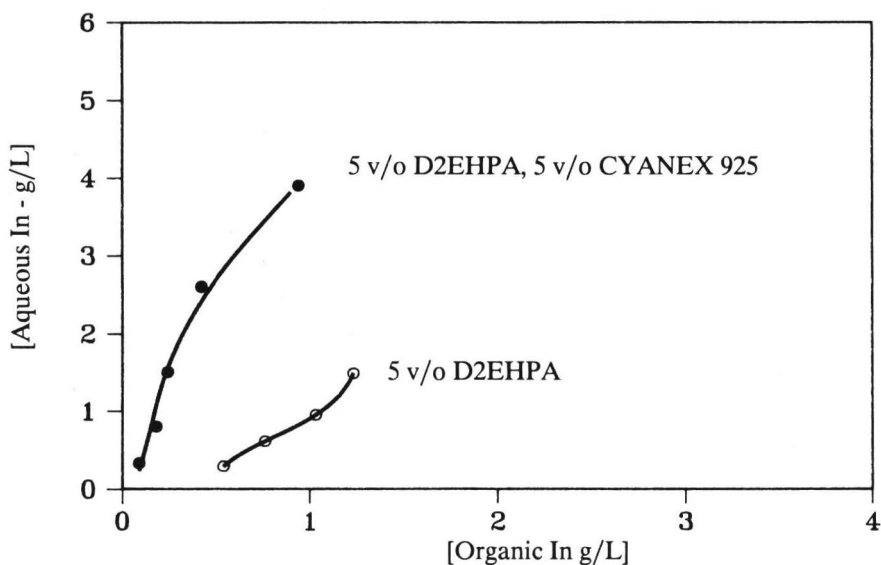


Fig. 3: Indium Stripping Isotherms Using 200 g/L H₂SO₄

The isotherms, plotted in Figure 3, indicate that indium is readily stripped from the solvent modified with 5 v/o CYANEX 925. For example, a McCabe-Thiele interpolation shows that 2 g/L In can be quantitatively stripped from the modified solvent with 200 g/L H_2SO_4 in three theoretical stages at $O/A=2$ to produce a strip liquor containing 4 g/L In. The unmodified solvent, containing 5 v/o D2EHPA, can only be stripped at lower O/A ratios. For example, one theoretical stage at $O/A=0.5$ will reduce indium in the solvent from 2 g/L to 0.5 g/L. This translates into using four times the amount of acid, producing a more dilute strip liquor containing only 0.38 g/L In and leaving 0.5 g/L of unstripped indium on the solvent which will adversely effect extraction performance on solvent recycle. Essentially equivalent results were obtained with a solvent modified with 10 v/o CYANEX 923 extractant.

Ferric Iron Stripping

The accumulation of ferric iron in a solvent containing D2EHPA can result in high viscosities, consequently poor phase disengagement rates and, eventually, solvent poisoning.

Ferric iron stripping isotherms plotted in Fig. 4 using the data in Table 3 show that the presence of CYANEX 925 extractant in the solvent produces efficient ferric iron stripping characteristics which cannot be obtained with D2EHPA alone or even when

TABLE 3

Effect of Phase Modifiers on Ferric Iron Stripping

Solvents	:	1) 5 v/o D2EHPA in Exxsol D-80 diluent loaded to 3.45 g/L Fe (3+)
		2) 5 v/o D2EHPA, 5 v/o CYANEX 925 extractant in Exxsol D-80 diluent, loaded to 2.37 g/L Fe (3+)
		3) 5 v/o D2EHPA, 15 v/o TBP in Exxsol D-80 diluent, loaded to 2.10 g/L Fe (3+)
Strip Feed	:	100 g/L H_2SO_4
Phase Contact	:	5 min at 24° C

A/O	Equilibrium Fe (3+) Concentration (g/L)					
	D2EHPA		D2EHPA + CYANEX 925 Extractant		D2EHPA + TBP	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
0.2	-	-	1.50	4.35	-	-
0.5	1.67	3.55	0.84	3.00	-	-
1	1.37	2.08	0.61	1.76	1.02	1.08
2	1.17	1.14	0	1.18	0.94	0.58
5	0.99	0.49	-	-	0.89	0.24
10	0.99	0.25	-	-	0.77	0.13
15	0.97	0.15	-	-	0.74	0.09

D2EHPA is modified with other solvating extractants, e.g. TBP. Solvents modified with 10% CYANEX 923 exhibit the same stripping characteristics as solvents modified with 5% CYANEX 925.

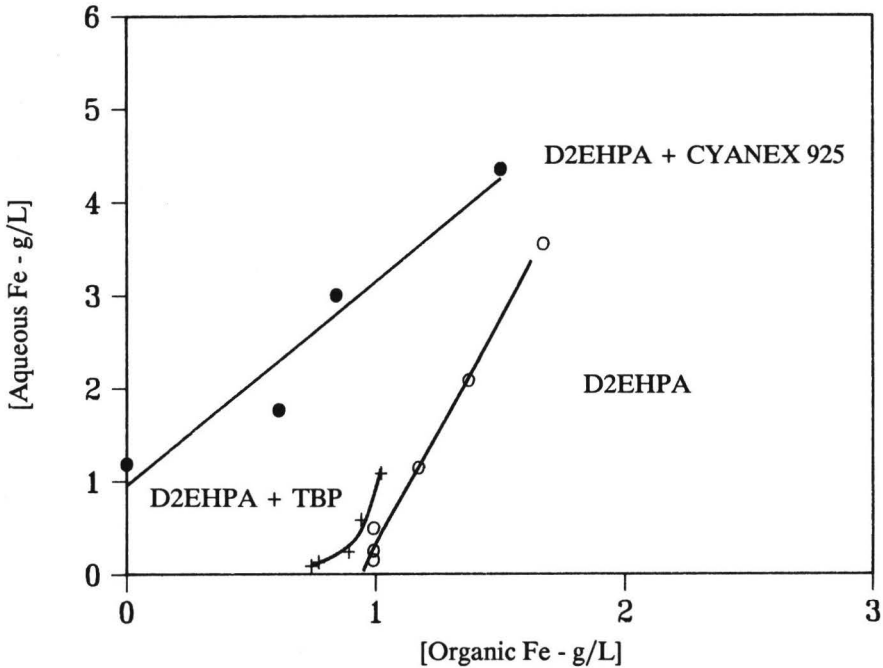


Fig. 4: Effect of Phase Modifiers on Iron [3+] Stripping

CONCLUSIONS

The conventional process for recovering indium involves solvent extraction from sulphate solution using D2EHPA. In this system, indium is strongly extracted and notoriously difficult to strip.

It has been demonstrated that adding trialkylphosphine phase modifiers to the solvent produces a synergic interaction which facilitates stripping with comparatively dilute sulphuric acid. An added benefit is that the phosphine oxide will prevent phase disengagement problems related to the accumulation of ferric iron in the solvent.

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5.4

**REAGENT DESIGN FOR THE SEPARATION OF TRANSITION AND POST
TRANSITION METAL IONS BY SOLVENT
EXTRACTION AND MEMBRANE TRANSPORT**

A. J. LEONG AND L. F. LINDOY*

Department of Chemistry and Biochemistry
James Cook University,
Townsville, 4811, Queensland, Australia.

P. A. TASKER AND D. THORP

ICI, Specialty Chemicals
Post Office Box 42, Hexagon House,
Blackley, Manchester M9 3DA. U.K.

ABSTRACT

An aim of the present studies has been to produce new mixed-donor cyclic systems which are selective for particular metal ions and to understand the reasons for such selectivity when it does occur. Emphasis in the program has been given to the recognition of and/or discrimination between ions such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), and Pb(II). The discussion has been limited to consideration of potentially pentadentate ligand systems of type (I) in which three structural parameters (namely, the macrocyclic ring size, the donor atom pattern, and the degree of ring substitution) are varied. The use of individual macrocyclic reagents in extraction and membrane transport studies is also described.

INTRODUCTION

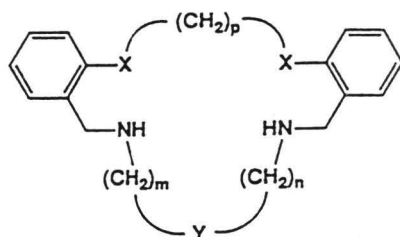
We have been concerned with developing strategies for achieving metal-ion recognition using mixed donor, macrocyclic ligands. In particular, our investigations have focussed on the design of such systems for the recognition (and/or discrimination) of ions within the following groups: Co/Ni/Cu; Zn/Cd; and Ag/Pb (Lindoy, 1987).

Although there are now many examples of the use of cyclic ligands for metal ion recognition (Lindoy, 1989), few such studies have been performed in conjunction with an integrated organic synthetic program involving both the synthesis of new cyclic ionophore types and their "tuning" in light of the results from the corresponding metal ion

complexation experiments. Thus, an important concept employed in the studies now discussed has been to investigate metal ion complexation across a matrix (or part of a matrix) of related macrocycles and to search for stability maxima at different points of the matrix; the ligand structures comprising the matrix normally bear a stepwise relationship to each other.

STRATEGIES FOR ACHIEVING METAL ION RECOGNITION

An aim of the discussion which follows is to give an overview of typical strategies employed in our studies for achieving metal ion recognition. Owing to limitations of space, the present discussion will be confined to dibenzo-substituted ring systems of type (1) (and their substituted derivatives). In our studies so far the attainment of metal ion discrimination has centered around the variation of (i) macrocyclic ring size, (ii) donor set, and/or (iii) ligand substitution. Although all three parameters would normally be varied during a particular discrimination investigation, for the present purposes it is convenient to discuss each of these approaches in turn.



(1) $X=O, NH, S$; $Y=O, NH, S$

Ring Size Variation

Two mechanisms contributing to macrocyclic ring-size discrimination have been established (Lindoy, 1989). The first type has been well investigated previously and results in maximum thermodynamic stability being achieved when there is a match between the radius of the metal ion and the cavity of the coordinated ligand (provided the ion is contained in cavity). As a consequence, the stability maxima for the complexes of two ions of different radii will often occur at different positions along a series of macrocycles exhibiting a regular gradation of ring size - especially when the ligand backbones are rigid.

The second mechanism for discrimination involving ring size variation has since been studied more recently by us (Adam *et al.*, 1988). Discrimination of this type differs from that mentioned above in that it does not necessarily depend on the match of the radius of the metal ion to the available macrocyclic cavity. Instead, it involves the occurrence of "dislocations" in the metal complexation behaviour along a series of closely related ligands. Such "dislocations" occur when the gradual change of properties along the ligand series

induces a sudden change in co-ordination for the complexes of adjacent ligands. The occurrence of dislocations at different points along a ligand series for different metal ions may form a basis for enhanced discrimination between these ions. Such behaviour may, for example, be a consequence of the build up of different steric strain along the series for the different metal ions. Several examples of dislocation discrimination have now been documented (Adam *et al.*, 1988; Adam *et al.*, 1983).

Donor Set Variation

The effect on complex stability of donor atom set variation has been well documented previously for a range of ligand types; it provides a further parameter for use in tuning macrocyclic ligand systems for metal ion discrimination. For example, the systematic variation of donor atom sets in the 17-membered macrocycles of type (**1**) has led to a system exhibiting extremely large discrimination for Ag(I) over Pb(II). The log K results obtained during this investigation are summarised in Table 1 (Adam, Baldwin, Barshall *et al.*, 1992).

TABLE 1
Effect of donor set on Ag(I)/Pb(II) discrimination^a

Ligand	Log K (Ag)	Log K (Pb)
1 , X=S, Y=S	12.4	~3.1
1 , X=S, Y=O	10.3	-
1 , X=S, Y=NH	~11.7	8.0
1 , X=O, Y=S	8.6	4.5
1 , X=O, Y=O	7.1	5.5
1 , X=O, Y=NH	8.7	8.1
1 , X=NH, Y=NH	10.3	9.4

^aLog K values at 25° (*I* = 0.1, Et₄NClO₄) in 95% MeOH.

Interaction of Ag(I) and Pb(II) with the parent 17-membered O₂N₃-donor macrocycle yielded a log K difference of less than an order of magnitude and the situation was only very slightly improved when the N₅-donor analogue was employed (even though the absolute values in this latter case are increased somewhat). Nevertheless, substitution of an ether oxygen for the NH donor in position Y (with X=O) results in enhanced discrimination for Ag(I) over Pb(II). Indeed, the log K data listed in Table 1 indicate that substitution of an N₂Y-fragment (Y=O or S) for an N₃-fragment results in a consistent lowering of the stabilities of the various Pb(II) species but has much less influence on the corresponding Ag(I) complexes. Moreover, the use of this effect coupled with the stepwise introduction

of sulfur donors results in a substantial increase in the discrimination for the "soft" Ag(I) over Pb(II). Indeed, for the final member of the series incorporating an S_3N_2 -donor set, exceptional discrimination was achieved. This ligand yielded a stability difference which is approximately 10^9 in favour of silver!

The X-ray structure of the Ag(I) complex of the macrocycle incorporating an ON_2S_2 -donor set shows that the metal has an irregular 5-coordination geometry. The macrocycle wraps around the silver in such a way that the respective donor to metal bond lengths are in each case typical of those found in a range of other silver complexes. In contrast to this "tight" 5-coordinate geometry, the X-ray structure of the Pb(II) complex of the related N_3S_2 -donor macrocycle reveals that the metal is now 7-coordinate and is bound to the five donor atoms of the macrocycle as well as to two perchlorato anions (which occupy axial positions). The macrocycle in this case adopts a flatter, more open, arrangement with the metal situated above the macrocyclic cavity. In addition, bond lengths tend to be long and clearly the macrocycle binds less strongly in this case in accordance with the results from the solution studies.

Substituent Variation

In the third approach, it has proved possible to "detune" the affinity of a particular cyclic ligand system for some (but not all) metal ions of interest by appending bulky substituent groups to the cyclic backbone. The effect of appending N-methyl and N-benzyl substituents to the parent 17-membered O_2N_3 -macrocycle of type (**1**; X=O, Y=NH) on metal ion discrimination is illustrated by the results listed in Table 2 (Adam, Baldwin, Leong *et al.*, 1992).

TABLE 2
Effect on log *K* appending N-methyl and N-benzyl substituents to the
17-membered macrocycle (**1**; X=O, Y=NH)

N-substituent	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
H	7.6	10.0	14.4	7.5	8.7	8.7	8.1
CH ₃	<3.5	<3.5	-	5.1	6.1	10.3	6.6
Benzyl	<3.5	<3.5	-	~3.5	~3.5	9.3	4.3

*Log *K* values at 25° (*I* = 0.1, Et₄NClO₄) in 95% MeOH.

The presence of N-substituents on all three nitrogen donors generally results in the formation of weaker complexes than those of the parent (unsubstituted) macrocycle. As expected, the effect increases with substituent bulk and is greatest for the bulky tribenzylated derivative. The latter yields 1:1 complexes with Co(II), Ni(II), Zn(II), Cd(II), and Pb(II)

whose log K values are all 4.3 or lower. In contrast, the log K value for the Ag(I) species is 9.3 (which is even slightly higher than that obtained for the complex of the parent ligand). Although the origins of this large selectivity for silver are still under investigation, modelling studies suggest that the macrocycle may adopt a relatively inflexible configuration in this complex thus providing an ideal cavity for this ion.

Selective detuning of the type outlined above thus represents a further potentially important means for achieving metal ion discrimination which is related (but subtly different) to the "dislocation discrimination" mechanism discussed earlier.

SOLVENT EXTRACTION AND MEMBRANE TRANSPORT

Extraction and membrane transport experiments involving Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Ag(I) and a selection of the mixed donor macrocycles are now complete. Quite substantial discrimination (and separation) of particular metals has been achieved during these studies but only a limited selection of these results will be presented here. Other results have been presented elsewhere in preliminary form (Lindoy, 1989).

As was expected, initial experiments indicated that there is a tendency for these amine-containing macrocycles to be lost from the organic phase (chloroform) to the aqueous phase(s) under certain conditions. Such behaviour is associated with loss of the ionophore as either its metal complex or as its protonated form. Because bleeding involves only charged species, it was reasoned that a lipophilic counter-ion introduced into the organic phase might impart a greater degree of lipophilicity to these charged species. Accordingly, transport experiments were undertaken in which palmitic (hexadecanoic) acid was added to the organic phase. As anticipated, the addition of this long-chain fatty acid greatly enhances the retention of the ionophore in the organic phase and results in a considerable increase in the efficiency of transport while maintaining metal ion selectivity in most instances.

We have strong evidence that the amine-containing macrocycles form host-guest adducts with one or two carboxylic acid moieties and the nature of the resulting assemblies has been studied in some detail (Adam, Antolovich *et al.*, unpublished work). The formation of such species in deuterio chloroform can be readily followed using an nmr titration procedure. For example, titration of the parent 17-membered macrocycle (**1**; X=O, Y=NH) in a nmr tube with hexadecanoic acid results in a clear inflection in the induced chemical shifts at a 2:1 molar ratio (hexadecanoic acid:macrocycle) for the methylene protons adjacent to the nitrogen donors. Moreover, for this and a number of other systems, such host-guest species have been isolated and characterised in the solid state; characterisation has included X-ray

and neutron diffraction structural determinations for individual adducts. The factors influencing the observed stoichiometries of the host-guest complexes have been investigated and were found to be strongly influenced by the relative basicities of the amine donors present in the respective macrocycles.

As well as adding to the lipophilicity of individual systems, particular host-guest species of the above type may be considered to act as "pre-organised assemblies" for metal-ion solvent extraction. Clearly, such pre-organisation has implications for metal-ion binding (and hence corresponding metal-ion extraction) since the components of the co-ordination sphere of the metal ion are pre-assembled for complex formation - an effect we refer to as the *pre-assembly effect*.

Aspects of the extraction of Cu(II) using (1, X=O, Y=NH) in the presence of palmitic acid are illustrated in Figure 1(a) and (b). Under the relatively low concentration of macrocycle employed, a 1:4 ratio of macrocycle to palmitic acid was necessary to optimise Cu(II) extraction. The 1:4 ratio (rather than the 1:2 ratio observed for the adduct stoichiometry in the nmr titration experiments and by X-ray diffraction in the solid state) is undoubtedly an equilibrium effect reflecting the significantly lower concentrations employed for the extraction experiments.

Extraction experiments involving the range of metal ions mentioned earlier and selected macrocycles of type (1) have been performed under a number of different experimental conditions (including solvent variation). For example, the extraction of Co(II), Ni(II), and Cu(II) by macrocycle (1, X=O, Y=NH) and palmitic acid (1:4) into chloroform is pH dependent and follows the expected order Cu(II) > Ni(II) > Co(II).

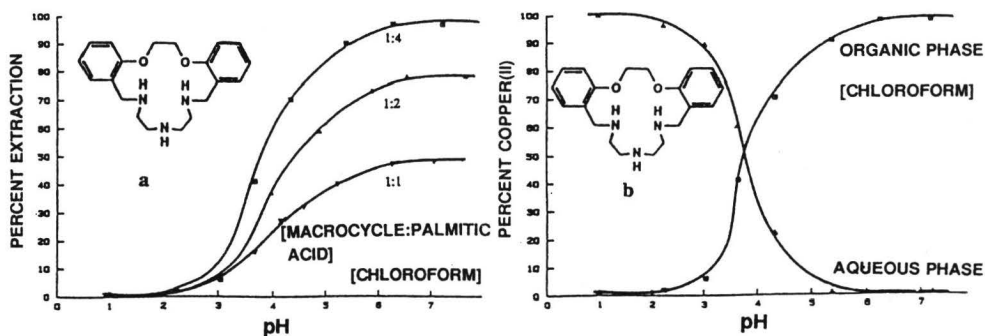


Fig. 1 Extraction of a solution of Cu(II) nitrate (0.01 mol dm^{-3}) into chloroform containing the 17-membered macrocycle (1, X=O, Y=NH) (0.01 mol dm^{-3}) in the presence of (a) various concentrations of palmitic acid and (b) palmitic acid at 0.04 mol dm^{-3} .

Metal ion transport across a chloroform membrane was studied using a cell of the type shown in Figure 2. The aqueous source phase, containing the metal ion(s) at 0.01 mol dm^{-3} (initial concentration), was buffered at pH 5.0 ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) while the receiving phase was buffered at pH 3.0. The membrane phase contained the ligand at $10^{-3} \text{ mol dm}^{-3}$ and hexadecanoic acid at $4 \times 10^{-3} \text{ mol dm}^{-3}$. The temperature in the cell was maintained at 25° and each run lasted 24 hours. To provide a background for the above investigations, parallel solvent extraction studies were also undertaken in which similar conditions were employed for the source and organic phases.

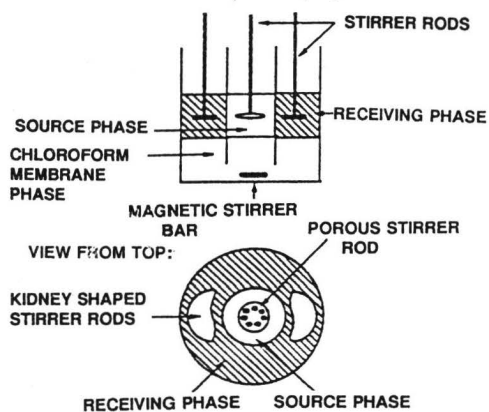


Fig. 2 The transport cell

The results of transport experiments, performed under the above conditions, are illustrated in Figure 3. The log K values for the corresponding metal-ligand systems have already been presented in Table 2. For the parent 17-membered macrocycle (**1**; $\text{X}=\text{O}$, $\text{Y}=\text{NH}$), selective transport of $\text{Cu}(\text{II})$ in the presence of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ was achieved. Although favourable thermodynamics of metal

complex formation may not be the only factor influencing selectivity of metal transport, for the macrocycle **1**, $\text{X}=\text{O}$, $\text{Y}=\text{NH}$, the complex stability is clearly highest for the $\text{Cu}(\text{II})$ ion (see Table 2). Unfortunately, in this case, owing to precipitation it was not possible to include $\text{Ag}(\text{I})$ in the mixture of metals present in the source phase.

The corresponding trimethylated and tribenzylated ligand results are also illustrated in Figure 3. Under the conditions employed, the transport results for these derivatives also parallel

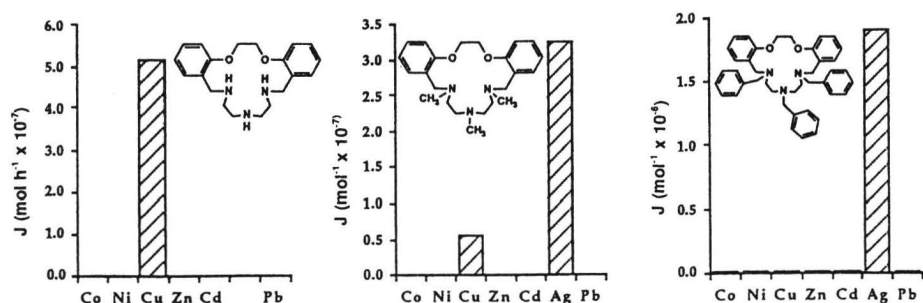


Fig. 3 Competitive mixed metal transport results for the 17-membered macrocycle (**1**; $\text{X}=\text{O}$, $\text{Y}=\text{NH}$) and its N-substituted derivatives.

the respective thermodynamic stabilities for complex formation (Table 2) - with the previously mentioned extraordinary selectivity of the latter ligand for Ag(I) being maintained.

Finally, while the work presented in this paper has largely been of a fundamental nature, it is our belief that the strategies discussed should serve as a guide for the rational development of new practical reagents for metal ion separation in the future.

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5.5

EXTRACTION OF $ZnSO_4$ BY ACID-BASE COUPLE EXTRACTANTS

Eyal Bressler * and Aharon M. Eyal **

* Department of Biological Chemistry, A. Silberman Institute of Life Sciences,

** Casali Institute of Applied Chemistry, Graduate School of Science and Technology
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

ABSTRACT

Acid-base couple (ABC) extractants are composed of a water immiscible amine and an organic acid in a diluent. They provide for reversible extraction of salts and mineral acids. The simplest mechanism for metal salt extraction is $M_n^{m+}X_m^{n-} (aq) + R_pNH_4-pA (org) \rightleftharpoons MA_m (org) + (R_pNH_4-p)X (org)$, where A, M, R, and X stand for an organic acid, a metal ion, an amine residue and an anion, respectively; aq. and org. refer to the aqueous and organic phases. It applies to the case where the metal ion does not form complexes with the anions in the system. Unlike the case of extraction by a liquid cation exchanger, a proton is not released. A neutral salt molecule is extracted. The amine binds the released acid and thereby facilitates the extraction. The extraction of zinc sulfate by various ABC extractants was studied. These results were analyzed for the effect of the properties of the amine and the organic acid in the organic phase. A method for the determination of pH of half-neutralization value, $pH_{(HN)}$, was applied. In this technique, the correlation between the acid-base properties of the extractants in the organic phase and their ability to extract the metal salt was obtained. These results provide for better understanding of the extraction mechanisms, facilitate the prediction of the extraction properties and allow one to use "tailor-made" extractants which fit best to the specific conditions of the chosen extraction system.

INTRODUCTION

The industries of hydrometallurgy, fertilizers, water treatment and others contain several liquid-liquid extraction operations, in which liquid ion-exchangers are the most common extractants. These extractants are traditionally divided into two main families: a. cationic liquid exchangers (such as carboxylic, phosphoric or sulfuric acids) and b. anionic liquid exchangers (amine salts, for example).

The action of anionic and cationic liquid exchangers is accompanied by the co-production of acids in stoichiometric amounts by two different mechanisms: a) the dissociation of a metal salt and b) proton release by the organic acid during the extraction. The higher the concentration of the acid formed during the extraction process, the lower is the efficiency of the extraction. The build up of the by-product increases the cost of the process because the aqueous phase should be further neutralized by the supplement of additional base or acid. Similarly, the extraction of metal salts from acidic solutions suffers from the same drawback. In the extraction stage, the feed solution should be neutralized. Further addition of acid or base is required in the back-extraction stage.

During the 1960's, Deptula (1967) and Grinstead (1969,1970) have introduced a new family of extractants which combines acidic-anionic liquid exchangers with basic-cationic ones in a diluent. Both types of liquid-exchangers are water-immiscible. The characteristics of the new family of extractants provide for extraction processes which lack the above discussed drawbacks. More data concerning the extraction of salts and acids by this extractant type have been added by other groups: Hadajiev (1988), Kholkin (1982), Kress (1989), Rice (1990) and Sato (1982) for example.

Acid-base couple (ABC) extractants present some useful advantages: a) a lower sensitivity to the acidity in the aqueous phase (as suggested by Nishimura 1976); b) a relatively high efficiency in the extraction of alkali and alkali-earth halides was mentioned by Gao (1988), Hanson (1982) and Hernandez (1981); c) the ability to participate in reversible extraction, which makes possible the recovery of extracted metal salts from the extractant by simple back-extraction with water. This leads to significant cuts in acid and base consumption as compared with acidic or basic single extractants; d) the suitability for the extraction of both acids and metal salts by a solution of a single extractant composition (Eyal 1990) and e) the multicomponent mixture of extractants with opposite properties which allows for a relatively high number of degrees of freedom in the adjustment of the extractant composition to the required separation system.

This paper will focus on the extraction of zinc sulfate. Several properties which determine its extraction by various ABC extractants will be presented and some extraction mechanisms will be discussed. A method to determinate the total acidity-basicity of the couple will be used. To conclude, a few correlations between the extraction of ZnSO_4 and the $\text{pH}_{(\text{HN})}$ value of the ABC extractant will be made.

MATERIALS AND METHODS

Materials

The diluent and most extractants were of technical grade. Other reagents were of the best commercially available grade. Unless otherwise indicated, all chemicals were used as received. JMT and AMBE were purchased from Rohm and Haas, TEHA and LA from Fluka, TCA and

MTCA from Henkel, DEHPA from Sigma, DN from King Industries, ABL from Miles Yeda (Israel) and zinc salts were obtained from Merck. The diluent used in all experiments was kerosene, produced by Paz (Israel), which contained up to 3-5% aromatic compounds.

Methods

The average molecular weights of the technical grade extractants were measured by titration with acid or base (ConvotTM standard solutions, by BDH), using a mixed-indicator (0.05% phenolphthalein, 23 mg Methyl-Red, 67 mg Bromo Cresol-Green and 10 mg Cresol-Purple in 100 ml absolute ethanol). ABC extractants were prepared by mixing the required organic acid and amine in the diluent to give a final concentration of 0.5 mol/kg of each ingredient. All ABC extractants which contained MTCA or DN were washed several times before use, in order to avoid contamination by traces of chloride or H₂SO₄, respectively. The assessment of the concentration of the above mentioned couples in the aqueous phases after equilibration with the extractant solution was performed by either pH determination, or by measurement of its chloride concentration by AgNO₃ titration, using potassium chromate in isopropanol as the indicator reagent. All extraction experiments were performed under "limiting-conditions", where the initial concentration of ZnSO₄ in the aqueous phase was near saturation (2.5 mol/kg). The solvent (5 g) and aqueous (50 g) phases were equilibrated in 250 ml Erlenmeyer flasks by shaking with a mechanical shaker for 30 min. at ambient temperature. After phase separation was obtained, usually by centrifugation, the aqueous phase was filtered through a Whatman paper-filter. The equilibrium aqueous phase salt concentration and pH were measured. The resulting organic phases were equilibrated with equal weight of 10% HNO₃ solution. The zinc salt's concentration was determined by titration with EDTA, using Eriochrome Black-T (0.2 g), triethanol amine (15 g) and absolute ethanol (5 g) as an indicator solution. An ammonium chloride/ammonia buffer was used. The reported results are the average of two or three such measurements. The pH of half-neutralization (pH_(HN) value) was initially described by Grinstead in 1966. It serves as a tool for the determination of amines' pK_a values in the organic phase, and is implemented here for the detection of the basicity (or acidity, by using pOH_(HN) value) of the ABC extractants and of single extractants. pH_(HN) was determined by the equilibration of 20 g of 0.5 mol/kg extractant with 50 g of aqueous solution containing 0.1 M HCl (or NaOH) and 1 M NaCl, using the procedure described above.

RESULTS AND DISCUSSION

The extraction of ZnSO_4 by ABC extractants which are composed of several amines and organic acids is described in Figure 1.

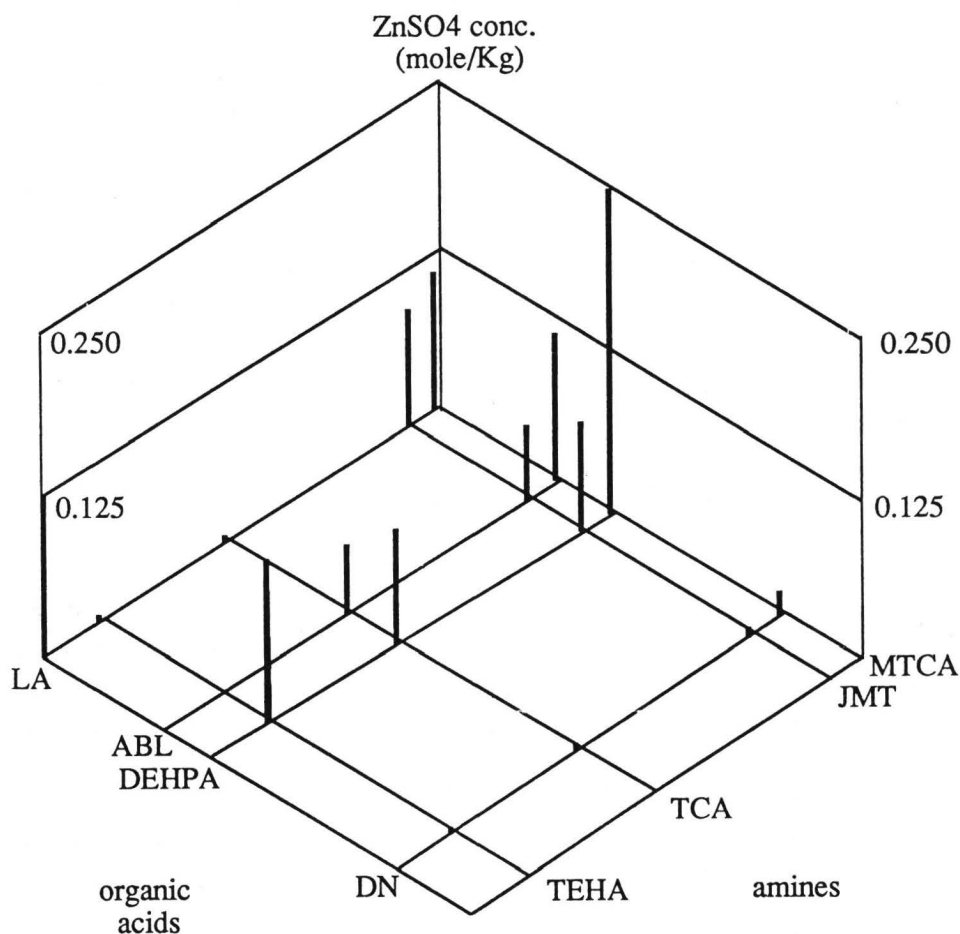


Figure 1. ZnSO_4 extraction by several acid-base couple extractants. The Z axis of the three-dimensional diagram represents the ZnSO_4 concentration (mole/Kg) in the organic phase equilibrated with an aqueous solution at ambient temperature. The salt's initial concentration in the aqueous phase is 2.5 mole/Kg. The X and Y axes represent increasing $\text{pH}(\text{HN})$ and $\text{pOH}(\text{HN})$ values of amines and organic acids, respectively.

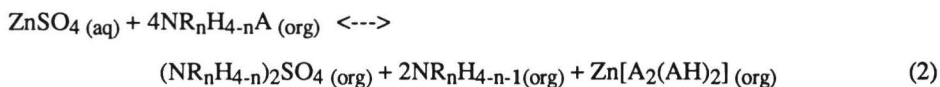
Maximum extraction is obtained by using amines-DEHPA couple extractants. A concentration of 0.25 mol/kg ZnSO_4 is found in the equilibrated organic phase. Under the conditions

described above, no significant extraction of ZnSO_4 was observed when amines are used as single extractants. Thus, it is possible to assume that the extraction mechanism which fits best under these conditions, is the one proposed by Grinstead (1970), and Davis (1970) and was later approved by others.



The above equation describes an extraction mechanism in which the organic acid serves as a cation-exchanger. The organic acid, which was initially bound to the amine and proton, binds during the extraction process to the Zn^{++} ion. The amine binds the released SO_4^{2-} anion.

The extraction by amines-LA couple extractants yields a maximum concentration of 0.125 mol/kg ZnSO_4 in the organic phase, although ZnSO_4 is in excess in the aqueous solution, as compared with the extractant. Thus, the suggested mechanism is:



The mechanism described in equation 2 resembles the extraction mechanism of $\text{Co}(\text{NO}_3)_2$ by alkyl phosphoric acid, as has been suggested by Teramoto (1988) and by others. Here, the organic acid acts partially as an ion-exchanger, exchanging the amine cation for the metal cation.

It can be concluded from the above equation that the organic acid has the role of a cation exchanger in systems which involve ZnSO_4 and ABC extractants (Eyal (1990)). A similar role is played by the organic acid in systems which involve a single extractant (Marcus (1969)). In the mechanism described by Eq. 1, the metal ion reacts with the organic acid in a 1:2 ratio. In mechanism 2, the stoichiometric ratio is 1:4. Two molecules of organic acid actually participate in the ion-exchange mechanism, as in mechanism #1, and the other two act as complexants to the metal ion.

In both mechanisms, the amine exchanges the organic acid for the sulfate anion. Mechanism #2 is not very sensitive to the nature of the amine moiety, as long as it is a strong base, and its couple is a weak organic acid. Hence, the concentration of the extracted ZnSO_4 is the same when extracted with the couples JMT-LA and MTCA-LA. This behavior is due to the complexing ability of the weak organic acid. It is capable of forming a stable complex with the metal cation, and thus its extraction mechanism is less dependent upon its ion-exchanging ability. In an opposite manner, the extraction of ZnSO_4 through mechanism #1 yields a much higher ZnSO_4 concentration when MTCA-DEHPA is used as compared with JMT-DEHPA.

In liquid-liquid extraction systems which contain a single extractant, the increasing strength of the organic acid results in a higher concentration of the extracted salt. A decrease in the pH of the aqueous phase is due to the release of protons in exchange for the metal-cations. Thus, protons from the aqueous solution compete with the metal cation for the carboxylic moiety of the organic acid, and the extraction decreases.

The influence of pH lowering on the extraction yield decreases with increasing strength of the organic acid because the acid has a lower affinity for protons and competes to a lesser extent with the zinc cation. There is, however, an advantage in working with weak organic acids, because of the reversible nature of the extraction process.

LA, as a single extractant, extracts a very low concentration of ZnSO_4 . However, in liquid-liquid extraction systems which contain coupled extractants (Fig. 1), the presence of the amine in the organic phase enables the extraction process to be carried out also by weak organic acids, such as LA. When compared to DEHPA, which is a stronger acid than LA, extensive extraction is obtained (similar to the case of single extractants). ABC extractants that contain strong organic acids (such as DN), yield only slight ZnSO_4 extraction. This is due to a relatively strong binding between the organic acid and the amine in the organic phase.

As a rule of thumb, one can say that the extraction of ZnSO_4 is greatest with ABC extractants of a lower organic acid acidity and of a higher basicity of the amine component.

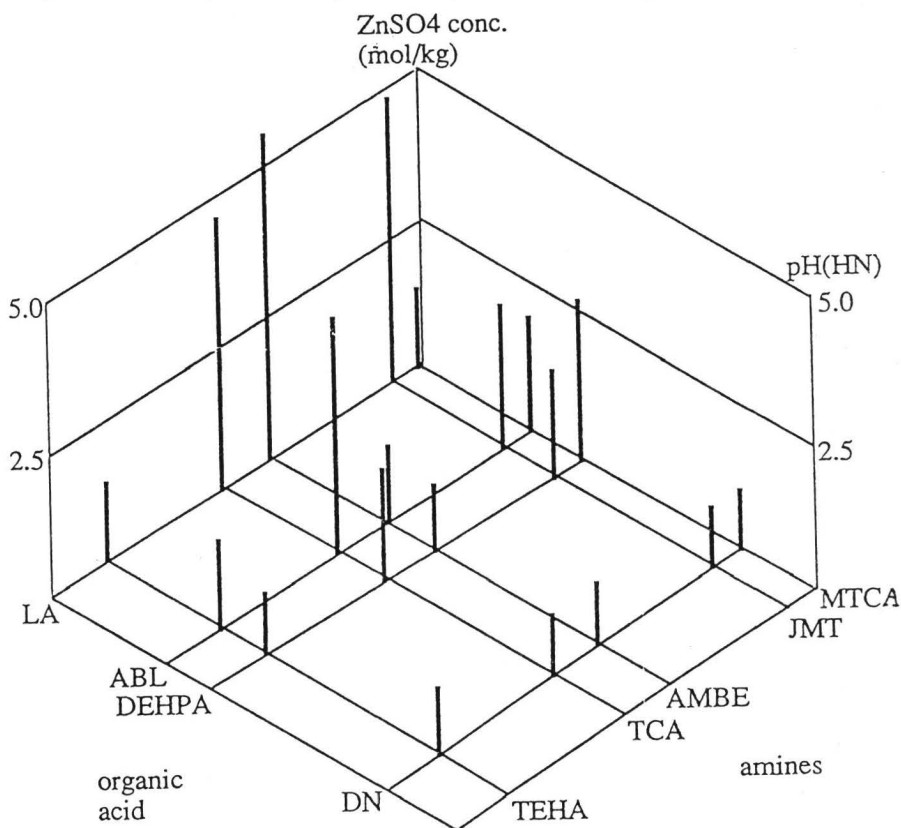


Figure 2. $\text{pH}(\text{HN})$ values of several acid-base couple extractants (on Z axis) The X and Y axes are arranged according to increasing $\text{pH}(\text{HN})$ and $\text{pOH}(\text{HN})$ values of 5 different amines and 4 organic acids are presented.

The strength of the amine has opposite effects on the extraction. On the one hand, a stronger amine basicity enables a stronger binding to the organic acid and lowers the extraction percentages. On the other hand, its ability to bind the proton which is released to the aqueous phase rises, and hence, increases the extraction. The sum of these opposing tendencies is presented in Fig. 2. ABC extractants which are composed of an organic acid of a relatively low acidity, and an amine of medium basicity, have maximum $\text{pH}_{(\text{HN})}$ values.

From the comparison of these two curves, especially in systems of ABC extractants which contain stronger organic-acids, it can be seen that there is a close connection between the $\text{pH}_{(\text{HN})}$ value of the ABC extractant and its ability to extract ZnSO_4 to the organic phase.

Some interesting properties of the $\text{pH}_{(\text{HN})}$ index appear from the comparison of its variation with ZnSO_4 extraction. Due to the similar trends which appear in both systems it is reasonable to say that the $\text{pH}_{(\text{HN})}$ value is useful for the achievement of a better understanding of the different role that each of the ABC extractant components plays during the process of extraction.

Comparing the $\text{pH}_{(\text{HN})}$ or $\text{pOH}_{(\text{HN})}$ values of each component and the total $\text{pH}_{(\text{HN})}$ value of the couple extractants will shed light on the fragile balance of the forces acting in solution between the various components during the extraction and the back-extraction processes. Thus, indirectly, the $\text{pH}_{(\text{HN})}$ index serves as a convenient tool for the assessment of the extraction mechanism.

It is evident that the determination of $\text{pH}_{(\text{HN})}$ is very useful for the tailoring of an ABC extractant composition for the desired extraction systems. In further, yet unpublished, experiments, we extend the scope of research to the extraction of transition-metal sulfates and for acidic aqueous solutions containing zinc chloride, by several ABC extractants.

GLOSSARY

A	organic acid
ABC	acid-base couple extractants
ABL	α -bromolauric acid
AMBE	AMBERLITE LA-2 (secondary amine)
aq.	aqueous phase
DEHPA	di-(2-ethylhexyl) phosphoric acid
DN	dinonylnaphthalene sulfonic acid
JMT	Primene JM-T (primary amine)
LA	lauric acid
MTCA	methyl tricapryl amine (ALQUAT 336)
org.	organic phase
$\text{pH}_{(\text{HN})}$	pH of half-neutralization
$\text{pOH}_{(\text{HN})}$	pOH of half-neutralization
TCA	tricapryl amine (ALAMINE 336)
TEHA	tri-(2-ethylhexyl) amine

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5.6

**GENERAL PROPERTIES OF BIS(2,4,4-TRIMETHYLPENTYL)
DITHIOPHOSPHINIC ACID (CYANEX 301®) IN ACIDIC LIQUID-LIQUID
EXTRACTION SYSTEMS**

S. FACON, M. AVILA RODRIGUEZ*, G. COTE and D. BAUER

Laboratoire de Chimie Analytique (Unité associée au C.N.R.S n°437),

E.S.P.C.I., 10, rue Vauquelin, 75005 Paris, France.

* University of Guanajuato, I.I.C., L. Retana No.5, 36000 Guanajuato, GTO, Mexico.

ABSTRACT

After presentation of some general properties of Cyanex 301®, the extraction properties of the latter are reported both in hydrochloric acid and in sulphuric acid media. The extraction of Ag, As, Au, Bi, Cd, Co, Cu, Cr, Fe, In, Ni, Pd, Pb, Pt, Sb, Sn and Zn has been more particularly investigated in hydrochloric acid media, while the extraction of As, Cu, Cd, Fe, In and Zn has been studied from aqueous sulphuric acid solutions. It is shown that some metal species create specific difficulties. For instance, copper(II) cannot be easily stripped, whereas cobalt(II) chelates are oxidized by atmospheric oxygen in the bulk of the organic phases. Possible solutions are discussed to overcome such problems. Finally, the long term stability of Cyanex 301® against hydrolysis is discussed in the conditions of extraction and stripping of the various metal species.

INTRODUCTION

Over the last three decades, lipophilic dithiophosphoric acids have attracted great attention for the solvent extraction of metal ions (Cote, 1989a). However, in spite of their fascinating properties, the use of these compounds has always been limited by their tendency to be susceptible to hydrolysis, especially at high temperatures (e.g. 50°C) (Cote, 1984, 1989a). Recently, it has been shown that the dialkyldithiophosphinic acids such as bis(2,4,4-trimethylpentyl) dithiophosphinic acid are significantly more resistant towards decomposition by hydrolysis than their phosphoro analogues (Rickelton, 1990). Bis(2,4,4-trimethylpentyl) dithiophosphinic acid is now commercially available as Cyanex 301®. Originally, Cyanex 301® was developed for the selective extraction of zinc from effluent streams containing calcium, such as those generated in the manufacture of rayon by the viscose process (Rickelton, 1988, 1990). Apart from some basic papers (Rickelton, 1988, 1990, 1992; Saito, 1989; Facon, 1991; Avila Rodriguez, 1992; Sole, 1992; Belfer, 1992) little information

concerning the extraction behaviour of Cyanex 301® is presently available. However, a typical feature of Cyanex 301® is its ability to extract many metal cations from highly acidic media. As a part of our ongoing examination of the properties of the organothiophosphorus reagents, the present work deals with the extraction of various metal ions from hydrochloric acid or sulphuric acid solutions with Cyanex 301®. In the discussion, special attention is paid to the behaviours of cobalt and copper which create some specific difficulties. Some general physico-chemical properties of bis(2,4,4-trimethylpentyl) dithiophosphinic acid such as its dimerization ability are also discussed.

EXPERIMENTAL

Reagents : Cyanex 301® which contained 85% (in weight) of bis(2,4,4-trimethylpentyl) dithiophosphinic acid was kindly supplied by the American Cyanamid Company and used as delivered. The Cyanex 301® concentrations given throughout the text are actually those of bis(2,4,4-trimethylpentyl) dithiophosphinic acid. Unless otherwise stated kerosene (Fluka) containing n-decanol (Aldrich) [10%v/v of final organic solution] was used as a diluent. All the other reagents were analytical grade.

Procedure and apparatus : The extraction and stripping experiments were carried out at 20 ± 2 °C by shaking the mixture of aqueous and organic solutions. After the settling and separation of the two phases, the various metals in the aqueous phase were determined by Inductively Coupled Plasma Atomic Emission Spectrometry with an ICP 1500 Plasma Therm Inc. equipment. The other spectroscopic instruments were a HP 8451A Diode Array Spectrophotometer for UV-visible spectrometry and a Brüker AM250 instrument for ^{31}P -NMR spectroscopy.

RESULTS AND DISCUSSION

General properties of Cyanex 301®

The chemical structure of bis(2,4,4-trimethylpentyl) dithiophosphinic acid (denoted R_2PSSH) which is the main component of Cyanex 301® has been given by various authors and is not recalled here (Rickelton, 1988, 1990, 1992; Facon, 1991; Sole, 1992). The aqueous pK_a of bis(2,4,4-trimethylpentyl) dithiophosphinic acid has been reported to be equal to 2.6 (Rickelton, 1990, 1992; Sole, 1992). We point out that bis(2,4,4-trimethylpentyl) dithiophosphinic acid has no tendency to protonate and thus does not extract mineral acids even from highly acidic (e.g. 6 M HCl) aqueous solutions (Facon, 1991). Cyanex 301® as delivered by the supplier contained three major impurities identified as R_2PSOCH_3 , $\text{R}_2\text{PS}_2\text{CH}_3$ and R_3PS by CG-MS analysis (Sole, 1992). In the proton decoupled ^{31}P -NMR

spectrum of Cyanex 301® in CDCl_3 , bis(2,4,4-trimethylpentyl) dithiophosphinic acid gives rise to two signals at 67.0 and 67.1 ppm, respectively (all chemical shifts refer to 85% H_3PO_4 as an external standard). According to Sole et al. (1992), these two signals can be attributed to the monomeric (67.1 ppm) and dimeric (67.0 ppm) forms of R_2PSSH . It is of interest that dithiophosphinic acids have already been reported to form cyclic dimers through $\text{SH}\cdots\text{S}$ bonds (Pogorelgi, 1974). Such an assignment suggests that the monomeric and dimeric forms of R_2PSSH coexist in solution both in appreciable quantities and thus, that the value of the dimerization constant (K_d) is as low as expected for these kinds of compounds. As the two peaks have about the same area, K_d can be roughly estimated to be equal to 4 ($\text{mol}^{-1}\cdot\text{L}$) in CDCl_3 which is low, compared for instance to $K_d = 10^{4.5}$ for bis(2-ethylhexyl) phosphoric acid (DEHPA) in hexane (Sella, 1988). However, it is surprising that the relative areas of the two peaks at 67.0 and 67.1 ppm are not significantly modified when deuterated methanol (which tends to inhibit the self-association of R_2PSSH) is added to the organic solution or when the latter is diluted by a factor of 10 by addition of CDCl_3 . Thus the two peaks observed at 67.0 and 67.1 ppm in the spectrum of Cyanex 301® in CDCl_3 may not be due to the monomeric and dimeric forms of R_2PSSH but rather to its diastereoisomers as a result of the presence of one asymmetrical carbon in each of its two hydrocarbon chains. Although further investigation is necessary, it is likely that bis(2,4,4-trimethylpentyl) dithiophosphinic acid is mainly monomeric in the organic diluents used in solvent extraction, especially in the presence of modifiers such as long chain alcohols (e.g., n-decanol).

Extraction properties.

Figures 1 and 2 show the percentage of extraction of various metal species by Cyanex 301® after overnight equilibration (about 15 h, but in most cases equilibrium was reached within a few minutes) as a function of aqueous HCl concentration. Figure 3 also gives the percentage of extraction of various metals, but as a function of aqueous H_2SO_4 concentration.

Comparison of Figures 1, 2 and 3 shows that Cyanex 301® behaves differently in concentrated hydrochloric acid and sulphuric acid media, as far as the extraction of metal species is concerned. For instance, indium(III) is efficiently extracted by Cyanex 301® at any concentration of sulphuric acid in the range of 0 to 8 M. Conversely, the yield of indium extraction sharply decreases as the concentration of hydrochloric acid exceeds about 5 M. Such a difference between hydrochloric acid and sulphuric acid media is mainly as a result of the high complexing power of chloride ions and the poor complexing power of hydrogenosulphate ions (Avila Rodriguez, 1992). Owing to such a difference, Cyanex 301® is a much more selective reagent in hydrochloric acid media than in sulphuric acid media. Thus, when Cyanex 301® is used in sulphuric acid media where it has a great affinity for many metal ions, a reasonable degree of selectivity can be achieved by performing a selective stripping in

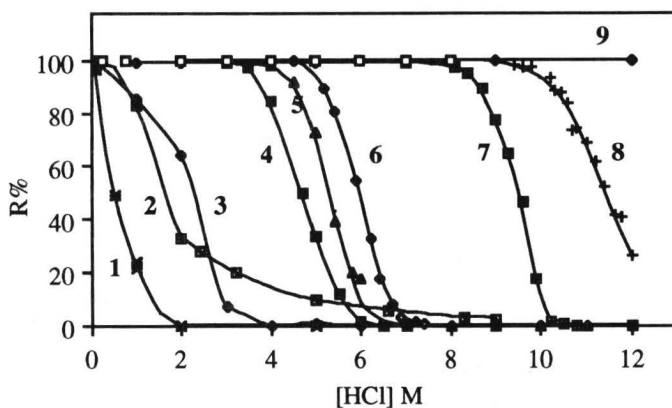


Fig. 1 Percentage of extraction of various metal species (considered separately) after 15 h equilibration as a function of aqueous HCl concentration. Organic phase : 0.2 M Cyanex 301®, phase ratio = 1. (1) Co(II); (2) Ni(II); (3) Zn(II); (4) Cd(II); (5) Pb(II); (6) In(III); (7) Bi(III); (8) Sb(III); (9) Cu(II), Pd(II), Ag(I), Au(III) and As(III) (precipitation of As compound was observed above 10 M HCl).

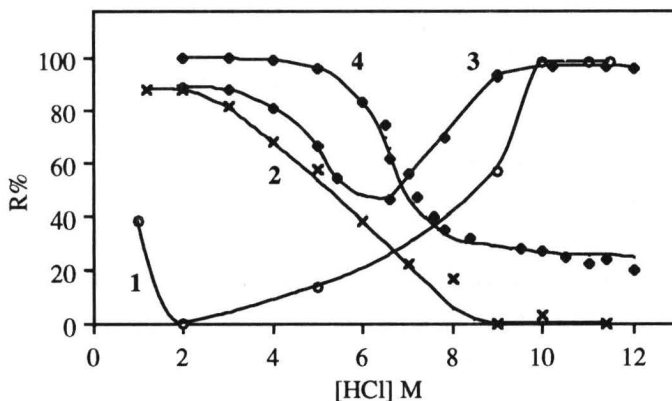


Fig. 2 Percentage of extraction of various metal species (considered separately) after 15 h equilibration as a function of aqueous HCl concentration. Organic phase : 0.2 M Cyanex 301®, phase ratio = 1. (1) Pt(IV); (2) Cr(VI); (3) Fe(III); (4) Sn(IV).

hydrochloric acid solutions of appropriate concentration. For instance, Cyanex 301® has recently been proposed for the recovery of indium from flue dust leaching solutions which typically contain a mixture of hydrochloric acid (typically 0.5 to 1 M) and sulphuric acid (2 to 4 M) (Avila Rodriguez, 1992). Most of the metal species present in such mixed solutions (i.e., As(III), Cd(II), Cu(II), Fe(III)) are co-extracted with In(III), but In(III) can be isolated during the stripping step on the condition that it is performed in HCl media. For Pb(II), Sn(IV),

Bi(III), Sb(III) and In(III), the extracted species from HCl solutions have been identified as PbL_2 , $SnCl_2L_2$, BiL_3 , SbL_3 and InL_3 , respectively, where L denotes the conjugated base of bis (2,4,4-trimethylpentyl) dithiophosphinic acid (HL) (Facon, 1991; Avila Rodriguez, 1992).

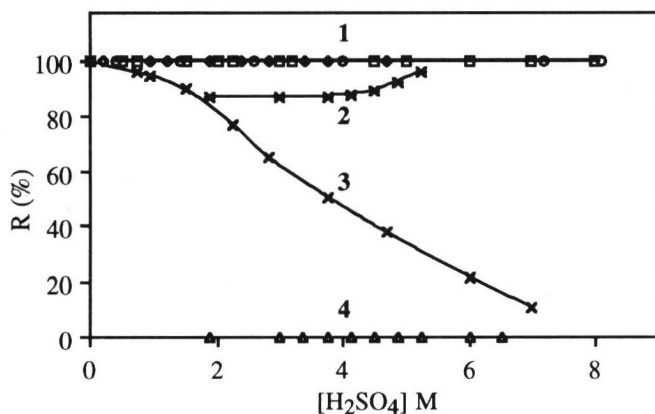


Fig. 3 Percentage of extraction of various metal species (considered separately) after 15 h equilibration as a function of aqueous H_2SO_4 concentration.

Organic phase : 0.2 M Cyanex 301®, phase ratio = 1. (1) In(III), Cd(II), Cu(II) and As(III) [the extraction of As was studied only up to 6 M H_2SO_4]; (2) Fe(III); (3) Zn(II); (4) Fe(II).

Among the particularities which appear in Figure 2, it is of interest that curve 3 corresponding to Fe(III) has a surprising shape. This is due to the existence of two different extraction mechanisms depending on the hydrochloric acid concentration. Up to about 6 M HCl, Fe(III) is extracted by formation of a chelate with the Cyanex 301® whereas above 6 M HCl, Fe(III) is mainly extracted by the mixture of kerosene and n-decanol itself, according to a solvation mechanism (the extraction occurs even in the absence of Cyanex 301®). Similar phenomena occur for the extraction of Sn(IV). Indeed, curve 4 corresponding to Sn(IV) exhibits a plateau region above 9 M HCl. Such a plateau region corresponds to an extraction yield of about 25% and is the result of the direct extraction of Sn(IV) by the mixture of kerosene and n-decanol. It is also likely that platinum(IV) is extracted according to a solvation mechanism at high HCl concentration. Examination of curve 9 in Figure 1 also shows that some elements such as Pd(II), Cu(II), Ag(I), Au(III), etc. cannot be stripped from the organic Cyanex 301® solution merely by using a concentrated solution of HCl (or H_2SO_4). This problem is further discussed below in the case of copper as this element is often present, at least as an impurity, in the aqueous solutions treated by solvent extraction.

From a kinetic point of view, there are some important differences between hydrochloric acid and sulphuric acid media. Here again, indium(III) is a relevant example. Indeed, as shown in Figure 4 the extraction of indium(III) by Cyanex 301® from sulphuric acid is slow ($t_{1/2} = 60$

min), but becomes rapid ($t_{1/2} < 1$ min) when hydrochloric acid is added to the solution, even at low concentrations.

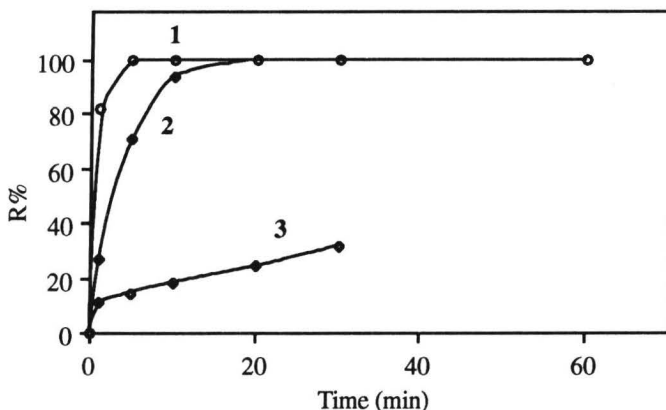


Fig. 4 Percentage of extraction of indium(III) (initially 10^{-2} M) by 0.2 M Cyanex 301® as a function of time. Phase ratio = 1; aqueous phase : (1) 1 M HCl in 5.2 M H_2SO_4 ; (2) 10^{-2} M HCl in 5.2 M H_2SO_4 ; (3) 5.2 M H_2SO_4 .

Such an enhancement is typically a result of the formation of asymmetrical indium(III) aquochlorocomplexes which are more labile than the aquocomplex $In(H_2O)_6^{3+}$ because of the "trans effect" of chloride ions (Al-Bazi, 1986; Cote, 1989b). We also point out that the extraction of nickel(II) is slow, especially above 1 M HCl. Thus, curve 2 in Figure 1 which has been obtained after 15 hours mixing does not correspond to the equilibrium state. For most of the other elements, extraction by Cyanex 301® is rapid ($t_{1/2} < 1$ min) in HCl media.

Specific behaviour of cobalt(II) chelates, stripping of copper and long term stability of Cyanex 301®

Behaviour of cobalt(II)

As shown in Figure 1, cobalt(II) is not extracted by Cyanex 301® from highly acidic solutions, i.e., for $[HCl] > 2$ M. Thus, in various applications such as the recovery of indium from flue dust leaching solutions, cobalt(II) will not interfere during extraction of the other metals. On the other hand, at a lower acidity the extraction of cobalt(II) occurs and creates some specific problems. Indeed, on exposing to air, the solution of Cyanex 301® containing cobalt(II) turns from blue to brown, while the stripping of cobalt(II) becomes more and more difficult (Figure 5). Such a phenomenon is due to the oxidation of cobalt(II) chelate into a cobalt(III) chelate by atmospheric oxygen and takes place in the bulk of the organic phase. It can be avoided by the formation of mixed ligand complexes by addition of appropriate modifiers such as pyridine derivatives, to the organic phase (Sabot, 1978; Guesnet, 1980a, 1980b, 1981).

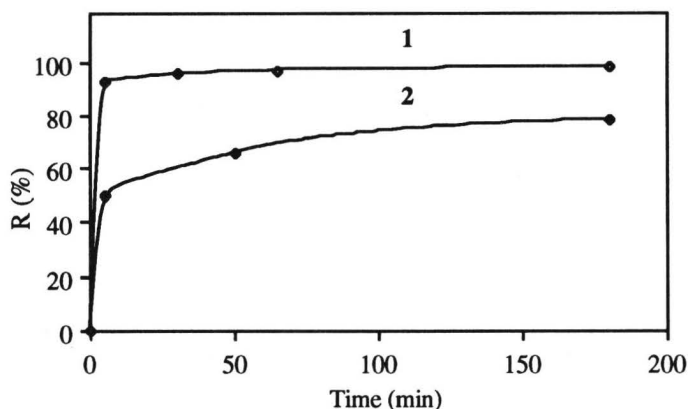


Fig. 5 Percentage of stripping of cobalt (initially 10^{-2} M) from a 0.2 M Cyanex 301® solution in kerosene + 10% (v/v) n-decanol with 5 M HCl. (1) just after extraction, (2) after the organic phase has been left 48 h in contact with atmospheric oxygen.

Stripping of Copper

As mentioned above, the stripping of copper from the organic Cyanex 301® solutions cannot be achieved by modifying the acidity of the aqueous phase. However, we have shown that copper can be efficiently removed from the Cyanex 301® solutions by precipitation of non-stoichiometric copper sulphides (Facon, 1993). This method is not as convenient as the usual liquid-liquid stripping, but allows a complete regeneration of Cyanex 301®.

Long term stability of Cyanex 301®

The preceding discussion shows that Cyanex 301® is an excellent reagent for extraction of

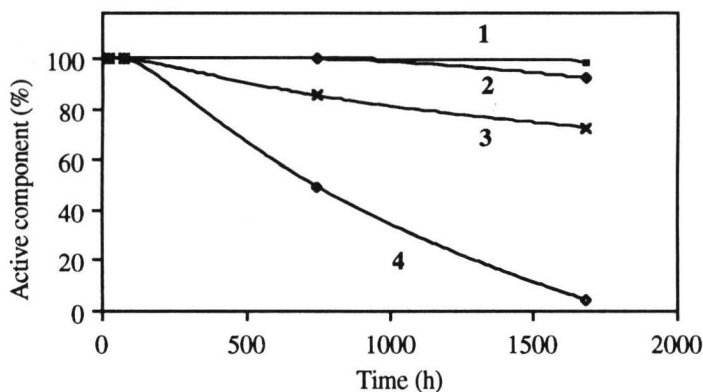


Fig. 6 Stability of a 0.2 M Cyanex 301® solution in kerosene + 10% (v/v) n-decanol in contact with various HCl solutions, at room temperature. HCl concentration : (1) 3 M; (2) 6 M; (3) 9 M; (4) 12 M.

metals from highly acidic solutions. Therefore we have investigated its stability in such media. Examination of Figure 6, where the percentage of active R₂PSSH (as determined by the loading method with bismuth(III)) has been plotted as a function of time, shows that the Cyanex 301® is fairly stable at room temperature up to about 6 M HCl. At higher HCl concentrations or at higher temperatures, Cyanex 301® decomposes more rapidly, but can still be used for stripping of some metals.

CONCLUSION

Cyanex 301® is a fascinating reagent which can find many original applications such as the removal of cadmium from phosphoric acid (Tjioe, 1989) or the recovery of indium from flue dust leaching solutions (Avila Rodriguez, 1992). However, because of the novelty of this reagent further investigations are still necessary to know better its physico-chemical properties and its extraction characteristics.

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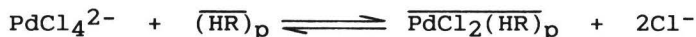
5.7

SOLVENT EXTRACTION OF PALLADIUM(II) AND PLATINUM(IV) WITH DI(2-ETHYLHEXYL)AMINOPHOSPHONIC ACID FROM CHLORIDE MEDIA

Yoshinari BABA, Yuji SHIMIZU
Joint Research & Development Center, Saga University,
Honjo 1, Saga 840, Japan

ABSTRACT

Solvent extraction of palladium(II) and platinum(IV) was investigated from acidic aqueous chloride media with di(2-ethylhexyl)aminophosphonic acid in toluene. The experimental results of the distribution equilibria suggested that palladium(II) is extracted according to the solvating reaction as follows:



The extraction equilibrium constant was evaluated as $K_e = 4.7 \text{ mol/dm}^3$ for palladium(II). The extraction reaction of platinum(IV) was assumed in the region of high concentration of hydrogen ion as follows:



The extraction equilibrium constant was evaluated as $K_e = 2.4 \times 10^2 \text{ dm}^3/\text{mol}$ for platinum(IV).

INTRODUCTION

Although many studies have been conducted on complex formation between metals such as copper(II), palladium(II) and platinum(IV), and amino-acids, peptides and related ligands in aqueous solutions(Pettit, Berger, 1985), there have been only a few publications on fundamental studies of solvent extraction with amino-acid types of extracting reagents(Zhang et al, 1985, 1987, Uhlig et al, 1986, Sevdic et al, 1974). In a fundamental study on the complex formation between palladium(II) and amino-acids, Wilson and Martin(1970) showed that palladium(II) forms extractable chelate complexes with amino acids with a 1:2 stoichiometry.

In the present work, the authors synthesized a novel extracting reagent of an amino-acid derivative, di-(2-ethylhexyl)aminophosphonic acid, to investigate the extraction equilibria of palladium(II) and platinum(IV) from acidic chloride media.

EXPERIMENTAL

Di(2-ethylhexyl)aminophosphonic acid, abbreviated as DEHAP and denoted by HR hereafter, was synthesized from di(2-ethylhexyl)amine, phosphorous acid and formaldehyde in benzene under a nitrogen atmosphere by using a conventional method according to the following reaction:



The product was dissolved in benzene and transferred to a separatory funnel to be washed with 2 mol/dm³ hydrochloric acid solution and subsequently with water to neutrality. After phase separation, benzene was removed by distillation under reduced pressure. Identification of the purified product was carried out by using NMR spectra and elemental analysis. The yield was 52% and the purity was 97%. An analytical grade of toluene was used as a diluent.

The apparent molecular weight of the reagent was measured by means of vapour-phase osmometry using a Hitachi model 117 osmometer to examine the degree of aggregation of the reagent in the organic solution. It was found that a great majority of the reagent exists as an octamer.

Equal volumes of aqueous and organic phases were shaken in a flask immersed in a thermostatted water bath maintained at 30°C for 24 h for both palladium(II) and platinum(IV) to attain equilibrium. The equilibration had been confirmed to be attained within this period in a preliminary experiment. The initial and equilibrium metal concentrations in the aqueous phase were determined by using a Seiko Instruments Japan model SAS 7500 atomic absorption spectrophotometer. The metal concentrations in the organic phase were calculated

from the mass balance of the metal contents in the aqueous phase before and after equilibration. The initial concentrations of palladium(II) and platinum(IV) were 1 mmol/dm^3 for all experiments.

RESULTS AND DISCUSSION

Figure 1 shows the effect of pH on the distribution ratios in the extraction from aqueous mixtures of hydrochloric acid and sodium chloride in which total chloride ion concentration was maintained at 1.0 mol/dm^3 . In this experiment, the pH was calculated from the hydrogen ion concentration determined by means of titration and the activity coefficient of hydrogen ion in the aqueous mixture of hydrochloric acid and sodium chloride (Ohtaki et al., 1969). The distribution ratio for the extraction of palladium(II) is independent of pH, which suggests that no hydrogen ion is involved in the extraction reaction. On the other hand, the extraction results of platinum(IV) were clustered on a straight line with a slope of -0.5 against pH, which suggests that one hydrogen ion participates or does not participate to form the chelate complex with one metal ion during extraction.

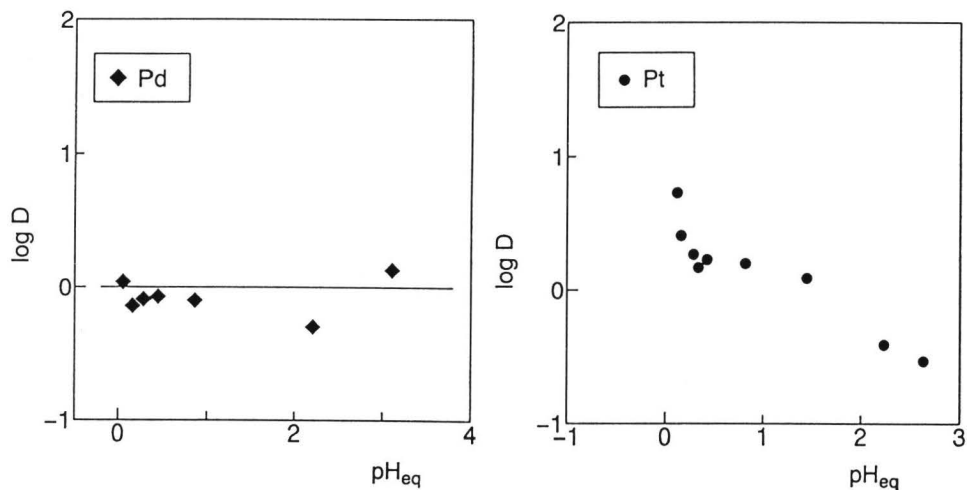


Fig. 1. Effect of pH on the distribution ratio (D) (reagent concentration = 50 mmol/dm^3 , total chloride ion concentration = 1.0 mol/dm^3).

Figure 2 shows the effect of the activity of the chloride ion on the distribution ratio in the extraction from aqueous chloride media in which the hydrogen ion concentration is maintained at 0.1 mol/dm^3 . Here, the activity of chloride ion was calculated from the chloride ion concentration and the activity coefficient of the chloride ion (Harned, 1959). The plots lie on straight lines with slopes of -2 and -1 for the extraction of palladium(II) and platinum(IV) respectively. This indicates that two and one chloride ions are released per unit metal ion during extraction of palladium(II) and platinum(IV) respectively.

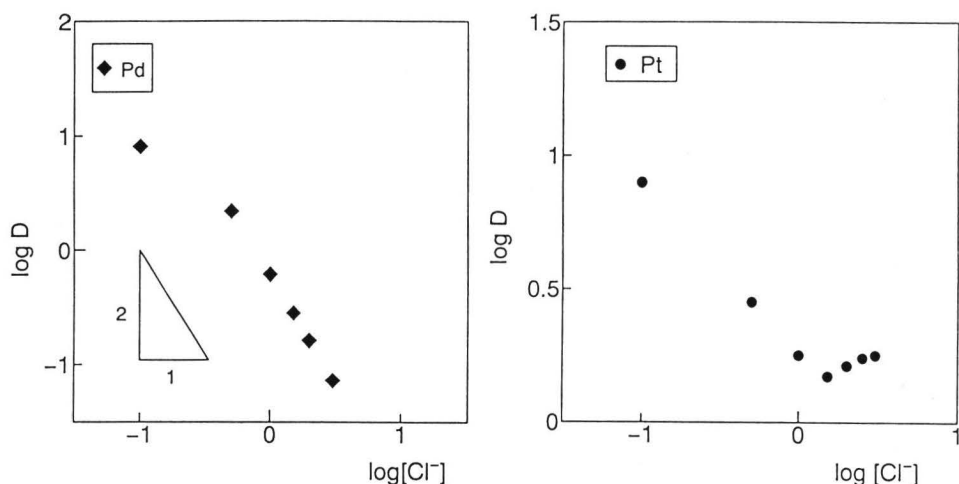


Fig. 2. Effect of the activity of chloride ion on the distribution ratio (D) (reagent concentration = 50 mmol/dm^3).

Figure 3 shows the effect of the concentration of the extractant on the distribution ratio in the extraction from 0.1 mol/dm^3 hydrochloric acid solution, where the concentration was an analytical extractant concentration. The plots lie on straight lines with slopes of unity for both metals. This fact suggests that the extractant behaves as a reversed micelle in the extraction of palladium(II) and platinum(IV) from the chloride media, since the majority of the reagent exists as an octamer in the organic phase as mentioned earlier.

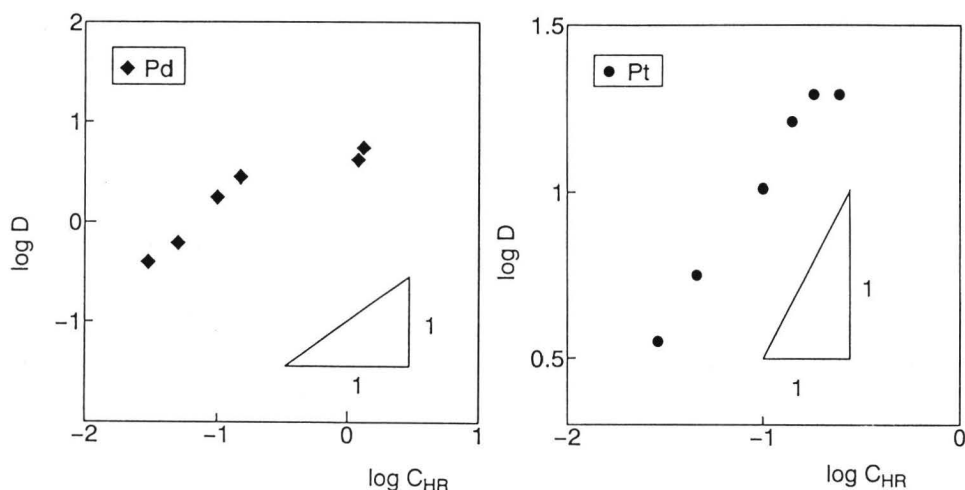
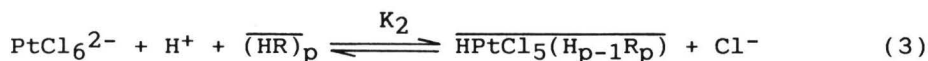
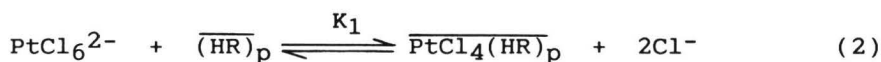
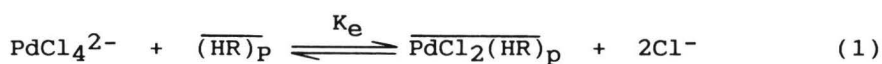


Fig. 3. Effect of the concentration of the extractant on the distribution ratio (D) in the extraction from 0.1 mol/dm^3 hydrochloric acid solution.

From the concentration dependencies of the reactant species on the distribution ratio mentioned above, and by taking into consideration that the majorities of palladium(II) and platinum(IV) exist as the tetrachloro and hexachloro complexes in the aqueous solutions, respectively, with high concentrations of chloride ion under the present experimental conditions, the following can be concluded: palladium(II) is extracted as a solvated complex according to the reaction shown in Eq.(1) whilst platinum(IV) is partially extracted as a metal-chelate complex according to the extraction reaction expressed by Eqs.(2) and (3).



Based on the above extraction reactions, the distribution ratio of palladium(II) or platinum(IV) is expressed as fol-

lows, respectively, since the tetrachloro complex of palladium(II) or hexachloro complex of platinum(IV) are predominant under the present experimental conditions:

$$\log D = -2\log[Cl^-] + \log([\overline{(HR)}_p]K_e) \quad (4)$$

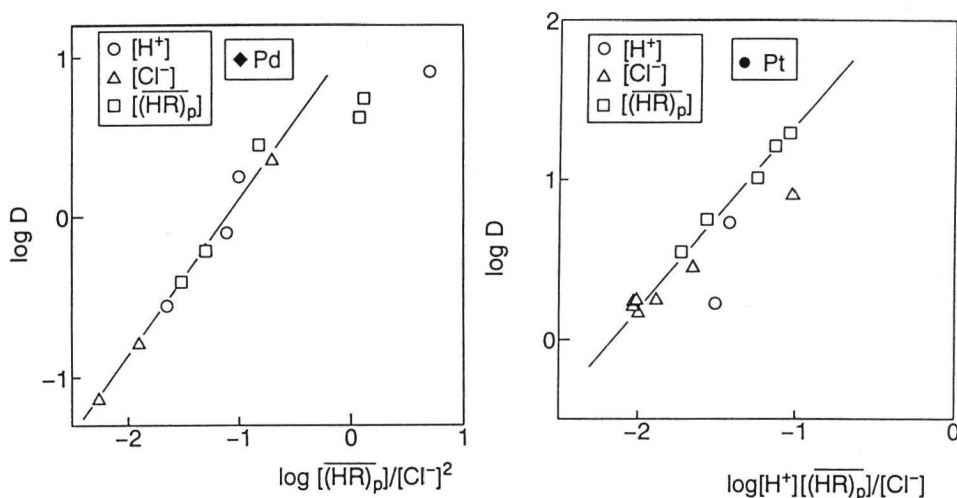
$$\log D = -\log[Cl^-] + \log[\overline{(HR)}_p] + \log(K_1/[Cl^-] + K_2[H^+]) \quad (5)$$

Eq.(5) obtained for the extraction of platinum(IV)) is approximated at high concentrations of hydrogen ion as follows:

$$\log D = -\log[Cl^-] - pH + \log[\overline{(HR)}_p] + \log K_2 \quad (6)$$

Eqs.(4)-(6) are consistent with the experimental results shown in Figs.1-3

Figures 4 and 5 show plots of all the data of palladium(II) and those of platinum(IV) at high hydrogen ion concentration respectively, which were calculated according to Eqs.(4) and (6). The plots lie on a straight line with a slope of unity in both figures as expected from Eqs. (4) and (6).



Figs.4 and 5. Plots of the experimental results based on Eqs.(4) and (6).

The equilibrium constants of the extraction reactions were evaluated as $K_e = 4.7 \text{ mol/dm}^3$ for palladium(II) and as $K_2 = 2.4 \times 10^2 \text{ dm}^3/\text{mol}$ for platinum(IV) from the intercept of the straight line with the ordinate in Figs. 4 and 5 respectively.

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5.8

EXTRACTION AND SEPARATION STUDIES OF BISMUTH (III) AND ANTIMONY(III) WITH TRIS-(2-ETHYLHEXYL) PHOSPHATE

A.D. BARVE, G.S. DESAI and V.M. SHINDE

Analytical Laboratory, Department of Chemistry, Institute of Science,
15 Madam Cama Road, Bombay 400 032, India.

ABSTRACT

Separation of bismuth (III) from lead, antimony, gold and tellurium and of antimony (III) from copper, bismuth and lead is achieved by selective extraction of bismuth (III) and antimony (III) from halide solutions into tris-(2-ethylhexyl) phosphate (TEHP) dissolved in toluene or xylene. The extracted species are evaluated by log D - log C plots. The method is applicable to the analysis of some 'real' samples. The separation and determination takes only 20 minutes.

INTRODUCTION

Tris-(2-ethylhexyl) phosphate (TEHP) has been earlier used in this laboratory for the extraction studies of uranium (VI) (Desai et al., 1990) thorium (IV) (Desai, Shinde, 1991) and tellurium (IV) (Desai, Shinde, 1992). An extension of this work has shown that the TEHP can also be used for extraction and separation of bismuth (III) and antimony (III) from associated elements. The methods are simple, fast and applicable for the analysis of some 'real' samples.

EXPERIMENTAL**Apparatus and Reagents**

Spectronic 20 D (Milton Roy Co.) spectrophotometer and Control Dynamics digital pH meter are used for the absorbance and pH measurements. Stock solutions of bismuth (III) and antimony (III) were prepared by dissolving 0.58 g of bismuth nitrate in 250 mL of distilled water containing 2 mL of concentrated nitric acid and by dissolving 0.100 g of powdered antimony metal in 25 mL of concentrated sulphuric acid and diluting to 100 mL. Both the solutions of bismuth (III) and antimony (III) are standardised by known methods (Vogel, 1961, p.442, 392) and are diluted as required for working solution.

Tris-(2-ethylhexyl) phosphate (TEHP) obtained from Aldrich Chemicals (b.p.215°) is used as an extractant.

Thiourea; 10% solution is used for the determination of bismuth (Sandell, 1958, p.337).

Potassium iodide; 20% solution is used for the determination of antimony (Marczenko, 1976, p.125).

All other reagents used are of analytical reagent grade.

GENERAL EXTRACTION PROCEDURE FOR BISMUTH (III) AND ANTIMONY (III)

Bismuth (III) (200 μg) is extracted from 0.09-0.3 mol dm^{-3} hydrobromic acid solution in a total volume of 10 mL with 50% TEHP dissolved in toluene. After phase separation, aqueous phase is discarded and bismuth from organic phase is stripped with two 5 mL portions of 0.1 mol dm^{-3} nitric acid and finally estimated spectrophotometrically with thiourea at 460 nm (Sandell, 1958, p.337).

To an aliquot of solution containing 75-300 μg of antimony (III), add hydrochloric acid solution so that its concentration is in the range of 2.0-3.0 mol dm^{-3} in a total volume of 10 mL. Transfer the solution into a separatory funnel and extract for 20s each time with two 5 mL portions of 50% TEHP dissolved in xylene. After phase separation, strip antimony from the combined organic layer with 8 mL of water and estimate spectrophotometrically with potassium iodide at 425 nm (Marczenko, 1976, p.125).

The bismuth and antimony contents are computed from a previously drawn calibration plot.

RESULTS AND DISCUSSION

Extraction conditions

The extraction of bismuth (III) and antimony (III) are studied at various concentrations of hydrochloric acid (0.025-8 mol dm^{-3}) and hydrobromic acid (0.025-7 mol dm^{-3}) with different concentrations of TEHP (10.0 - 50.0% dissolved in toluene or xylene). The results show that two 5 mL portions of 50% TEHP in xylene extract antimony (III) quantitatively from 2.0-3.0 mol dm^{-3} hydrochloric acid solution whereas extraction is incomplete from hydrobromic acid solution. In the case of bismuth (III) the quantitative extraction is feasible with 5 mL of 50% TEHP in toluene, from 0.09 to 0.3 mol dm^{-3} hydrobromic acid solution. The extraction of bismuth from hydrochloric acid media is incomplete.

Nature of extracted species

The nature of the extracted species is established using log-log plots. The log-log plots of distribution ratio versus TEHP concentration for antimony (at 2.0 mol dm^{-3} hydrochloric acid concentration) and bismuth (at 0.1 mol dm^{-3} hydrobromic acid concentration) give a slope of 1.7 indicating metal to TEHP ratio of 1:2 in the extracted species. Hence the extracted species is an ion association complex formed by solvation. The possible species are $\text{HBiBr}_4 \cdot 2\text{TEHP}/\text{HSbCl}_4 \cdot \text{TEHP}$.

Effect of various foreign ions

Microgram amounts of foreign ions are added to a fixed amount of antimony (150 µg) or bismuth (200 µg) to study interference in the recommended procedure. The tolerance limit is set at the amount required to cause $\pm 2\%$ error in metal recovery. The tolerance limit is caused by inhibiting antimony/bismuth extraction. For 150 µg of Sb (III), there is no interference from 150µg each of tin (II), gold (III), tellurium (IV), 300 µg of tungsten (VI), 500 µg each of bismuth (III), selenium (IV) 750 µg each of silver (I), citrate, tartrate, oxalate, nitrite, 1000 µg each of mercury (II), thorium (IV), vanadium (V), molybdenum (VI), thiourea, thiosulphate, 2000 µg each of arsenic (III), iron (III), titanium (IV), uranium (VI), ascorbate, EDTA, 4000 µg each of sulphate, nitrate, 5000 µg each of lead (II), nickel (II), copper (II), manganese (II), barium (II), calcium (II), cadmium (II), magnesium (II), zinc (II), cobalt (II), chloride, phosphate show no interference. However, chromium (VI) gives serious interference in the extraction of antimony. For 200 µg of Bi (III), there is no interference from 200 µg of thiosulphate, 500 µg each of tin (II), antimony (III), 1000 µg each of silver (I), aluminium (III), tellurium (IV), selenium (IV), vanadium (V), 1500 µg of titanium (IV), 2000 µg each of barium (II), tungsten (VI), arsenic (III), uranium (VI), nitrite, sulphate, nitrate, chloride, phosphate, ascorbate, thiourea, 2500 µg of nickel (II), 3000 µg of gold (III), 4000 µg of each mercury (II), molybdenum (VI), oxalate, 5000 µg each of lead (II), copper (II), manganese (II), calcium (II), cadmium (II), magnesium (II), zinc (II), cobalt (II), iron (III), thorium (IV), chromium (VI), citrate do not show interference. However EDTA shows serious interference.

BINARY SEPARATION OF BISMUTH (III) FROM ANTIMONY (III), LEAD (II), GOLD (III), TELLURIUM (IV) AND ANALYSIS OF SYNTHETIC MIXTURE

Bismuth is often found in association with lead, antimony, gold and tellurium. Hence separation of bismuth from binary mixtures is achieved. Bismuth and antimony are separated by extracting antimony from 3 mol dm⁻³ hydrochloric acid solution with 50% TEHP dissolved in toluene. It is then stripped with water (8 mL) and determined in the aqueous phase spectrophotometrically using iodine method (Marczenko, 1976, p.125). Bismuth which remains quantitatively in water phase is determined using thiourea (Sandell, 1958, p.337). Lead and bismuth are separated as lead does not show any extraction and remains quantitatively in the aqueous phase. It is determined in the aqueous phase spectrophotometrically using 4-(2-pyridylazo) resorcinol (PAR) (Yadav, Khopkar, 1971). Gold co-extracts with bismuth but they are separated by selective stripping of bismuth with nitric acid. Gold does not strip and is estimated in the organic phase directly by measuring the absorbance of the yellow complex at 400nm. Tellurium and bismuth are separated by extracting bismuth from 0.1 mol dm⁻³ hydrobromic acid solution with 50% TEHP dissolved in toluene. Tellurium which remains quantitatively in the aqueous phase is estimated

spectrophotometrically with stannous chloride (Desai, Shinde, 1992). The method also permits extraction and determination of bismuth (III) from synthetic mixtures containing titanium, vanadium, iron, arsenic, antimony, tin and lead.

The recovery of separation and of a synthetic mixture for bismuth (III) is >99.9%.

BINARY SEPARATION OF ANTIMONY (III) FROM COPPER (II), BISMUTH (III), LEAD (II) AND ANALYSIS OF SYNTHETIC MIXTURE

The method permits separation and determination of antimony (III) from binary mixtures containing either copper, bismuth or lead. Separation of antimony and bismuth is described above. Antimony is separated from copper and lead by its extraction with 50% TEHP dissolved in xylene from 2 mol dm⁻³ hydrochloric acid solution. Under this condition copper and lead remain quantitatively in the aqueous phase where they are determined spectrophotometrically using 1-(2-pyridylazo) naphthol (PAN) (Pease, Williams, 1959) and 4-(2-pyridylazo) resorcinol (PAR) (Yadav, Khopkar, 1971) respectively. Antimony is stripped from the organic phase with water and estimated spectrophotometrically using potassium iodine (Marczenko, 1976, p.125). The proposed method is applied for the extraction and determination of antimony (III) in different synthetic mixtures.

The recovery of separation and of a synthetic mixture for antimony (III) is >99.9%.

ANALYSIS OF ALLOYS AND PHARMACEUTICAL SAMPLES

Since bismuth containing alloy samples are not available, a known amount of bismuth is added to standard alloy solution and the proposed method is used for the recovery of bismuth. Leaded brass (BCS 385), leaded bronze (BCS 364), leaded gunmetal (BCS 183/4) and Woods alloy (Indalloy 158) are analysed by the proposed method. Once the alloy is dissolved in concentrated nitric acid, 2.5 mg of bismuth is added to each alloy solution except Woods alloy which contains 50% bismuth. An aliquot of the alloy solution is taken for the extraction and determination of bismuth. The recovery of bismuth (III) is >99.9%.

Analysis of Denol Tablet, Pectomycin Suspension and Sodium Antimony Gluconate Injection

The method is also used for analysis of pharmaceutical samples. Denol tablet is dissolved in 10 mL of perchloric acid, evaporated to dryness and the residue is taken up in water (while dissolving Denol, continuous heating is avoided to eliminate the probability of spurting). Filter the precipitate and filtrate is diluted to 500 mL. Agrawal and Bhatt (Agrawal, Bhatt, 1984) have determined bismuth in pectomycin suspension (Manufactured by Lyka Labs, India). The samples of pectomycin available in the Bombay market, however does not contain bismuth and hence 2.5 mg of bismuth is added to 5 mL of pectomycin suspension and dissolved in 10 mL of 2.5 mol dm⁻³ sulphuric acid, the solution is filtered and diluted to 50 mL. 1 cm³ and 4 mL

aliquots of Denol and pectomycin solution are taken for the extraction and determination of bismuth by the proposed method. The results reported in Table 1 are reproducible.

1 mL of injection containing 100 mg of antimony (V) is evaporated to dryness, the residue is decomposed with perchloric acid, leached and diluted to 500 mL with 0.5 mol dm⁻³ sulphuric acid. 1 mL of this solution containing 200 µg of antimony is reduced with ascorbic acid and subsequently antimony is extracted and determined as for the general extraction procedure. The results are reported in Table 1.

TABLE 1
Analysis of Pharmaceutical samples

Name of Drug/ Injection	Composition	Certified or added value of Bi/Sb mg	Bi/Sb found mg ^a	Standard deviation	Coefficient of variation %
Denol (Elder Pharmaceuticals, India)	Colloidal bismuth subscitrate calculated as Bi ₂ O ₃ 120mg	107.64	107.63	0.016	0.01
Pectomycin Suspension (Lyka Labs Limited, India)	Each 15 mL contains light kaolin 1.P 2.5 mg, Pectin 1.P. 50mg; Streptomycin Flavoured Syrupy base q.s.+2.5mg Bi	2.5	2.49	0.004	0.15
Sodium Antimony Gluconate Injection(I.P.)	Each mL contains Sodium Antimony Gluconate I.P. 0.333g (Equivalent to 100 mg of total Antimony).	0.200	0.199	0.068	0.03

a = Average of six determinations

The methods are accurate and permit rapid separation and determination of micro amounts of antimony (III) and bismuth (III). The average recovery of antimony and bismuth is >99.9%. Each determination takes a total of 15-20 min.

ACKNOWLEDGEMENTS

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5.9

SYNTHESIS AND EXTRACTION PROPERTIES OF N-ALKYL- AND N,N-DIALKYL-3-PYRIDINECARBOXAMIDES

A. BOROWIAK-RESTERNA, J. SZYMANOWSKI, R. CIERPISZEWSKI*
K. PROCHASKA and I. BANCZYK

Institute of Chemical Technology and Engineering
Poznan Technical University

P1. Skłodowskiej-Curie 2, 60-965 Poznan, Poland

*Academy of Economics, A1. Niepodległości 10, Poznan, Poland

ABSTRACT

Model individual N-alkyl-3-pyridinecarboxamides and N,N-dialkyl-3-pyridinecarboxamides were synthesized and used for copper (II) extraction from chloride solutions. Equilibrium and interfacial activity of extractants were determined. N-alkyl-3-pyridinecarboxamide is a stronger extractant and more surface active than N,N-dialkyl-3-pyridinecarboxamide. However, N-alkyl-3-pyridinecarboxamide extracts copper slower than N,N-dialkyl-3-pyridinecarboxamides.

INTRODUCTION

Hydrometallurgical processes, particularly those using chloride leachants, may be used as an alternative to conventional pyrometallurgical methods for the treatment of sulphide ores. That is why solvent extraction reagents that will selectively extract individual metals from concentrated chloride solutions are required. Using extractants of the hydroxyoxime type, which belong to a class of weakly acidic chelating ligands, makes the extraction of copper from concentration solutions ($40\text{--}45\text{ g dm}^{-3}\text{ Cu}^{2+}$) uneconomical.

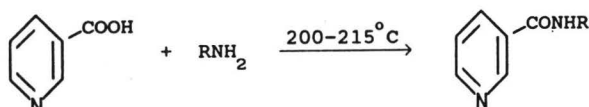
In the 1980's ICI proposed to use a new type of extractant, DS5443 (now known as ACORGA CLX 50), which extracts copper from chloride solutions (Dalton et al., 1983, Danielssen et al., 1983, Price et al., 1982 Soldenhoff, 1986). A demonstration plant, which was built in Spain, had to show whether a process using DS5443 for the recovery of copper from complex ores by a purely hydrometallurgical route is technically and commercially feasible (Dalton et al., 1987). DS5443 is probably a pyridinedicarboxylate ester (Soldenhoff, 1987). The aim of this work is synthesis of some model N-alkyl- and N,N-dialkyl-3-pyridinecarboxamides and studies of copper extraction from concentrated chloride solutions.

EXPERIMENTAL

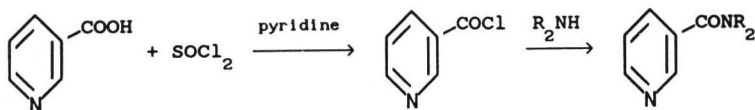
Synthesis of extractants

N-dodecyl-3-pyridinecarboxamide (DPCA) and N-octadecyl-3-pyridinecarboxamide (OPCA) were obtained according to the scheme I and N,N-dihexyl-3-pyridinecarboxamide (DHPCA) and N,N-dioctyl-3-pyridinecarboxamide (DOCPA) - according to the scheme II:

Scheme I:



Scheme II:



Purity of these amides was determined by gas chromatography (Hewlett-Packard 5890A with detector MSD HP 5970B).

Studies of extraction equilibrium

Extraction was carried out in a typical way. $2 \cdot 10^{-2}$ or $5 \cdot 10^{-2}$ mol dm⁻³ solutions of N-alkyl- and N,N-dialkyl-3-pyridinecarboxamides in toluene were used as the organic phase. The aqueous phase contained 10^{-2} mol dm⁻³ CuCl₂ and 0.1-8 mol dm⁻³ Cl⁻. Initial pH of the aqueous phase was 3.2. chloride ion concentration was adjusted by addition of aqueous lithium chloride. 10 cm³ volumes of both phases were efficiently stirred for 15 minutes at room temperature. Copper concentration was determined in the initial aqueous solutions and in the aqueous phases after extraction by the spectrophotometric method using sodium diethyldithiocarbamate (Marczenko, 1979).

Extraction rate measurements

The ascending drop method was used. Four different columns of the same inner diameter, 25 mm, and various length, 85, 565, 980 and 1600 mm, were applied. The drops were formed with approximately similar rates 60-90 drops/minute. The inner diameter of the capillary used for drop formation was 0.27 mm. The surface of the drops was calculated assuming their ideal spherical shape. The copper concentration in the aqueous chloride solution used as the continuous phase was 0.1 mol dm⁻³ and was adjusted by lithium chloride solution to 4 mol dm⁻³. The amide concentration in toluene was $5 \cdot 10^{-3}$ mol dm⁻³.

Interfacial tension measurements

The interfacial tension was measured by means of the drop method according to the method described previously for hydroxyoximes (Szymanowski et al., 1988). The aqueous phase was 3.9 mol dm⁻³ LiCl solution of pH 3.2. Toluene was used as the diluent. The interfacial tension data were interpreted in the same way as in previous works for hydroxyoximes (Szymanowski et al., 1987, 1988, 1988a).

RESULTS AND DISCUSSION

N-alkyl-3-pyridinecarboxamides (DPCA and OPCA) were obtained in the acylation reaction of the respective alkylamine by nicotinic acid at 200-215°C (scheme I) (Badgett et al., 1945). The yield was 60-70%. N,N-dialkyl-3-pyridinecarboxamides (DHPCA and DOPCA) were obtained in the two-stage reaction (scheme II): i) the synthesis of 3-pyridinecarboxyl chloride from nicotinic acid and thionyl chloride in presence of pyridine and ii) the acylation reaction of the dialkylamine by raw 3-pyridine-carboxyl chloride (not separated from the post-reaction mixture) [Badgett et al., 1945]. The yield was about 60%. The presence of pyridine considerably increased the yield of reaction and the best molar ratio of pyridine to nicotinic acid was 2:1. N,N-dialkyl-3-pyridinecarboxamides could not be obtained in one-stage reaction (scheme I). The purity of all amides was 98-99%. UV, IR, PMR and MS spectra prove the structure and purity of the obtained compounds. The extraction investigations showed that the alkylamides of nicotinic acid form blue-coloured complexes with copper and chloride. Individual monoalkylamides of nicotinic acid, and particularly their complexes, dissolve slightly in the hydrocarbon diluents. The highest solubility of DPCA in toluene is 5*10⁻² mol dm⁻³, and of OPCA is 2*10⁻², and of OPCA is 2*10⁻² mol dm⁻³. Monoalkylamides are stronger extractants than dialkylamides (Fig. 1). The extraction of 90% was obtained for DPCA at 5*10⁻² mol dm⁻³ already at low chloride concentration (1 mol dm⁻³). For DHPCA and DOPCA degrees of extraction of 85-90% were obtained at 8 mol dm⁻³ chloride concentration. Such great differences in the extraction ability between mono- and dialkylamides are probably caused by differences in the stabilities of formed complexes. It is difficult to determine unequivocally the influence of the alkyl chain length on the extraction. Equilibrium curves for DPCA and OPCA are similar, but for the dialkylamides slightly better results are obtained for the amide with short alkyl chains. While comparing properties of amides and esters of nicotinic acid (curves 2,4 and 6 in Fig. 1), one can observe that monoalkylamide is the most effective extractant. When the concentration of chloride ions falls below 5 mol dm⁻³ N,N-dihexyl-3-pyridinecarboxamide shows higher copper extraction ability than dodecyl 3-pyridinecarboxylate. Kinetics studies were carried out only for DPCA, DHPCA and DOPCA (Fig.2). The extraction rate increases in a sequence DPCA < DOPCA < DHPCA, i.e. in the opposite direction to the extraction equilibrium. The replacement of the

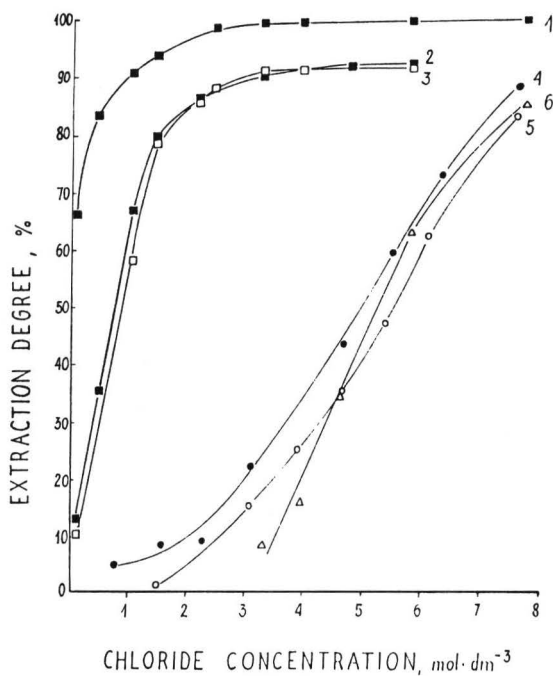


Fig. 1. Copper (II) extraction from chloride solutions with hydrophobic alkylpyridinecarboxamides (1 and 2, ■, DPCA; 3, □, OPCA; 4, ●, DHPKA; 5, △, DOPCA; 6, △, dodecyl 3-pyridinecarboxylate; 1,4,5 and 6, $c = 0.05 \text{ mol dm}^{-3}$; 2 and 3, $c = 0.02 \text{ mol dm}^{-3}$).

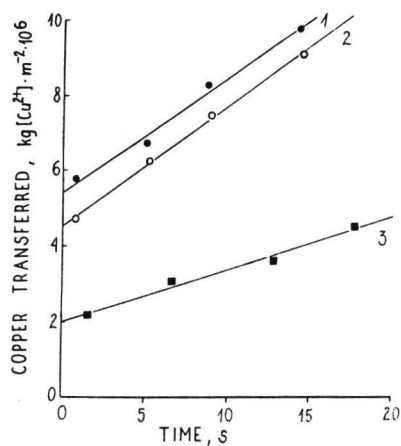


Fig. 2. Copper transfer from chloride solutions with hydrophobic alkylpyridinecarboxamides (1, ●, DHPKA; 2, △, DOPCA; 3, ■, DPCA).

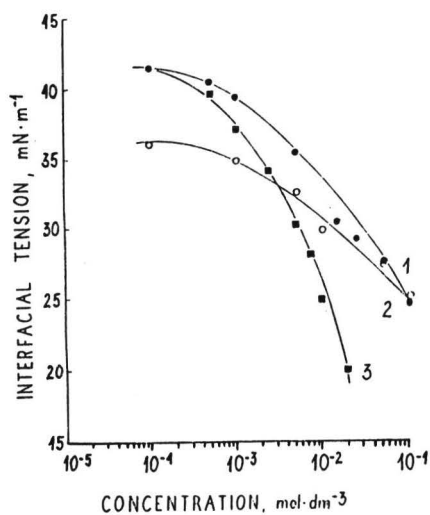


Fig. 3. Interfacial activities of hydrophobic alkylpyridinecarboxamides (1, ●, DHPKA; 2, ○, DOPKA; 3, ■, DPKA).

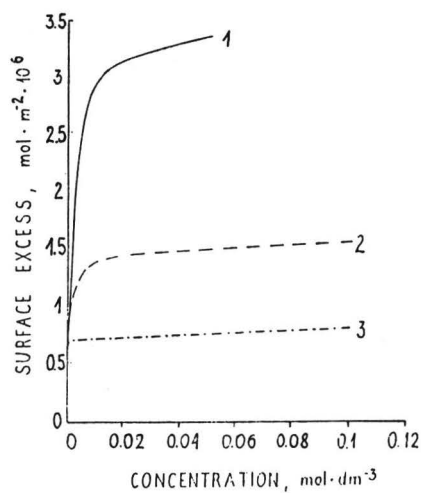


Fig. 4. Surface excess of hydrophobic alkylpyridinecarboxamides calculated according to the Gibbs and Szyszkowski equations (1, —, DPKA; 2, ---, DHPKA; 3, - · -, DOPKA)

12-carbon chain by two 6-carbon chains in the amide group increases the amount of copper transferred in unit time by about 2.5 times. When the number of carbon atoms in the alkyl chains of N,N-dialkyl-3-pyridinecarboxamides increases the rate of extraction decreases. Alkylamides of nicotinic acid adsorb at the toluene-water interface decreasing the interfacial tension to about 20 mN m^{-1} (Fig.3). Interfacial activity of the studied amides depends both upon their hydrophobicities, i.e. the length of the alkyl group and the number of alkyl substituents. Monoalkylamide (DPCA) is more surface active than dialkylamides (DHPCA and DOPCA). DOPCA permits obtaining lower values of the interfacial tension than DHPCA. The surface excess (concentration at the interface) of studied extractants decreases with the increase of both the alkyl chain length and the number of alkyl substituents (Fig.4). The interfacial concentration of monoalkylamide (DPCA) is twice as high as for dialkylamide containing the same number of carbon atoms (DHPCA). The sequence of surface activities is opposite to the sequence obtained in kinetics experiments. This supports our previous idea, that the location of the adsorbed molecules at the interface and the distribution of extractant between both extraction phases are more important parameters than the extractant interfacial concentration. The presented results prove good extraction properties of N,N-dialkyl-3-pyridinecarboxamides. The use of N-alkyl-3-pyridinecarboxamides needs an important improvement of their solubilities in the organic phase which can be achieved by using mixtures of monoalkylamides with alkyls of different lengths and structures.

CONCLUSIONS

N-alkyl- and N,N-dialkyl-3-pyridinecarboxamides are strong copper extractants for chloride solutions. The solubility and kinetics data favour use of N,N-dialkyl-3-pyridinecarboxamides. Monoalkylamides are stronger than dialkylamides but the latter extract copper quicker than monoalkylamides. Monoalkylamides are more surface active than dialkylamides. The effect of extractant structure upon the rate of copper extraction cannot be explained by different interfacial activity of extractants and their interfacial concentration.

ACKNOWLEDGEMENTS

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5.10

**LIQUID-LIQUID EXTRACTION OF METAL IONS WITH
CYCLIC DIAZATETRATHIOETHER DERIVATIVES**

Kenji CHAYAMA, Koji HARA, Yuzo TAMARI, Haruo TSUJI AND Yuzuru KUSAKA
Department of Chemistry, Faculty of Science
Konan University
Okamoto, Higashinada, Kobe 658, JAPAN

Eiichi SEKIDO AND Yoshihiro MORI
Department of Chemistry, Faculty of Science
Kobe University
Rokkodai, Nada, Kobe 657, JAPAN

ABSTRACT

Liquid-liquid extraction of metal ions with 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (ATCO) and its derivative were examined using picrate as the anion of ion pair. Liquid-liquid partition of these reagents between 1,2-dichloroethane (DCE) and water were estimated for each pH value of aqueous phase. It was shown that these reagents transferred from dichloroethane phase to acidic aqueous phase. Soft metals such as Ag(I), Cu(I), and Hg(II) were extracted with ATCO and ATCO-Bzl₂, as well as 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO). Not only soft metals, but Co(II), Ni(II) and Cu(II) were also extracted.

INTRODUCTION

A cyclic polythioether (thiacrown ether) reacts selectively with soft Lewis acids such as Ag⁺, Cu⁺, Pd²⁺ and Hg²⁺ etc., to form a cation complex. This can form an ion pair complex with an appropriate anion such as perchlorate ion and picrate ion. The ion pair can be extracted into a suitable organic solvent. Several studies on the liquid-liquid extraction of metal ions with 1,4,8,11-tetrathiacyclo-

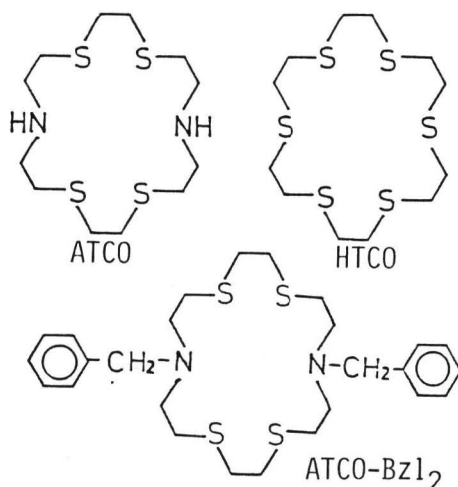


Fig.1 Ligands discussed in this work

tetradecane (TTCT) (Sevdic,1977,1977, Saito,1983,1984, Sekido,1985) and 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO)(Sekido,1988) have been reported. These studies made possible the application of thiacycrown compounds to the extractive spectrophotometric determination of soft metals such as Ag^+ and Cu^+ , by using coloured anions or by using chromogenic thiacycrown compounds. (Saito,1984, Sekido,1985,1986, Muroi,1986) Recently, a macrocyclic tetrathioether containing two nitrogen atoms 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (ATCO) and its derivatives have been studied in the field of the coordination chemistry (Atkinson,1989,1990). Although some of metal complexes of the azathiacycrown compounds have been isolated and characterized, there are few studies concerning the extraction of the metal complexes. In the present study, liquid-liquid extraction of metal ions with ATCO and the dibenzylated ATCO, N,N'-bis-benzyl-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (ATCO-Bzl₂) were examined. The behaviour of liquid-liquid partition of reagents, picrate ion and metal complexes was investigated.

EXPERIMENTAL

Apparatus

Extraction was performed in a Taitec Personal Lt-10 incubator with a thermocontroller. A Hitachi Z-6000 atomic absorption spectrophotometer was used to determine the concentration of the metal ion. UV and visible absorption spectra of aqueous and organic phases were measured with Hitachi double-beam spectrophotometer U-2000. The pH of aqueous phase was measured with a Horiba M-12 pH meter.

Reagents

The method described by Black and McLean was used to prepare ATCO. ATCO-Bzl₂ was synthesized described as follows: in a 500 mL of three necked flask, ATCO (2.94 g, 9.0 mmol) was dissolved in 200 mL of dichloroethane. Triethylamine (1.83 g, 18.1 mmol) was added to this solution and stirred for 30 min. Then, benzylbromide (3.18 g, 18.1 mmol) dissolved in dichloromethane was added and refluxed for 24h. The dichloromethane solution was washed with water and dried over magnesium sulphate. The solution was filtered and evaporated in vacuo. The resulting white precipitate, ATCO-Bzl₂ was recrystallized twice from dichloromethane/ethanol; m.p. 74-76°C, yield 0.82g (18%). ¹H NMR (CDCl₃), δ=2.67-2.80 (24H, d and s, CH₂CH₂), 3.64 (4H, s,

CH_2Ph), 7.26-7.33 (12H, d and s, aromatic H). Ms (70 eV) m/z (rel. intensity) 506(M^+).

Liquid-liquid partition of reagents

An aliquot of aqueous solution containing the buffer solution ($1 \times 10^{-2}\text{M}$) ($\text{M} = \text{mol} \cdot \text{dm}^{-3}$) and sodium sulphate to keep the ionic strength at 0.1 was taken in a 50 mL glass cylindrical tube with a glass stopper. After the addition of 10 mL of $5 \times 10^{-5}\text{M}$ ATCO-Bzl₂ solution of DCE, the mixture was shaken for 30 min at 180 strokes/min at $25 \pm 0.1^\circ\text{C}$. After the mixture had been centrifuged for 5 min, the pH of the aqueous phase was measured. A portion of the organic phase (5 mL) was taken into another tube. After the addition of aqueous solution (5 mL) containing the silver sulphate solution ($1 \times 10^{-3}\text{M}$), picrate ion ($1 \times 10^{-3}\text{M}$), and the buffer solution, the mixture was shaken for 30 min. Thus, ATCO-Bzl₂ in the organic phase was converted into the silver complex, of which the composition was 1:1:1 ($\text{Ag}:\text{ATCO-Bzl}_2:\text{Pic}^-$). After the phase separation, 3 mL of the organic phase was allowed to evaporate, the residue was dissolved in concentrated nitric acid and diluted to 6 mL with water. The concentration of the silver ion in this solution was determined by atomic absorption spectrometry. The silver concentration was regarded as the concentration of ATCO-Bzl₂.

Liquid-liquid partition of picrate ion

The aqueous solution (10 mL) containing the picrate ion ($1 \times 10^{-3}\text{M}$), the buffer solution ($1 \times 10^{-2}\text{M}$) and sodium sulphate to keep the ionic strength at 0.1 was added to the $5 \times 10^{-4}\text{M}$ ATCO-Bzl₂ solution of DCE (10 mL). The mixture was shaken for 30 min. After two phases were separated, a portion of the aqueous phase (1 mL) was diluted with 0.1M NaOH solution to 15 mL. The concentration of the picrate ion in this solution was determined spectrophotometrically at 354 nm. The picrate ion in the organic phase (3 mL) was back-extracted into an 0.1M NaOH solution (25 mL), and the concentration was determined spectrophotometrically.

Liquid-liquid extraction of metals

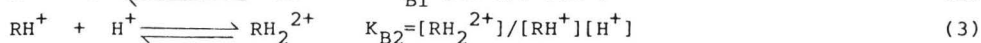
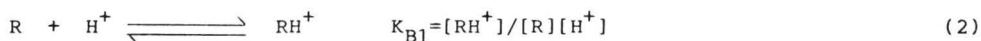
An aliquot (10 mL) of aqueous solution containing the metal ion ($5 \times 10^{-5}\text{M}$), picrate ion ($1 \times 10^{-3}\text{M}$) and the buffer solution ($1 \times 10^{-2}\text{M}$) was taken in the 50 mL glass tube. For the copper (I) solution, hydroxylammonium sulphate was added to the copper (II) sulphate solution. After the addition of 10 mL of $5 \times 10^{-3}\text{M}$ ligand solution of DCE, the mixture was shaken for 30 min at 180 strokes/min at $25 \pm 0.1^\circ\text{C}$. After the mixture had been centrifuged for 5 min,

the pH of the aqueous phase was measured. The concentration of the metal of both the aqueous and the organic phase was measured by atomic absorption spectrometry at the resonance line for each metal.

RESULT AND DISCUSSION

Liquid-liquid partition of reagents

The cyclic hexathioether HTCO is not very soluble in aqueous solution. However ATCO and ATCO-Bzl₂ which have two nitrogen and four sulphur atoms, are soluble in aqueous solution. In order to examine the distribution of reagents between water and DCE, the concentration of reagents in the both aqueous and the organic phase were determined in the pH range 1-8. Figure 2 shows the plots of the concentration of ATCO-Bzl₂ in both the aqueous and the organic phase vs. pH in the aqueous phase. The concentration of the ATCO-Bzl₂ in the organic phase decreased with decrease of pH. Fifty percent of the ATCO-Bzl₂ in the organic phase transferred to the aqueous phase at pH2.0. On the other hand, that of ATCO transferred at pH6.5. This result suggests the protonation of the ligand. If the protonated species of ATCO-Bzl₂ (R) is expressed as RH⁺ and RH²⁺, the distribution constant (K_{DL}) and the protonation constants (K_{B1} and K_{B2}) are expressed as follows:



where the subscript "O" denotes the species in the organic phase. Initial concentration of the ATCO-Bzl₂ (C) is written as

$$C = [R]_O + [R] + [RH^+] + [RH_2^{2+}] \quad (4)$$

Equation (4) is expressed in the term of above constants and the acid concentration as follows:

$$[H^+]K_{B1} + [H^+]^2K_{B1}K_{B2} + (1 - C/[R]_O)K_{DL} = -1 \quad (5)$$

These constants were calculated from the data sets of R_O and pH, as

$\log K_{B1}=3.10$, $\log K_{B2}=1.62$ and $\log K_{DL}=0.55$.

Liquid-liquid partition of the picrate ion

Picrate ion forms an ion pair with the metal complex cation, and facilitates the extraction of the metal ion from the water phase into the organic phase. However, in the case of ATCO and ATCO-Bzl₂, the protonated ligand forms an ion pair with the picrate ion (without the metal ion). This causes the reduction of picrate ion in the aqueous phase, which results in the decrease

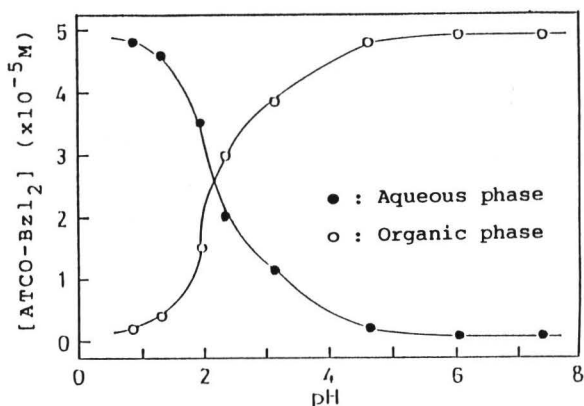


Fig.2 Distribution of ATCO-Bzl₂ between DCE and water

of metal extraction. Therefore, extraction behaviour of the picrate ion with ATCO and ATCO-Bzl₂ was examined. Figure 3 shows the plots of the concentration of the picrate ion in both the aqueous and the organic phase vs. pH in aqueous phase. As the pH value of aqueous phase decreased, the concentration of picrate ion in the organic phase increased. The increase of the protonated species of ATCO-Bzl₂ (RH⁺ and RH²⁺) results in increase of the ion pair of the protonated species of ATCO-Bzl₂ with picrate ion which is easily extractable. The concentration of picrate ion was $8.2 \times 10^{-4} \text{ M}$, at pH 3.5, which is about twice the ligand concentration. Therefore, the composition of the ion pair is (RH₂²⁺)(Pic⁻)₂. On the other hand, in the case of ATCO with picrate ion, the composition of that was 1:1 (ATCO:Pic⁻).

Liquid-liquid extraction of various metals

Results of the liquid-liquid extraction of various metal ions with ATCO and ATCO-Bzl₂ in the presence of picrate ion are summarized in Table 1. In order to compare the extraction behaviour of various metals with ATCO to that of HTCO (having the same number of donor atoms as sulphur atoms in its rings), the previous extraction data for HTCO (Sekido, 1988) are also shown in Table 1. The following ions were examined: Mg²⁺ (class a), Mn²⁺, Zn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ (class ab), and Ag⁺, Cu⁺ and Hg²⁺ (class b). As described in the

previous paper, metal ions belonging to class a and ab except Cu^{2+} are not extracted with HTCO at all. On the other hand, Zn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} belonging to class ab metal ion were extracted with ATCO and ATCO-Bzl₂ which have a donor set of S4N2. It is thought that two nitrogen atoms in the ligand contribute to the extraction of the class ab metals. Class b metal ions such as Ag^+ , Cu^+ and Hg^{2+} were extracted well with each of three ligands. Class b metal ions were also extracted with the ligand which

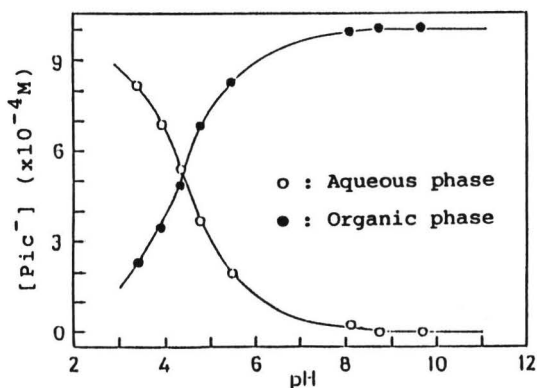
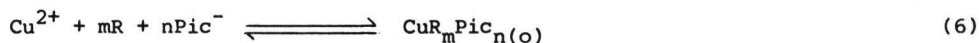


Fig.3 Distribution of picrate ion with ATCO-Bzl₂

contains four sulphur atoms such as 1,4,8,11-tetrathiacyclotetradecane (TTCT), as previously reported(Saito,1983). The extraction behaviour of metal ions with the ATCO-Bzl₂ is similar to that of ATCO. Extractability of ATCO-Bzl₂ is larger than that of ATCO for Cu^+ , Cu^{2+} , and Hg^{2+} . It was found that two benzyl groups of ATCO-Bzl₂ contributed to the increase of the distribution constant of the ion pair complex. This result suggests the extractability of the diazatetrathioether having lipophilic groups is larger than that without lipophilic groups.

Extraction behaviour of copper(II)

Liquid-liquid extraction of Cu^{2+} was examined. The extraction constant K_{ex} and the distribution ratio D are defined as follows:



$$K_{\text{ex}} = [\text{CuR}_m\text{Pic}_n]_{\text{O}} / [\text{Cu}^{2+}] [\text{R}]_{\text{O}}^m [\text{Pic}^-]_{\text{O}}^n \quad (7)$$

and

$$D = [\text{CuR}_m\text{Pic}_n]_{\text{O}} / ([\text{Cu}^{2+}] + [\text{CuR}_m^{2+}] + [\text{CuR}_m\text{Pic}_n]) \quad (8)$$

From Eqs. (6), (7), (8) and suitable approximation, the following logarithmic expression is obtained:

$$\log D = \log K_{\text{ex}} + m \log [R]_O + n [\text{Pic}^-] \quad (9)$$

TABLE 1

Data for the extraction of various metals
with HTCO, ATCO and ATCO-Bzl₂
(α : parameter of softness(Ahrland,1958,Yamada,1975))

metal	class		HTCO		ATCO		ATCO-Bzl ₂	
			5x10 ⁻⁴ M pH	%E	5x10 ⁻⁴ M pH	%E	5x10 ⁻⁴ M pH	%E
Mg(II)	a	0	5.3	0	5.6 9.4	0 0	5.3	0
Mn(II)	ab	1.04	5.4	0	5.3 9.4	0 0	5.0	18
Zn(II)	ab	1.25	5.3	0	5.3 9.4	1 6	5.3	3
Co(II)	ab	1.39	5.3	0	5.3 9.4	1 15	5.4	1
Ni(II)	ab	1.41	5.3	0	5.6 9.4	3 21	5.4	1
Cu(II)	ab	1.64	5.4	4	5.6 9.5	15 33	5.6	53
Ag(I)	b	3.60	5.4	100	5.5 9.4	100 83	5.5	100
Cu(I)	b	3.92	5.4	100	5.2 9.4	61 99	5.8	100
Hg(II)	b	5.83	5.2	34	5.4 9.3	33 16	5.4	100

The plots of the logarithmic distribution ratio of copper(II) vs. the logarithmic concentration of ATCO-Bzl₂ in the organic phase are shown in Fig.4. The plots gave a straight line with slope +0.9 at $\log[\text{ATCO-Bzl}_2]_{O,i} < -2.4$. Therefore, "m" in Eqn.(9) is taken as m=1. However logD values decreased with the increase of the ligand concentration at $\log[\text{ATCO-Bzl}_2]_{O,i} > -2.4$. Figure 4 also shows the plots of the logarithmic concentration of picrate ion in aqueous phase vs. $\log[\text{ATCO-Bzl}_2]_{O,i}$. The plots reveal the picrate ion concentration in the aqueous phase decreased with the increase of the ligand concentration. It is thought that the formation of the ion pair $(\text{RH}_2^{2+} (\text{Pic}^-)_2)$ prevents the extraction of Cu^{2+} . The relationships between logD and logarithm of picrate ion concentration are shown in Fig. 5. A straight line with the slope +1.0 was obtained. Therefore, "n" in Eq. (9) is 1. These results suggest that the mole ratio of

the extracted species is 1:1:1 ($\text{Cu}^{2+}:\text{R}:\text{Pic}^-$). Another anion associated with the complex cation for the charge compensation may be hydroxide ion (Chayama, 1990, 1991).

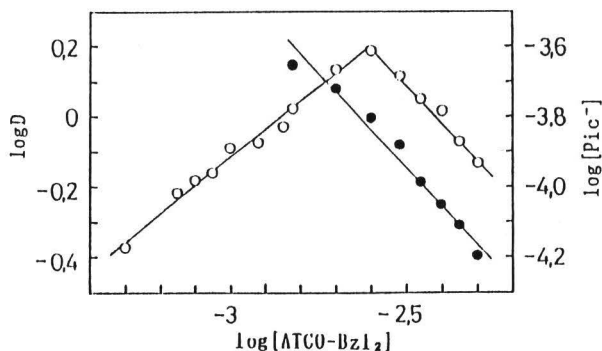


Fig.4 Plots of $\log D_{\text{Cu(II)}}$ vs. $\log[\text{ATCO-Bzl}_2]_{\text{O,i}}$ and $\log[\text{Pic}^-]$ vs. $\log[\text{ATCO-Bzl}_2]_{\text{O,i}}$ at pH 4.9

○ : $\log D_{\text{Cu(II)}}$ vs. $\log[\text{ATCO-Bzl}_2]_{\text{O,i}}$
● : $\log[\text{Pic}^-]$ vs. $\log[\text{ATCO-Bzl}_2]_{\text{O,i}}$

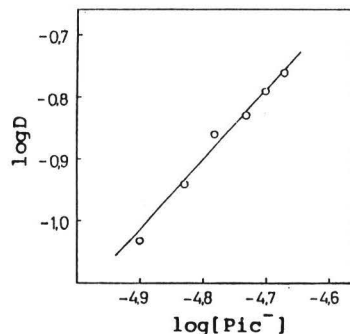


Fig.5 Plots of $\log D_{\text{Cu(II)}}$ vs. $\log[\text{Pic}^-]$ at pH 4.9

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5.11

**EXTRACTION OF PALLADIUM FROM NITRIC ACID SOLUTIONS
BY TRIPHENYLPHOSPHINE SULPHIDE IN CHLOROFORM**

S.A.EL-REEFY, J.A.DAoud AND H.F.ALY

Hot Laboratories Centre
Atomic Energy Authority
Post Code 13758, Egypt**ABSTRACT**

The extraction of Pd(II) by triphenylphosphine sulphide(Ph_3PS) in chloroform from nitric acid solutions was investigated. The effect of the different parameters affecting the extraction of palladium was studied. The stoichiometry of the extracted species was elucidated and found to be $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{Ph}_3\text{PS}$. The data were compared with those previously obtained using triphenylphosphine in chloroform as the extractant under similar conditions. Possible interference with selected radionuclides that might exist in high level liquid wastes was investigated and is discussed.

INTRODUCTION

Platinum group metals are used in high technology industries and are strategically very important materials whose supply is limited. These metals are present in substantial quantities in the high level waste (HLW) produced from reprocessing operations of spent nuclear fuel, IAEA(1989). Therefore, the recovery and purification of platinum metals from fission products is of major importance.

The investigations of the solvent extraction of palladium have been mainly carried out from chloride media with different extracting agents. Katsutoski et al.(1988) investigated the extraction of Pd(II) with trioctylammonium chloride in toluene from hydrochloric acid solutions and reported that palladium is

extracted as a mononuclear ion pair at high hydrochloric acid concentrations. El-Bazi and Freiser(1987) studied the extraction of Pd(II) with dioctyl sulfide(R_2S) in chloroform from chloride solutions and found that the extracted species was $PdCl_2(R_2S)_2$. Daamach et al.(1987) studied the extraction of Pd(II) with dialkylsulphides from hydrochloric acid solutions and showed that the addition of long-chain amines to the organic phase significantly enhances the Pd(II) extraction. However, the extraction of palladium from nitric acid solution so far reported is rather limited, Popczyk and Zaitsev(1987), Gorski et al.(1984), Rizni and Natarajan(1990). The extraction of Pd(II) from nitrate medium by triphenylphosphine and triphenylphosphine oxide in chloroform from nitrate medium was reported in a previous communication (El-Reefy et al.(1992)). In the present work, extraction of Pd(II) by triphenylphosphine sulphide from nitrate medium was investigated and the results obtained in both systems are discussed in order to develop and optimize the selective extraction of Pd from HLW.

EXPERIMENTAL

Chemicals and reagents

Triphenylphosphine sulphide and $Pd(NO_3)_2$ were of purum grade and supplied by Fluka. The chloroform used was an AR product of Prolabo. The mother solution of palladium was prepared by dissolving the salt in concentrated nitric acid and then diluting to the desired molarity and storing in a dark bottle.

Measurement techniques

The palladium concentration in the aqueous nitric solutions was determined spectrophotometrically using a Shimadzu UV-visible recording spectrophotometer, type UV-160A. A maximum absorption band was observed at $400\pm 3nm$ for $Pd(NO_3)_2$ in nitric acid solutions ranging from 1-6M, as previously reported (El-Reefy et al.(1992)).

The radioactive Co-60 and Eu-152+154 were prepared by neutron irradiation of spectroscopically pure cobalt carbonate and europium oxide. Ru-103 was obtained from Amersham, England. The

radionuclides were used in tracer concentrations ($<10^{-6}\text{M}$). The radiometric measurements were carried out by using a NaI(Tl) scintillation counting assembly.

Procedure

The extraction was carried out by shaking 5 cm^3 of the aqueous nitric acid solutions containing Pd(II) with 5 cm^3 of the organic phase containing Ph_3PS at the desired molarity. Preliminary experiments showed that equilibrium Pd(II) extraction was reached after 45 min of vigorous shaking in a thermostated shaker at $25\pm 1^\circ\text{C}$. After centrifugation and phase separation, the concentration of palladium in the aqueous phase was measured and its concentration in the organic phase was calculated by difference. The distribution ratio, D , of Pd(II) as well as the partition investigations of the different radionuclides investigated were carried out and calculated as previously reported (El-Reefy et al.(1992)).

RESULTS AND DISCUSSION

The effects of the different parameters affecting the extraction of Pd(II) by Ph_3PS from nitric acid solutions were separately investigated. The effect of HNO_3 molarity was investigated in the range 1-6M. The distribution ratio increased with increasing $[\text{HNO}_3]$ and reached a maximum around 3.5M, followed by a gradual decrease, Fig.1.

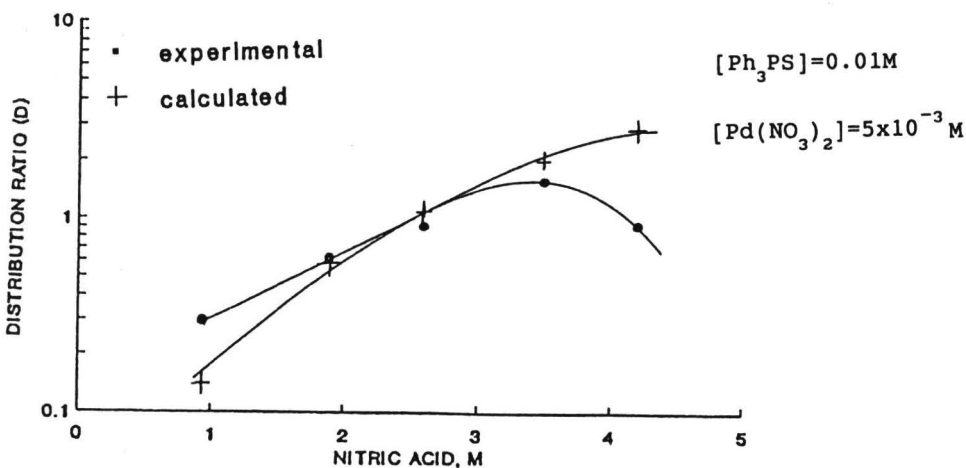


Fig. 1 Effect of $[\text{HNO}_3]$

The increase in $[H^+]$ of the aqueous phase at constant $[NO_3^-]$ of 6M, had visually no effect on the distribution ratio. The effect of $[NO_3^-]$ was investigated in the range 2-6M at constant $[H^+]$ of 2M. The distribution ratio was found to increase with the increase in $[NO_3^-]$ and a slope of 2 was obtained from the log-log relation, Fig.2.

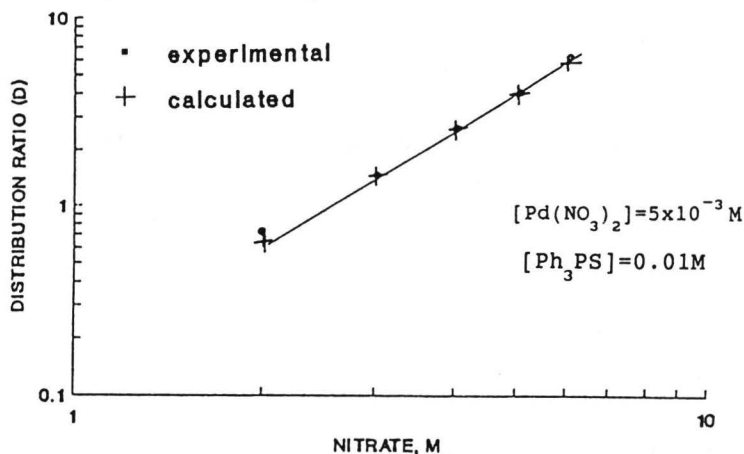


Fig. 2 Effect of $[NO_3^-]$ at constant $[H^+]$ (2M)

The increase in $[Ph_3PS]$ from 5×10^{-3} - $4 \times 10^{-2} M$ was found to increase the value of the distribution ratio with a slope of 2, Fig.3.

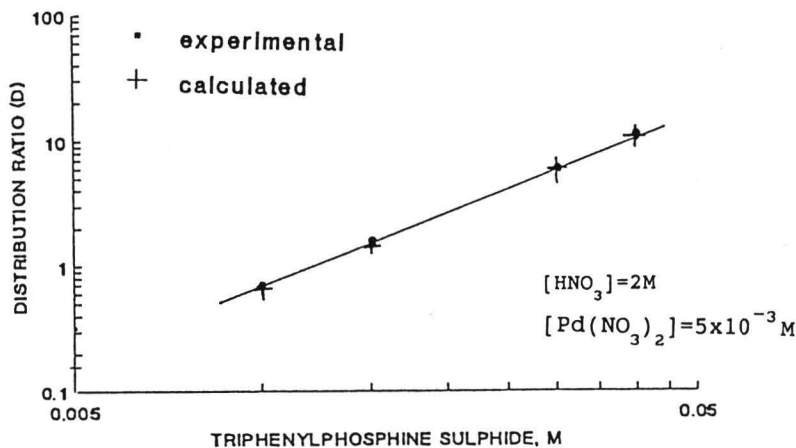
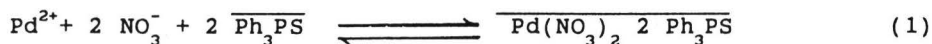


Fig. 3 Effect of $[Ph_3PS]$

Slope analysis of the results indicates that the reaction is second power dependent of both the nitric acid and the extractant concentration while it is independent of $[H^+]$. The extraction reaction in this case can be represented by the following equation :



$$K_{ex} = \frac{[\overline{Pd(NO_3)_2 \cdot 2 Ph_3PS}]}{[Pd^{2+}] [NO_3^-]^2 [\overline{Ph_3PS}]^2} = \frac{D}{[NO_3^-]^2 [\overline{Ph_3PS}]^2} \quad (2)$$

The values of K_{ex} calculated at different $[NO_3^-]$ and $[\overline{Ph_3PS}]$ using equation (2) are given in Table 1 and a mean value of $K_{ex} = 1.61 \pm 0.01 \times 10^3$ is obtained. The tabulated data show deviations in the value of K_{ex} at $[\overline{Ph_3PS}] < 10^{-2} M$.

TABLE 1
Extraction constant, K_{ex} , of $\overline{Pd(NO_3)_2 \cdot 2 Ph_3PS}$ at different nitrate and extractant concentration

* $[\overline{Ph_3PS}] \times 10^3 M$	$K_{ex} \times 10^{-3}$	** $[NO_3^-], M$	$K_{ex} \times 10^{-3}$
5	3.17	2	1.70
10	1.70	3	1.56
15	1.67	4	1.56
30	1.56	5	1.60
40	1.56	6	1.60
Mean value	$1.62 \pm 0.07 \times 10^3$		$1.60 \pm 0.01 \times 10^3$
Total mean value			$1.61 \pm 0.04 \times 10^3$

* at constant $[NO_3^-] = 2M$,

** at constant $[\overline{Ph_3PS}] = 10^{-2} M$

The distribution ratios calculated for different nitric, nitrate and $\overline{Ph_3PS}$ concentrations using the average value of the extraction constant show good agreement with the experimental values, within the accepted experimental error, Figs.1-3. Deviations at high nitric acid concentrations may be related to the co-extraction of nitric acid or formation of less

extractable Pd(II) species, as reported by Zaitsev and Inkova (1981) and Schmidt et al.(1986).

The effect of temperature on the extraction of Pd(II) by Ph_3PS in chloroform was investigated and the different thermodynamic parameters, namely, the enthalpy change (ΔH), the Gibbs standard free energy (ΔG) and the standard entropy change (ΔS) are calculated and given in table 2 together with those previously reported by El-Reefy et al.(1992) and Daoud et al.(1992).

TABLE 2
Thermodynamic functions for the extraction of Pd(II) by Ph_3PS in chloroform

Extractant	$\Delta H, \text{kJ/mol}$	$\Delta G, \text{kJ/mol}$	$\Delta S, \text{J/mol/K}$
$\text{Ph}_3\text{P}/\text{chloroform}$	-27.13	-33.10	19.90 *
$\text{Ph}_3\text{PS}/\text{benzene}$	-35.69	-22.13	-45.50 **
$\text{Ph}_3\text{PS}/\text{chloroform}$	-29.71	-19.06	-35.75

* data obtained from El-Reefy et al.(1992).

** data obtained from Daoud et al.(1992).

The tabulated data show that the stability of the Pd(II) complex extracted by $\text{Ph}_3\text{PS}/\text{chloroform}$ is enthalpy favoured like the complex extracted by $\text{Ph}_3\text{PS}/\text{benzene}$, while the complex formed by $\text{Ph}_3\text{P}/\text{chloroform}$ is favoured by both the enthalpy and the entropy changes of the reaction. The positive entropy and negative heat changes in the Ph_3P system favour the complex formation of Pd with Ph_3P rather than with Ph_3PS . This is justified by the higher extraction constants of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{Ph}_3\text{P}$ over that of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{Ph}_3\text{S}$ in chloroform or benzene under the same experimental conditions.

Recovery of palladium from some fission products

The feasibility of recovery of palladium by Ph_3PS from some fission products which can exist in high active liquid waste (HLW), namely, Co-60, Eu-152+154 and Ru-103 was preliminarily investigated. The results obtained showed that more than 97% of Pd(II) was extracted from 3.5M HNO_3 by $5.1 \times 10^{-2}\text{M}$

Ph_3PS /chloroform while less than 0.3% of the other nuclides were extracted under the same conditions. In a previous work, El-Reefy et al (1992), it was shown that Pd(II) was extracted by Ph_3P /chloroform, but more than 70% of Ru was also extracted by the same extractant. Consequently, Ph_3PS /chloroform can be considered as a better extractant, compared with Ph_3P /chloroform for the extraction of Pd(II) less contaminated with Ru .

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5.12

A SPECTROSCOPIC APPROACH TO SOME LIQUID-LIQUID EXTRACTION SYSTEMS

G.J. GOETZ-GRANDMONT, A. TAYEB and J.P. BRUNETTE
Laboratoire de Chimie Minérale et Analytique, E.H.I.C.S.,
(URA 405 du Centre National de la Recherche Scientifique),
1, rue Blaise Pascal, BP 296, 67008 STRASBOURG CEDEX, FRANCE

ABSTRACT

IR, ^1H and ^{31}P NMR spectroscopic studies related to the phase-transfer of some divalent or trivalent metal ions, Cu(II), Co(II), Zn(II), In(III), with 4-acylpyrazol-5-ols derivatives are presented. The extractants are the 1-phenyl-3-methyl-4-acyl-5-hydroxypyrazoles "HL" (acyl: benzoyl, thenoyl, lauroyl) and the bis(1-phenyl-3-methyl-5-hydroxypyrazol-4-oyl)octane HL-8-LH. The studies mainly deal with the three topics: structural studies of extractants, structural studies of (isolated) extractable complexes, and studies of loaded extraction phases or of model synthetic solutions. The latter give additional information, unattainable by the usual analytical methods, to determine the extraction processes.

INTRODUCTION

Increasing interest is observed in spectroscopic studies related to phase-transfer of metal ions using more and more sophisticated techniques. They deal with the following main topics:

- *Spectroscopic studies of the extractants*: extractants in pure form or in solution (structure, isomerization, dimerization or aggregation, solute-solvent interactions), interactions in synergistic mixtures of extractants.

- *Simulation of extraction systems* to obtain direct evidence of the conclusions drawn from analytical studies: preparation and structural studies of metal-extractant complexes supposed to be extracted (nature of metal-ligand bonds, hydration, hydrolysis), single-phase simulation of reactions supposed to occur in the extraction system (e.g.: synergistic reaction). In both cases, comparisons with organic extraction phases are needed. This is not so easy because, generally, the phases must be loaded and even saturated with the metal for accurate spectroscopic measurements, which may shift the equilibria under study.

- Studies of complex extraction phases:

In many systems, analytical studies fail to determine the extraction process owing to its complexity (e.g., Stoyanov (1991): co-extraction of Zr(IV) and Fe(III) with (HDEHP)₂). Sometimes they give the overall composition of the extracted species (e.g., Huang (1987): UO₂H₃R₄NO₃ with H₂R₂ = (HDEHP)₂) but this latter cannot be synthesized and structural information is missing. Spectroscopic studies, generally combining several techniques, may solve such problems.

- Interfacial studies:

This is a more recent research field which generally requires sophisticated techniques, save for micellar (transparent) solutions. However, indirect information about the interface may sometimes be obtained by studying the bulk phases.

The aim of this communication is to show that a number of useful, even indispensable, pieces of information may be obtained from IR and NMR studies using currently available apparatus and rather unsophisticated methods. Studies deal with the extraction systems: In³⁺ / HL (respectively HL + TOPO) in toluene, and Zn²⁺ or In³⁺ / HL-8-LH (respectively HL-8-LH + TOPO) in chloroform,

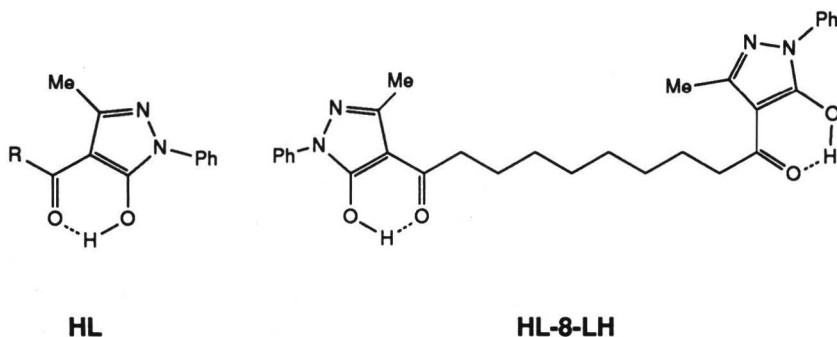


Fig. 1 The extractants

HL: 1-phenyl-3-methyl-4-acyl-5-hydroxypyrazole

(R = phenyl: HPMBP; R = undecyl: HPMLP; R = thienyl: HPMTTP)

HL-8-LH: bis(1-phenyl-3-methyl-5-hydroxypyrazol-4-oyl)octane

METHODOLOGY

Most measurements were performed using an IR Perkin-Elmer 457 spectrometer and FT Brücker WH 90 (2.11 T field) and WH 200 SY (4.7 T field) NMR spectrometers. Thermogravimetric analyses were performed on a Setaram TG-DTA 92 apparatus, under

argon. FAB⁺ mass spectra of InL₃ complexes were recorded on a ZAB HF VG Analytical, and negative CI mass spectra were recorded on a TSQ 70 Finnigan MAT.

Most of our conclusions have been drawn from the same sort of data, namely:

- the chemical shift and the width of the ³¹P NMR peaks of TOPO, that show respectively the extent of P=O donation and the exchange of TOPO between its various sites, if any,
- for PMR, the chemical shift of the CH₃(pyrazole) protons of HL and HL-8-LH, that is very sensitive to any perturbation of the HL group,
- for IR, the frequencies of the C=O and OH stretching vibrations, that describe the chelating part of the extractant and the coordination of water molecules.

RESULTS

Extractants: structure and interactions

Figure 1 shows the chelated 4-acylpyrazol-5-ol form, that corresponds to the major tautomer in solids, and in toluene or CHCl₃ solutions at room temperature. However, other forms might exist, e.g. acylpyrine, acylpyrazolone, (alkylhydroxymethylene)pyrazolone. In fact, ¹³C and ¹H NMR, and IR spectroscopies allow the observation of the acylpyrine and acylpyrazolol forms only [Kurkovskaya (1977), Okafor (1984), Brunette (1985)]. The intramolecular chelate bond (Figure 1) may be loosened or broken when intermolecular interactions occur. This is observed for one of the crystalline forms of HPMBP and of "HL-Ph-LH", i.e. 1,3-bis(1'-phenyl-3'-methyl-5'-hydroxypyrazol-4'-oyl)benzene. It is also observed in toluene solutions of HL + TOPO : for the most acidic chelant, HPMTp, an IR free C=O stretching frequency is observed. However, ³¹P NMR is the most sensitive technique to observe TOPO - HL interactions. It shows that the order of magnitude of the interaction strength is the same as the TOPO - CHCl₃(solvent) one: δ(³¹P) of TOPO is 39.9 ppm/H₃PO₄ in toluene, 48.8 ppm in CHCl₃ and ≈ 50 ppm for equimolar mixtures of HL + TOPO in toluene.

Note that, even when the strongest interaction occurs, it has no influence upon the synergistic extraction.

Metal-extractant complexes, comparison with extraction phases

Indium complexes of mono-acylpyrazolols

Solid complexes In(PMBP)₃.xH₂O and In(PMTp)₃.xH₂O (x = 0, 2) have been prepared, studied by IR, PMR and mass spectroscopies, TGA and conductimetry, and their solutions in toluene have been compared to loaded extraction phases [Goetz-Grandmont (1992)]. Undoubtedly, tris-chelates are extracted.

In the solid "InL₃.2H₂O" complexes, H₂O is strongly perturbed with respect to free H₂O:

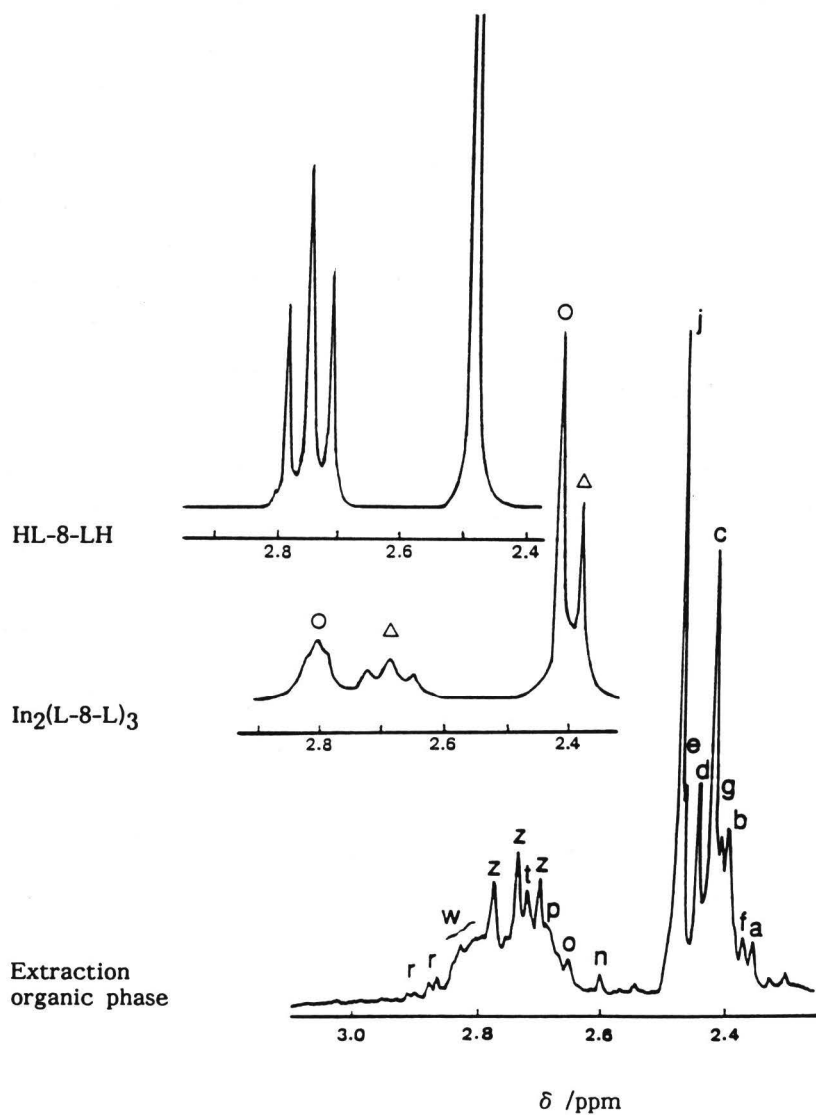


Fig. 2 PMR spectra (solvent: CDCl_3)

Extraction phase from the system:

In^{3+} , $(\text{Na,H})+\text{ClO}_4^-$ 1M in D_2O , $\text{pD} = 1.9$ / HL-8-LH 10^{-2}M in CDCl_3

Spectra from the reference "Tayeb (1991)" by courtesy of Springer-Verlag KG

$\nu(\text{O-H})$ appears at 3070 cm^{-1} . Such a frequency might well be due to H_2O coordinated upon indium or upon oxygen atoms of the "L" moiety, thus some ambiguity exists.

Complexes of some divalent metals with HL-8-LH

Solid $\text{Co}(\text{L-8-L})(\text{H}_2\text{O})_2$, $\text{Cu}(\text{L-8-L})$ and $\text{Zn}(\text{L-8-L})(\text{H}_2\text{O})$ have been prepared and studied. IR shows that, as expected, all the L⁻ groups act as chelatants and that one H_2O molecule per metal atom probably form a coordination bond with Zn, respectively Co. The latter is in agreement with TGA data. Those are monomers: thus, the L-8-L^{2-} ligand is folded around the cationic center. For such small-size ions, this probably causes some constraint in the ligand. Indeed, for $\text{Zn}(\text{L-8-L})(\text{H}_2\text{O})$, [Tayeb (1990)], PMR shows a restricted rotation of the " CH_2, α " protons, i.e. protons of the CH_2 group linked to the carbonyl of the coordinated acylpyrazolol group.

Owing to experimental problems (poor solubility or/and paramagnetic complexes, precipitates in the extraction phases), it is impossible to effectively compare the spectra of extraction phases and those of solutions of these complexes. However, it is noticeable that the analytical treatment of Cu extraction with HL-8-LH, either in 1,2-dichloroethane [Miyazaki (1989)] or in CHCl_3 , gives evidence of the extraction of a $\text{Cu}(\text{L-8-L})(\text{H}_2\text{O})_x$ (x unknown) monomer species. Moreover, since the $\text{Cu}(\text{L-8-L})$ complex is anhydrous, it is not surprising that it does not accommodate any other donor molecule: thus, no synergy is observed in the presence of TOPO. However, the extracted complexes may be different from the complexes obtained by synthesis. For Co^{2+} , analytical studies show that HL-8-LH and HL-8-LH + TOPO extract the metal as $\text{Co}(\text{L-8-LH})_2$ [Lu(1991)], $\text{Co}_2(\text{L-8-L})_2$ and $\text{Co}(\text{L-8-L})(\text{TOPO})_1$ or 2 respectively. Only the latter complexes may be related to the solid $\text{Co}(\text{L-8-L})(\text{H}_2\text{O})_2$. For Zn^{2+} , $\text{Zn}(\text{L-8-L})$ and $\text{Zn}(\text{L-8-L})(\text{TOPO})$ are extracted in 1,2-dichloroethane [Miyazaki (1991)], while $\text{Zn}(\text{L-8-LH})_2$ and $\text{Zn}(\text{L-8-L})(\text{TOPO})$ are extracted in chloroformic solutions. However, only $\text{Zn}(\text{L-8-L})(\text{H}_2\text{O})$ precipitates from the latter extraction phases when they are strongly loaded.

Complex of In^{3+} with HL-8-LH

$\text{In}_2(\text{L-8-L})_3$ is easily prepared in aqueous-ethanolic solution. Its PMR spectrum, recorded just after dissolution [Fig.2, Tayeb(1991)] shows that two different "L" functional groups are present in a 1:2 ratio, corresponding to a L-8-L bridge (Δ) and to two folded L-8-L ligands ($\circ$). The profile of the downfield signal ($\circ$), that corresponds to the CH_2, α protons of the folded ligands, agrees with a restricted rotation of the $\text{C}(\text{O})\text{-CH}_2$ bond, due to steric constraints. On standing, new signals corresponding to one sort of unfolded L-8-L appear and grow. They probably correspond to a dimeric complex with three L-8-L bridges or to oligomeric species.

Complex extraction phases: In^{3+} / HL-8-LH system in chloroform

Analytical studies fail to solve this system. Evidence is given that, at rather low pH and for low extractant concentrations, the major extracted species are $\text{In}(\text{L-8-L})(\text{L-8-LH})$ and $\text{In}_2(\text{L-8-L})_3$ but their extraction cannot describe the whole process. The PMR spectra of some

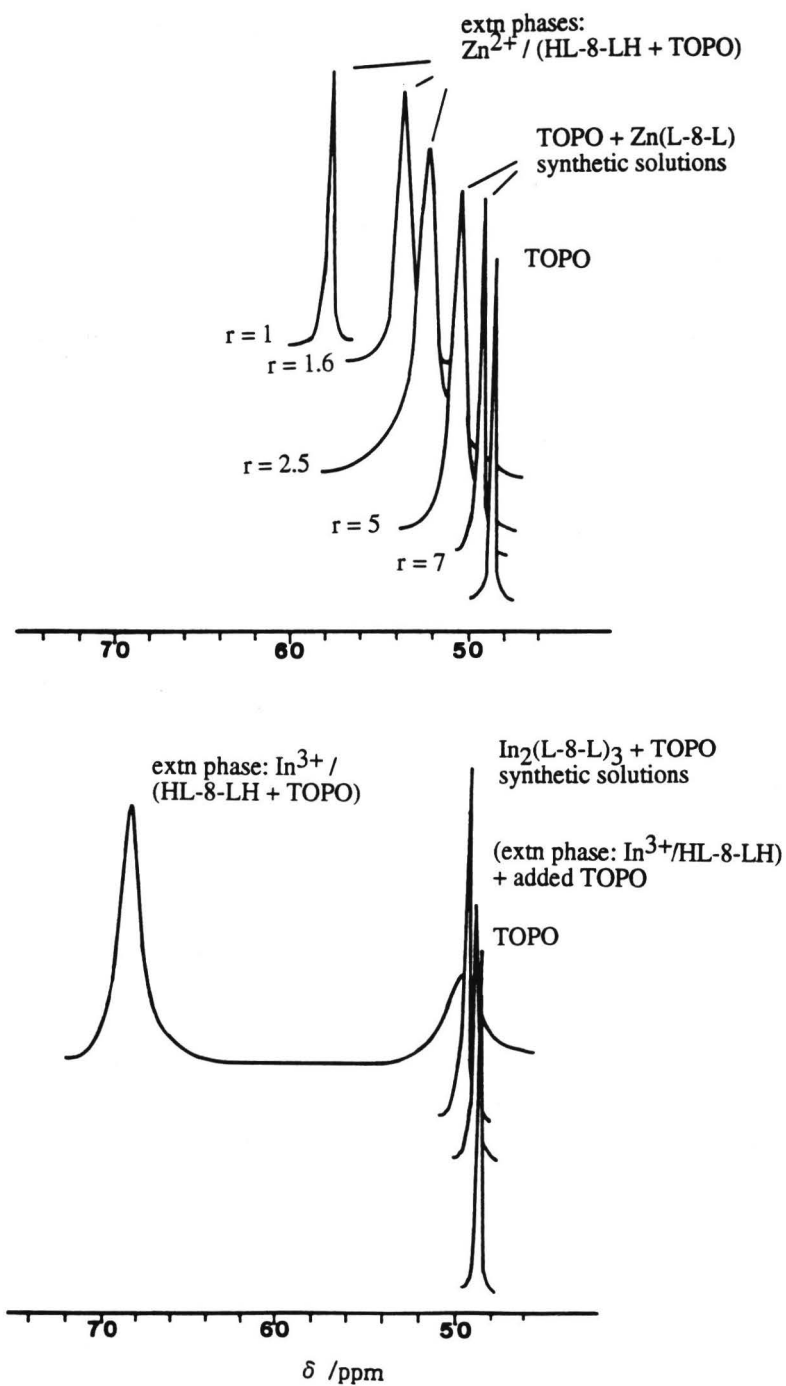
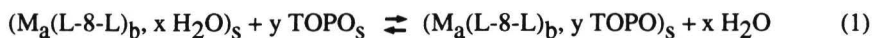


Fig. 3 ^{31}P NMR spectra of synthetic solutions and extraction organic phases in CDCl_3
 $(r = c(\text{TOPO}) / c(\text{"L-8-L"}))$

extraction phases show the great complexity of the system: e.g. Figure 2, each singlet (a to e, j) corresponds to a different ligation of a "L" functional group. HL-8-LH and $\text{In}_2(\text{L-8-L})_3$ signals are known. Other species are identified from the variation of the spectra of the extraction phases with pH and initial concentrations, namely, $\text{In}(\text{L-8-LH})(\text{L-8-LH})$ and $\text{In}_2(\text{L-8-L})_3$. In view of these results, the analytical data may be explained and hence an approximate solution may be obtained. Both methods show that polymeric species are formed at highest pH's.

Study of synergistic effects: M^{n+} / HL-8-LH (HL) + TOPO systems

H_2O - TOPO substitutions or TOPO additions on complexes in the organic phase, according to the equilibrium (1), are most often used to describe the synergistic effect obtained by using a cation exchanger (e.g. HL-8-LH) and a solvating agent (e.g. TOPO).



(It is often supposed that $y = x$).

Thus, synthetic mixtures of $(\text{M}_a(\text{L-8-L})_b)_s + x \text{H}_2\text{O}$ complexes and TOPO in chloroform have been studied by ^1H and ^{31}P NMR. Their spectra have been compared with those of organic extraction phases from the systems Zn^{2+} (respectively In^{3+}) / HL-8-LH + TOPO in CHCl_3 , where $c(\text{TOPO}_{\text{total,s}})$ and $c(\text{"L-8-L"}_{\text{total,s}})$ were in the same proportions. Figure 3 reports the ^{31}P NMR studies.

For Zn^{2+} , synthetic solutions and organic extraction phases are similar, the ^{31}P peak position and its width only depend on r . Therefore, equilibrium 1 may occur in the organic phase.

For In^{3+} , a strong TOPO-In bonding, i.e. with $\delta(^{31}\text{P}_{\text{TOPO}}) > 65$ ppm, is observed only for the extraction phases. Thus, the reaction 1 is not a step of the extraction mechanism.

The same conclusion holds for the system: In^{3+} / HL + TOPO in toluene (perchlorate or chloride aqueous medium).

The formula of its synergistic complexes suggest that indium may be heptacoordinated, even octacoordinated. Indeed, IR spectra of the extraction phases show that, simultaneously, all the L⁻ groups form chelates and TOPO is strongly bonded: this is rather convincing evidence of a coordination higher than 6.

CONCLUSION

By combining spectroscopic data, much valuable information may be obtained about extraction systems. The structures of the acylpyrazolol derivative extractants and of their metal complexes have been studied, as well as their interactions with TOPO. Considerable help has been brought by NMR to solve the extraction system In^{3+} / HL-8-LH. Comparison

of synthetic ML_n + TOPO solutions with extraction phases showed that, depending on the metal, equilibrium (1) may (Zn^{2+}) or may not (In^{3+}) be a step of the extraction mechanism.

ACKNOWLEDGMENTS

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5.13

**SYNERGISTIC EXTRACTION OF IRON(III) WITH DI(1-METHYLHEPTYL)
METHYL PHOSPHONATE AND PRIMARY AMINE N1923**

Shumin HAN, Deqian LI and Genxiang MA

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

ABSTRACT

The synergistic extraction of Fe (III) from HCl or NaCl and LaCl_3 solutions with di(1-methylheptyl)methyl phosphonate (abbreviated as B) and primary amine N1923 (RNH_2) in n-heptane has been studied at constant high ionic strength. The composition of the synergistic extraction complex was determined to be $\text{RNH}_3\text{FeCl}_4\text{B}_2$. The mechanism of synergistic extraction of Fe(III) has been obtained. The salting-out effect of LaCl_3 and NaCl on the distribution ratio of Fe(III) was also investigated, and the results show that effective separation is possible with the RNH_3Cl and B system for removal of Fe (III) from LaCl_3 solution.

INTRODUCTION

It has been considered that no synergism is usually present in the extraction of ferric iron (Xu et al., 1984); in fact, the synergistic extraction of Fe(III) has been reported (Reddy et al., 1978; Yu and Chen, 1989). The synergistic extraction of Fe(III) from chloride media with di(1-methylheptyl)methyl phosphonate (B) and primary amine N1923 (RNH_3Cl) is reported in this paper from HCl, NaCl and LaCl_3 solutions at constant high ionic strength.

It is well known that Fe(III), which often co-exists with rare earth ions, is disadvantageous in separation processes for rare earth ions. The results reported here show that effective separation is possible with RNH_3Cl and B for removal of Fe(III) from LaCl_3 solutions.

EXPERIMENTAL

B and primary amine N1923((R₁)(R₂)-CHNH₂ with a total number of carbon atoms of 19-23) were supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. B was purified as described in a previous paper (Hu and Zhang, 1981). All other chemicals were analytical reagents.

Equal volumes of the aqueous and organic phases were placed in a thermostatic box at $25 \pm 1^\circ\text{C}$ for 30 min., and were shaken for 20 min.. After centrifugal separation, the concentration of Fe(III) in the aqueous phase was determined spectrometrically by the o-phenanthroline method. The concentration of Fe(III) in the organic phase was obtained by difference. The contents of B and primary amine were determined as described previously (Hu and Zhang, 1981; Le et al., 1987).

RESULTS AND DISCUSSIONS

Extraction of Fe(III) with B and RNH₃Cl

Under the conditions used, the extraction of Fe(III) with RNH₃Cl is negligible. The extraction of Fe(III) with B can be seen in Fig. 1.

The slope of the straight line in Fig. 1 is determined to be 2.12, and thus the extraction reaction of Fe(III) can be expressed as follows:



$$K_B = \frac{[\text{FeCl}_3\text{B}_2]_{(\omega)}}{[\text{FeCl}_3][\text{B}]_{(\omega)}^2} = \frac{D_B(1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i)}{\beta_3 [\text{Cl}^-]^3 [\text{B}]_{(\omega)}^2} \quad (2)$$

Taking logarithms on both sides of Eqn. (2) and rearranging.

$$\log K_B = \log D_B - 2\log [\text{B}]_{(\omega)} + \log Y \quad (3)$$

$$\text{Where } Y = \frac{(1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i)}{\beta_3 [\text{Cl}^-]^3}$$

The terms of equation (3) can be replaced by the relevant values of $\log D_B$, $\log [\text{B}]_{(\omega)}$ and $[\text{NaCl}] = 5.0\text{M}$ from literature data for β_i (Chem. Depart. Hangzhou Univ., 1979) ($\beta_1 = 10^{1.48}$, $\beta_2 = 10^{2.13}$, $\beta_3 = 10^{1.99}$, $\beta_4 = 10^{0.01}$) then the equilibrium constant of reaction (1) is calculated to be $\log K_B = 2.14$.

Synergistic extraction of Fe (III) from HCl, NaCl and LaCl₃ solutions with "RNH₃Cl+B"

The total concentration of "B+RNH₃Cl" in the organic phase was maintained to be 0.10 M during the experimental series, while the concentration ratio of "RNH₃Cl+B" was changed.

The synergistic diagrams of the distribution ratio (Dt) versus mole fraction ($X_{\text{RNH}_3\text{Cl}}$) were thus obtained [Fig. 2]. The results indicate that the synergistic effect is present

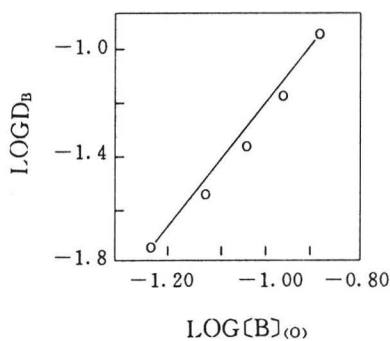


Fig. 1 $\log D_B$ vs $\log [B]_{(O)}$

$C_{\text{Fe(III)}} = 1.07 \text{ mM}$
 $\text{pH} = 1.07$ $C_{\text{NaCl}} = 5.0 \text{ M}$

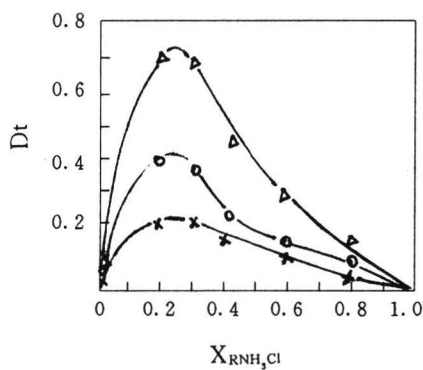


Fig. 2 Dt vs $X_{\text{RNH}_3\text{Cl}}$

Δ -NaCl; $C_{\text{NaCl}} = 5.0 \text{ M}$
 $\text{pH} = 1.07$ $C_{\text{Fe(III)}} = 1.07 \text{ mM}$
 $\circ$ -LaCl₃; $C_{\text{LaCl}_3} = 1.8 \text{ M}$
 $\text{pH} = 0.67$ $C_{\text{Fe(III)}} = 1.34 \text{ mM}$
 $\times$ -HCl; $C_{\text{Fe(III)}} = 1.09 \text{ mM}$
 $C_{\text{HCl}} = 1.0 \text{ M}$

in the extraction of FeCl₃ with "B+RNH₃Cl" not only from high HCl concentration solutions but also from high NaCl or LaCl₃ concentration solutions at lower acidities.

No synergism was found when the concentration of HCl, NaCl or LaCl₃ was much lower, which suggests that the synergistic extraction of Fe(III) mainly depends on the salting-out effect.

The salting-out effect of NaCl, LaCl₃ on the synergistic extraction of Fe (III) with "RNH₃Cl+B"

Fig. 3 shows the effect of LaCl_3 and NaCl concentrations on the synergistic extraction of Fe(III) with " $\text{RNH}_3\text{Cl} + \text{B}$ ". The extraction distribution ratio of Fe(III) increases with increasing LaCl_3 or NaCl concentration. The slope of the straight line of the effect of LaCl_3 on the distribution ratio of Fe(III) is much bigger than that of NaCl , which shows that LaCl_3 is a more effective salting-out agent than NaCl . This may be explained by higher cationic charge density and greater anion concentration of LaCl_3 than that of NaCl . It is expected that effective separation will be possible with B and RNH_3Cl as solvents for the removal of Fe(III) in rare earth(III) solutions.

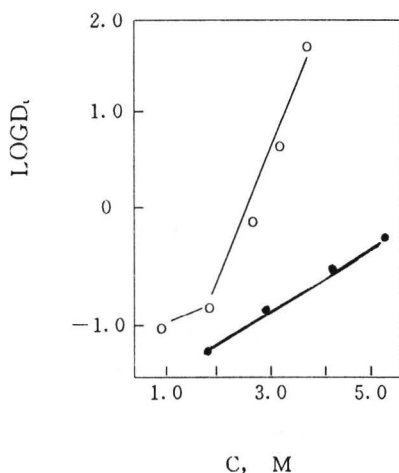
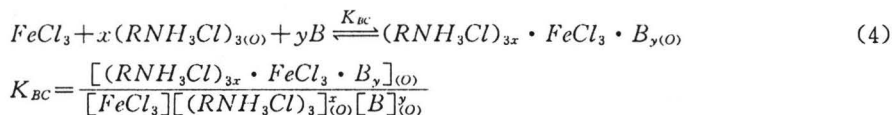


Fig. 3 Relationship between $\log D_t$ and C_{NaCl} or C_{LaCl_3}

o — $\text{B-RNH}_3\text{Cl-Fe(III)-LaCl}_3$ • — $\text{B-RNH}_3\text{Cl-Fe(III)-NaCl}$
 $C_{\text{B}} = 0.08 \text{ M}$, $C_{\text{RNH}_3\text{Cl}} = 0.02 \text{ M}$, $C_{\text{Fe(III)}} = 1.04 \text{ mM}$, $\text{pH} = 0.70$

Synergistic extraction mechanism of Fe(III) with " $\text{B} + \text{RNH}_3\text{Cl}$ " and calculation of equilibrium constants

In the experimental program, the salting-out agents NaCl and LaCl_3 have been proved not to be extracted into organic phase. Considering the polymeric degree of RNH_3Cl and Eqn. (1). The synergistic reaction of the system can be assumed to be:



$$= \frac{D_{BC}Y}{[(RNH_3Cl)_3]_{(O)}^x [B]_{(O)}^y} \quad (5)$$

Where $Y = \frac{1 + \sum_{i=1}^4 \beta_i [Cl^-]^i}{\beta_3 [Cl^-]^3}$

and D_{BC} stands for the distribution ratio of binary synergistic extraction of Fe(III). Since $[Cl^-]$ in the aqueous phase was maintained at 5.0 M, Y is a constant. Taking logarithms on both sides of Eqn. (5) and replacing $[(RNH_3Cl)_3]_{(O)}$ by $[RNH_3Cl]_{(O)}/3$ and rearranging:

$$\begin{aligned} \log K_{BC} &= \log D_{BC} - x \log [RNH_3Cl]_{(O)} - y \log [B]_{(O)} + \log 1.41 + x \log 3 \\ &= \log D_{BC} - x \log (RNH_3Cl)_{(O)} - y \log [B]_{(O)} + x \log 3 + \log 1.41 \end{aligned} \quad (6)$$

where $\log Y = \log 1.41$

A series of D_t (the total distribution ratio of Fe(III) in this extraction system) values were obtained at constant aqueous phase ($C_{Fe(III)} = 1.07$ mM, $NaCl = 5.0$ M, $pH = 1.07$) and B concentrations while varying the RNH_3Cl concentrations. Similarly, the B concentration was changed, to obtain a second series of D_t values. Because $D_c \approx 0$ under the present experimental conditions, the distribution ratio of binary synergistic extraction can be expressed as $D_{BC} = D_t - D_B - D_c \approx D_t - D_B$. In the experimental process, $\log D_{BC}$ is plotted against $\log [RNH_3Cl]_{(O)}$ or $\log [B]_{(O)}$ in Fig. 4 and 5 respectively, and

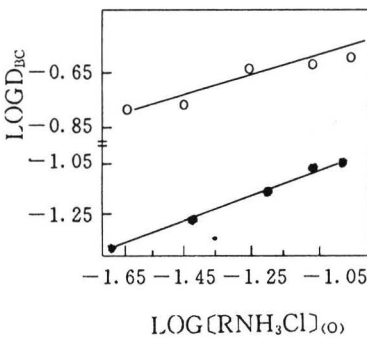


Fig. 4 Relationship between $\log D_{BC}$ and $\log [RNH_3Cl]_{(O)}$

$C_B(M)$: o—0.04; •—0.02
 $C_{Fe(III)} = 1.04$ mM,
 $C_{NaCl} = 5.0$ M, $pH = 1.07$

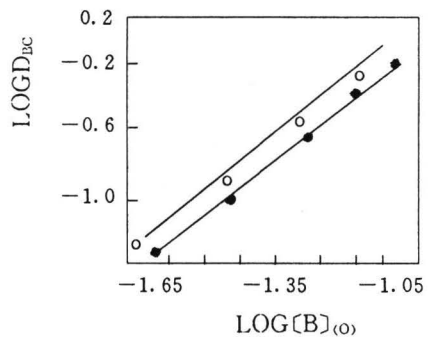


Fig. 5 Relationship between $\log D_{BC}$ and $\log [B]_{(O)}$

$C_{RNH_3Cl}(M)$: o—0.04; •—0.02
 $C_{Fe(III)} = 1.04$ mM,
 $C_{NaCl} = 5.0$ M, $pH = 1.07$

the slopes of the straight lines are determined to be $x=1/3$, $y=2$. Thus the synergistic extraction reaction can be represented by the following reaction, i.e.,



The terms of Eqn. (6) were replaced by the relevant values, and the equilibrium constant of reaction (7) was calculated to be $\log \bar{K}_{BC} = 2.92$. The formation of the synergistic complex in the organic phase can be written as:



$$\beta = \frac{[(RNH_3)_3FeCl_4 \cdot B_2]_{(O)}}{[FeCl_3 \cdot B_2]_{(O)} [(RNH_3Cl)_3]_{(O)}^{1/3}} \quad (9)$$

Eqn. (9) is replaced by Eqn. (2), (5) and rearranging, then

$$\log \beta = \log K_{BC} - \log K_B = 2.92 - 2.14 = 0.78$$

Effect of temperature on the synergistic extraction of Fe(III)

In order to ascertain the heat effect of the synergistic extraction of Fe(III) with "RNH₃Cl+B", the values of D_{BC} at different temperatures (14–34°C) were determined. $\log D_{BC}$ is plotted against the reciprocal of the temperature ($1/T$) in Fig. 6; the slope of

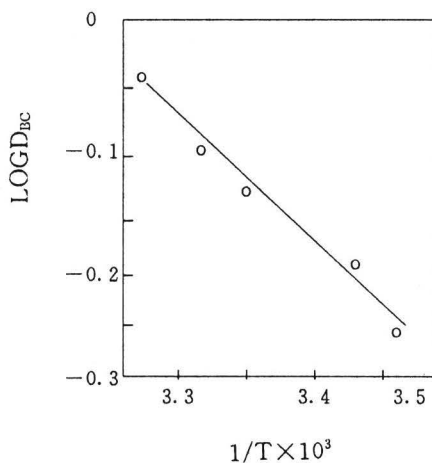


Fig. 6 Relationship between $\log D_{BC}$ and $1/T$

$$C_{Fe(III)} = 1.04 \text{ mM}, C_{NaCl} = 5.0 \text{ M} \\ C_B = 0.08 \text{ M}, C_{RNH_3Cl} = 0.02 \text{ M}, pH = 1.04$$

the straight line is calculated to be 921.6 using the least square method. Thus, the thermodynamic functions of the synergistic reactions can be expressed as $\Delta \log D_{BC} / \Delta (1/T) = -\Delta H / 2.303R$, hence $\Delta H = 17.56 \text{ kJ} \cdot \text{mol}^{-1}$. This result shows that reaction (7) is exothermic and the other thermodynamic functions are calculated to be $\Delta G^0 = 16.66 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^0 = 115 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

ACKNOWLEDGMENT

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EXTRACTION CHARACTERISTICS OF METAL IONS WITH REAGENT IMPREGNATED POLYMER RESINS

H. MATSUNAGA, Y. WAKUI and T.M. SUZUKI
Government Industrial Research Institute, Tokohu
4-2-1, Nigatake, Miyaginoku, Sendai 983 JAPAN.

ABSTRACT

Reagent impregnated polymer resins have been prepared with hydrophobic reagents and a macroporous resin as the polymer support. The resins with tertiary amines showed distinct characteristics different to those with solid quaternary ammonium salts with respect to the concentration of anionic complexes of noble metals. Similar differences were observed between the resins with liquid and solid chelating reagents for several heavy metal ions. Extraction characteristics of metal ions suggested that the prepared resins could be classified into at least two types including those having a solvent extraction mechanism, depending on the physical properties of the reagents impregnated.

INTRODUCTION

Reagent-impregnated polymer materials (RIPOM) are relatively new types of ion-selective exchangers suitable for not only hydrometallurgical but also analytical purposes, due to their high selectivity and ease of preparation. In a RIPOM system, a hydrophobic organic reagent is physically retained in the actual pores of an inert polymer without any chemical bonds to the matrix (Flett 1977). If the reagent impregnated is sufficiently hydrophobic, leaking of the reagent from the polymer matrix should not be significant and consequently the material can be used as a conventional ion-exchanger. There is a wide choice of reagents of desired selectivity to make RIPOM, since many of the reagents used for solvent extraction are generally hydrophobic and selective for certain metal ions. For the hydrophobic polymer supports, macroporous resins with a large surface area and minimum volume change are generally preferred. Although many kinds of RIPOM type adsorbents have been reported for the preconcentration and separation of metal ions (Suzuki 1991), the mechanism of uptake of metal ions has not been clarified yet. The selectivity of RIPOM is generally considered to depend on the properties of the reagent impregnated. Hence, the solvent extraction behaviour

of the reagents has been considered to be the most important property to understand the extraction characteristics of the RIPOM. Tertiary amines and quaternary ammonium salts having long alkyl chains have been impregnated into Amberlite XAD-7 beads. Since the alkylated amines and ammonium salts are effective extractants for various anionic species, the RIPOM with these reagents are expected to show anion exchange properties. The extraction characteristics of anionic chloro-complexes of noble metals with the RIPOM have been studied and compared with those of the conventional anion-exchanger and the solvent extraction system. Another type of ion-selective RIPOM has been also prepared with 4-dodecyl-6-(2-thiazolyazo)resorcinol (DTAR) and 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (PC-88A), which is known to be a good extractant for separation of rare earth metals. The extraction characteristics of rare earth metals with these RIPOM systems (Wakui 1988) have been compared to the corresponding solvent extraction (Sawai 1987).

EXPERIMENTAL

Reagents and Apparatus

The quaternary ammonium salts were synthesized from tertiary amines and ethylbromide by the conventional method. A DTAR was prepared in the manner reported by Matsunaga (1986). PC-88A (more than 95%) was kindly donated by Daihachi Chemical Co., and used as received. Amberlite XAD-7 beads (20-26 mesh) were washed with 2M nitric acid followed by acetone and water. All other chemicals used were of analytical grade. Each reagent was impregnated into XAD-7 by the method described in our previous paper (Matsunaga 1986). The concentration of metal ions was determined with a SEIKO SP-1200 ICP Atomic Emission Spectrometer. A TOA HM-50V pH-meter was used for the measurement of pH.

Extraction Procedure

An aliquot of the stock solution of the metal ion was placed in a 50cm³ glass bottle. The acidity of the solution was adjusted with a hydrochloric acid or a suitable buffer solution and diluted to the desired volume with distilled water. To the solution was added a certain amount of RIPOM. Then, the mixture was shaken until equilibrium was attained. The distribution ratios (D , cm³/g) were calculated from the concentrations of the metal ion in the solution before and after shaking, based on the following equation.

$$D = \frac{\text{The amount of the metal ion in the RIPOM (mol g}^{-1}\text{)}}{\text{The amount of the metal ion left in the solution (mol cm}^{-3}\text{)}}$$

RESULTS AND DISCUSSION

Tertiary amines and quaternary ammonium salts having bulky substituents are often used for the extraction of anionic species including chloro-complexes of noble metals. Therefore the RIPOM containing such a reagent was expected to show an affinity toward the anion. It has been already confirmed that the RIPOM prepared with trioctyl amine can extract anionic chloro-complexes of noble metals from acidic solution (Matsunaga 1986). Distribution ratios, D , for a series of RIPOM prepared from three kinds of tertiary amines and four kinds of quaternary ammonium salts with XAD-7 as a polymer support are shown in Table 1 along with that for commercially available anion exchanger, Amberlite IRA-400.

TABLE 1
Distribution Ratio of Au (III) with various types of RIPOM

Type	log D	Type	log D
TOA-XAD7	4.6	TOEA-XAD7	4.1
TDA-XAD7	4.9	TDEA-XAD7	4.2
TLA-XAD7	5.3	TLEA-XAD7	4.4
		IRA-400	4.5

Adsorbent Weight; 100 mg. Initial Au Concentration; 5×10^{-5} mol dm⁻³

Volume of Aqueous Phase; 20 cm³, HCl Concentration; 1 mol dm⁻³,

TOA; Tri-*n*-octylamine,

TDA; Tri-*n*-decylamine,

TLA; Tri-*n*-dodecylamine

TOEA; Ethyltri-*n*-octylammonium Bromide,

TDEA; Ethyltri-*n*-decylammonium Bromide,

TLEA; Ethyltri-*n*-dodecylammonium Bromide.

Figure 1 shows the relationship between log D and the carbon number (CN) for the amines and ammonium salts. The relationship between CN and log D for the amines gave a different trend to that for the ammonium salts. The Distribution ratios for amines more clearly depend on the carbon number than those for the ammonium salts. It is well known that there is a linear relationship between the extraction constants of an ion-pair and the carbon number of the organic ions extracted (Biles 1966). The present RIPOM system with amines is very similar to the ion-pair extraction system on this point. On the other hand, the sets of RIPOM with ammonium salts are less sensitive to the number of carbon atoms in the ammonium salts used. If the alkyl moiety of ammonium salts are so rigidly immobilized in the matrix of the

RIPOM that they would behave as a part of the polymer, the effect of the change in the carbon number on the extraction characteristics should be small. The ammonium salts used in this study are remarkably hydrophobic and solid at room temperature. Hence, the movement of the ammonium salts must be considerably restricted in the polymer matrix, while the amines used are liquid and might act like an extractant as in the solvent extraction.

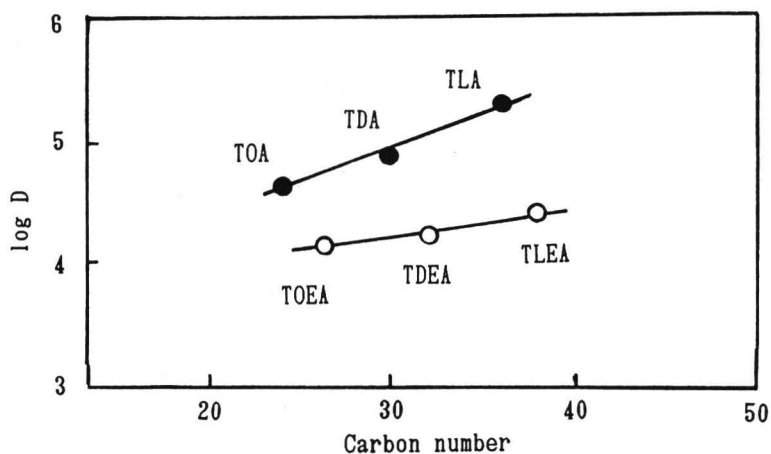


Fig.1 The relation between log D and the carbon number of the amines and ammoniums

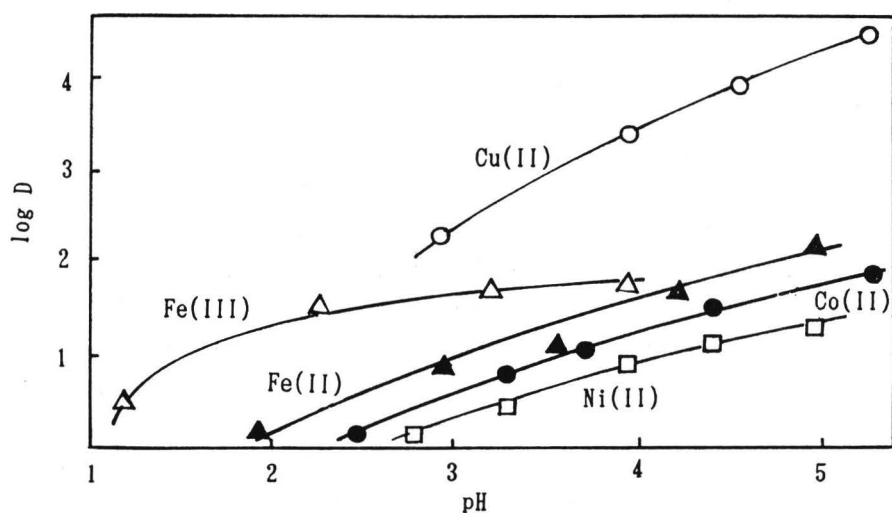


Fig.2 The effect of pH on the extraction of metal ions with TADR-XAD7

In order to provide another example for this speculation, the extraction characteristics of RIPOM systems with chelating reagents were also studied. Figure 2 shows the effect of pH on the distribution constants for several heavy metal ions with DTAR impregnated XAD-7 (DTAR-XAD7). The formation constants for 4-(2-thiazolylazo)resorcinol (TAR) which have been already reported by Stanley (1966) and Nickless (1967) are listed in Table 2.

TABLE 2
Formation constants of metal-TAR complexes

Metal ion	log K ₁	log β ₂
Fe(II)		21.6
Co(II)	12.1	23.3
Ni(II)	12.9	24.7
Cu(II)	12.3	22.2.

K₁: Formation constant of 1:1 Complex

β₂: Over all formation constant of 1:2 complex.

When the alkyl groups are structurally sufficiently apart from the chelating groups as in DTAR, the effect of them on the complex formation is considered to be very small. Hence, we can compare the formation constants for TAR with the distribution ratios for DTAR-XAD7. The order of the formation constants of TAR complexes does not agree with the order of distribution in the RIPOM system with DTAR. An additional example for the chelating-type RIPOM was investigated with 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (PC-88A). The distribution ratios for eight rare-earth metal ions are shown in Fig.3. The order of increase in the value of log D is in good accordance with that for the solvent extraction constants with PC-88A. The difference between DTAR and PC-88A in their extraction behaviour is considered to be attributable to their mobility in the polymer matrix. Since PC-88A is a liquid in the standard state, it can move more easily inside polymer than a solid DTAR. While the liquid PC-88A could behave as in the solvent extraction system, the solid DTAR might act almost like a functional group in a chelating resin, where the chelating moiety is often restricted to form a metal complex compared to that in the homogeneous medium, because of a lack in the structural flexibility.

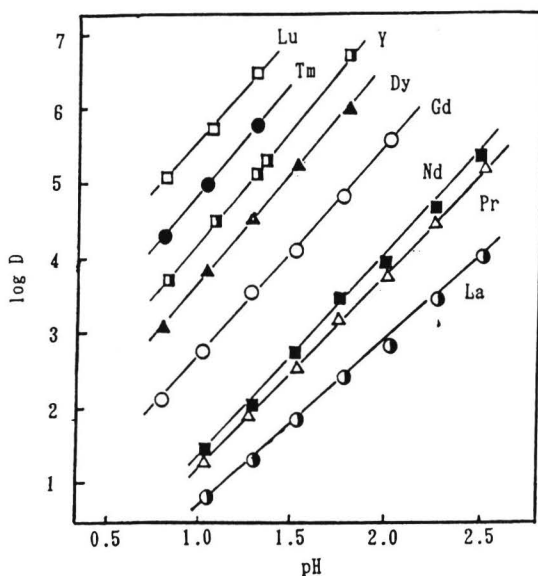


Fig. 3 The Effect of pH on the extraction of rare earths with PC-88A impregnated XAD7.

CONCLUSION

For both ion-exchanger type RIPOM and chelating resin type RIPOM, there are at least two primarily different mechanisms, which are based on the solvent extraction and ion-exchange system. When a reagent is present as a liquid in the polymer matrix, the selectivity of the RIPOM with the reagent for metal ions is explained by the behaviour of the reagent in a solvent extraction system. The extraction characteristics of RIPOM prepared from a solid reagent are considered to be similar to those of a solid adsorbent and are different from the solvent extraction system with the corresponding reagent. It is also very important to consider the physical properties of the reagents as well as the chemical properties in order to design and prepare an efficient extractant based on the RIPOM system.

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5.15

THE INFLUENCE OF MODIFIERS ON EXTRACTION OF METALS WITH
TERTIARY AMINES, TRIALKYLBENZYLAMINE AND TRIBUTYLPHOSPHATE

M.A.MEDKOV, N.I.STEBLEVSKAYA, A.A.SMOLKOV, V.V.ZELEZNOV

The Institute of Chemistry
Russian Academy of Sciences, Far-Eastern Branch
Vladivostok, Russia

ABSTRACT

The influence of polar organic solvents (modifiers) on extraction of metals with tertiary aliphatic amines, trialkylbenzylamine and tributylphosphate (TBP) has been investigated. The mechanism of this influence is discussed. A method for calculating the distribution coefficients dependent on modifiers concentration is offered to forecast the behaviour of metals in extraction systems with modifiers.

INTRODUCTION

Polar organic solvents - modifiers - are widely used in metal extraction to prevent formation of a second organic phase. In some cases modifier introduction into an extraction system leads to suppression of extraction, in others synergism takes place. It was interesting to carry out a mathematical description of metals distribution coefficients dependent on modifier concentration to forecast the metals behaviour in extraction systems with modifiers.

RESULTS AND DISCUSSION

As a rule, the bismuth, indium, and zinc distribution coefficient (D) dependencies on modifier concentration - octanol (Oct) and methylhexylketone (MHK) in bilogarithm coordinates $\lg D - \lg c_M$ are straight lines with breaks at molar ratio

$c_{\text{TOA}} : c_{\text{M}} = 1 : 2$ (c_{TOA} , c_{M} - initial molar concentrations of trioctylamine and modifiers). These diagrams for systems examined at $c_{\text{M}} > 0,01$ mol/L can be described by the equation:

$$\lg D = \lg D_0 + k + m(\lg c_{\text{M}} - \lg 2c_{\text{TOA}}) + q/\lg c_{\text{M}} - \lg 2c_{\text{TOA}} \quad (1)$$

where k is constant for this system, m and q are the coefficients, the difference $(m - q)$ corresponds to the slope tangent for the initial part of the diagram $\lg D - \lg c_{\text{M}}$ (for $c_{\text{M}} < 2c_{\text{TOA}}$), and the sum $(m + q)$ corresponds to the slope tangent for $c_{\text{M}} > 2c_{\text{TOA}}$. The results of calculations for extraction systems with TOA are given in Fig.1 and Table 1.

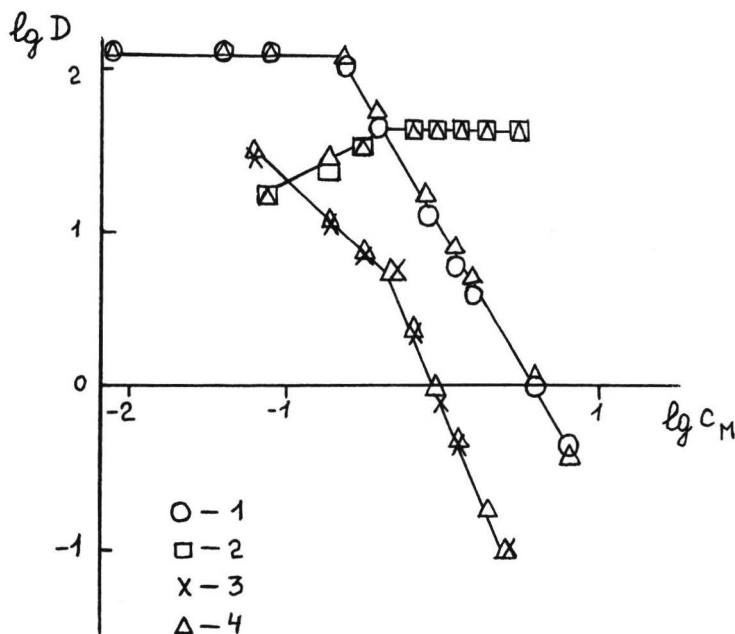


Fig.1. Distribution ratios of metals vs. initial concentration of octanol (1,3) and methylhexylketone (2):1 - bismuth (0,11 mol/L TOA); 2,3 - indium (0,23 mol/L TOA); 4 - calculation according to equation (1).

The diagrams of $\lg D$ dependencies on $\lg c_{\text{M}}$ for extraction sys-

tems of different initial extractant concentration are parallel (Medkov et al., 1990). Hence, only magnitudes of D_0 would change for different concentrations of extractant while k , m , and q would be constant. Earlier Ochkin et al., (1985) offered the following linear regression equation to describe extraction systems dependent on n-tetradecanol concentration:

$$\lg D = \lg D_0 - b \cdot c_M \quad (2)$$

where b is the coefficient which depends on solvation parameters of amine salt and extractable metal compound, c_M - molal concentration of n-tetradecanol. The equation (2) describes satisfactorily the extraction of metals dependent on n-tetradecanol concentration at small amine salt and n-tetradecanol concentration (10^{-3} - 10^{-2} mol/L). However, for practical

TABLE 1
Coefficients of equation (1)

Extraction system	$\lg D_0$	k	m	q
Bi - TOA - Oct	2,090	0,000	-0,900	-0,900
Zn - TOA - Oct	2,820	-0,740	-1,400	-0,600
Zn - TOA - MHK	2,820	0,000	0,000	0,000
In - TOA - Oct	1,570	-0,850	-1,700	-0,700
In - TOA - MHK	1,200	0,420	0,250	0,250
Bi - TBP - Oct	1,210	-0,720	-0,400	-0,300
In - TBP - MHK	-1,040	0,640	1,700	0,700
Zn - TBP - MHK	-0,052	0,059	0,420	0,280
Zn - TBP - Oct	-0,052	0,000	0,000	0,000
Bi - TBP - MHK	1,210	0,180	0,400	0,000
W - TOA - Oct	0,860	-0,370	-0,370	0,000

hydrometallurgical processes, higher concentrations of both extractants and modifiers are conventionally used. Moreover, equation (2) is preferable, since the coefficient "b" can be obtained from independent data. The possibilities of joint use of the equations (1) and (2) for the prediction of metal behaviour in extraction systems dependent on modifier concentration at extractant concentration 0,1 - 0,5 mol/L have been shown.

The distribution coefficients of metals for the extraction

with 50% TBP dependent on MHK and octanol concentrations can also be calculated according to the equation (Fig.2, Table 1):

$$\lg D = \lg D_0 + k + m(\lg c_M - \lg c_{TBP}) + q/\lg c_M + \lg c_{TBP} \quad (3)$$

The breaks on diagrams $\lg D$ on $\lg c_M$ for some metals in systems with both TBP and TOA show a change of modifier influence mechanism.

In order to determine the mechanism of modifier influence on

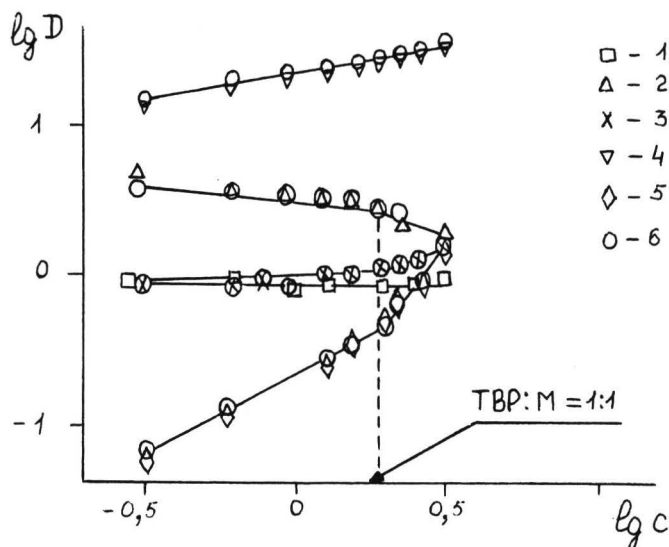


Fig.2 Distribution ratios of metals vs. initial concentration of modifiers (1,2 - octanol; 3,4,5 - methylhexylketone): 1,3 - zinc; 2,4 - bismuth; 5 - indium; 6 - calculation according to equation 3. Solvent - 50% tributylphosphate.

extraction of bismuth with TOA the interaction of the extract $(TOAH)_2BiCl_5$ with various organic solvents was studied by UV spectroscopy method. The transformation of UV spectra of extracts containing polar organic solvents in second ($d^2A/d\lambda^2$) and fourth derivatives allows to resolve wide absorption bands separating the components related to $BiCl_3$ (307 nm), $[BiCl_4]^-$ (317 nm) and $[BiCl_5]^{2-}$ (328 nm). The rise of ethylacetate and

pentanol concentration (Fig. 3) in $(\text{TOAH})_2\text{BiCl}_5$ extract leads to its dissociation with consequent formation of TOAHBiCl_4 and BiCl_3 . The $[\text{BiCl}_4]^-$ anion is known to be coordinatively solvated and have the composition $[\text{BiCl}_4 \cdot \text{H}_2\text{O} \cdot \text{ROH}]^-$ in a system with alcohol (ROH). For instance, dissociation in organic

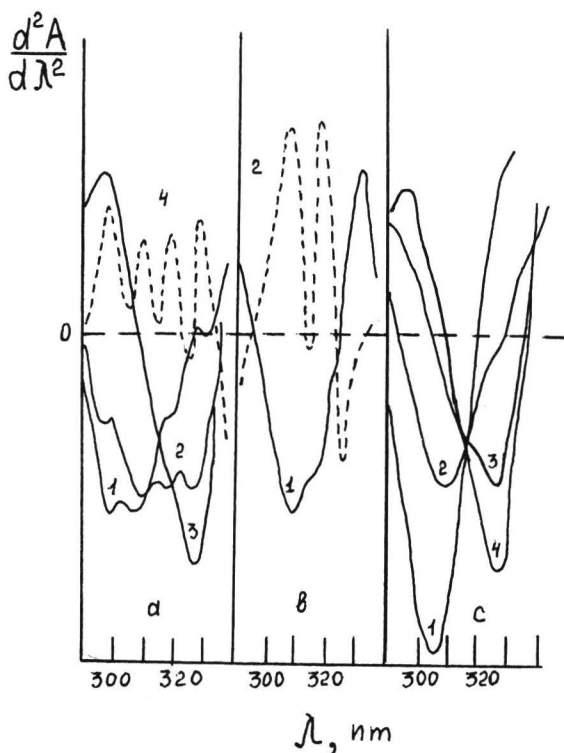
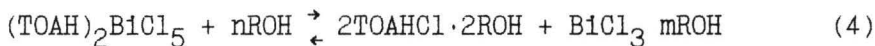


Fig.3. The second and fourth (the broken line) derivative of UV spectra of extracts containing different amounts of ethylacetate (a, b) and pentanol (c): 1a - 80%; 2a, 4a - 50% ethylacetate in TOAHCl excess; 1c - 10%, 2c - 5%, 3c - 2%, 4c - 0,5%.

phase with alcohol occurs according to the following scheme:



through the formation of $\text{TOAH}[\text{BiCl}_4 \cdot \text{H}_2\text{O} \cdot \text{ROH}]$. The process of transition from $[\text{BiCl}_5]^{2-}$ to BiCl_3 with the break of Bi-Cl bond must go through formation of hydrogen $\text{O} \dots \text{H}$ and $\text{H} \dots \text{Cl}$ bonds. It follows from our data that the equilibrium of the reaction of BiCl_3 formation in the organic phase shifts to the left by an addition of TOAHCl excess (Fig. 3; 1c). The dissociation of $[\text{BiCl}_5]^{2-}$ anion begins to a significant extent only at Oct : TOA ratio in organic phase more than two, i.e. a rise of alcohol concentration in organic phase leads firstly to the process of extractant solvation and then an excess of alcohol interacts with $[\text{BiCl}_5]^{2-}$ -anion.

The data obtained show that up to Oct : TOA = 2 : 1 in the organic phase alcohol practically does not influence bismuth extraction ; in other words, extractant solvation by alcohol does not cause depression of bismuth extraction. This depression results mainly from the dissociation of complex $[\text{BiCl}_5]^{2-}$ anion. Thus, long-chain aliphatic alcohols can be used as modifiers without any worsening of extraction indexes in extraction of bismuth with TOA from sulphate-chloride solutions, if their molar concentration does not exceed twice the extractant concentration.

TABLE 2

Coefficients in equation (1)
for systems with TABAC

Extraction system	$\lg D_0 + k$	m	q
Zn - TABAC - Oct	2,32	-1,05	-0,65
Bi - TABAC - Oct	2,02	-1,57	-0,64
In - TABAC - Oct	1,06	-1,32	-0,58
Fe - TABAC - Oct	2,10	-0,97	-0,56
Zn - TABAC - MHK	2,56	-0,38	-0,22
Bi - TABAC - MHK	2,80	-0,62	-0,58
In - TABAC - MHK	1,63	-0,37	-0,19
Fe - TABAC - MHK	2,43	-0,24	-0,06

IR data also show that complex $[\text{InCl}_4]^-$ -anion interacts with modifiers in a similar way while the extractable form of tungsten from fluoride media is, according to NMR ^{19}F , $[\text{WO}_2\text{F}_4]^{2-}$, independent of modifier concentration.

It was experimentally investigated how the concentration of such modifiers as octanol and methylhexylketone influences extraction of zinc, iron, indium, and bismuth with tribenzylammonium chloride (TABAC). The distribution coefficients of metals extracted with TABAC, in the presence of MHK and octanol can be calculated in the same way as for systems with TOA according to equation (1). The results of these calculations are given in Table 2.

Non-Standard nomenclature:

A	absorption of UV radiation
b	solvation parameter coefficient
D	distribution coefficient
λ	wavelength (nm)
M	modifier
m, n, q	coefficients

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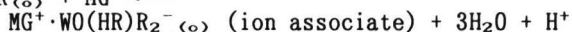
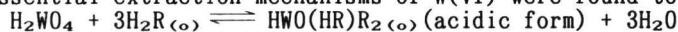
SOLVENT EXTRACTION OF METAL IONS WITH CATECHOL DERIVATIVES AND CATIONIC DYES

Shoji MOTOMIZU AND Mitsuko OSHIMA

Department of Chemistry, Faculty of Science,
Okayama University, 3-1-1 Tsushimanaka, Okayama, 700 JAPAN

ABSTRACT

Catechol derivatives containing a hydrophobic tert-butyl group were synthesized, and were used for solvent extraction of Mo(VI), W(VI), V(V), Sn(IV) and Sb(III). These chelates were anionic, and were extracted into toluene as ion associates with a dye cation, such as Malachite Green (MG^+). The chelates were also extracted into the organic phase without any dye cation as acidic forms. The extraction mechanism was examined stoichiometrically by spectrophotometric measurements. For example, the essential extraction mechanisms of W(VI) were found to be as follows;



where H_2R and subscript (o) denote catechol derivatives and organic phase, respectively. The molar ratios of metals to catechol derivatives were 1:3 for Mo(VI), W(VI), Sn(IV) and 1:2 for V(V) and Sb(III). The extraction constants and the exchange extraction constants for Mo(VI) and W(VI) were obtained.

INTRODUCTION

Metal ions which are likely to coordinate with oxygen atoms will preferably react with oxygen-containing chelating agents to form chelate ions. Some of them can be extracted into organic solvents as ion associates formed with cationic ions (Vrcklabsky, Sommer, 1968; Bailey, Chester, Dagnall, West, 1968; Kohara, Ishibashi, Abe, 1970; Tikhonov, Mikhailova, Myasnikova, Bangurkia, 1983; Singh, Kummar, 1985; Sato, Iwamoto, Uchikawa, 1987; Zhang-Fa, Xi-Man, 1988). To improve the extractability of the chelates, we synthesized several catechol derivatives containing bulky and hydrophobic tert-butyl groups (Oshima, Motomizu, Tdei, 1984; Oshima, Shibata, Gyouten, Motomizu, Tdei, 1988). As metal chelates of these reagents are highly extractable, extraction solvents of a low dielectric constant and a relatively high boiling point, such as toluene, can be used. Therefore, the interference from coexisting ions is expected to be low and the toxicity of extraction solvents is less. In this paper, stoichiometrical studies on Mo(VI), W(VI), V(V), Sn(IV) and Sb(III) che-

lates have been made to clarify the extracted species.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were made on a Shimadzu UV-300 scanning spectrophotometer and a Hitachi 100-10 spectrophotometer. A Hitachi-Horiba F-5 SS pH meter and an Iwaki KM shaker were used.

Reagents. Standard metal ion solutions. Ammonium heptamolybdate tetrahydrate (Nakarai Kagaku Ltd.), sodium tungstate dihydrate (Wako Pure Chemicals Ind.Ltd.), ammonium vanadate (Nakarai Kagaku Ltd.) were used. Metallic Sn and Sb_2O_3 were dissolved in sulfuric acid. Working solutions were prepared by accurate dilution with water or sulfuric acid.

Catechol and its derivatives: Catechol derivatives used are shown in Fig.1. These derivatives were synthesized in the same way as in our previous paper (Oshima, Motomizu, Tōei, 1984; Oshima, Shibata, Gyouten, Motomizu, Tōei, 1988). These were dissolved in toluene. Commercially available catechol was recrystallized from ethanol. Purified material was dissolved in water.

Cationic dyes. Malachite green (MG), crystal violet (CV) and brilliant green (BG) were purchased from Tokyo Kasei Kogyo Co. (purity is more than 98%) and structural formulas are shown in Fig.1. They were dissolved in water.

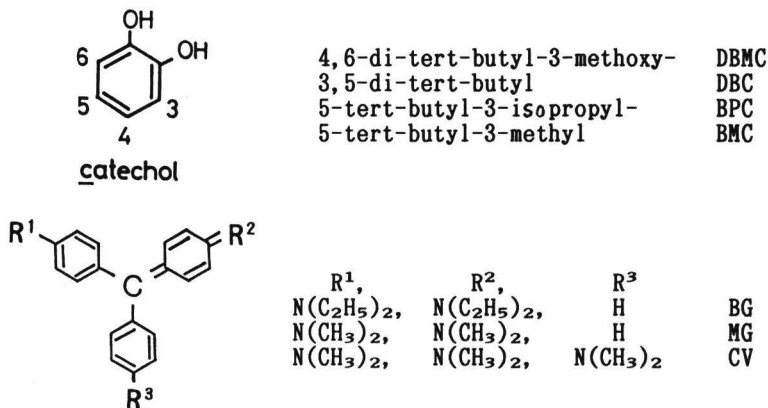


Fig.1 Abbreviations of catechol derivatives and cationic dyes

Procedures. (1) Distribution of chelates as acidic form In all experiments, ionic strength was adjusted to 0.1 M with sodium sulfate. To a 25-mL test tube with stopper, transfer a metal ion solution, a pH-adjusting solution and an ionic strength adjusting solution, and then make up to 10 mL with water. Shake with 5 mL of a catechol derivative toluene solution. To determine the total concentration of a metal ion in the organic phase, transfer 4 mL of the equilibrated organic phase to another 25 mL test tube and shake with 10 mL of a pH-adjusted aqueous solution containing 5×10^{-5} M cationic dye, the condition of which is the same as that of the calibra-

tion graph. After phase separation, measure the absorbance of the organic phase at each maximum wavelength, and calculate the concentration of the metal ion.

To determine the total concentration of the metal ion remaining in the aqueous phase, transfer 5 mL of the equilibrated aqueous phase to another 25 mL test tube and adjust to the optimum condition, and then make up to 10 mL. Shake with 5 mL of adequate concentration of catechol derivative toluene solution. Calculate the concentration of the extracted ion associate by using the calibration graph.

Calculate the distribution ratio, D , of the metal ion by using the concentrations of the metal ion in the organic and/or the aqueous phase.

(2) **Distribution of ion associates in the presence of cationic dye** The procedure was similar to the procedure (1), except for the presence of the dye. To determine the concentration of an ion associate extracted into the organic phase, measure the absorbance of the equilibrated organic phase at each maximum wavelength, and calculate the concentration from the molar absorptivity (ϵ) of each cationic dye (ϵ for MG = $9.6 \times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ cm}^{-1}$).

The concentration of a metal ion in an organic phase and the total concentration remaining in an aqueous phase were also determined as described above.

The apparent molar absorptivities used for the determination of the total metal concentrations are summarized in Table 1.

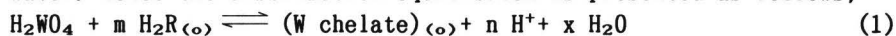
TABLE I
Apparent molar absorptivities (ϵ) of the ion associates
 $\epsilon / 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

	Mo(VI)-MG	W(VI)-MG	V(V)-MG	Sb(III)-BG	Sn(IV)-2MG
DBMC	8.39	6.50	9.70*	9.85	
DBC	9.21	7.47	7.92	8.29	
BPC	9.11	7.50	8.78		
BMC	8.50	7.50	6.78	8.25	14.0
catechol	4.14		2.40		

* The pairing cationic dye is crystal violet.

RESULTS AND DISCUSSION

Extraction stoichiometry for acidic form chelates in the absence of dye. The chelate of Sn(IV) could not be extracted without cationic dye, and that of V(V) changed in absorption spectrum in the organic phase. Therefore, the stoichiometrical experiments were carried out for the other three metals. The treatment for stoichiometry is almost the same for each metal ion, so the subsequent equations are represented by the W(VI) chelate. The catechol derivatives, except for catechol, are hardly soluble in water. Hence the distribution equilibrium is presented as follows;



The extraction constant, $K_{E(H)}$, is defined as;

$$K_{E(H)} = [W \text{ chelate}]_o \cdot [H^+]^n / ([H_2WO_4] \cdot [H_2R]_o^m) \quad (2)$$

where subscript (H) means the acidic form of the extracted chelate. The distribution ratio of W(VI), $D_{W(H)}$, and the side reaction coefficient of W(VI) in the aqueous phase, α_w , are presented as follows;

$$D_{W(H)} = [W \text{ chelate}]_o / C_w \quad (3)$$

$$\alpha_w = C_w / [H_2WO_4] \quad (4)$$

where C_w denotes the total concentration of W(VI) in the aqueous phase. From Eqs. (2), (3) and (4), Eq. (5) is derived.

$$\log D_{W(H)} = \log K_{E(H)} + m \log [H_2R]_o + n \text{ pH} - \log \alpha_w \quad (5)$$

The plots of $\log D_{W(H)}$ against $\log [H_2R]_o$ are expected to be linear, provided that pH and α_w are kept constant. Figure 2 (a) shows such plots at pH 2.2 for W(VI). The slopes, m , were 3 in all plots for four catechol derivatives. The values $D_{W(H)}$ calculated from the metal concentrations obtained using the equilibrated organic phases were identical to the ones calculated from the concentrations obtained using those of the equilibrated aqueous phases within the error of ± 0.03 in logarithmic unit. The molar ratios of metal to catechol derivatives were 1:3 for Mo(VI) and 1:2 for Sb(III).

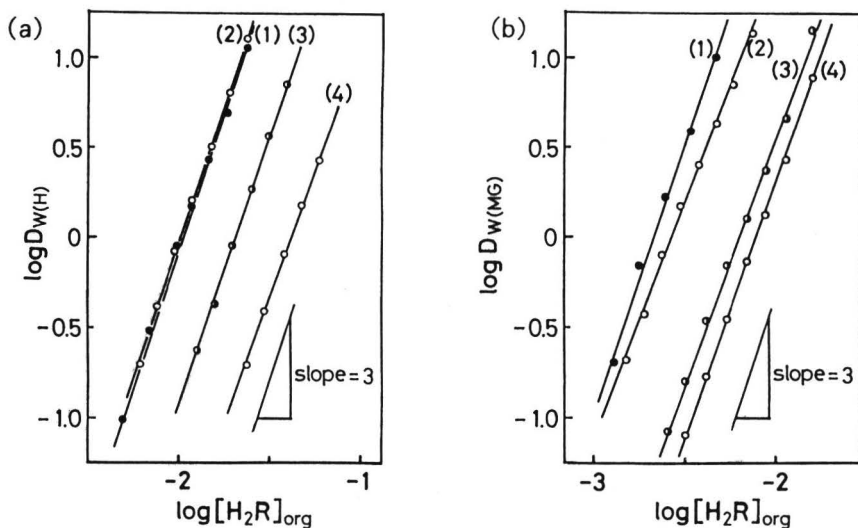


Fig. 2 The plots of $\log D_{W(H)}$ or $\log D_{W(MG)}$ against $\log [H_2R]_o$.

(a) acidic form chelates; (b) ion associate.

1, DBMC; 2, DBC; 3, BPC; 4, BMC.

In the case of the absence of a cationic dye, the chelates of W(VI) and Sb(III) with catechol were not extracted into the organic phase.

The extraction constants, $K_{E(H)}$, for Mo(VI) and W(VI) can be calculated from Eq. (5). The results are summarized in Table 2.

The values of $\log K_{E(H)}$ for Mo(VI) are larger by 0.55~0.64 log units than

those for W(VI), and the order of the extractability of chelates is almost the same as that of the hydrophobicity of the chelating agents. Hansch et.al.(1979) presented π values which is a parameter of the contribution of a substituent to the partition coefficient: π values for tert-butyl, isopropyl, methyl and methoxy groups are 1.98, 1.53, 0.56 and -0.02, respectively. Thus, the total π values for DBMC, DBC, BPC and BMC are calculated to be 3.94, 3.96, 3.51 and 2.54, respectively. The values of $\log K_{E(H)}$ for both Mo(VI) and W(VI) are in the following order: DBMC~DBC>BPC>BMC. This order is almost the same as that expected from the total π values, though the extractability of DBMC is estimated to be the same as or a little smaller than that of DBC.

pKa values of tungstic acid. Schwarzenbuch et al.(1962) obtained the acid dissociation constants, pK_{a1} and pK_{a2} , of tungstic acid. However, acid dissociation constant, pK_{a3} , of H_2WO_4 is not known. Therefore, in this work, the pK_{a3} value was determined.

$$K_{a3} = [H_2WO_4][H^+]/[H_3WO_4^+],$$

$$K_{a2} = [HWO_4^-][H^+]/[H_2WO_4] = 3.16 \times 10^{-4} \text{ \{Schwarzenbuch et al.(1962)\}}$$

$$K_{a1} = [WO_4^{2-}][H^+]/[HWO_4^-] = 2.51 \times 10^{-5} \text{ \{Schwarzenbuch et al.(1962)\}}$$

$$\alpha_w = ([H_3WO_4^+] + [H_2WO_4] + [HWO_4^-] + [WO_4^{2-}])/[H_2WO_4]$$

$$= [H^+]/K_{a3} + 1 + K_{a2}/[H^+] + K_{a2} \cdot K_{a1}/[H^+]^2 \quad (6)$$

Figure 3 shows the relationship between $\log D_{W(H)}$ and pH when $\log[H_2R]$ is kept constant. The value of pK_{a3} could be calculated as 1.26 ± 0.02 by the distribution method using Eqns (5) and (6). The precise pK_{a1} and pK_{a2} values, however, were not obtained by the distribution method or UV

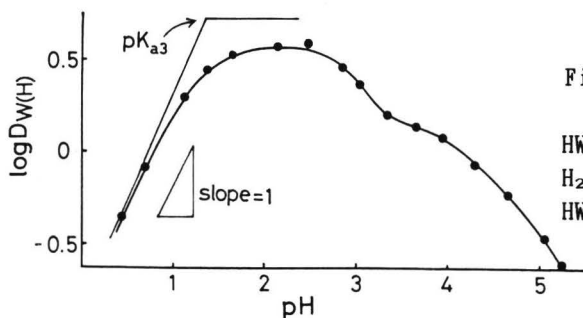
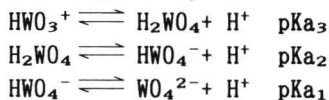


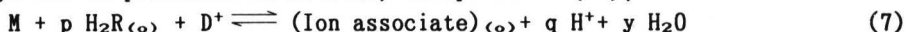
Fig.3 The plots of $\log D_{W(H)}$ against pH



spectrophotometry in an aqueous medium. This is probably because tungstic acid forms a higher aggregate in the higher pH region. As seen from Fig. 3, the plot of $\log D_{W(H)}$ against pH shows the abnormality at pH region above 3. In this work, the pK_{a2} and pK_{a1} values obtained by Schwarzenbuch et al.(1962) were used for the calculation of $\log K_{E(H)}$ of W(VI) chelate.

Distribution equilibria of ion associates in the presence of cationic dye. The molar ratios of metals to a dye cation were found to be 1:1 for Mo(VI), W(VI), V(V) and Sb(III) by molar ratio method, as shown in Fig.4

as an example, and hence the distribution equilibrium in the presence of a dye can be presented as follows, except for Sn(VI);



$$K_{E(D)} = [\text{Ion associate}]_o \cdot [H^+]^q / ([M] \cdot [H_2R]_o^p \cdot [D^+]) \quad (8)$$

where M, D and $K_{E(D)}$ denote metal, dye and the extraction constant for the ion associate, respectively. When $D_{M(D)}$, α_M , and side reaction coefficient of D^+ , α_D , are taken into consideration, the following equation is derived.

$$K_{E(D)} = D_{M(D)} \cdot [H^+]^q \cdot \alpha_M \cdot \alpha_D / ([H_2R]_o^p \cdot C_D) \quad (9)$$

or,

$$\log D_{M(D)} = \log K_{E(D)} + p \log [H_2R]_o + \log C_D + q \text{ pH} - \log \alpha_M - \log \alpha_D \quad (10)$$

where $D_{M(D)}$ is defined as:

$$D_{M(D)} = [\text{Ion associate}]_o / C_M \quad (11)$$

and the total distribution ratio of M, D_M^T , is defined as follows;

$$D_M^T = ([\text{acidic form chelate}]_o + [\text{Ion associate}]_o) / C_M \\ = D_{M(D)} + D_{M(H)} \quad (12)$$

The values of D_M^T were calculated by using the total concentrations of the metal ions of the organic phase or the aqueous phase, and the values of $D_{M(D)}$ were calculated by using the absorbances of the ion associate of the equilibrated organic phase and the total concentrations of the metal ions remaining in the aqueous phase. Figure 2(b) shows the plots of $\log D_{M(MG)}$ against $\log [H_2R]_o$, from the slopes of which we can estimate $p=3$. The extraction constants with MG, $K_{E(D)}$, were listed in Table 2.

Extraction schemes. The molar ratios of Mo(VI), W(VI), V(V) and Sb(III) chelates to MG^+ or BG^+ were 1:1 and that of Sn(IV) to MG^+ was 1:2. In Table 1 are shown the optimum pairing dye cations selected for each chelate with respect to the molar absorptivity and the absorbance of the reagent blank.

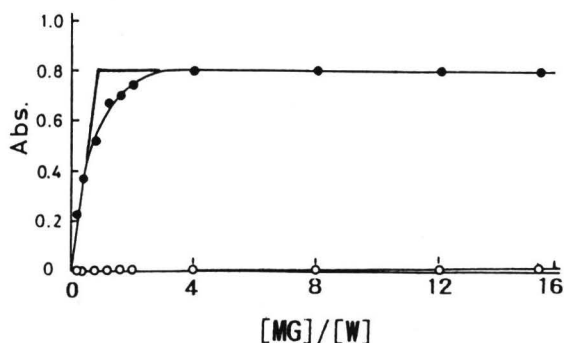
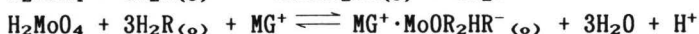
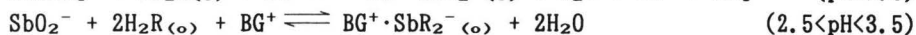
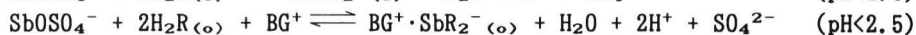
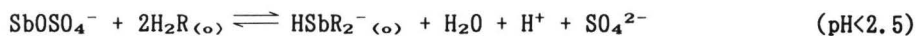
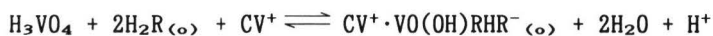
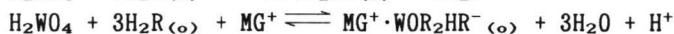


Fig.4 Molar ratio method
for W(VI)
 $\lambda = 630 \text{ nm.}$

The extraction schemes were considered as follows;





In the case of Sn(IV), only the molar ratio was clear: Sn: H₂R: MG = 1:3:2. Then, the ion associate is seemed to be [(MG⁺)₂(SnR₃)²⁻].

TABLE 2

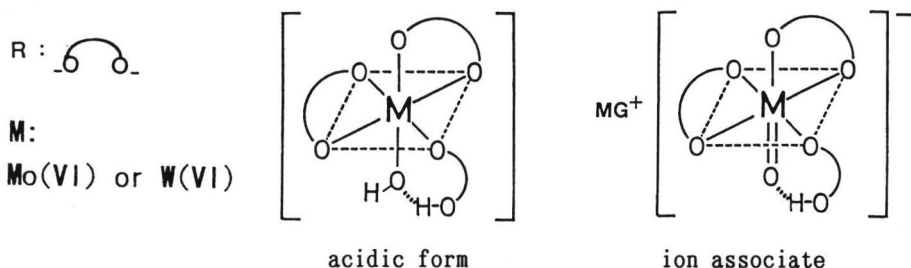
Extraction constants of Mo(VI) and W(VI) chelates and their ion associates

Catechols	log K _{E(H)} ^{a)}	log K _{E(MG)} ^{b)}	log K _(exch)
Mo(VI)			
DBMC	6.73 ± 0.04	12.07 ± 0.18	5.34
DBC	6.64 ± 0.03	11.42 ± 0.15	4.78
BPC	5.70 ± 0.01	11.00 ± 0.08	5.30
BMC	4.93 ± 0.03	10.63 ± 0.11	5.70
W(VI)			
DBMC	5.99 ± 0.06	12.54 ± 0.08	6.55
DBC	6.04 ± 0.02	12.15 ± 0.17	6.11
BPC	5.12 ± 0.02	11.14 ± 0.13	6.02
BMC	4.21 ± 0.05	10.75 ± 0.08	6.54

a) Obtained by varying log[H₂R]_o at pH 2.4.

b) Obtained by varying log[H₂R]_o at the constant C_{MG}.

The structural formulas for the acidic form and the ion associate of Mo(VI) and W(VI) were considered to be as follows;



Both extraction constants of an acidic form and an ion associate for Mo(VI) and W(V) were obtained. Then, K_(exch), corresponding to the cation exchange constant for H⁺ to MG⁺, was defined as follows;

$$K_{(\text{exch})} = [\text{MG}^+ \cdot \text{A}^-]_{\text{o}} \cdot [\text{H}^+] / [\text{H} \cdot \text{A}]_{\text{o}} \cdot [\text{MG}^+] = K_{\text{E}(\text{MG})} / K_{\text{E}(\text{H})} \quad (14)$$

These values are also listed in Table 2. The K_(exch) values of Mo(VI)

and W(VI) are very large, which means that the ion associates are more extractable than the acidic forms. In Fig.5, the absorption spectra of Mo(VI)-DBMC-MG extraction system are shown. It is clear that highly sensitive methods for Mo(VI) and W(VI) determination can be accomplished with MG.

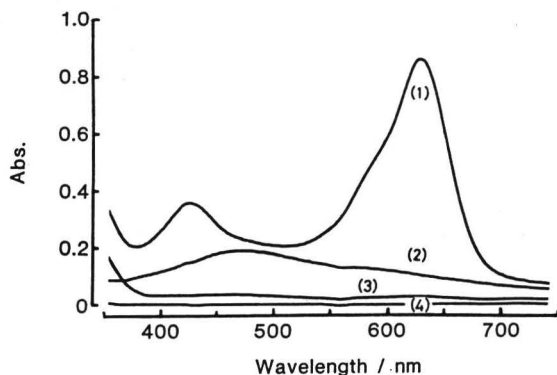


Fig.5 Absorption spectra
 1 $\text{MG}^+(\text{Mo chelate})^-_{\infty}$
 2 $\text{H}^+(\text{Mo chelate})^-_{\infty}$
 3 reagent blank for curve 1
 4 reagent blank for curve 2

CONCLUSIONS

Catechol derivatives substituted tert-butyl group(s) were synthesized and used as extraction reagents for metal ions. The stoichiometries for the chelates of Mo(VI), W(VI), V(V), Sb(III) and Sn(VI) and their ion associates with a cationic dye were discussed and the compositions of the extracts were determined. The extraction method for ion associates can be applied to the practical samples as a highly sensitive spectrophotometry.

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ENHANCEMENT OF METAL CHELATE EXTRACTION BY FORMATION OF ADDUCT CHELATES AND OF ANIONIC CHELATES IN THE ORGANIC PHASE.

T.SEKINE, NGUYEN Thi Kim Dung, AND J.NORO*

Department of Chemistry, Science University of Tokyo

1-3 Kagurazaka, Shinjuku-ku Tokyo, 162 JAPAN.

* Research Department, Nissan ARC Ltd.,

Natsushima-cho, Yokosuka-shi, 273 JAPAN.

ABSTRACT

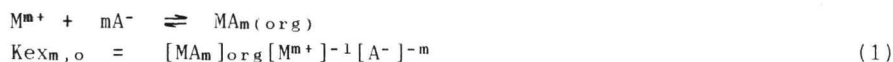
The enhancement of solvent extraction of a metal ion, M^{m+} , with a chelating extractant, HA, by an addition of a bulky cation, B^+ , which is due to the extraction of the ternary complex, $MA_m+1^-B^+$, is statistically treated as the over-all equilibrium of the solvent extraction of the MA_m and the addition of the ion-pair of reagents, A^-B^+ , on it in the organic phase. This is demonstrated with the extraction data of some divalent and trivalent metal ions with β -diketones and tetrabutylammonium. This statistical approach is compared with that for the enhancement in synergistic extraction systems. Lanthanum, europium, lutetium, scandium, indium, magnesium, nickel, cobalt and zinc were treated under this investigation.

INTRODUCTION

In a solvent extraction system of a metal ion, M^{m+} , with a chelating extractant, HA, such as a β -diketone, the extracted species is usually the non-charged chelate, MA_m . However, other species may also be extracted when a certain third component is added. The synergistic extraction with a chelating extractant and an organophilic neutral ligand, L, such as tributylphosphate (TBP) is one typical example (Irving 1967, Healy 1969) and the extraction of ternary complex with a chelating extractant and a bulky cation, such as a cationic dye is the other example.

The equilibrium of the synergistic extraction is often treated as the association of the extracted neutral chelate with the L in the organic phase. The extraction of a ternary complex is, on the other hand, often treated as the extraction of the anionic chelate, MA_m+1^- , with the bulky cation B^+ as ion-pairs and thus the stability and the extractability of the anionic complex are considered to be the essential factors. However, the anionic complex is usually not recognized in the aqueous phase and thus the estimation of such properties is not possible. At the same time, it is pointed out that even when a stable anionic complex is formed, it is not always extractable as ion-pairs (Sekine, Ishizaki, Hieda,

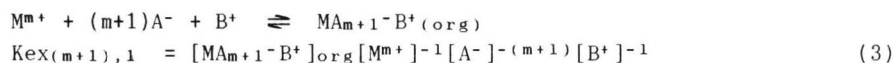
Murai, Iwahori 1987) and thus a statistical method was proposed to treat the extraction equilibrium in the following way (Noro, Sekine 1992). The extraction equilibrium of MA_m can be written as:



The association of the MA_m with n molecules of L in the organic phase may be written as:



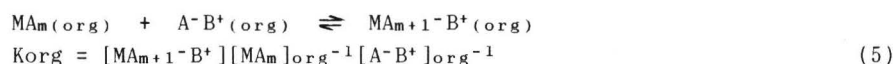
The extraction of the anionic chelate with a bulky cation B^+ may be written as:



The extraction equilibrium of the ion-pair of reagents may be written as:



The association equilibrium of the anion in this ion-pair with the MA_m in the organic phase may be written as:



The formation of " p "th complex with the extractant in the aqueous phase may be written as:



The distribution ratio in the absence and presence of L and B^+ may be written as:

$$\begin{aligned} D_0 &= [MA_m]_{org} / ([M^{m+}] + [MA_m^{-1}] + \dots) \\ &= K_{exm,0} [A^-]^m / (1 + \beta_1 [A^-] + \dots) \end{aligned} \quad (7)$$

$$\begin{aligned} D_L &= ([MA_m]_{org} + [MA_mL]_{org} + [MA_mL_2]_{org} + \dots) / ([M^{m+}] + [MA_m^{-1}] + \dots) \\ &= K_{exm,0} [A^-]^m (1 + \Sigma \beta_{(org)n} [L]^n_{org}) / (1 + \beta_1 [A^-] + \dots) \end{aligned} \quad (8)$$

$$\begin{aligned} D_{B^+} &= ([MA_m]_{org} + [MA_{m+1}B^+]_{org}) / ([M^{m+}] + [MA_m^{-1}] + \dots) \\ &= (K_{exm,0} [A^-]^m + K_{ex(m+1),1} [A^-]^{m+1} [B^+]) / (1 + \beta_1 [A^-] + \dots) \end{aligned} \quad (9)$$

$$= K_{exm,0} [A^-]^m (1 + K_{exAB} K_{org} [A^-] [B^+]) / (1 + \beta_1 [A^-] + \dots) \quad (10)$$

EXPERIMENTAL

The experiments were made at 298K. A 5 cm³ portion of the aqueous solution containing a certain amount of the metal ion, a buffer, and none or a certain amount of tetrabutylammonium (tba⁺) was placed in a stoppered glass tube (capacity 20 cm³) and the same volume of carbon tetrachloride containing 0.1 M benzoyltrifluoroacetone (Hbfa) or 2-thenoyltrifluoroacetone (Htta) was added. The two phases were agitated with a mechanical shaker for 30 minutes and centrifuged off. The metal content in the both phases was determined by ICP-AES or atomic absorption spectrometry. The hydrogen-ion concentration in the equilibrated aqueous phase was determined by potentiometry.

RESULTS AND DISCUSSION

An addition of tba⁺ into the aqueous phase enhanced the extraction of metal ions with Hbfa, Htta or other -CF₃ containing β -diketones. However, it did not change the extraction with acetylacetone or benzoylacetone. This was explained in terms of difference in the extractability of the ion-pair, A-B⁺; the ion-pair of the -CF₃ containing β -diketonate ion was extracted but that of acetylacetonate or benzoylacetate ion was not extracted. Thus the addition of A-B⁺ on the MA_m in the organic phase was not possible with the latter β -diketones.

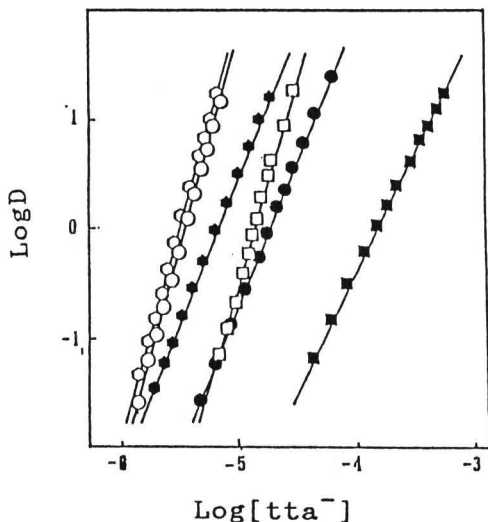


Figure 1. Extraction curves of La(III)(□, ■), Eu(III)(○, ●) and Lu(III)(◊, ◐) with Htta and tba⁺. Closed symbols: no tba⁺, open symbols: 1mM tba⁺ at initial in the aqueous phase. The metal concentration is 0.1 mM in the initial aqueous phase. The plots are calculated by Eq. 10 using the values in Table 1.

The extraction constant of the reagents as ion-pairs in Eq.4 was determined at several initial concentration of tba^+ . The value of K_{exAB} was not affected by the concentration of A-B^+ in the organic phase from 0.03 to 0.3 mM with bfa-tba^+ and from 0.07 to 3 mM with tta-tba^+ . Thus the associated species of the ion-pairs to form $(\text{A-B}^+)_n$ where n is larger than unity should be negligible.

Figure 1 gives the extractions of La(III) , Eu(III) , and Lu(III) with Htta and tba^+ . The enhancement of Htta extraction of Sc(III) and In(III) by tba^+ under similar conditions was negligible. The equilibrium constants obtained from these data are given in Table 1.

TABLE 1*
Equilibrium constants for the extraction of M(III)
with 2-thenoyltrifluoroacetone and tetrabutylammonium
or tributylphosphate into carbon tetrachloride.

	$\log K_{\text{ex}3,0}$	$\log K_{\text{ex}4,1}$	$\log K_{\text{org}}$	$\log \beta_1$	$\log \beta_{(\text{org})1}$	$\log \beta_{(\text{org})2}$
La^{3+}	12.2	22.6	8.5	4.4	4.83	9.33
Pr^{3+}	13.2	23.8	8.5	4.3	—**	—**
Nd^{3+}	13.5	24.0	8.4	4.4	—**	—**
Eu^{3+}	14.4	24.8	8.5	4.4	5.15	8.89
Lu^{3+}	15.7	25.0	7.4	4.8	5.69	6.60
Sc^{3+}	22.3	nil	nil	—**	3.44	nil
In^{3+}	20.4	nil	nil	—**	nil	nil

* (Noro, Sekine 1992; Sekine, Dyrssen 1967)

** not determined

*** $\log K_{\text{exAB}}$ is 1.94 in 0.1 M $\text{NaNO}_3\text{-CCl}_4$ system.

Cf: $K_{\text{ex}m,0}$:Eq.1; $K_{\text{ex}(m+1),1}$:Eq.3; K_{org} :Eq.5; β_p :Eq.6; $\beta_{(\text{org})n}$:Eq.2.

The enhancement at a certain tba^+ concentration is greater when $[\text{A}^-]$ is higher. This is because the extraction of the $\text{MA}_4\text{-B}^+$ species is dependent on the quantity $[\text{A}^-][\text{B}^+]$, as seen from Eq.10. In Fig.1, the addition of 1mM tba^+ enhanced the extraction of La(III) more than Eu(III) and Lu(III) . However, this is not due to the fact that the La(tta)_3 accepts more the tta-tba^+ than the Eu(tta)_3 in this solvent. It is seen from Table 1 that the constant, K_{org} , of La(tta)_3 is similar to that of Eu(tta)_3 though the value is lower with Lu(tta)_3 : it accepts tta-tba^+ less than these two complexes. As seen from this, the enhancement can be understood systematically by comparing the values of K_{org} .

It is seen from the $\beta_{(\text{org})2}$ values in Table 1 that Sc(tta)_3 and In(tta)_3 cannot add two TBP molecules thus they may not be able to accept one bidentate ligand such as tta^- .

This type of evaluation of the enhancement of metal extraction by extracting the ternary complex can also be made when the charge of the metal ions is different or even when the aqueous phase is different. This is because the value of K_{org} is the equilibrium constant for the reaction in the organic phase which is essentially not affected by the chemical

property of the aqueous phase and also by the charge of the metal ions. Figure 2 gives the extraction curves of Mg(II), Co(II), Ni(II), and Zn(II) with Hbfa in carbon tetrachloride and also that of Eu(III) in the absence and presence of tba⁺. Table 2 summarizes the equilibrium constants of the extraction of these metal ions obtained from the data and the adduct formation constants with TOPO in carbon tetrachloride.

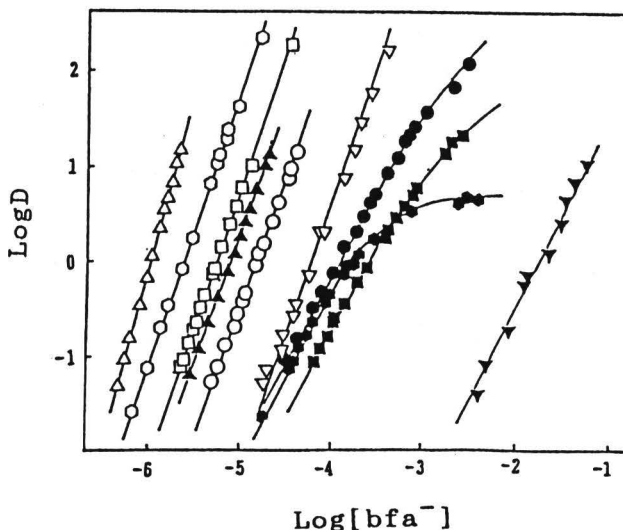


Figure 2. Extraction curves of Mg(II)($\nabla, \blacktriangledown$), Ni(II)($\bigcirc, \bullet$), Co(II)($\square, \blacksquare$), Zn(II)($\bigcirc, \bullet$) and that of Eu(III)($\triangle, \blacktriangle$) with Hbfa and tba⁺. Closed symbols: no tba⁺, open symbols: 1mM tba⁺ at initial in the aqueous phase. The metal concentration is 0.05 mM for Mg(II), 0.1 mM for Co(II) and Ni(II) and 0.02 mM for Zn(II). The plots are calculated by Eq. 10 using the values in Table 2.

The enhancement of the extraction due to the extraction of ternary complex can be compared by this way with that due to the adduct metal chelate formation, the "synergistic enhancement". However, no direct comparison of the values of $\beta_{(\text{org})2}$ with K_{org} is possible because the dimensions of these two constants are different. From Tables 1 and 2, it is seen that those which are poor acceptors of two molecules of the monodentate ligand in the organic phase are also poor acceptors of the chelating β -diketonate ions in the organic phase. This is reasonable because the vacant coordination sites are combined with two oxygen atoms of the ligand to form the complexes of the higher coordination number in the both cases. However this does not seem to be quite general because the $\text{Zn}(\text{bfa})_2$ does not add two molecules of TOPO but it adds one bfa⁻ to form $\text{Zn}(\text{bfa})_3^- \text{tba}^+$. It is seen from Table 2 that K_{org} of $\text{Zn}(\text{bfa})_2$ is smaller than for the other chelates. This is similar to that the TOPO adducts of the $\text{Zn}(\text{bfa})_2$ are less stable than those of the other chelates.

TABLE 2*

Equilibrium constants for the extraction of M(II) and M(III) with benzoyltrifluoroacetone and tetrabutylammonium or trioctylphosphine oxide into carbon tetrachloride.

	logKex _{2,0}	logKex _{3,r}	logKorg	logβ ₁	logβ ₂	logβ _{(org)1}	logβ _{(org)2}
Mg ²⁺	3.48	15.65	10.90	-	-	6.78	11.64
Co ²⁺	7.20	18.87	10.89	3.40	5.24	6.15	9.34
Ni ²⁺	7.60	19.96	11.58	3.60	6.68	5.19	8.98
Zn ²⁺	7.77	17.70	9.15	2.81	5.18	6.71	***

	logKex _{3,0}	logKex _{4,1}	logKorg	logβ ₁	logβ ₂	logβ _{(org)1}	logβ _{(org)2}
Eu ³⁺	15.30	26.5	9.93	4.81	-	7.49***	12.26***

The aqueous phase for these extraction data is, 1 M NaCl for Co(II) and Ni(II), 1 M NaNO₃ for Zn(II) and 0.1 M NaNO₃ for Mg(II) and Eu(III).

*Sekine, Murai, Konno 1984, Sekine, Ishizaki, Hieda, Murai, Iwahori 1987, Noro, Sekine 1992, and unpublished data

** This data is not determined.

***No data with Eu(bfa)₃ has been reported but they should not be very much different from those values of Eu(tta)₃ adducts given here.

Cf:Kex_{m,0}:Eq.1; Kex_{(m+1),1}:Eq.3; Korg:Eq.5; β_p:Eq.6; β_{(org)n}:Eq.2.

The solvent extraction of the anionic chelate complex with a bulky cation has often been discussed but as long as this is considered from the standpoint that the anionic chelate formed in the aqueous phase or on the liquid-liquid interface is extracted as ion-pairs with the bulky cation, a general discussion is difficult. The approach developed in the present paper should be useful for this purpose and in this way a similarity is shown between the synergistic extraction and the ternary complex extraction.

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SOLVENT EXTRACTION OF METALS WITH STRONGLY ACIDIC EXTRACTANTS DERIVED FROM HETEROCYCLIC COMPOUNDS

S. UMETANI, Q. T. H. LE, H. TAKAHARA AND M. MATSUI

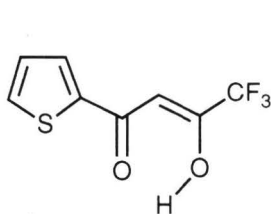
Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611, Japan

ABSTRACT

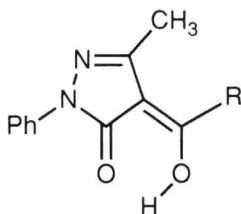
Highly acidic β -diketones, 1-aryl-3-methyl-4-acyl-5-pyrazolones and 3-phenyl-4-benzoyl-5-isoxazolone (HPBI), were derived from heterocyclic compounds and the acid dissociation constants and the partition constant between an organic solvent and an aqueous 0.1 M sodium perchlorate solution were determined by a liquid-liquid distribution method. The solvent extraction of lanthanides was investigated in the presence or absence of tri-*n*-octylphosphine oxide (TOPO). HPBI was found to be a very powerful extractant for lanthanides owing to its strong acidity. The acidity and extractability are discussed on the basis of the molecular structure optimized by a semi-empirical MNDO/H calculation.

INTRODUCTION

In the solvent extraction of metals ions, a fluorinated substituent has often been introduced to extractants. The acidity of the extractant is enhanced by the strong electron withdrawing nature of the fluorinated substituent, therefore metal ions are extractable from an acidic region. The acid dissociation constant (pK_a) of 2-thenoyltrifluoroacetone (HTTA), one of the most representative β -diketones, is reported to be 6.23, while that of acetylacetone is 8.82 (Keller et

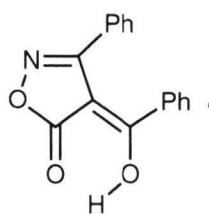


HTTA



HPMBP (R=Ph)

HPMTPF (R=CF₃)



HPBI

al. 1969). Actually, many metal ions are extractable from highly acidic regions with HTTA. On the other hand, 4-acyl-5-pyrazolones are known to be promising extractants. Their acid dissociation constants are 2.5-4.0, being much stronger than HTTA (Umetani et al. 1980, 1983); derivation from five membered heterocyclic compounds clearly brings strong acidity. In addition, the combination of acylpyrazolones and neutral ligands such as TOPO and polydentate phosphine oxides has made it possible to extract quantitatively alkaline earths (Umetani et al. 1982, 1986) and lithium (Umetani et al. 1987, Mukai et al. 1989), known to be one of the most unextractable elements.

Recently, novel extractants derived from 5-isoxazolone have emerged (Jothi et al. 1987, 1988, 1989, 1990). Their acid dissociation constants are reported to be about 1.3 (Wiley et al. 1962), which are much more acidic than acylpyrazolones. In the present work, synthesis of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) is described, and its acid dissociation constant and the partition constant between the organic phase and 0.1 M sodium perchlorate aqueous phase was determined precisely by a liquid-liquid distribution method. The solvent extraction of lanthanides in the presence or absence of TOPO was examined.

EXPERIMENTAL

Chemicals

HPBI was synthesized according to the method analogous to 3-phenyl-4-acetyl-5-isoxazolone (Korte et al. 1961). 3-Phenyl-5-isoxazolone (3.2 g) and benzoic anhydride (4.5 g) were dissolved in dioxane (100 mL). After adding sodium benzoate (5.8 g), the mixture was refluxed for 2 hours. The mixture turned to red-brown. After the mixture was cooled, sodium benzoate was removed by filtration. Adding water (200 mL) and acidifying by hydrochloric acid solution gave a yellow precipitate. This precipitate was collected, washed with water and dried in vacuo. Yield: 3.3 g (62 %). HPBI: m.p. 146 °C; analysis, calculated for $C_{16}H_{11}NO_3$, C 72.45, H 4.18, N 5.28; found, C 72.43, H 4.10, N 5.23 %. 1H -NMR ($CDCl_3$): 7.06-7.46 ppm (m, Ph).

TOPO was purchased from Dojindo and used without further purification. Other chemicals were of analytical-reagent grade. Water was demineralized and distilled.

A semi-empirical MNDO/H calculation was performed on a CRAY Y-MP2E/264 using UniChem MNDO90 (CRAY Research Inc.).

Distribution of HPBI and lanthanides

Distribution experiments for HPBI and lanthanides were performed in a 30 mL centrifuge tube in a similar manner as described previously (Umetani et al. 1983). The concentration of HPBI was measured spectrophotometrically. The metal concentration in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry and that in the chloroform phase was determined after stripping with 1 M hydrochloric acid solution.

RESULTS AND DISCUSSION

Distribution of HPBI

In general, β -diketone type chelating agents have a keto-enol tautomerism. However, the absence of a methyne proton (CH) peak for the 4-position of isoxazolone ring characteristic of keto form in the $^1\text{H-NMR}$ spectrum indicates that HPBI exists quantitatively as an enol form in CDCl_3 .

The acid dissociation constant (K_a) and the partition constant (P_{HA}) were determined by a liquid-liquid distribution method. The distribution ratio of HPBI (HA) between the organic and the aqueous phase, D_{HA} , can be written as

$$D_{\text{HA}} = \frac{[\text{HA}]_{\text{o}}}{([\text{HA}] + [\text{A}^-])} = \frac{P_{\text{HA}}}{(1 + K_a[\text{H}^+]^{-1})} \quad (1)$$

where P_{HA} and K_a are the partition constant and the acid dissociation constant defined by $[\text{HA}]_{\text{o}}/[\text{HA}]$ and $[\text{H}^+][\text{A}^-]/[\text{HA}]$, respectively. Subscript o denotes the species in the organic phase.

When the hydrogen ion concentration is high enough, D_{HA} agrees with P_{HA} , while $\log D_{\text{HA}}$ agrees with $\log P_{\text{HA}} + \text{p}K_a - \text{pH}$ for low hydrogen ion concentrations. In Fig. 1 is shown the relationship between $\log D_{\text{HA}}$ and pH for the cyclohexane/water system. Analyzing the plots on the basis of Eqn. 1 gives the values of $\log P_{\text{HA}}$ and $\text{p}K_a$ as 1.24 and 1.23, respectively. The $\text{p}K_a$ value are close to the reported value. Although the molecular weight is similar, the $\log P_{\text{HA}}$ value is much smaller than that of HPMBP, of which $\log P_{\text{HA}}$ is 2.33 (Umetani et al. 1983). The oxygen atom at the 1-position of the isoxazolone ring which is exposed to the solvent unlike the nitrogen atom at the 1-position of the pyrazolone ring would decrease the hydrophobicity.

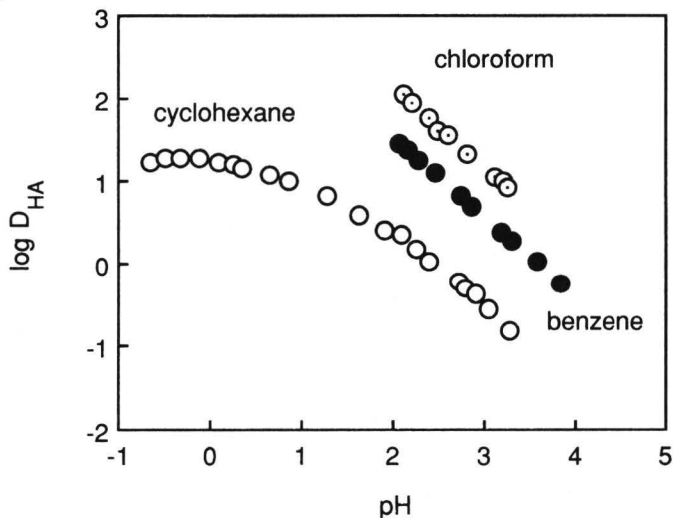


Fig. 1 Distribution of HPBI.

The distribution of HPBI between chloroform/water and benzene /water were also examined and shown in Fig. 1. The plots were found to fall on the straight lines with a slope of -1. The $\log P_{HA}$ values were obtained employing pK_a value of 1.23 to be 2.88 and 2.33 for the chloroform/water and benzene/water systems, respectively.

Ball-and-stick representation based on the MNDO/H optimized structure is shown in Fig. 2. All geometric parameters were fully optimized. Two phenyl groups are fixed face to face and this structure is supported by the 1H -NMR spectral data. The phenyl signals of HPBI appear as multiplet at 7.06-7.46 ppm, whereas those of benzoic anhydride and 3-phenyl-5-isoxazolone appear at 7.5-8.2 ppm. This clearly indicates that the stacking of two phenyl groups brings upfield shifts of the ring protons due to the ring current effect.

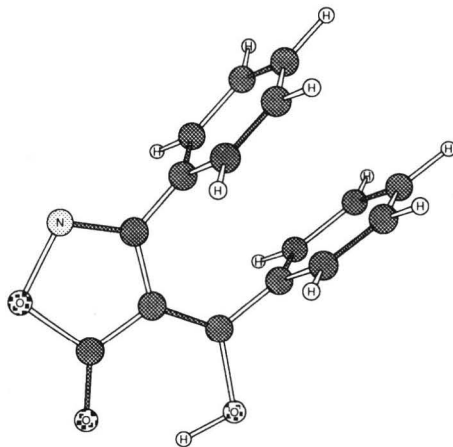


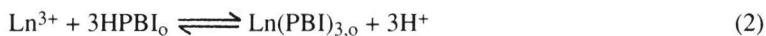
Fig. 2 HPBI

The strong acidity of acylpyrazolones and acylisoxazolones could be partly attributed to the heterocyclic π -electron conjugation system that contains electronegative nitrogens and oxygens. It is more interesting to compare the distance between the two donating oxygen atoms. The O-O distances for HTTA, HPMBP and HPBI obtained from MNDO/H optimized structure are 2.5, 2.7 and 2.9 Å, respectively. The O-O distance should be significant in the stability of the intramolecular hydrogen bonding and the formation of metal complexes. Electronegativity of oxygen is larger than that of nitrogen, however such great enhancement in acidity changing from acylpyrazolone to acylisoxazolone could not be merely attributed to replacement of nitrogen by oxygen.

The larger O-O distance in HPBI would increase the stability of the intramolecular hydrogen binding, resulting in the great enhancement of acidity. The effect of the O-O distance in acidity and complex formation is now under examination in further detail (Umetani et al. 1992).

Extraction of lanthanides with HPBI

In the extraction of lanthanides (Ln^{3+}), the overall extraction equilibrium and the extraction constant can be written as



$$K_{\text{ex}} = [\text{Ln}(\text{PBI})_{3,o}][\text{H}^+]^3 / [\text{Ln}^{3+}][\text{HPBI}]_o^3 \quad (3)$$

$$\log K_{\text{ex}} = \log D - 3\log [\text{HPBI}]_o - 3\text{pH} \quad (4)$$

where D is the distribution ratio of Ln^{3+} defined as $[\text{Ln}(\text{PBI})_{3,o}] / [\text{Ln}^{3+}]$. From the effects of pH and $[\text{HPBI}]_o$ on D , it was confirmed that the extracted species are $\text{Ln}(\text{PBI})_3$ with no neutral HPBI as self-adduct taking part in the extracted species. After having confirmed the validity of Eqns. 3 and 4, the $\text{pH}_{1/2}$ values, (at which half of metal ions is extracted, read from the plots of $\log D$ vs. pH for each lanthanide), were employed to obtain K_{ex} on the basis of Eqn. 4. In Table 1 are summarized the $\text{pH}_{1/2}$ and the $\log K_{\text{ex}}$ values for HPBI together with those for HTTA, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP) for comparison. The extraction constants referred to were obtained employing chloroform as organic solvent except for HTTA, where the organic phase is benzene. It was found to be possible to extract lanthanides quantitatively below pH 3 with 0.01 M HPBI. The extraction constants obviously increase as acidity increases.

TABLE 1

Extraction constants for lanthanides with HPBI, HPMTFP, HPMBP and HTTA

	HPBI		HPMTFP	HPMBP	HTTA
pK_a	1.23		2.56 ^a	3.92 ^a	6.23
	$\text{pH}_{1/2}^c$	$\log K_{\text{ex}}$	$\log K_{\text{ex}}^d$	$\log K_{\text{ex}}^e$	$\log K_{\text{ex}}^f$
La^{3+}	2.59	-1.77	-6.18	-7.18	-10.51
Pr^{3+}	2.40	-1.20	-4.98	-6.17	-8.85
Eu^{3+}	2.13	-0.39	-3.78	-5.33	-7.66 (-8.68) ^g
Ho^{3+}	2.12	-0.36	-3.36	-4.71	-7.25
Yb^{3+}	2.10	-0.36	-3.15	-4.24	-6.72

^aUmetani et al. 1983. ^bKeller et al. 1969. ^c $[\text{HPBI}]_o = 0.01$ M in chloroform.

^dUmetani et al. 1987. ^eRoy et al. 1978. ^fStary 1964. ^gSekine et al. 1964. Extraction into chloroform.

Figure 3 shows the typical plots of $\log K_{\text{ex}}$ vs. pK_a for each extractant in the extraction of europium, where the $\log K_{\text{ex}}$ value for HTTA is also that into chloroform (see Table 1). As seen in the figure, $\log K_{\text{ex}}$ increases linearly as pK_a decreases. The separation of lanthanides is getting poorer as the extractability increases. These results would strongly suggest the relationship between the separability and the acidity, that is, the O-O distance.

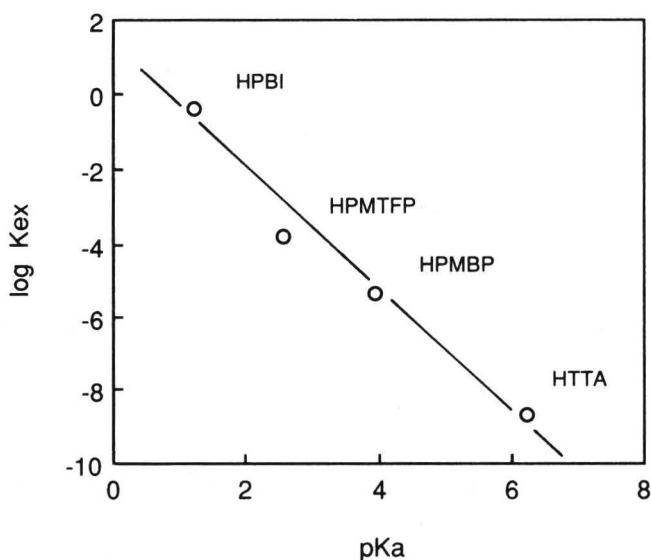


Fig. 3 log K_{ex} vs. pKa

Extraction of lanthanides with HPBI and TOPO

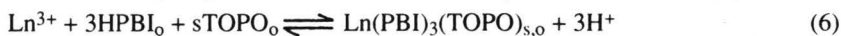
In the extraction of lanthanides in the presence of TOPO, the distribution ratio, D^* , can be expressed as

$$D^* = ([\text{Ln}(\text{PBI})_3]_o + [\text{Ln}(\text{PBI})_3(\text{TOPO})]_o + \dots + [\text{Ln}(\text{PBI})_3(\text{TOPO})_s]_o) / [\text{Ln}^{3+}]$$

when the species in the aqueous phase except for $[\text{Ln}^{3+}]$ are negligible, dividing D^* by D , the distribution ratio in the absence of TOPO, gives

$$D^*/D = 1 + \sum \beta_s [\text{TOPO}]_o^s \quad (5)$$

where β_s is an adduct formation constant defined as $[\text{Ln}(\text{PBI})_3(\text{TOPO})_s]_o / [\text{Ln}(\text{PBI})_3]_o [\text{TOPO}]_o^s$. In the higher $[\text{TOPO}]_o$ region where $\text{Ln}(\text{PBI})_3(\text{TOPO})_s$ could be considered the predominant extracted species, the extraction equilibrium and the synergistic extraction constant, $K_{\text{ex},s}$, are expressed simply as follows.



$$K_{\text{ex},s} = [\text{Ln}(\text{PBI})_3(\text{TOPO})_s]_o [\text{H}^+]^3 / [\text{Ln}^{3+}] [\text{HPBI}]_o^3 [\text{TOPO}]_o^s \quad (7)$$

The synergistic extraction of lanthanides with the combination of 0.01 M HPBI and 0.01 M TOPO has been examined. The plots of $\log D^*$ vs. pH fall on a straight line with a slope of 3 as predicted from Eqn. 7. The dependency of $\log D^*$ on $\log [\text{TOPO}]_o$ indicates that the extracted species with HPBI and TOPO depends on $[\text{TOPO}]_o$ and that the extracted species, $\text{Ln}(\text{PBI})_3(\text{TOPO})$, in the lower TOPO concentration region changes to $\text{Ln}(\text{PBI})_3(\text{TOPO})_2$ at higher concentrations. The adduct formation constants were calculated by non-linear least-square methods on the basis of Eqn. 5 and summarized in Table 2 together with those for some

acylpyrazolones for comparison.

In the synergistic extraction of lanthanides with acylpyrazolone and TOPO, the number of TOPO in the extracted species is one when the substituent at 4-position of pyrazolone ring is aliphatic (Tochiyama et al. 1981, Sasayama et al. 1983, Sasaki et al. 1983), and two when that is aromatic or perfluorinated (Sasayama et al. 1983, Umetani et al. 1987, Mukai et al. 1990). The number of TOPO in the extracted species with HPBI is two in analogy with aroyl or perfluoroacyl pyrazolones. The adduct formation constant for HPBI are larger than those for 1-phenyl-3-methyl-4-octanoyl-5-pyrazolone (HPMOP) and smaller than those for HPMTFP. The stability for the HTTA/TOPO/Eu system ($\log \beta_1=4.95$, $\log \beta_2=7.68$, Akiba et al. 1981) is similar to the HPBI/TOPO/Eu system. It is known that stable adduct formation reactions are usually brought about by strong acidic extractants. But the order of the adduct formation reaction does not obey the order of the acidity of extractant to the extent discussed in the present paper. The stability of the adduct formation reaction would probably depend on the acidity of extractants, however, the strong acidity has some different causes, namely the electron withdrawing substituent such as perfluoroalkyl group, the heterocyclic structure and the O-O distance that gives significant effect on hydrogen bonding. These modes seem not to be equivalent for the stability of adduct formation reaction. The difference in the extraction constants between HPMTFP and HPBI decrease on adding TOPO owing to the very stable adduct formation in the HPMTFP/TOPO system. Nevertheless, those for HPBI are still larger than those for HPMTFP.

TABLE 2
The stability constants of the adducts with TOPO

		La	Pr	Eu	Ho	Yb
HPBI	$\log K_{ex,2}$	6.38	7.25	7.50	7.20	6.46
	$\log \beta_1$	5.05	5.14	5.11	5.13	5.53
	$\log \beta_2$	8.15	8.45	7.89	7.56	6.76
HPMTFP ^a	$\log K_{ex,2}$	4.20	5.19	6.06	6.08	5.68
	$\log \beta_1$			5.88	5.90	6.31
	$\log \beta_2$	10.38	10.17	9.84	9.44	8.70
HPMOP ^b	$\log K_{ex,1}$		-4.51	-2.82		-0.08
	$\log \beta_1$		4.34	4.15		4.40

^aUmetani et al. 1987. ^b1-Phenyl-3-methyl-4-octanoyl-5-pyrazolone. Tochiyama et al. 1981.

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KINETICS OF SOLVENT EXTRACTION OF PALLADIUM(II) WITH A NEW TYPE OF SULFUR-CONTAINING EXTRACTANT

Kazuharu YOSHIKAWA, Masashi KOBAYASHI, Ritsuo YASUKAWA and Katsutoshi INOUE
Department of Applied Chemistry
Saga University,
Honjo 1, Saga 840 JAPAN

ABSTRACT

3,3-Diethylthietane (DETE) was synthesized to investigate its extraction behavior for palladium(II) from acidic aqueous chloride media, together with the interfacial adsorption and aqueous distribution equilibria of DETE between the organic and aqueous phases.

From the extraction equilibrium of palladium(II) with DETE, it was concluded that these metals were extracted with DETE as $\text{PdCl}_2\cdot\text{S}_2$ into the organic phase. It was found that the interfacial activities of DETE was negligibly small and aqueous solubility of DETE was slightly higher than for usual commercial extractants.

A kinetic study on the solvent extraction of palladium(II) with DETE from chloride media was conducted at 303 K using a hollow fiber membrane extractor. The apparent reaction orders of permeabilities for the extraction were determined by the dependencies of hydrogen ion activity, concentrations of metal, chloride ion and DETE, respectively. The diffusional effects were reasonably explained by the diffusion model accompanied by a proposed reaction, taking into account the velocity distributions of the aqueous and organic phases through the inner and outer sides of a hollow fiber.

INTRODUCTION

Solvent extraction is an effective method for recovery, separation and purification of metals, and it is used for hydrometallurgical refining of uranium and reprocessing of the spent nuclear fuel in the field of atomic industry. In recent years a more efficient extraction process is desired for producing highly purified rare metals. For this purpose, development of new types of extractants with high selectivity to a specified metal are necessary. It is well known that extractants having sulfur atoms have high affinity and selectivity for precious metals (Mikhailov et al., 1973).

Recently, the application of hollow fiber modules to membrane extraction process has been attempted for metal recovery (Kim, 1984). In order to improve the membrane extraction process, the extraction kinetics through the hollow fiber membrane must be elucidated because these processes are governed by kinetics rather than equilibria. If the difference between the extraction and stripping rates of the metals of interest is greater than that of the

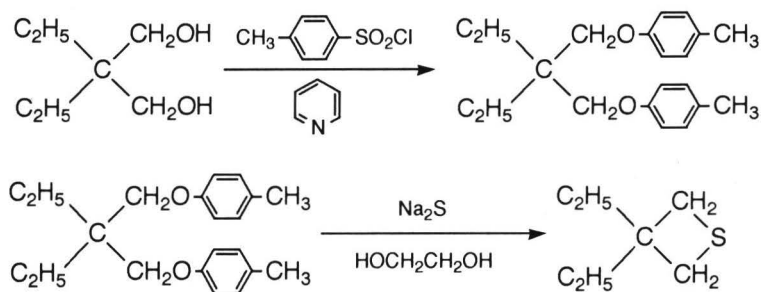
distribution ratios at equilibrium, the separation using the membrane extraction processes could represent an attractive alternative to the conventional solvent extraction processes based on distribution equilibrium. However, only a few investigations have been reported that deal with the membrane extraction processes since the mechanism is strongly dependent on the combination of metals and the extractants (Danesi and Cianetti, 1982).

In the present paper, we investigated the synthesis of the 3,3-diethylthietane (henceforth, DETE, abbreviated as S) used as the extractant, and the extraction rate of palladium(II) with DETE from acidic chloride media carried out by a hollow fiber membrane extractor (Yoshizuka et al., 1986b), together with the measurements of the interfacial adsorption and aqueous distribution equilibria of DETE, in order to obtain more detailed information on the extraction kinetics of palladium(II) with DETE.

EXPERIMENTAL

Synthesis of DETE

DETE was synthesized according to the reaction expressed as follows (Tazaki et al., 1988):



2,2-Diethyl-1,3-propanediol and *p*-tosyl chloride were mixed together with pyridine. The mixture solution was stirred for 1 hour at 20 °C. Lumps of ice were added to the reaction mixture for the purpose of hydrolysis of excess *p*-tosyl chloride, and then crystalline 2,2-diethyl-1,3-propanediol ditosylate was precipitated. To the 2,2-diethyl-1,3-propanediol ditosylate, sodium sulfide and ethylene glycol were added to be stirred and refluxed at 150 °C. 3,3-diethylthietane and water were distilled from the reaction mixture. Hexane was added to the distillate. The mixture was washed with 1 M sodium hydroxide, the aqueous phase was discharged and the organic phase was evaporated to remove hexane and to obtain the final product. The identification of the product was carried out by infrared and ¹H-n.m.r. spectroscopies. The elemental analysis of the product was obtained as follows; Found: C, 64.51; H, 10.81%. Calcd. for C₇H₁₄S: C, 64.55; H, 10.83%. This reagent was found to exist as monomeric species in toluene from the measurement of the apparent molecular weight.

The organic solution was prepared by dissolving DETE in reagent grade of toluene to a re-

quired concentration gravimetrically. The aqueous solution for studying the palladium(II) extraction was prepared by dissolving palladium(II) dichlorides in aqueous mixtures of 1 M hydrochloric acid – ammonium chloride. Palladium(II) dichlorides, PdCl_2 , were kindly supplied from Tanaka Kikinzoku Kogyo. Co., Ltd..

Extraction equilibria

In the extraction equilibrium of palladium(II), the metal was completely extracted into the organic phase over the whole experimental conditions. Thus, the extraction constant of palladium(II) can not be evaluated. However, from the loading test of palladium(II) with DETE, it was found that palladium(II) was extracted with DETE as $\text{PdCl}_2 \cdot \text{S}_2$ into the organic phase.

Interfacial tension of DETE

Interfacial tension between the organic phase and 0.1 M hydrochloric acid solution was measured at 30 °C by the pendant drop method to examine the interfacial adsorption equilibrium of DETE (Yoshizuka et al., 1986a).

Aqueous distribution of DETE

Aqueous distribution of DETE between the organic and hydrochloric acid solutions was measured at 303 K by the same method reported previously (Yoshizuka et al., 1986a). The concentration of sulfur in the aqueous phase was measured by a Shimadzu model ICP-1000III inductively coupled plasma atomic emission spectrometer to determine the concentration of DETE.

Extraction rate

The extraction rate of palladium(II) with DETE from chloride media was measured at 303 K using a hollow fiber membrane extractor as shown in Fig.1. The experimental procedures were as the same as in the previous paper (Yoshizuka et al., 1986b).

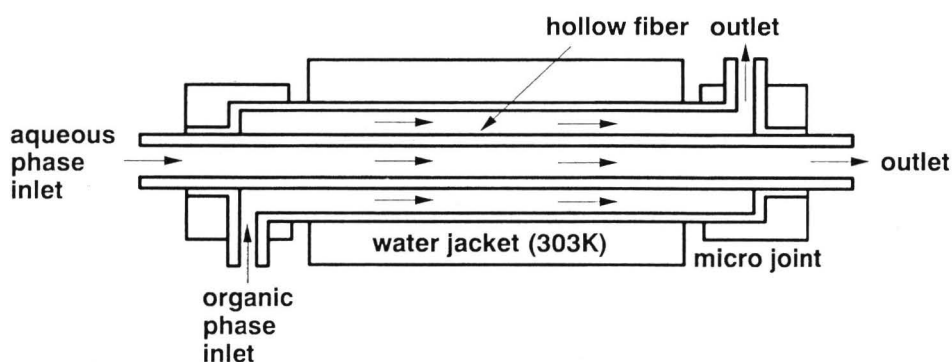


Fig. 1. Hollow fiber membrane extractor.

The extraction rate of palladium(II), J_M , was calculated according to the following equation;

$$J_M = (F_{aq}/2\pi r_1 L) \cdot (C_{Pd0} - C_{Pd}) = (F_{org}/2\pi r_1 L) \cdot C_{Pdorg} \quad (1)$$

Palladium(II) concentration in the aqueous phase was measured by a Seiko model SAS7500 atomic absorption spectrophotometer. Palladium complex in the organic phase was stripped by 2 M aqueous ammonia to determine the concentration by atomic absorption spectrophotometer.

RESULTS and DISCUSSION

Interfacial tension of DETE

Figure 2 shows the relation between interfacial tension and the concentrations of DETE, C_S^- . Since the interfacial tension of DETE is not affected by the concentrations of DETE, it can be concluded that the adsorption of DETE at the interface is negligibly small.

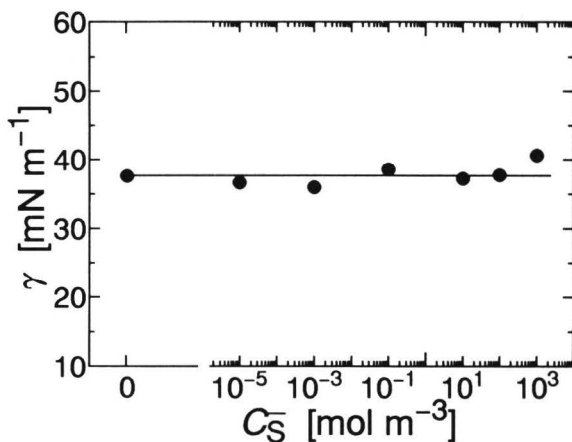


Fig. 2. Interfacial tension of DETE.

Aqueous distribution of DETE

From the measurement of the apparent molecular weight, DETE was found to exist as monomeric species in toluene. Therefore, the distribution equilibrium of DETE between the organic and aqueous phases is expressed as follows:



Figure 3 shows the relation between the concentration of DETE in the aqueous phase, C_S , and that in the organic phase, $C_{\bar{S}}$ in the case of various concentrations of hydrochloric acid. From the linear relationship, the distribution equilibrium constant, K_D , was found to be equal to 8.2×10^{-4} . The K_D value of DETE is nearly equal to that of benzoylacetone ($K_D = 7.2 \times 10^{-4}$; Stry, 1964), and that is 60 times higher than that of usual commercial extractants such as *E*-2-hydroxy-5-nonylbenzophenone oxime isolated from LIX 65N ($K_D = 1.4 \times 10^{-5}$; Komasaawa et al., 1980).

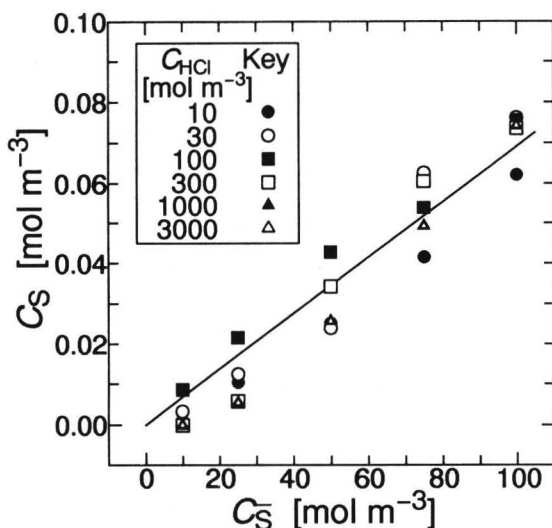


Fig. 3. Aqueous distribution of DETE.

Extraction rate

Figure 4 shows the relation between the extraction rate of palladium(II), J_M , and hydrogen ion concentration in the aqueous phase, C_H , and that between J_M and palladium(II) concentration in the aqueous phase, C_{Pd} , respectively. From the figure, hydrogen ion does not affect on the extraction rate of palladium(II), while the extraction rate is proportional to the palladium(II) concentration.

Figure 5 shows the relation between J_M and the extractant concentration in the organic phase, $C_{\bar{S}}$, and that between J_M and the chloride ion concentration in the aqueous phase, C_{Cl} , respectively. It was found that the extraction rate is proportional to the extractant concentration, while J_M decreases with increasing chloride ion concentration.

From the experimental results, the mechanism of palladium (II) extraction with DETE is expressed by the following reaction in the aqueous phase adjacent to the interface:

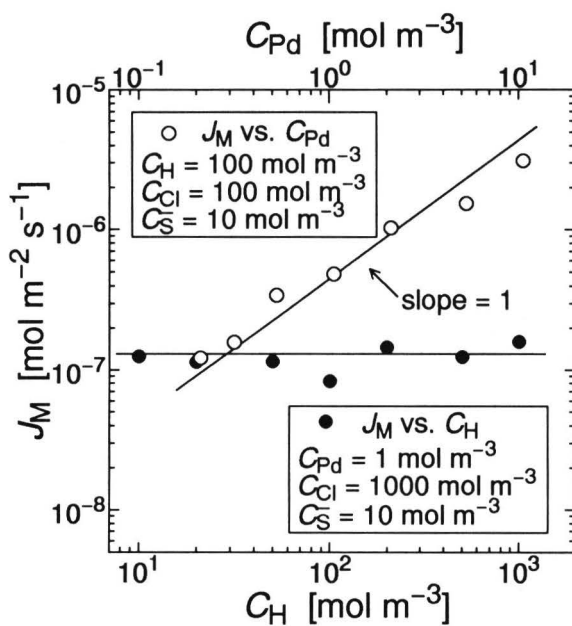


Fig. 4. Relation between J_M and C_H and that between J_M and C_{Pd} .

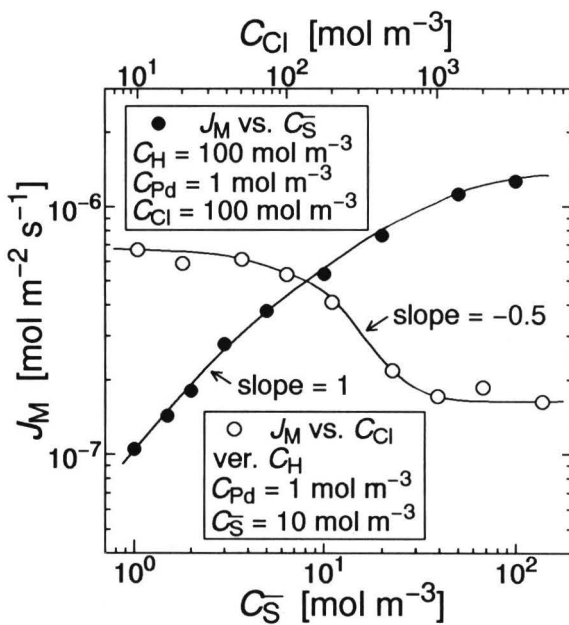


Fig. 5. Relation between J_M and C_S and that between J_M and C_{Cl} .



Since palladium(II) exists as tri- and tetrachloro complexes in the present experimental conditions, the concentrations of chloro-complexed palladium(II) are expressed as follows :

$$[\text{PdCl}_3^-] = \frac{\beta_3}{\beta_3 + \beta_4 C_{\text{Cl}}} \cdot C_{\text{pd}} \quad (5)$$

$$[\text{PdCl}_4^{2-}] = \frac{\beta_4 C_{\text{Cl}}}{\beta_3 + \beta_4 C_{\text{Cl}}} \cdot C_{\text{pd}} \quad (6)$$

The apparent reaction rate of palladium(II) extraction, R , is expressed by the following equation :

$$R = r_3 + r_4 = \frac{k_3 \beta_3 + k_4 \beta_4 C_{\text{Cl}}}{\beta_3 + \beta_4 C_{\text{Cl}}} \cdot C_{\text{pd}} \cdot K_D C_{\text{S}}^- \quad (7)$$

The data in the region of high extraction rate should be analyzed on the basis of the diffusion model accompanied by the reaction expressed by Eq.(7), taking into account the velocity distributions of the laminar flows of aqueous and organic phases in the extractor shown in Fig.1 (Yoshizuka et al., 1986b).

The unknown parameters in Eq.(7) are the reaction rate constants, k_3 and k_4 . These constants were evaluated by the trial-and-error method so as to minimize the standard deviation between the experimental and calculated results. The values of constants used for the calculation are listed in Table 1. The values of k_3 and k_4 are equal to $9.8 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and $8.5 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, respectively. The solid lines in Figs. 4 and 5 show the calculated results. It is found that the calculated results agree well with the experimental results within the range of experimental error.

CONCLUSION

Kinetic studies of the extraction of palladium(II) with 3,3-diethylthietane were carried out in a hollow fiber membrane extractor, together with the interfacial adsorption and aqueous distribution equilibria of DETE. The following can be concluded:

- (1) The extracted species of palladium(II) with DETE is $\text{PdCl}_2\cdot\text{S}_2$.
- (2) 3,3-Diethylthietane is scarcely adsorbed at the interface between the organic and aqueous phases.
- (3) The experimental results for the extraction rate can be explained by the diffusion model

accompanied by a reaction rate expression which is described by Eq.(7), taking into account the velocity distributions of laminar flows of both phases in the extractor.

TABLE 1
Constants used for numerical analysis.

Kinetic and equilibrium constants	
D_{Pd}	$= 1.0 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, $D_S^* = 1.0 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$,
$D_{PdCl_2 \cdot S_2}^*$	$= 5.0 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$
β_3	$= 15.85 \text{ m}^9 \cdot \text{mol}^{-3}$, $\beta_4 = 0.316 \text{ m}^{12} \cdot \text{mol}^{-4}$.
Physical properties of membrane extractor	
hollow fiber material : polytetrafluoroethylene (Japan Goretex Co. Ltd.)	
r_1	$= 5.3 \times 10^{-4} \text{ m}$, $r_2 = 9.0 \times 10^{-4} \text{ m}$, $r_3 = 1.2 \times 10^{-3} \text{ m}$,
L	$= 0.25 \text{ m}$, $\tau = 1.60$, $\epsilon = 0.70$,
F_{aq}	$= 1 \times 10^{-9} \text{ m}^3 \cdot \text{s}^{-1}$, $F_{org} = 2 \times 10^{-9} \text{ m}^3 \cdot \text{s}^{-1}$.

* estimated value by Wilke-Chang correlation

NOMENCLATURE

C_j	concentration of species j	$[\text{mol} \cdot \text{m}^{-3}]$
D_j	diffusivity of species j	$[\text{m}^2 \cdot \text{s}^{-1}]$
J_M	extraction rate of palladium	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$
K_D	distribution equilibrium constant of DETE	$[\text{m}^3 \cdot \text{mol}^{-1}]$
k_3	rate constant of reaction of Eq.(3)	$[\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$
k_4	rate constant of reaction of Eq.(4)	$[\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$
L	length of membrane extractor	$[\text{m}]$
F	volumetric flow rate	$[\text{m}^3 \cdot \text{s}^{-1}]$
R	reaction rate in extraction	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$
r_1	inner radius of hollow fiber	$[\text{m}]$
r_2	outer radius of hollow fiber	$[\text{m}]$
r_3	inner radius of membrane extractor	$[\text{m}]$
β	stability constant of i -th chloro complex of palladium(II)	$[(\text{m}^3 \cdot \text{mol}^{-1})^i]$
γ	interfacial tension	$[\text{N} \cdot \text{m}^{-1}]$
ϵ	porosity of hollow fiber	$[-]$
τ	tortuosity of hollow fiber	$[-]$
Superscript		
—	organic phase	
Subscripts		
aq	aqueous phase	
j	species ($= \text{Pd}^{2+}$, S, H^+ , Cl^- , PdCl_3^- , PdCl_4^{2-} , $\text{PdCl}_2 \cdot \text{S}$, $\text{PdCl}_2 \cdot \text{S}_2$)	
org	organic phase	
0	initial state	

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N-methyl-2-pyrrolidone	8.25
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3-phenyl-3-methyl-4-p-nitrobenzoyl-5-pyrazolone	3.20
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