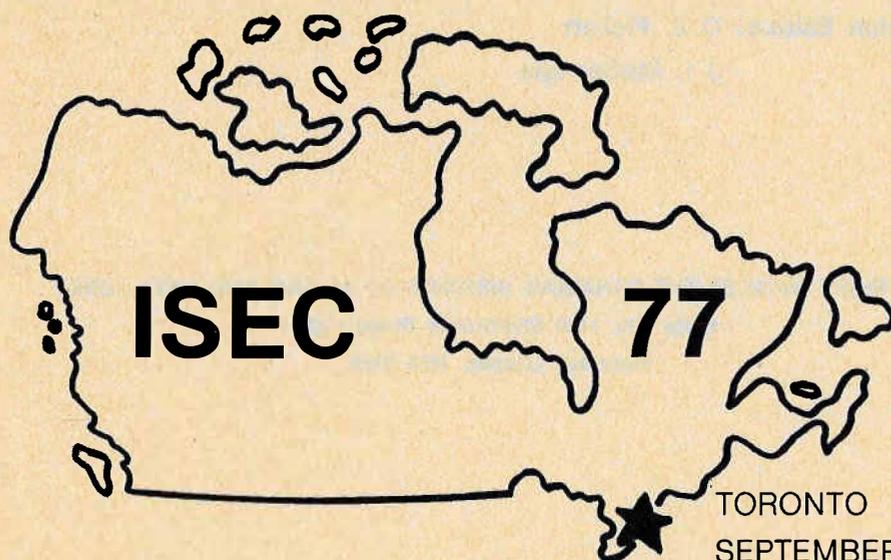

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TORONTO
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1977

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ISEC '77 Reception

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John Hawley, Ruth Blumberg, Gordon Ritcey**



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Charles Cooper and Mr. and Mrs. Gus Van Weert



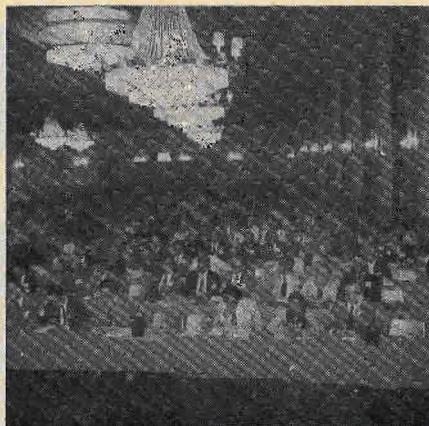
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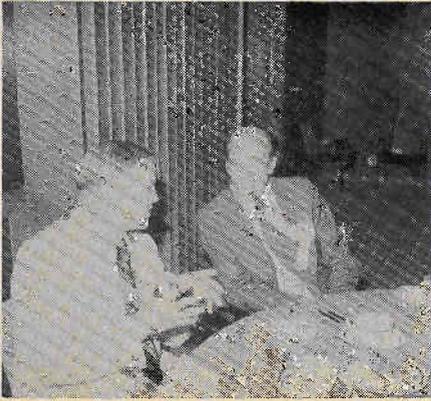


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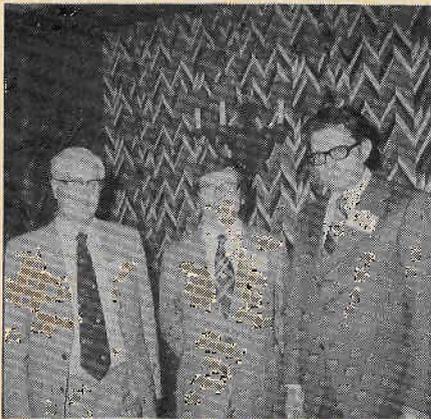


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Author's Breakfast



Doug Flett, R.F. Dalton, B.F. Myasoedov



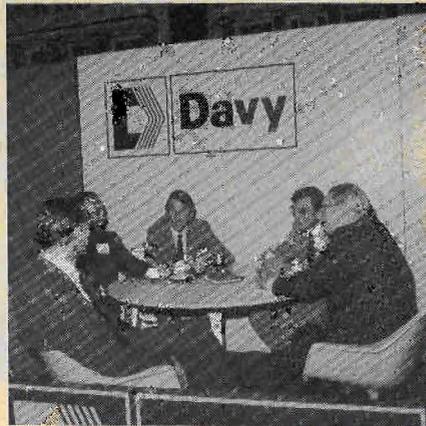
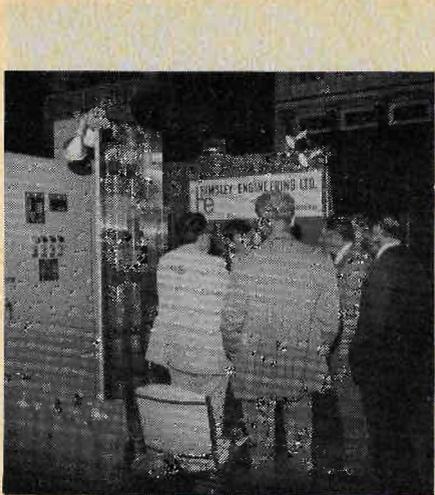
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Coffee Breaks

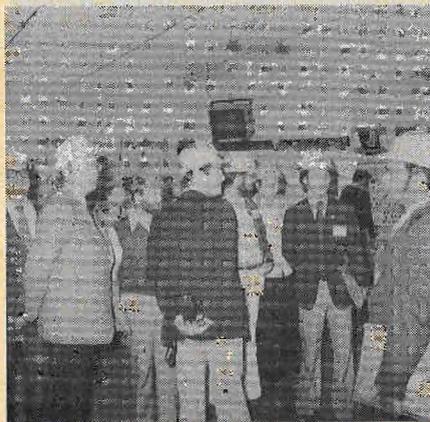


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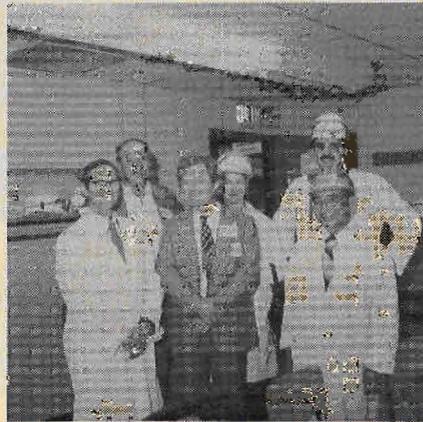
Serge Berkovitch and Walter Sowa



Equipment Displays



Pickering Nuclear Power Plant

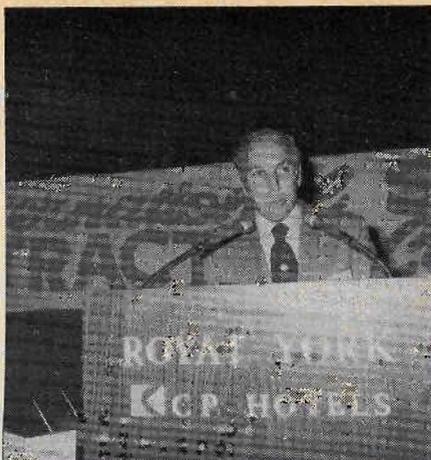


Eldorado Port Hope Uranium Refinery



McMaster University

Banquet



Closing Remarks, ISEC '77
Chairman Gordon Ritcey



On to ISEC '80 — Co-Chairmen
Dr. A.W. Ashbrook and Mr. G. Ritcey
(Canada) handing over ISEC banner to
Mr. T. Van Peteghem and
Dr. I.F. Desreux (Belgium)



Irwin and Betty Itzkovitch



Gladys and Gordon Ritcey



Not all business —
Walter Kusters and Friend

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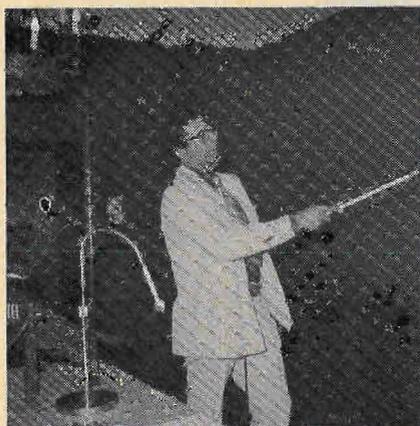
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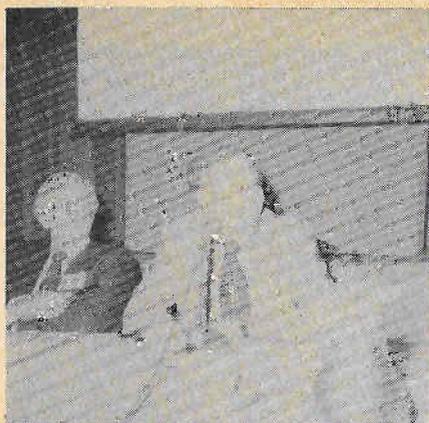
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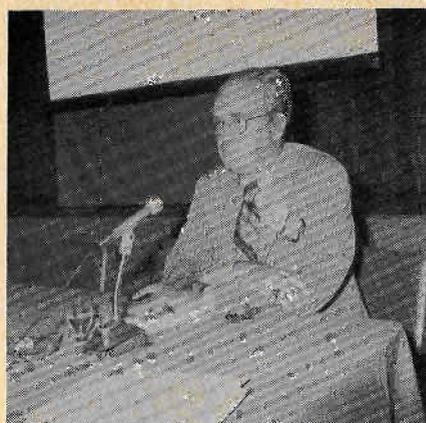
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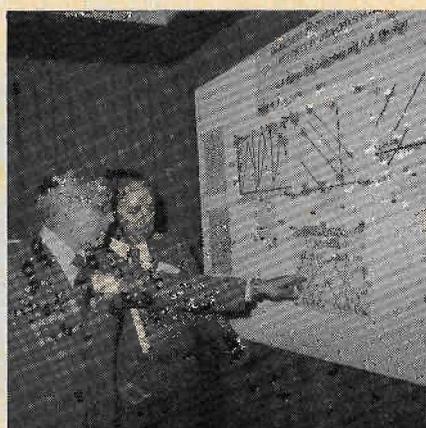
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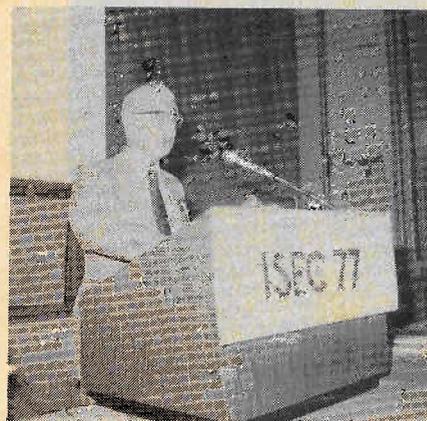
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Dr. V. Sefton

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Chapter 3

Inorganic Processes

Section 3.1 and 3.2
Printed in the United States of America



Dr. K. S. Thirumangalakudi



Dr. K. S. Thirumangalakudi

Section 3.3 and 3.4

The Recovery of Gallium from Bayer Process Aluminate Solutions by Liquid-Liquid Extraction

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ABSTRACT

Liquid-liquid extraction is an attractive technique for the recovery of gallium from Bayer process aluminate solutions. Highly selective extraction of gallium is obtained using an alkylated hydroxyquinoline (KELEX 100). The characteristics of this extractant, acting as a cationic and anionic exchanger, allow an important purification of gallium during the stripping.

Introduction

SODIUM ALUMINATE SOLUTIONS from the Bayer process are at present the main raw material for gallium. In such solutions mass ratio Al/Ga runs approximately from 150 to 400/1, and the recovery of gallium requires a highly selective technique. Processes used are usually based on the amalgamation of the gallium by direct electrolysis or exchange with sodium amalgam. These processes are carried out directly^(1,2) or after treatment of the aluminate solutions by fractional carbonation⁽⁴⁾ or caustic addition⁽³⁾. This leads to a smaller Al/Ga ratio and gives better yields. However in these last cases, solutions are spoiled and cannot then be recycled in the Bayer circuit. Pollution, resulting from the need for large stocks of mercury, will forbid the use of such processes in the future. Solvent extraction thus appears to be a good method for the recovery of gallium.

In the very basic aluminate solutions, no known complex-forming agent is effective or selective enough to fix the $\text{Ga}(\text{OH})_4^-$ anions in the presence of large quantities of $\text{Al}(\text{OH})_4^-$ anions and hydroxyl ions, OH^- . On the other hand, some cationic complex-forming agents have a sufficiently strong affinity for Ga^{3+} ions in such a medium. Oxine (*o*-hydroxyquinoline) and acetylacetone are well known for their high selectivity for gallium in a basic medium⁽⁶⁻⁸⁾. However, these products are analytical reagents, too soluble in aqueous phases, and the conditions that are used to get significant recovery yields for gallium also lead to a high dilution of the Bayer solutions, which will then be unsuitable for industrial use. We show in this paper that an alkylated-8-hydroxyquinoline⁽⁹⁾, KELEX 100®, extensively studied for copper hydrometallurgy, is a suitable extractant for an industrial process of gallium recovery from Bayer solutions by solvent extraction⁽¹⁰⁾.

Experimental

Sodium aluminate solutions considered in this study have been taken from the Pechiney Bayer circuit at Salindres (France). KELEX 100 (Ashland Chemicals) con-

tains about 2% of free 8-hydroxyquinoline (gas chromatography analysis) which is eliminated by prior washing with a 2 M HCl solution. Kelex concentration is determined by potentiometric titration in anhydrous acetic acid. — Atomic absorption spectrophotometry is used for analysing gallium in aqueous and organic phases.

Extraction Reactions

The sodium aluminate solutions from the Bayer process are described as "decomposed" when the alumina has been precipitated. Their average composition corresponds approximately to the following concentrations:

$$\text{Al}_2\text{O}_3 \text{ 80 g.l}^{-1} (\text{Al}^{\text{III}} \text{ 4.7 eq. l}^{-1})$$

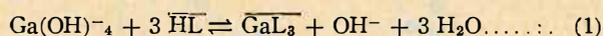
$$\text{Na}_2\text{O 160 g.l}^{-1} (\text{Na}^+ \text{ 5.2 eq. l}^{-1})$$

$$\text{Ga 0.1 to 0.3 g.l}^{-1} (\text{Ga}^{\text{III}} \text{ 0.004 to 0.012 eq. l}^{-1})$$

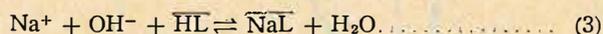
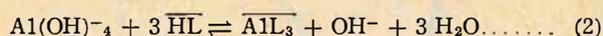
Gallium concentration is variable with Bayer circuits and depends on the Bauxite source.

These solutions form a highly basic medium ($[\text{OH}^-] \sim 3.6 \text{ M}$) from which the extraction of metals by KELEX (HL) leads to a total exchange of the solvent's equivalents according to the following reactions:

— to a low degree, as far as gallium is concerned, due to the respective concentrations



— to a very high degree, as for aluminium and sodium



Thus, the basicity of the solutions which is favorable for sodium extraction is highly unfavorable for gallium extraction. However, the partition coefficient and selectivity towards gallium obtained with KELEX are sufficient to give excellent yields in the recovery. A relatively low kinetics is observed for gallium.

We consider several parameters affecting the extraction of gallium:

- (i) — temperature which especially affects the kinetics,
- (ii) — Kelex concentration in the diluent (kerosene), and
- (iii) — modifier concentration (*n*-decanol) which is necessary to avoid demixing during the acidic stripping.

Temperature

Temperature is a powerful parameter on the kinetics of gallium extraction as shown in Figure 1. On the other hand, the equilibrium is slightly affected. Concentrations of the different elements in the solvent are given in Table I. High selectivity towards gallium can be observed: at 50°C for example, the Al/Ga ratio is 147 in the Bayer solution and falls to 6.6 in the loaded solvent with a recovery yield close to eighty percent.

TABLE 1 — Temperature Effect on Equilibrium

$V_o/V_A = 1$
 Initial Bayer solution: Al_2O_3 75 g.l⁻¹
 Na_2O 194 g.l⁻¹
 Ga 270 mg.l⁻¹
 Solvent: KELEX 8.5% v/v — kerosene — 10% n-decanol

t°C	\overline{Ga} mg.l ⁻¹	\overline{Al} g.l ⁻¹	\overline{Na} g.l ⁻¹
28	216	1.50	1.59
50	210	1.38	1.92
75	206	1.21	2.36

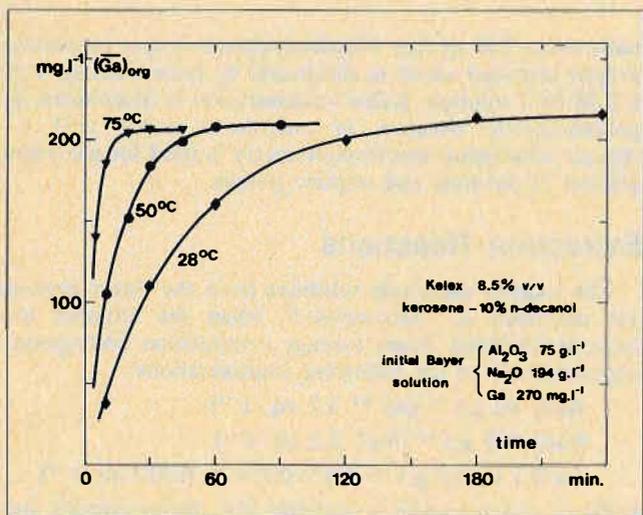


FIGURE 1. Temperature effect on gallium extraction.

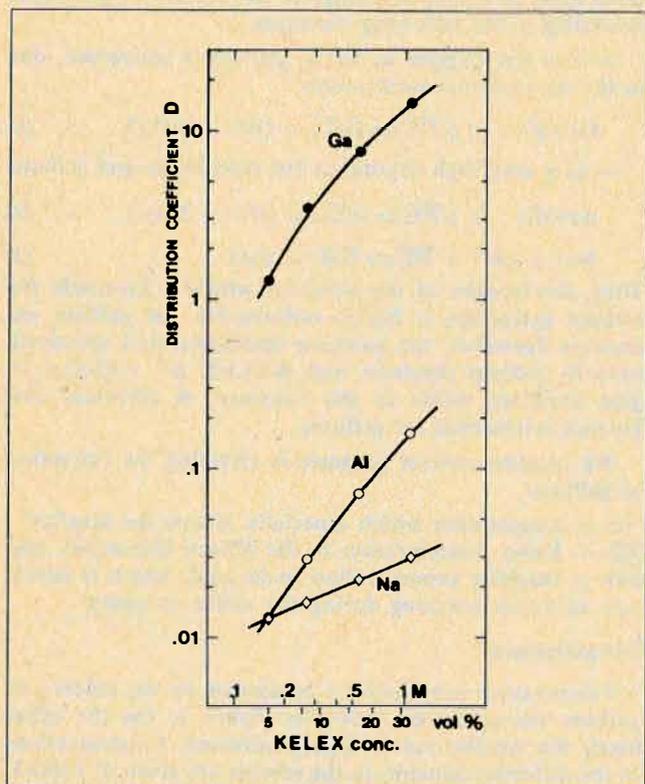


FIGURE 2. Effect of KELEX concentration (at 50°C)
 Bayer solution: Al_2O_3 84 g.l⁻¹
 Na_2O 217 g.l⁻¹
 Ga 300 mg.l⁻¹

KELEX Concentration

Reaction (1) shows that increasing the KELEX concentration will have a great effect on the distribution coefficient of gallium. Results obtained after equilibrium at 50°C are given in Figure 2. In accordance with the total exchange of the H⁺ equivalents of KELEX, we do not observe a third power dependency of D_{Ga} with the KELEX concentration.

Modifier Concentration

Excellent hydrodynamic conditions are obtained during the extraction operation from Bayer solutions with KELEX in kerosene without a modifier. On the other hand, during acidic strippings, a modifier must be added to the solvent to get good phase separation and to avoid a third phase formation. We chose n-decanol and we have studied its consequences on the selectivity of KELEX (Figure 3). Increasing n-decanol in the solvent leads to a loss of selectivity towards aluminium and gallium with respect to sodium. However, the evolution is weak and the gallium load is slightly affected.

Stripping

The stripping of the KELEX loaded with Ga, Al and Na, is conventional in an acidic medium according to (e.g. for gallium):



As in the reaction with copper⁽¹¹⁾, the stripping is promoted by KELEX protonation when the acid concentration is sufficient (Figure 4). However, for gallium, two situations must be considered, according to whether or not the acid leads to the formation of anionic complexes. These complexes are then extractable by KELEX acting as a tertiary amine. This is the case when hydrochloric acid is used.

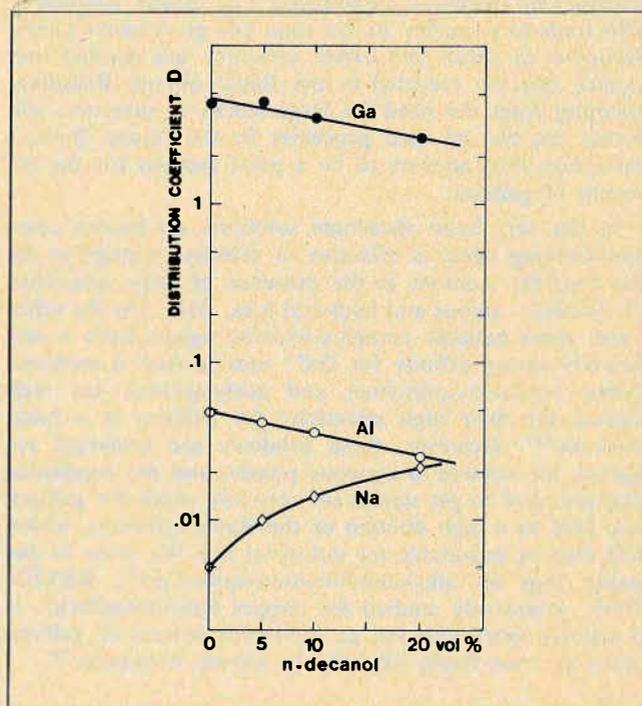


FIGURE 3: Effect of n-decanol (at 50°C)
 KELEX 8.5% v/v
 Bayer solution: Al_2O_3 75 g.l⁻¹
 Na_2O 194 g.l⁻¹
 Ga 270 mg.l⁻¹

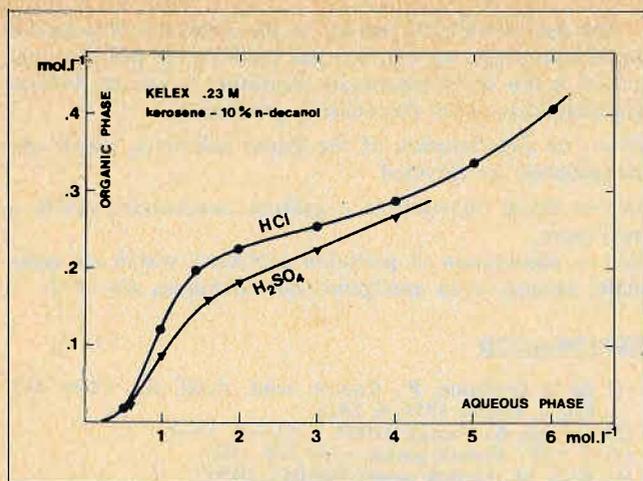


FIGURE 4. Extraction of HCl and H₂SO₄ (T = 20°C)

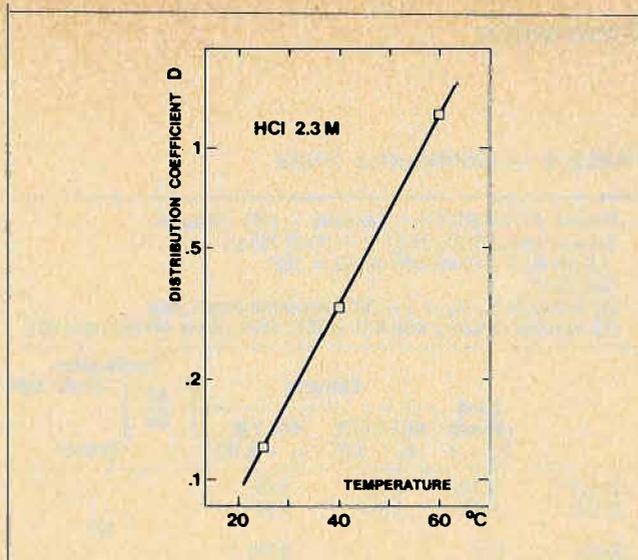


FIGURE 6. Temperature effect on gallium extraction in HCl medium (KELEX 8% v/v).

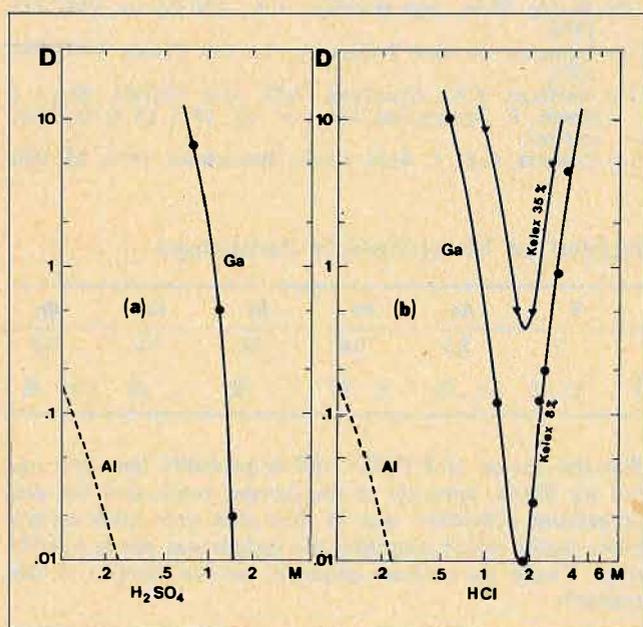
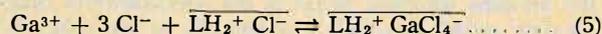


FIGURE 5. Stripping of gallium with (a) H₂SO₄ or (b) HCl.

The first observed reaction is (4), but when the acid concentration increases over approximately 2M, KELEX is in the hydrochloride form $\text{LH}_2^+ \text{Cl}^-$ and the anionic complex GaCl_4^- is extracted by the following reaction



These reactions are similar to those obtained with iron (III)⁽¹²⁾. Evolutions of distribution coefficients are given for sulfuric acid (Figure 5a) and hydrochloric acid (Figure 5b). Sodium and aluminium are more easily stripped than gallium according to reaction 4, which is not dependent on the kind of acid. In the case of HCl, we note an important temperature effect which increases gallium extraction in the high concentration levels where the extracted species is GaCl_4^- (Figure 6).

On the other hand, with sulfuric acid, the stripping can be efficient even with a relatively high KELEX concentration, but with acid consumption. With hydrochloric acid, a condition for a good stripping of gallium is a low minimum distribution coefficient, and that involves a KELEX concentration below 10% (Figure 5b).

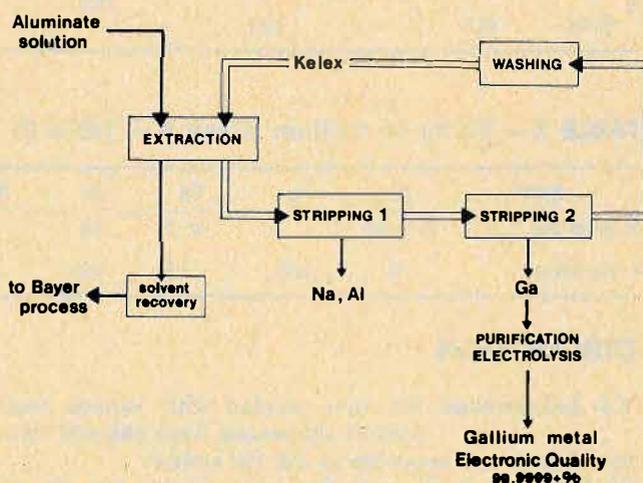


FIGURE 7. Scheme of the process.

Gallium Purity

After the extraction stage, KELEX is essentially loaded with aluminium and sodium (in Table 1, gallium is only 3 to 4% of the solvent loading). A possible result of the selectivity of KELEX in an acidic medium is the purification of gallium during the stripping operation. A first selective stripping of Al and Na is carried out (Figure 7), with (i) 0.5 M H₂SO₄ and (ii) 0.5 M or 6 M HCl, or (iii) 1.8 - 2 M HCl. After (i), Ga stripping can be carried out at (i) > 1.5 M H₂SO₄.

The highest purity of gallium is obtained with a HCl 6N primary stripping as shown in the results of continuous tests, given in Table 2; moreover this arrangement excludes the small loss of gallium recorded during a first stripping with a dilute acid (case A).

Another point of interest in the process is the purity of the gallium in the extract as compared to other metallic ions present in the Bayer solutions. Results are given in Table 3. We observe a very high degree of purity close to 95% at this stage. Aluminium is the major contaminant.

Conclusion

TABLE 2 — Continuous Tests

	Load solvent $V_o = 1$	Extracts		Purification $\left[\frac{Al}{Ga} \right]$ Bayer soln Extract
		HCl 0.67M $V_A = 1.05$	HCl 2 M $V_A = 0.182$	
— Solvent: KELEX 8% v/v — kerosene — 10% n-decanol				
— Bayer solution: Al_2O_3 91 g.l ⁻¹ — Na_2O 185 g.l ⁻¹ Ga 300 mg.l ⁻¹ (mass ratio Al/Ga = 160)				
— Conditions: (a) extraction $V_o/V_A = 1$ — 50°C residence-time 1 hour. (b) selective stripping with HCl at 25°C dilute (A) or concentrated (B).				
A	Ga g.l ⁻¹	0.175	0.017	400
	Al g.l ⁻¹	1.43	1.31	
	Al/Ga	12.3	0.385	
— HCl 6.4 M $V_A = 0.463$ HCl 2 M $V_A = 0.272$				
B	Ga g.l ⁻¹	0.175	not detected	3200
	Al g.l ⁻¹	1.43	3.07	
	Al/Ga	12.3	0.05	

TABLE 3 — Purity of Gallium (Case B — Table 2) Expressed as Metal/Gallium Percentage

Metal	Al	Fe	Cu	Zn	Mo	V	As	Pb	Ni	Co	Mn
In Bayer soln.	16×10^3	7	< .3	2.5	57	33	8.3	0.6	0.6	0.6	0.8
In the extract	5	0.65	0.2	0.15	< .2	< .2	< .04	< .05	< .02	< .02	< .01

DISCUSSION

V.I. Lakshmanan: We have worked with various commercial extractants from chloride solution. I have two questions to ask the author:

(1) From our work, extraction and stripping rate for trivalent ions from chloride solution should be very interesting. Could the authors give some comments on stripping Ga^{3+} , after extracting into the KELEX phase from HCl solution.

(2) In my opinion, reagent loss, under the conditions the authors have worked at, can be important. Have the authors done any work on treating raffinates for environmental control?

A. Leveque: (1) The rate of the stripping from the loaded solvent with acid solutions is acid dependent. With the HCl solution, the rate is faster than with H_2SO_4 solutions. But in the two cases, at the acid concentrations which are used for the shifting of gallium, the rate is quite fast.

(2) Considering the respective size ratio between the KELEX process for gallium and the Bayer process, there are no environmental problems. Effluents from the gallium process are quite easily integrated into those of the Bayer circuit, especially the red muds.

D.S. Flett: Some time ago at Warren Spring Laboratory, we examined the extraction of gallium from Bayer Process liquors with KELEX 100. We would agree

The use of KELEX has led to the definition of a liquid-liquid extraction process for the recovery of gallium contained in the Bayer aluminate solutions. It has the following advantages over the existing processes:

- (i) — no deterioration of the Bayer solutions, which can immediately be recycled,
- (ii) — direct recovery of a gallium concentrate which is very pure,
- (iii) — elimination of pollution problems, which are especially intense when amalgamation techniques are used.

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that the choice of KELEX 100 is probably the right one but we found, contrary to the current work, that the rate of gallium extraction was so slow that even after several hours under reflux condition the system was not at equilibrium. Could the authors comment on the kinetics of this system?

A. Leveque: We found that the purity of KELEX has some influence on kinetic results, but not in such a way as you report. We do not understand the reason of your observations.

T. Sato: (1) The Bayer process uses highly concentrated sodium hydroxide solutions. When we apply the extraction of gallium by KELEX to the Bayer process, the stability of KELEX depends on the concentration of the alkaline solution. What is the concentration range of alkaline media in which it is possible to use KELEX?

(2) The solubility of KELEX in alkaline solution is an important problem in the application of KELEX to the Bayer process. Could you explain this point to us, if possible?

A. Leveque: KELEX is used for the extraction of gallium from the "decomposed aluminate solutions"; the extraction can be achieved in such solutions without any trouble of economic consideration for the solvent stability. From more concentrated solutions, the loss of KELEX could become important, but such solutions lead to lower partition coefficients for gallium and are not of practical interest.

The Solvent Extraction of B_2O_3 Carried by the Borax and Boric Acid Slurries

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Gaziantep Extension Campus, Gaziantep, Turkey.

ABSTRACT

Several borax and boric acid factories in Turkey produce slurries containing up to 19% B_2O_3 as an end product. (See Table 1) These slurries are obtained either in the form of filterpress-cake or thickener tailing of aqueous tincal and sulfuric acid solutions of roasted colemanite and are usually dumped into the sea causing pollution problems⁽¹⁾. This work aims at recovering boron trioxide present in these slurries using polyalcohols as extractants.

Introduction

SINCE ALL KNOWN CHELATE RINGS OF BORON have boron-oxygen bonds, organic compounds carrying hydroxy groups at the cis-position on the neighboring carbon atoms such as polyalcohols, hydroxy organic acids or B-diketones, will usually form complexes with boron which contain five and six-membered chelate rings.

Many polyalcohols have been used for selective extraction of borax and other boron compounds. Practical⁽²⁻⁸⁾ and analytical⁽⁹⁻¹³⁾ applications of this type of liquid-liquid extraction have been reported.

Experimental

Chemicals

The boric acid and borax slurries used in this work were supplied by the Etibank Bandirma Borax and Boric Acid factories. After solar drying in air the cakes were ground into powder and stored in a dessicator.

EHD, TMPD, ND* and mannitol obtained from Fluka of Switzerland were utilized without further purification. CTMP was prepared in the Marmara Research Institute of Turkish Scientific and Technical Research Council⁽¹⁴⁾. All the other chemicals used were of reagent grade.

Procedure

Slurries of different pulp densities have been prepared by adding 1-100 grams of dry samples into 100 ml of water. The percentages of dissolved B_2O_3 in water of these samples were a function of pulp density. In the extraction experiments, borax and boric acid solutions or slurries of different pulp densities and also one-to-one mixtures of boric acid and borax slurries were shaken by means of a shaking machine with an equal volume of organic phase containing diol - solvent (1:1). The two phases were separated by means of centrifugation.

The pregnant organic phases were stripped by shaking with an equal volume of dilute NaOH when aliphatic 1,3-diols were extractors and by dilute mineral acids in the case of aromatic diols.

*See notation following text.

TABLE 1. Analysis Report — May 1973 Averages

	Borax Slurry (%)	Boric Acid Slurry (%)
B_2O_3	17.30	7.55
SiO_2	15.35	7.46
Fe_2O_3	0.38	0.27
Al_2O_3	5.16	1.91
CaO	14.16	30.80
MgO	12.55	2.38
As	0.005	0.194
SO_3	—	45.33

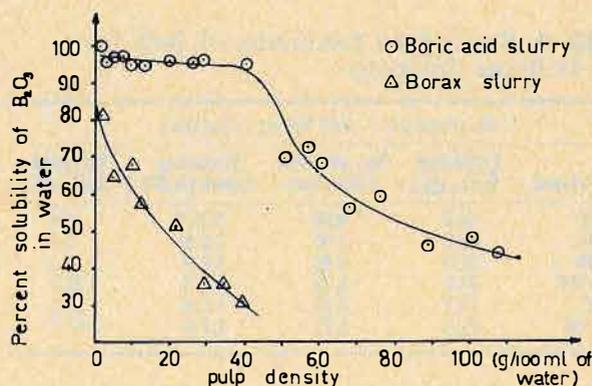


FIGURE 1. Change of solubility of B_2O_3 in water with pulp density.

The amounts of B_2O_3 remaining in the aqueous phases were determined before and after each step by alkaline titration in the presence of mannitol and the percentage of extractions and strippings were computed.

Results and Discussion

Solubility of B_2O_3 Present in the Slurries

In Figure 1 the change of solubility of B_2O_3 in water with pulp density at $22 \pm 2^\circ C$ is shown. B_2O_3 present in boric acid slurries was found to be almost completely soluble in water and the solubility remained above 95 percent up to a pulp density of "40 g/100 ml of water". On the other hand, the solubility of B_2O_3 present in the borax slurry was around 85% at most and dropped sharply as the pulp density increased. This may be due to the colloidal nature of the borax slurry.

Extraction

Table 2 shows the results of extraction and stripping of B_2O_3 from a 0.01 M borax solution. Percent extraction is around 50% with the exception of ND (74.9%). The

stripping yields are very low in the case of EHD and TMPD which are aliphatic 1,3-diols. ND and CTMP, both aromatic diols, show very high stripping yields with dilute mineral acids.

Another important observation is the change in pH of the aqueous layer after extraction. For EHD and TMPD, pH increases from 9.20 to 9.90, while decreasing from 9.20 to 6.40 in the case of ND and CTMP. The former case indicates that the acidic species are extracted by EHD or TMPD, while the latter is caused by the extraction of only the basic species by ND or CTMP.

In fact, in a borax solution, the hydrolysis of the tetraborate ion leads to the formation of boric acid and metaborate ion at equal concentrations:



If the acidic species, namely boric acid, is extracted, the pH of the solution increases due to the equilibrium shift in favor of the metaborate ion or vice versa. As indicated by Equation 1 the percent extraction can be 50% at most, for either case. In fact it is around 50% with the exception of ND in which case phase separation is difficult due to the formation of a third phase.

Another remarkable observation is the Stripped % B_2O_3 (see Table 2). The values are very low for EHD -

TABLE 2. Single-Step Extraction of B_2O_3 from 0.01 M Borax Solutions

(Aqueous pH = 9.20 before Extraction)				
Diol/Solvent	Extracted B_2O_3 (%)	Aq. pH after Extraction	Stripping Agent (H_2SO_4)	Stripped B_2O_3 (%)
EHD/PE	56.0	9.90	0.05 N	6.8
EHD/IPE	53.2	9.90	1.0 N	9.7
EHD/BN	52.6	9.90	1.0 N	4.3
TMPD/IPE	48.0	9.95	1.0 N	31.2
ND/IPE	74.9	6.30	1.0 N	97.6
CTMP/PE	51.3	6.25	1.0 N	97.7

TABLE 3. Extraction from Acidified 0.01 M Borax Solution

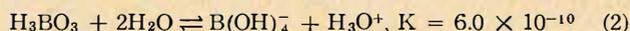
(Aqueous pH = 8.90 before Extraction)		
Diol Solvent	Extracted B_2O_3 (%)	Aq. pH after Extraction
EHD PE	63.5	10.22

TABLE 4. Extraction of B_2O_3 from Boric Acid Slurry

Solvent : EHD/PE (1:1) Stripping Agent : NaOH			
Pulp-density g/100 ml water	Extracted B_2O_3 (%)	NaOH	Stripped B_2O_3 (%)
3.82	94.1	0.1	86.7
6.28	93.1	0.1	64.2
8.08	94.4	0.1	35.1
10.80	94.0	0.5	65.8
12.68	92.1	0.5	72.6
13.74	95.0	0.1	25.3
21.96	95.7	0.5	65.6
30.88	96.1	0.5	56.4
36.14	96.0	0.5	46.1
37.92	87.8	1.0	59.2
40.82	86.6	0.5	43.0
40.00	86.8	1.0	54.3
48.20	78.6	1.0	42.8
48.00	78.0	1.0	57.9

and TMPD-diol complexes, but very high for ND- and CTMP-diol complexes when mineral acids (according to the suggestions of Garret^(7,8)) have been used as stripping agent. This point will be discussed later.

A pH of 9.20 for 0.01 M borax solution indicates the presence of boric acid - metaborate buffer of 1:1 ratio. Since pK for boric acid is 9.22, when this solution is acidified the following equilibrium shifts in favor of boric acid formation:



Thus the extraction by EHD or TMPD from such an acidified borax solution is expected to give a higher yield as shown in Table 3. EHD and TMPD, as aliphatic 1,3-diols, therefore, seem to extract boric acid only. On the other hand, metaborate ion is extracted by ND and CTMP, both of which are aromatic and the former one is a 1,2-diol.

In order to verify this statement, a successive two-step extraction from a 0.01 M borax solution has been carried out. In the first step ND and in the second step EHD have been used and a combined extraction yield of 99% has been reached. Table 4 shows the results of solvent extraction from boric acid slurries of different pulp densities by EHD/PE (1:1). Very high extraction yields indicate again that EHD is a very good extractant for boric acid. Here, NaOH was used as the stripping agent instead of mineral acids (see Table 2) and very high yields were obtained. At high pulp densities, higher concentrations of NaOH were required to increase the stripping yield as shown in Table 4. A multistep (or continuous) stripping with 0.1 N NaOH gave also high values (Table 5):

Extraction from Mixtures of Boric Acid and Borax Slurries

50g-samples from each slurry were taken and mixed with one-liter of water using a magnetic stirrer for an hour. The sample was allowed to rest for over two hours and then a clear solution was obtained over the solid phase. The pH of this solution was 8.20. 40 ml-samples from this supernatant solution were shaken with CTMP/PE at equal volumes. Phase separations were easy. Stripping was done by 1 N H_2SO_4 . The same experiments were repeated after the aqueous pH has been increased to 9.20-9.30 by adding sodium hydroxide. The results are given in Table 6. Extracted % B_2O_3 in Table 6 has two values for the same experiment. For the computation of the first (higher) values, initial B_2O_3 concentration was taken as the concentration of supernatant solution. But the second values were computed with respect to the total B_2O_3 (i.e. B_2O_3 in supernatant + B_2O_3 in the solid phase). From these values it is understood that 60-65% of B_2O_3 present in this slurry-mixture was carried to the aqueous and 30-60% of that was extracted to the diol-petroleum ether phase depending on pH.

TABLE 5. Stripping in Three Steps

Aqueous Phase : Boric acid slurry Organic Phase : EDH + PE Stripping Agent : 0.1 N NaOH		
Pulp density g/100 ml water	Extracted B_2O_3 (%)	Stripped Total B_2O_3 (%)
29.24	87.0	71.2
33.38	88.0	81.0
35.68	89.7	79.7
39.74	89.0	68.0

TABLE 6. Boron Extraction from Mixtures of Boric acid — Borax Slurries

Exp. No.	Aq-pH before Extraction	Organic Phase : CTMP/PE		Stripping Agent (H ₂ SO ₄)	Stripped B ₂ O ₃ (%)
		I	II		
1	8.20	28.9	18.4	1 N	93.9
2	8.20	27.6	17.5	1 N	94.9
3	9.20	58.4	38.6	1 N	93.8
4	9.30	60.9	37.0	1 N	90.9

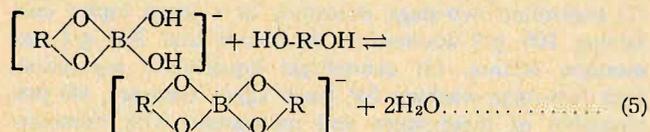
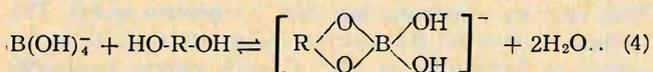
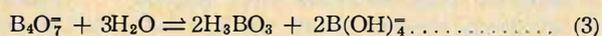
Multistep Extraction from the Mixture

A three-step extraction from the mixture of boric acid-borax slurry supernatant gave a total extraction yield of 94%, provided that the pH of the aqueous phase was continuously kept at 9.20 by adding NaOH. (See Table 7). When these results are compared with the literature, especially with those dealing with the practical application^(2,8), we do not observe any indication of differences in extractive behavior of aliphatic 1,3-diols with respect to aromatic and 1,2-aliphatic diols. Especially the suggestion of dilute mineral acids as the unique stripping agent for all kinds of diols was found misleading in this study as seen in Tables 2 and 4.

Some supporting evidence has also been found^(15,16,17) in the literature. Grannen⁽¹⁷⁾ extracts boron from an aqueous solution at pH 5 with the derivatives of salicylic acids which are very similar in structure to CTMP where a drop in pH after extraction is observed. Although no mention is made of the extraction mechanism, this dropping pH indicates that salicylic acid derivatives extract metaborate ion as CTMP does.

Dyrssen, et al⁽¹⁵⁾ have reported that the distribution coefficient of boron drops above pH 8 when EHD and DEPD were used, due to the metaborate, B(OH)₄⁻, formation. Egneus and Uppstrom⁽¹⁶⁾ report that aliphatic 1,3-diols are superior with respect to 1,2-diols in extracting boric acid.

The extraction of boron from alkaline solutions, in other words the extraction of metaborate ion (by polyalcohols such as ND and CTMP), may follow the following steps:



As it is seen, the final product is an ion-pair. In fact Dyrssen⁽¹⁵⁾ indicates that polyalcohols extract boron from alkaline solutions in the form of ion-pairs. Acidic stripping required for ND- or CTMP-boron ion-pairs supports the above given mechanism.

On the other hand, 1,3-diol-boron complexes can be stripped only by alkaline stripping agents and this indicates that these complexes are not ion-pairs but esters⁽¹⁵⁾: [B-(OH)₂-(OH)₂R].

These differences may arise from the symmetry differences of metaborate ion and boric acid. Complex formations with diols should follow the mechanism which leads to the most stable ring formations.

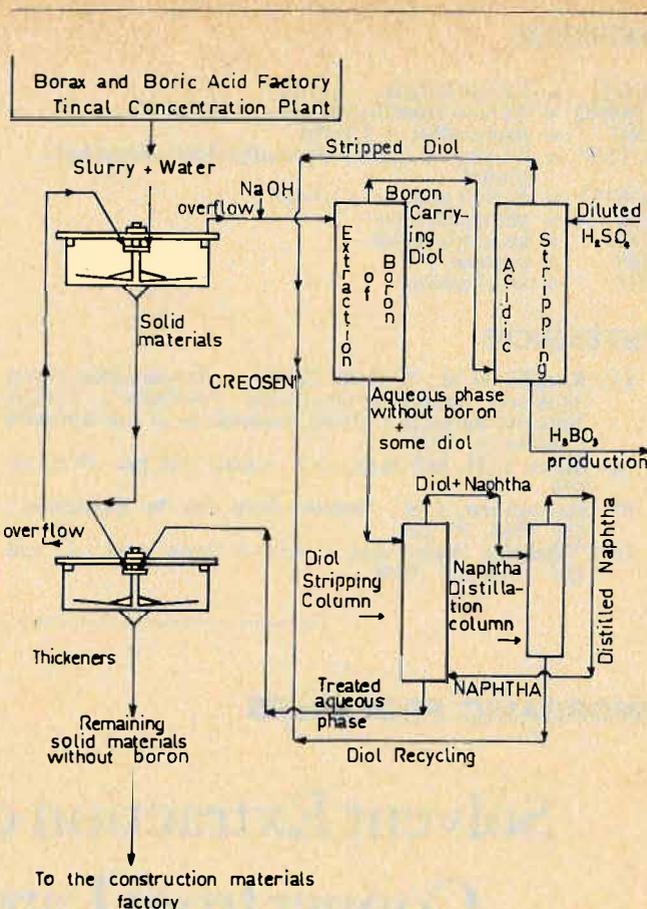


FIGURE 2. Solvent extraction flowsheet.

TABLE 7. Multistep Extraction from the Mixture of Slurries

Organic Phase : CTMP/PE	
Aq. pH before Ext. : 9.20	
	Extracted total B ₂ O ₃ (%)
1. step	47.6
2. step	80.6
3. step	94.0

Conclusion

1. Extraction of boron from slurries may lead to the diol-losses. Therefore, thickeners should be used and the extraction must be carried with the supernatant solution.
2. Extraction from the mixtures of boric acid and borax slurries may be done most economically by using 1,2-diols or aromatic diols (such as ND or CTMP) by keeping the aqueous pH above 9. Since in this case acidic stripping is required, the final product will be boric acid.
3. A flow-sheet is proposed according to the above conclusions. (see Figure 2)

Acknowledgment

The authors wish to thank the Turkish National Research Council for financial support.

NOTATION

EHD	= 2-ethyl hexane — 1,3-diol
TMPD	= 2,2,4 — trimethyl pentane — 1,3-diol
ND	= naphthaline — 2,3-diol
CTMP	= 2-Chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol phenol
DEPD	= diethyl propane — 1,3-diol
PE	= petroleum ether
IPE	= iso propyl ether
BN	= benzene
DA	= decyl alcohol

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INORGANIC PROCESSES

Solvent Extraction of Nickel, Cobalt and Copper from Laterite-Ammoniacal Leach Liquors

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ABSTRACT

The U.S. Department of the Interior, Bureau of Mines, is investigating a method to recover nickel, cobalt, and copper from laterites containing less than 1.2 percent nickel by reduction roasting, leaching, solvent extraction, and electro-winning unit operations. This method includes three Bureau of Mines objectives: (1) production from low-grade domestic laterites of critical metals that are domestically in short supply, (2) lower processing energy requirements, and (3) solution recycling.

Nickel and copper are coextracted with LIX 64N* from an ammoniacal-ammonium sulfate batch leach liquor containing 1.00 grams per liter (g/l) nickel, 0.30 g/l cobalt, 0.03 g/l copper, and 0.02 g/l zinc. Nickel and copper are then separated by selective stripping with spent nickel and copper electrolytes.

Cobalt(III) in the nickel- and copper-barren raffinate is reduced to cobalt(II) with cobalt metal. General Mills XI-51 extracts cobalt(II) from the treated raffinate. Extracted cobalt is stripped from the XI-51 with spent cobalt electrolyte.

*Reference to specific equipment, trade names, or manufacturers does not imply endorsement by the Bureau of Mines.

Introduction

THE U.S. DEPARTMENT OF THE INTERIOR, Bureau of Mines, is conducting research to maintain an adequate supply of minerals to meet national economic and strategic needs by making major improvements in metals and minerals processing technology. The Bureau is developing a reduction roast-ammonia leach method^(1,2,3) (Figure 1) to selectively recover nickel, copper, and cobalt as metals from laterites containing less than 1.2 percent nickel. The method involves (1) the selective reduction of nickel in the laterite to ferronickel at 525° C with carbon monoxide, (2) controlled two-stage oxidation in a leach liquor containing 100 g/l ammonium hydroxide and 300 g/l ammonium sulfate, (3) centrifugal liquid-solid separations with two-stage washing for leach agent recovery, (4) precipitation of magnesium and manganese with monoammonium phosphate, (5) stripping leach liquor of its free ammonia to 20 g/l to improve nickel loading, (6) solvent co-extraction of nickel and copper with General Mills LIX 64N* followed by a very dilute sulfuric acid wash and selective stripping of nickel and copper, (7) solvent extraction of cobalt from the nickel-copper raffinate with General Mills XI-51, (8) solvent extraction of zinc from the cobalt electrolyte with di-(2 ethylhexyl) phosphoric acid followed by crystallization of zinc sulfate in an evaporator, and (9) electro-winning of nickel, cobalt, and copper metals from pregnant electrolytes with the spent electrolyte being replenished in the respective strip circuits. With the exception of low or periodic bleed requirements, recycled streams include reduction offgas, leach

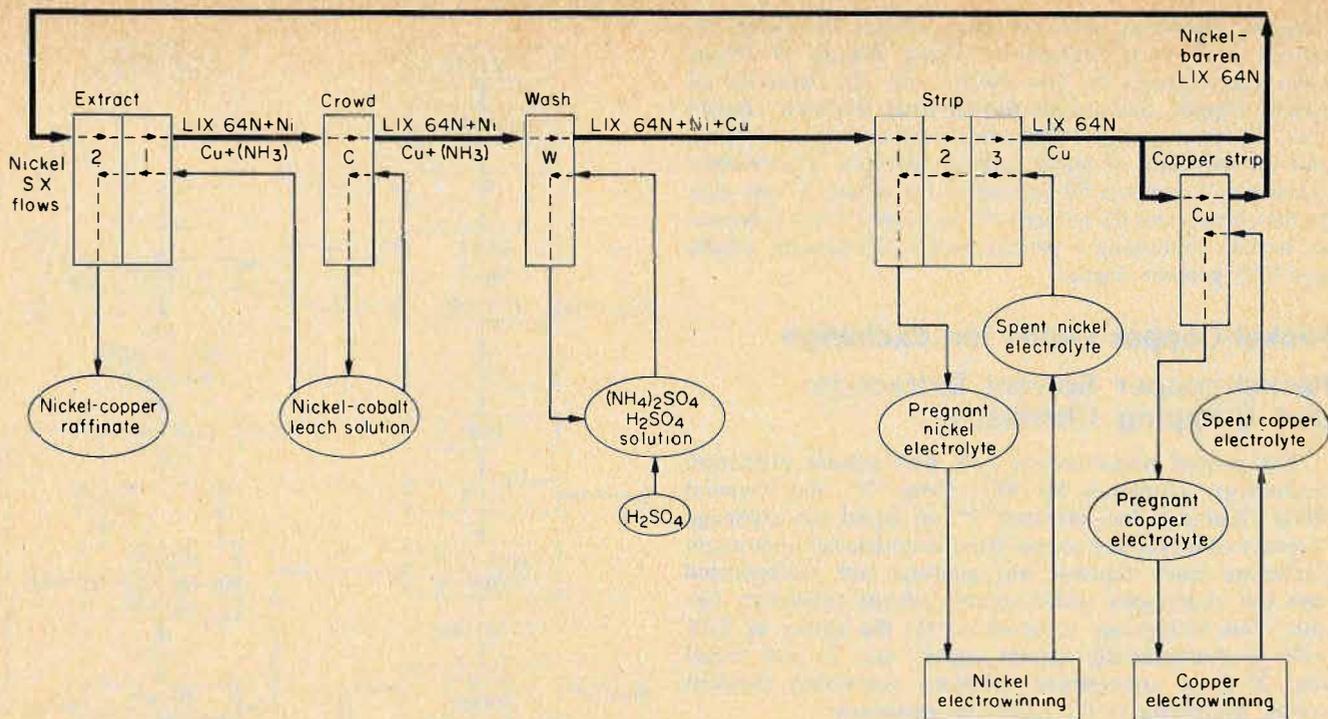


FIGURE 3. Nickel-copper solvent extraction system.

xide, and 294 g/l ammonium sulfate. The resulting raffinate is fed to the cobalt solvent extraction circuit and contains 0.30 g/l cobalt, 0.02 g/l zinc, 0.01 g/l nickel, and < 0.0001 g/l copper.

The first two stages of the nickel-copper extraction circuit are counter-current (Figure 3), the third stage is co-current and maximizes nickel loading and crowds or displaces zinc off the LIX 64N. The nickel extraction profile is shown in Figure 4, and the crowd extraction profile is shown in Figure 5. Organic to aqueous (O:A) ratios are reported on the figures. The organic phase loaded with nickel and copper passes to the wash circuit for removal of sorbed ammonia.

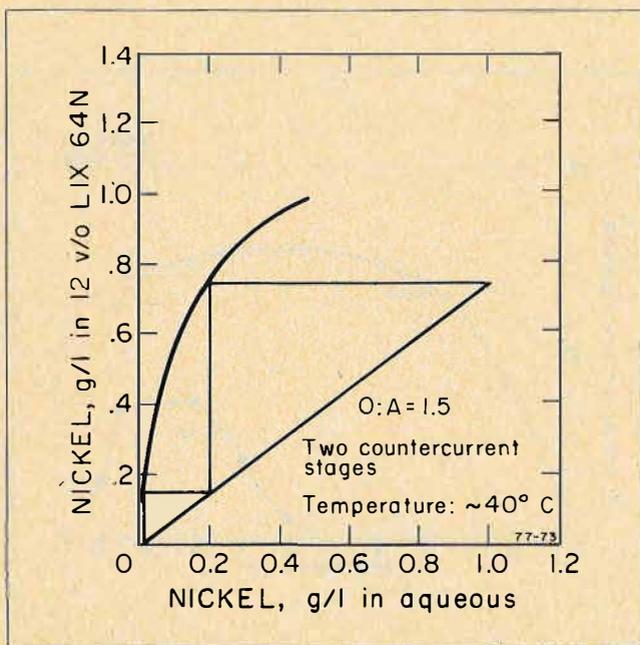


FIGURE 4. Nickel extraction profile.

Washing

The ammonia sorbed in the loaded organic phase is removed in a mixer-settler (Figure 3) by washing with pH 3.2 sulfuric acid in 250 g/l ammonium sulfate. The pH 3.2 sulfuric acid solution is added to the mixer to maintain a settler pH between 4.5 and 5.5. This removes ammonia without stripping nickel. Nickel and copper are then selectively stripped from the ammonia-free organic phase.

Nickel Stripping

The nickel in the 12 v/o LIX 64N is selectively stripped to 0.04 g/l in three countercurrent stages (Figure 3) with spent nickel electrolyte containing 83 g/l nickel and about 5 g/l sulfuric acid. The pregnant electrolyte produced during nickel stripping serves as feed to electrowinning and contains 90 g/l nickel at pH 2. The stripping profile is shown in Figure 6.

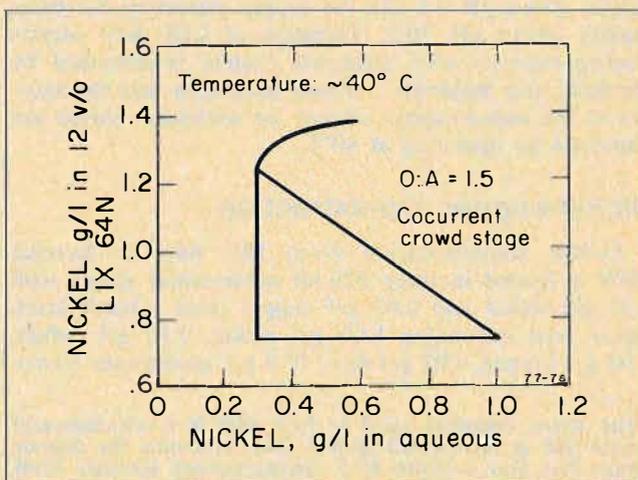


FIGURE 5. Nickel crowd extraction profiles.

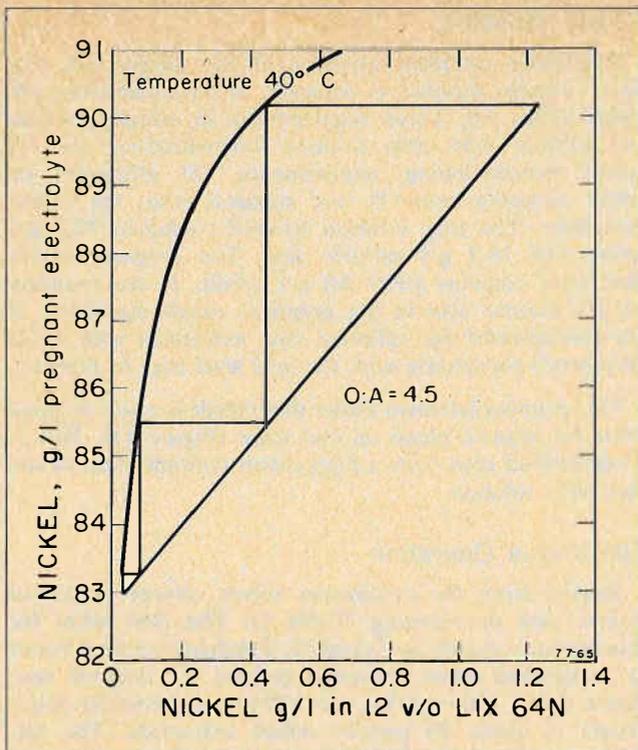


FIGURE 6. Nickel stripping profile.

Copper Stripping

Since copper loading of the organic phase is low, only one-fifth of the nickel-barren 12 v/o LIX 64N is stripped. The organic phase is stripped to 0.005 g/l copper in one mixer-settler with 180 g/l H_2SO_4 and 25 g/l copper electrolyte. The resulting barren 12 v/o LIX 64N flows into the nickel-barren LIX 64N.

Cobalt Liquid Ion Exchange

The experimental liquid ion exchange reagent XI-51, developed by General Mills, is being used to recover cobalt from the ammoniacal nickel-copper raffinate. Although XI-51 is not an oxime, it operates on a hydrogen ion cycle, forming metal-organic chelates.

Cobalt Extraction

The nickel-copper raffinate feed to cobalt solvent extraction from batch leach liquor contains 0.3 g/l cobalt (III), 0.02 g/l zinc, 10 to 20 g/l ammonium hydroxide, and 300 g/l ammonium sulfate. An organic solution consisting of 3 v/o XI-51, 15 v/o isodecanol, and 82 v/o Kermac 470B loads less than 0.1 g/l cobalt(III) from typical raffinates. Synthetic cobalt(II) solutions have a much higher loading capacity of about 1.5 g/l. A cobalt metal shot column is used to reduce cobalt(III) to cobalt(II) before extraction [eq. 5].



The effectiveness of the cobalt reduction column is illustrated in Figure 7. Clearly, high extraction of cobalt(II) is possible. The relative ease of cobalt extraction is also illustrated by the extraction isotherm, Figure 8. The S-shaped characteristic probably results from cobalt that is not reduced to cobalt(II). One extraction stage (Figure 8) produced a raffinate containing about 0.12 g/l cobalt, provided the loading of the organic phase did not exceed about 85 percent. Otherwise two stages are necessary.

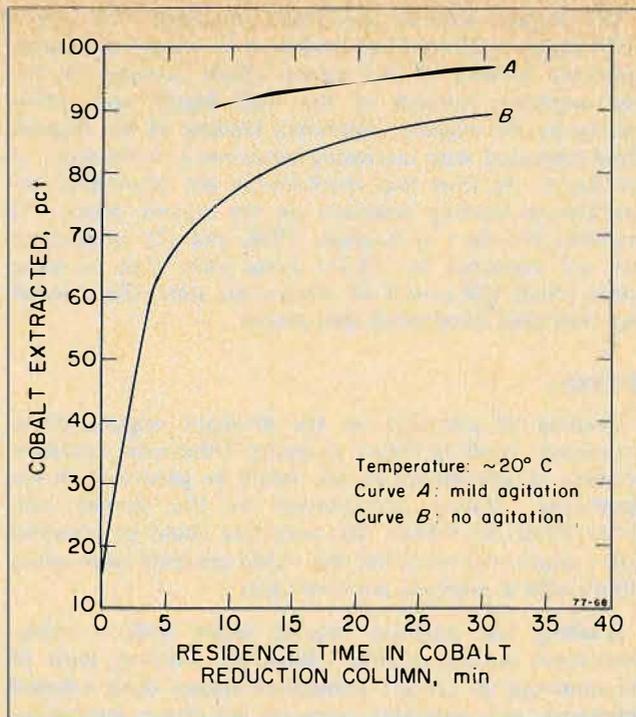


FIGURE 7. Cobalt extraction versus column residence time.

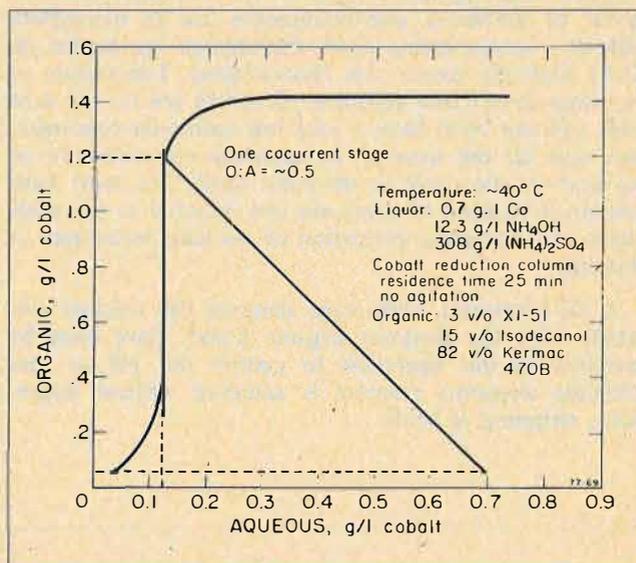


FIGURE 8. Extraction isotherm.

Longer retention time or increased agitation in the cobalt reduction column would reduce the cobalt concentration of the raffinate still further.

The loading of cobalt(II) on XI-51 is strongly pH dependent (Figure 9). Cobalt(II) just begins to load above about pH 4.5, with maximum loading taking place between pH 7.5 and 9. Increased free ammonia concentration above pH 9 probably provides an increased driving force to form amine complexes, thus inhibiting cobalt(II) extraction by XI-51. The maximum cobalt(II) loading capacity of 3 v/o XI-51, 15 v/o isodecanol, and 82 v/o Kermac 470B is about 1.4 g/l from actual nickel-copper raffinate at pH 9.5.

Zinc and nickel are also extracted by XI-51. The extent of their extraction is more strongly dependent on free ammonia content than that of cobalt. Zinc and nickel may be at least partially displaced off XI-51 by cobalt(II).

The organic solution also loads ammonia. The 3 v/o XI-51 organic solution has loaded up to 1.1 g/l ammonia. Ammonia loading of the organic phase depends on the free ammonia content of the feed liquor and cobalt loading on the organic. Ammonia loading of the organic phase increased with increasing ammonia concentration in the liquor. At least two mechanisms are apparently responsible in loading ammonia on the organic phase: (1) ammonia dissolves in Kermac 470B, and (2) ammonium ions are extracted by XI-51. Tests show that to some extent cobalt will crowd off ammonium ions. Other metal ions may also accomplish this action.

Washing

Loading of ammonia on the pregnant organic phase necessitates washing before stripping. Otherwise, excessive amounts of ammonium sulfate would be generated in the electrolyte, causing precipitation of the double salt, $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. The ammonia could be removed with a dilute acid wash, but this would generate ammonium sulfate with a resultant ammonia loss.

Washing the pregnant organic phase with a water-ammonium sulfate solution effectively removes most of the ammonia. A 120-g/l ammonium sulfate wash solution optimized both ammonia removal and phase separation. Two counter-current wash stages typically remove 70 to 80 percent of the total ammonia from the organic. The J-shaped washing curve (Figure 10) indicates that removal of ammonia and ammonium ion is incomplete without a neutralization wash. Ammonium ion loaded on XI-51 probably causes this characteristic. Limitations of the water-ammonium sulfate wash system are (1) the feed wash solution must have a very low ammonia concentration, and (2) the increase in ammonia concentration of the wash solution will be relatively small. The used wash solution is stripped of ammonia and recycled to the wash stages. An economic evaluation of washing techniques is planned.

A pH-controlled wash stage removes the residual ammonia from the pregnant organic phase. Care must be exercised in this operation to control the pH so that adequate ammonia removal is achieved without appreciable stripping of cobalt.

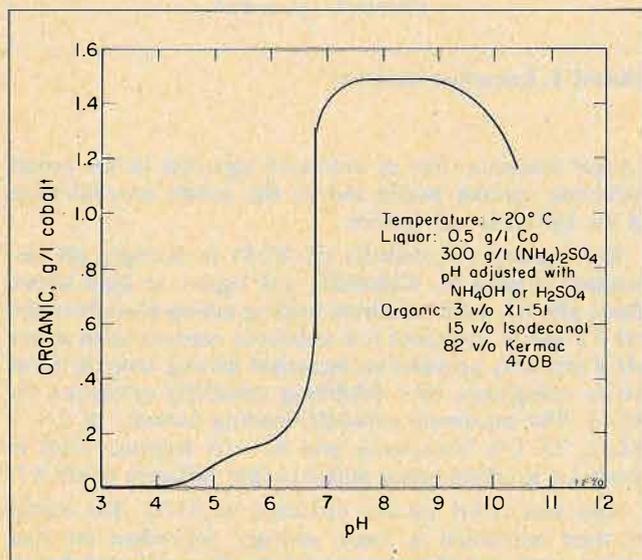


FIGURE 9. Cobalt(II) loading versus pH.

Cobalt Stripping

Essentially complete stripping of the pregnant 3 v/o XI-51 organic solution is achieved at an equilibrium pH below about 3.0. Three requirements in selecting cobalt and sulfuric acid strip solution concentrations are (1) cobalt electro-winning requirements, (2) efficiency of cobalt stripping, and (3) zinc removal from the cobalt electrolyte. The strip solution selected contained 77.3 g/l cobalt and 18.3 g/l sulfuric acid. The pregnant cobalt electrolyte contains about 80 g/l cobalt. If the resulting 10 g/l sulfuric acid in the pregnant cobalt electrolyte is too concentrated for efficient zinc extraction with di-(2-ethylhexyl) phosphoric acid, the acid level may be reduced.

The stripping isotherm shows that cobalt is easily stripped from the organic phase on one stage (Figure 11). This is accomplished even with a high cobalt concentration in the feed strip solution.

Continuous Operation

Results from the continuous cobalt solvent extraction system look encouraging (Table 1). The flow sheet for this system is shown in Figure 12. Treatment of feed liquor in an agitated cobalt reduction column (11 minutes' residence time), followed by one 180-ml mixer-settler stage, results in about 94 percent cobalt extraction. The raffinate contains only 0.02 g/l cobalt, while the pregnant organic contains 0.85 g/l cobalt and 0.77 g/l ammonia.

A two-stage water-ammonium sulfate wash circuit, using recycled wash solution, recovers about 73 percent of the ammonia from the pregnant organic phase. After a final pH-controlled wash (pH ~ 5.5), the pregnant organic phase ammonia level is reduced to about 0.013 g/l. This results in about 98 percent overall ammonia removal from the pregnant organic phase. At pH 5.5 about 0.03 g/l cobalt is stripped in this wash stage.

The pregnant organic phase is then stripped in one stage with a solution containing 77.3 g/l cobalt and 18.1

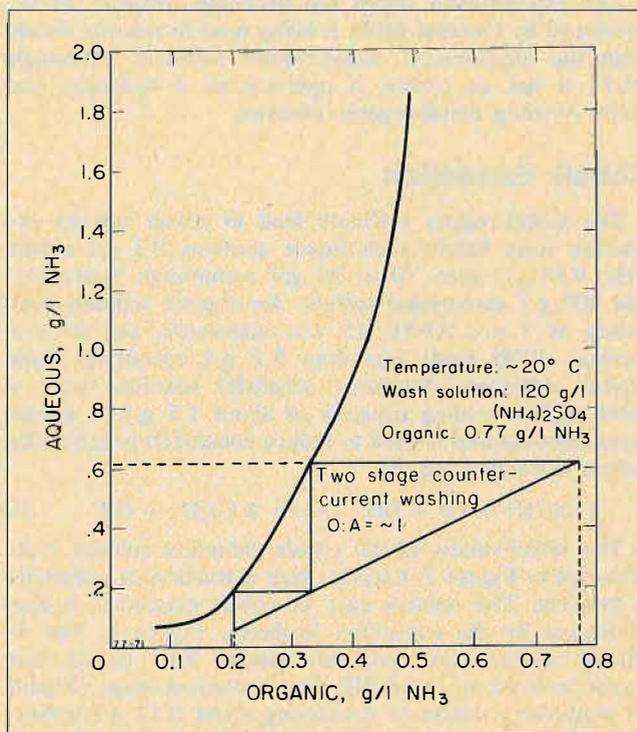


FIGURE 10. Washing curve.

TABLE 1. Continuous Cobalt Solvent Extraction System

Solution	Co	NH ₃	Grams per liter			ml/min	Flows O:A	O:A overall
			NH ₄ OH	(NH ₄) ₂ SO ₄	H ₂ SO ₄			
Ni-Cu raffinate	0.24	—	10.0	302	—	47.4 } 0.43	1.04	
Column effluent	0.36	—	9.8	296	—			
Raffinate	0.02	—	9.0	298	—			
Pregnant organic	0.85	0.77	—	—	20.5			
Wash water feed	0.006	—	0.1	118	—	18.8 } 1.1	1.1	
Wash water exit	0.005	—	1.3	118	—			
Water washed organic	0.86	0.206	—	—	20.5			
pH washed feed	0.03	—	—	113	0.05	18.8 } 1.1	1.1	
pH wash exit	0.06	—	—	106	0.04			
pH washed organic	0.83	0.013	—	—	20.5			
Strip feed	77.3	—	—	0.1	18.1	4.0 } 5.125	1.6	
Strip exit	81.3	—	—	0.5 ¹	10.9			
Stripped organic	0.05	0.0	—	—	20.5			

¹ Includes transfer of residual NH₃-NH₄⁺ loaded on the organic and (NH₄)₂SO₄ transfer through aqueous entrainment (~260 ppm) from the pH-controlled wash stage.

g/l sulfuric acid. This results in a pregnant strip solution containing about 81.3 g/l cobalt and a stripped organic phase containing 0.05 g/l cobalt. The corresponding ammonia build-up in the strip solution from residual ammonia and ammonium ion loaded on the organic phase is about 0.066 g/l. The balance of the ammonium sulfate generation in the strip solution is through aqueous entrainment (~260 ppm) in the organic phase from the pH-controlled wash stage. Continued work will concentrate on reducing the transfer and generation of ammonium sulfate in the stripping solution.

Conclusions

Solvent extraction is successfully utilized to (1) co-extract 99 percent of the nickel and 97 percent of the copper from batch laterite leach liquors (1.00 g/l nickel, 0.05 g/l copper, 0.30 g/l cobalt, 0.02 g/l zinc, 17.8 g/l ammonium hydroxide, 294 g/l ammonium sulfate) with LIX 64N, (2) prepare cell-grade nickel and copper electrolytes by selectively stripping and concentrating nickel and copper from loaded LIX 64N with the spent electrolytes, (3) extract 94 percent of the cobalt from the nickel and copper barren raffinate with a 3 v/o XI-51 organic solution, and (4) prepare cell-grade cobalt electrolyte by stripping cobalt-loaded XI-51 with spent electrolyte.

NOTATION LIST

- g/l Grams per liter
- v/o volume-percent
- O:A Ratio of organic flow to aqueous flow
- Kermac 470B A kerosine produced by Kerr-McGee Corp. containing 10 to 15 percent aromatic fraction. Formerly designated as Napoleum 470B.
- org organic phase

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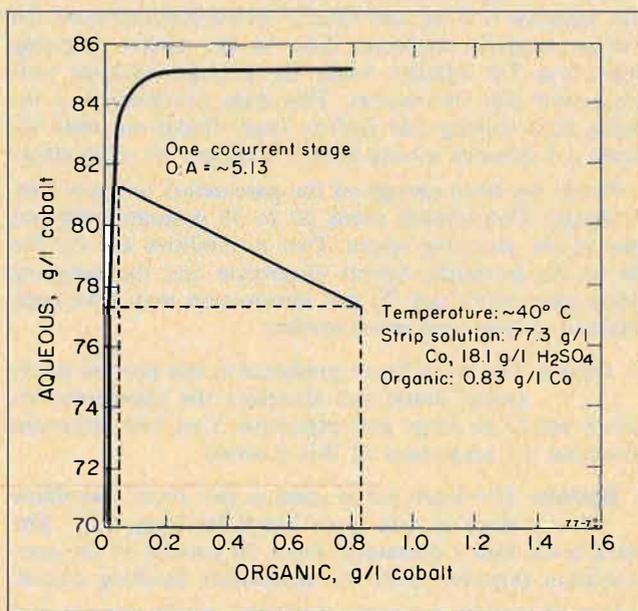


FIGURE 11. Stripping isotherm.

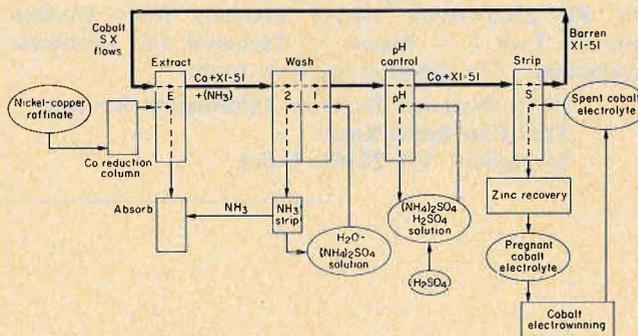


FIGURE 12. Cobalt solvent extraction system.

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DISCUSSION

S. Andersson: 1. What is the pH of incoming and outgoing nickel electrolyte and what is the residence time in the stripping stages?

2. In view of your answer, I would like you to comment on the results reported by Kennecott Corporation that residence times of 20-30 minutes are needed in their ammonia-ammonium carbonate system.

S. Rhoads: Depending on electrowinning and solvent extraction operating conditions, the incoming (spent) nickel electrolyte pH is 1.3 to 1.8, and the outgoing nickel electrolyte pH is 2.2 to 2.6.

Due to stage operating conditions, fixed mixer-settler size, aqueous recycle, and extract nickel concentration the average organic residence time in the nickel stripping stages was 7.6 minutes while the average aqueous residence time was 34 minutes. This stage residence time includes both mixing and settling time. Shake out tests indicate 3.5 minutes mixing time is adequate for each stage.

We do not have enough of the parameters to know why Kennecott Corporation needs 20 to 30 minutes residence time in the stripping stages. Two possibilities are (1) the pH of the incoming (spent) electrolyte and the outgoing nickel electrolyte, and (2) this information may have been obtained in oversized mixer-settlers.

A. Oliver: The leach liquor produced in this process seems rather dilute and therefore the equipment required would be large and expensive. Can you comment please on the economics of this process?

S. Rhoads: The leach liquor used in this study was dilute since it was from batch leaching tests. The batch leach liquor contained about 50 percent of the concentration expected from the continuous leaching circuit.

A technical and economic evaluation of the process was done by Singmaster and Breyer within the last two years. Since this evaluation, process improvements have been made that enhance the process and the economics. This evaluation is titled: Report No. USBM OFR 65-76, NTIS No. PB 256574/AS "Nickel Recovery from Western Sources. Task 1 — Report — Technical and Economic Evaluation". The report is available from:

NTIS (National Technical Information Service)
5285 Port Royal Road,
Springfield, VA 22161, U.S.A.

The printed paperback edition is \$5.50 and on microfilm it is \$2.25.

B. Lucas: After reducing the cobaltic to cobaltous, do you maintain a neutral atmosphere or non-oxygen atmosphere in the extraction of the cobaltous by SX?

S. Rhoads: An argon atmosphere is maintained during reduction of cobalt III to cobalt II. The solution containing the cobalt II remains in an argon atmosphere until it enters the extraction mixer. On a larger scale nitrogen will probably replace argon for the neutral atmosphere.

D. Flett: I suppose the \$64,000 question is what is XI 51 but I suppose we must ask General Mills that question. I don't believe you said anything about the problem of organic entrainment in the nickel and cobalt electrolytes and perhaps you might comment on this with regard to your zinc problem. Zinc SX with D2EHPA is well known and in particular Davy Powergas in collaboration with Technicas Reunidas in Spain have just developed an SX-EW process for zinc recovery from pyrite.

S. Rhoads: We have an agreement with General Mills not to analyze XI-51. However, we can disclose that it forms metal-organic chelates and operates on a hydrogen ion cycle.

Organic entrainment in the nickel and cobalt electrolytes has been controlled by (1) operating the mixer organic continuous for the stage that electrolytes are discharged from, and (2) use of polypropylene coalescers for the electrolytes. The extractant from the coalescers is treated with diatomaceous earth before being returned to the circuit. We plan to obtain more definitive entrainment information from the larger process development unit mixer-settlers that will process about one gallon per minute of leach solution.

V.B. Sefton: For a commercial plant, the author noted that the NH_3 will be stripped from the pregnant liquor by boiling. Experience at Sherritt indicates that during boiling, a portion of the cobalt will be reduced to Co^{++} by thiosulphates; the Co^{++} would subsequently be absorbed irreversibly by the LIX64N. In the author's pilot plant, was the NH_3 stripped by boiling?

S. C. Rhoads: NH_3 was adjusted by acid addition and not by boiling.

Panel Discussion

Introduction

Y. Sefton, V. Lakshmanan: DURING THE PAST FEW YEARS we have witnessed a large portion of our efforts being directed to the recovery of elements, mainly copper, using solvent extraction technique. However, the current market situations and future requirements suggest the needs for increased efforts to recover elements such as molybdenum, vanadium and zirconium. These are relatively more expensive but their demand for the next few years looks promising.

We have here assembled a group of panelists with considerable experience in the field of solvent extraction. They are A. W. Ashbrook, Eldorado Nuclear Limited, Canada, V. I. Lakshmanan, Eldorado Nuclear Limited, Canada, D. R. Spink, University of Waterloo, Canada, G. H. Beyer, Virginia Polytech, U.S.A., H. Ottertun, Mx Processor, Sweden, G. M. Ritcey, CANMET, Canada, and D. S. Flett, Warren Springs, U.K. Ashbrook will speak on organic extractants, Lakshmanan on molybdenum, Spink on zirconium, Beyer on zirconium, Ottertun on vanadium, Ritcey on current processes and Flett on future developments. This will be followed by a general discussion on these topics.

Panelists' Presentations

Organic Reagents

A.W. Ashbrook: Having had little time to think about what to say, this dissertation will be rather brief. In looking at the current and future situations with respect to extractants in the solvent extraction field, perhaps I can best review these in terms of extractant types.

First, the acidic extractants. We have seen during the sixties considerable activity with carboxylic acids, but the initial promise of these extractants has never been fulfilled to the extent predicted. Thus to-day, while some activity still persists, the properties associated with this class, solubility especially, has precluded use in the large industrial operations. As a result, I can see only limited use in the future for the carboxylic acid extractant.

The other major acidic extractant type, phosphoric acid ester, has been examined exhaustively for some 25 years. The amount of data on this type, especially D2EHPA, is now overwhelming. But out of this emerges, I suggest, the fact that D2EHPA is probably still the most versatile extractant available. While it is not the specific reagent that the hydroxyoxime-type is, nevertheless, I think that it still can provide a versatility which has not yet been fully exploited.

Turning now to the ion-association type of extractant, we see that the tertiary amine of the early days of solvent extraction is still with us in the uranium processing field. I would venture to predict that the tertiary amine will be with us for a long time to come. Other amines, the primary and secondary types, have come and gone, which leads me to think that interest and study of these extractants will continue in an up-and-down manner. The quaternary amines show particular promise in the base-metals metallurgical field, but again in specific instances. Generally,

I see little change in the next half decade in the use of amine extractants.

In the solvating extractant class, the use of TBP has been consistent over the last two decades or so, especially in the nuclear field and I can see no reason why this should change. Alcohols and esters have been looked at as commercial extractants and have found application in some areas. I do not see any substantial increase in the use of such extractants over the next decade.

The application of crown ethers to light metals extraction shows promise, but I don't see any major applications here before ISEC 80.

Finally, a few words about the chelating extractants. As I said in my opening remarks at this conference, I feel we have been having a love affair with the hydroxyoxime extractants. Another way of looking at this situation in the last decade is as a variation on a theme. There has been, to my way of thinking, far too much effort devoted to this copper-specific reagent, to the point where I wonder whether some of us have not lost sight of the objective of the solvent extraction process.

It seems to me that in the love affair with oximes, another reagent, oxine, has been forgotten. When one looks at the analytical literature one finds little about oximes — especially monohydroxy oximes — but a considerable amount on oxine and its derivatives. I suggest that consideration of the available data on oxines will provide new applications of this extractant type, and that more study in this area will be rewarding.

In general, there has, I believe, been too much emphasis placed on metal-specific (that is copper-specific) extractants, and not enough on the non-specific extractants. I suggest to you that reagents such as D2EHPA — the non-specific type — have a versatility which, in many situations, is more promising for the future than are the specific chelating extractants.

Inorganic Processes

Molybdenum

V.I. Lakshmanan: Molybdenum, like tungsten, can form a large number of isopoly and heteropoly complexes. Vanadium is the only other element showing a somewhat similar behaviour. Hence, extraction and separation of molybdenum from various accompanying valuable and gangue materials will depend upon the type of leaching procedures chosen initially.

If the pH of the leach solution is around 10, molybdate ion will be present. Formation of polyanions will commence as the pH is lowered. Paramolybdates may be predominant at pH 6, tetramolybdate at about pH 3 and octamolybdate at about pH 1. Generally, it has been known that a series of polymolybdate anions predominate above pH of ca 2 and cationic species predominate below pH of ca 2. Molybdic acid or cationic molybdenum chloro or sulphate complexes may be present as the pH is lowered further. Hence, any extraction study planned, should primarily seek for a detailed knowledge on the aqueous conditions including pH, nature of anions and their concentrations, molybdenum concentrations, and the nature of the impurities present.

When molybdenum is present as an anion in molybdate, isopoly-molybdate or heteropolymolybdate, extractants such as amines, alcohols, esters and ketones can be potentially good extractants. Alcohols, esters and ketones solvate the protons accompanying various forms of molybdic acids.

When amine extraction systems are considered from acidic solutions, amine salts act as extractants. However, with quarternary ammonium salts, extraction from acidic, neutral and slightly alkaline media can be considered. In general, molybdenum from the aqueous solutions can be extracted by either anion exchange mechanism or compound formation. This depends on the nature of molybdenum species present in the aqueous phase which in turn depends on the pH of the aqueous phase. When extraction from aqueous solutions at $\text{pH} \geq 2$ is considered, the extraction is basically an anion exchange process. However, from highly acidic solutions, molybdenum can be extracted by compound formation.

Cationic extractants, including chelating and acidic extractants, can be used when molybdenum exists in the aqueous phase as a cation, such as in MoO_2^{2+} ion. Oximes, oxines, alkyl phosphoric acid have been used at various times. Kennecott and Union Carbide have studied molybdenum extraction with amines and Molycorporation has studied the extraction using tertiary amine and alkyl phosphoric acid.

My final note is that solvent extraction as a purification method deserves more attention in molybdenum extraction, particularly due to the increased mining activities and demand for molybdenum.

Zirconium and Hafnium Separation

D.R. Spink: Very little research has been conducted in this area over the past 20 years due to poor markets, so there is not much news to report. The separation of hafnium from zirconium is still the most difficult separation of elements in the periodic table, and solvent extraction is still the only industrially acceptable method employed.

Two systems have been fully developed and employed on an industrial scale: (1) TBP extraction of zirconyl nitrate from a mixed zirconyl-hafnyl nitrate solution; (2) MIBK extraction of the hafnium thiocyanate complex from a mixture of Zn and Hf thiocyanate complexes. While both processes are capable of producing specification-grade zirconium, only the MIBK process is capable of producing "pure" hafnium.

SX research to develop better Hf-Zn separation processes is being conducted in Russia and in the U.S. separation of Hf from Zn via SX does introduce a number of problems such as: (a) cost, both capital and operating, (b) pollution (both air and water) (c) the final products (oxides) must be chlorinated for further processing.

As a consequence, most current research on zirconium-hafnium separation is directed to methods which do not involve aqueous chemistry, but rather separate the tetrachlorides. Methods currently being investigated are:

- (1) Eutectic fused salt distillation employing the system $\text{ZrCl}_4\text{-HfCl}_4\text{-NaCl-KCl}$,
- (2) Relative stabilities of complex fused salts such as KrZnCl_6 vs KrHfCl_6 , and
- (3) The selective reduction of one tetrachloride in the presence of the other.

Other approaches are probably being studied and it is predicted that one such method will be successfully de-

veloped and employed commercially within the next ten years.

Zirconium

G.H. Beyer Zirconium is one of my favorite elements and I am always eager to talk about it . . .

Zirconium is obtained from zircon sand which is found on beaches in Australia and elsewhere. The sand is a zirconium silicate, ZrSiO_4 , containing approximately 25,000 ppm of hafnium silicate and only small amounts of iron, titanium, etc.

The usefulness of zirconium for the cladding of nuclear fuel elements requires the removal of hafnium to very low levels (less than 100 ppm) because of hafnium's high neutron absorption cross section. Purification is accomplished by fractional solvent extraction which provides an overall separation factor of 250 to 500 with less than 10 theoretical stages.

The sand may be opened up by reaction with caustic soda. Aqueous treatment of the resulting "frit" forms insoluble zirconium hydroxide and soluble sodium silicate. The removal of silicate can be critical to the success of the subsequent solvent extraction step.

Tributyl phosphate diluted with kerosine is an effective solvent, preferential for zirconium and rejecting hafnium. But the presence of substantial amounts of silica can seriously inhibit the clean separation of organic and aqueous phases.

The point to be made is that feed preparation is inexorably coupled to the choice of solvent extraction equipment. The intensity of mixing must be carefully matched to providing adequate time for separation of phases and removal of interfacial "crud" which always seem to develop in industrial-scale operation. Provision for cleaning up interfacial accumulation and restoring solvent quality are essential to continuous operation.

Vanadium

H. Ottertun: A short review of our experiences in solvent extraction of vanadium is given. We are working in this field in connection with two different vanadium projects concerned with recovery of vanadium from a uranium ore and soot waste residues from power stations based on fossil fuels.

In the first project investigations have been made in conjunction with two different ore processing schemes. In one of these the ore is leached directly in a conventional way with a moderately acid sulfate solution. Uranium is then extracted with an amine. The possibility of extraction of vanadium from the uranium-barren raffinate has been investigated. The liquor contains only 0.3 g/l vanadium and large amounts of iron and aluminium (15 and 10 g/l respectively). Vanadium is fourvalent and iron is divalent to more than 90%. Because of the large amount of divalent iron, vanadium must be extracted as tetravalent (oxidation economically prohibitive). Selective extraction of vanadium with di-(2-ethylhexyl)phosphoric based on differences in kinetics between vanadium, iron and aluminium has been tried. However, due to the high feed temperature (50°C), determined by the uranium processing, the mass transfer rate for iron and aluminium turned out to be so high that vanadium was crowded out after a contact time of the order of one minute.

In the other processing scheme, being in the early development stage, the ore is roasted or pyrolyzed prior to a strong sulphuric acid leach. In this case oxidation of vanadium to its pentavalent state is easily accomplished (low

iron content). However, problems with oxidative attacks on organic components have arisen when using amines or organophosphorus compounds for extraction of vanadium. This is due to the high oxidation potential of the feed liquor under the prevailing high acidity (2 to 6 M free sulphuric acid). Efforts are now being made to study this problem more closely.

In our second vanadium project concerned with soot residues di-(2-ethylhexyl) phosphoric acid has been successfully used for the extraction of vanadium(IV). In this case the vanadium concentration in the leach liquor is high, 25 g/l and the iron concentration is moderate (about 3 g/l). The temperature is optional and will be selected in the interval 25 to 40°C. The vanadium is partially extracted (~ 80%) at a comparatively high acidity (pH ~ 1) and a high organic loading (5 to 6 g/l). Under these circumstances the coextraction of iron is low.

Summary of Inorganic Processing

G.M. Ritcey The growth of solvent extraction processing, although slow to begin, has been increasing in popularity and use particularly during the past ten years. The first solvent extraction plant commenced operation in 1942 for the recovery and purification of uranium from nitric acid solutions using ether as the extractant. This refinery was followed by two others, and then during the 1950's by additional uranium refineries using tributyl phosphate (TBP). Solvent extraction and ion exchange were also used to replace non-selective precipitation techniques for uranium recovery from solutions resulting from sulphuric acid leaching of uranium-bearing ores. The first such solvent extraction plant was installed in 1956, and by the end of 1960 a total of 20 similar plants were established throughout the world. During the period 1960-1970 came the uranium reprocessing plants, and in addition, the use of solvent extraction for the recovery of base metals. This growth of solvent extraction is depicted in Figure 1 indicating, by extrapolation, possibly more than 200 plants by 1980. There are now many applications of solvent extraction in plants throughout the world that are presently using this technique to recover such metals as uranium, thorium, lanthanides, copper, nickel, cobalt, zirconium, hafnium, platinum metals, molybdenum, tungsten, niobium, tantalum, beryllium, boron, and possibly some of the rarer metals not shown here.

But more applied research is required if solvent extraction technology is going to advance at an equal or greater pace.

Regarding plant design, many changes have occurred over the 30-year period, with a multitude of contactor designs of the stage-wise and differential types now available. More attention is now being paid to the optimization of the process and to contactor selection to suit particular applications. We require now more understanding of how to best utilize these various contactors in order to optimize the economics.

Materials of construction have improved over the period, particularly in the past decade, so that now we are not forced to use the sulphuric acid system that has been the predominant route. Nitric acid, because of its environmental problems, is not a desirable dissolving medium but hydrochloric acid offers much potential. With the refractories, fiberglass reinforced plastics and other materials, it would appear that more effort should be devoted towards the design of flowsheets incorporating hydrochloric acid. In a solvent extraction process for treating such a solution, improved kinetics and metals selectivity are usually achieved. Such results from the

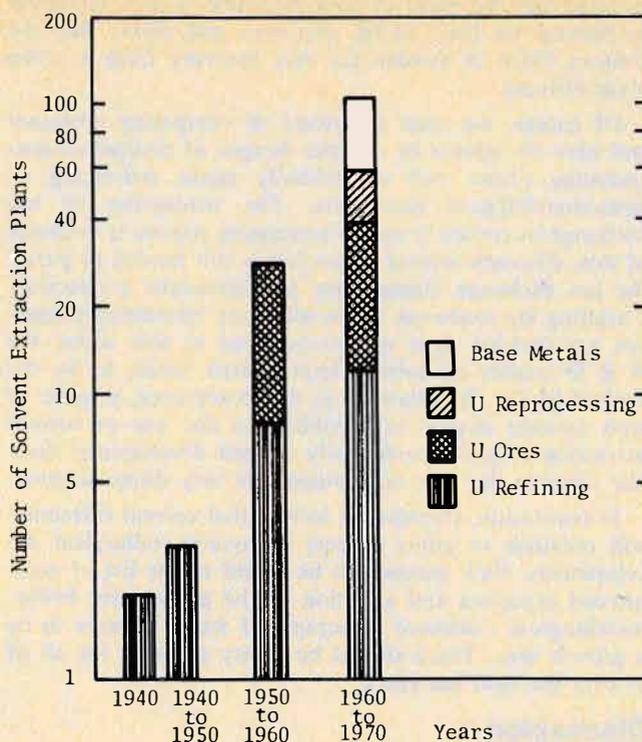


FIGURE 1. Growth of solvent extraction processing.

chloride system should improve the economics when compared to the sulphate system, as well as being capable of providing a more environmentally-acceptable effluent.

Regarding the effluent disposal, the regulatory agencies are becoming more strict, and thus more attention has to be paid to clean-up of any solution prior to discharge from the plant. Solvent extraction has been proposed, but it would seem more likely that ion-exchange, particularly continuous ion-exchange, is more suited to the bulk removal of contaminants at a lower cost than solvent extraction. The effluents may also have to be treated for the removal of toxic organics prior to disposal.

Hydrometallurgy

D.S. Flett With regard to the future of solvent extraction in hydrometallurgy, I believe that solvent extraction is now an accepted process and that we have come of age. Research and development seem to be at a plateau stage and this is particularly true with regard to kinetic investigation. However, a major advance here could lead to a radical rethink of contactor design. While there is little doubt that the continuing low price of copper is materially affecting the development rate of further plants in this sector, the growth areas seem to me to be uranium (and here particular mention of uranium from phosphoric acid liquors should be made), manganese nodules, and platinum group metals (for example, see Dr. Edwards paper at this conference). Zinc too is coming to the fore and here the Espindesa Process can be cited (joint development between Davy Powergas and Technis Reunidas in Spain) and the work that Anaconda and General Mills have done with LIX 34. However, it seems to me that significant applications are likely to come forward in the secondary processing field. Already processes such as recovery of copper from silver electrolyte at Brookside Metals, Watford, U.K. and the Proteus Reclamation plant for treatment of spent copper in Manchester, U.K. serve

to underline this trend as does the work of MX Processor in Sweden on their MAR processes and plants like the Valberg Plant in Sweden for zinc recovery from a rayon plant effluent.

Of course, we must be aware of competing processes and here the advent of realistic designs of continuous-ion-exchange plants will undoubtedly cause rethinking of hydrometallurgical flowsheets. The readoption of ion exchange in certain uranium processing sectors is evidence of this, although solvent extraction is still needed to purify the ion exchange eluate prior to yellowcake production. Chelating ion exchange resins with very interesting properties are making their appearance and in this sector the R & D studies on solvent impregnated resins, to be described by Dr. Warshawsky in this conference, provide us with another degree of flexibility in our use of solvent extraction reagents, particularly as their development looks like opening the way to treatment of very dilute solution.

In conclusion, therefore, I believe that solvent extraction will continue to enjoy success in hydrometallurgical developments. New metals will be added to the list of commercial processes and adoption of the process for hydrometallurgical treatment of scrap and waste appears to be a growth area. There should be plenty of work for all of us over the next ten years.

Discussion

V.I. Lakshmanan, V. Sefton: The contribution from the panel speakers, besides the extraction of molybdenum, zirconium and vanadium specifically, covered topics such as selectivity, universal extractant (D2EHPA?), cost, pollution, agitation, crud formation, contactors and recovery from secondary sources, etc. These are all valuable points to consider while choosing a process. The session is now open for discussion.

P.J. Lloyd: I do not believe it is worthwhile paying too much attention to selectivity determined in a batch manner. We successfully ran a Zr/Hf process in sulphate solution using amines where the batch selectivity

(Zr/Hf) was only 1.5, but a carefully controlled 6-stage extraction and scrub section gave over 95% Zr recovery at less than 1 ppm. Hf. Of course, you need "well behaved" equilibrium curves to avoid pinch regions, but some "badly behaved" systems can be modified slightly to overcome this (e.g. local pH modification in S shaped equilibrium regions).

H. Reinhardt: Mr. Chairman, I would like to make a comment on the selectivity of reagents: di(2-ethylhexyl) phosphoric acid (D2EHPA) is today a commonly used extractant for zinc. It is, however, not very selective so many people are therefore looking for a more selective reagent. I am afraid that they will never find such a reagent, especially if they compare their efforts with the selectivity of the copper reagents.

The practical selectivity of a reagent is a function of the demand for purity in the product solution. In the case of electrolytic production of zinc, a few ppm of impurity metals such as nickel and copper will spoil the electrolytic procedure. This means that the selectivity for zinc over other metals in the extraction has to be very good. Reagents with sufficient selectivity may therefore never be found.

S. Andersson: The different views put forward here on the possibility to separate metals with a given reagent must depend on different reference points. Certainly a difference in selectivity for the metals will make it possible to obtain almost any degree of separation, given the necessary conditions and required number of stages.

However, from the practical or economical point of view, this may not be feasible. Undoubtedly there is some room for further development also for the well known reagents by using crowding techniques, scrubbing of extract and selective stripping, which all may improve our present processes.

C. Bozec: Concerning D2EHPA, we have noted difficulties due to significant fixation of Ca, Mg in the organic phase which then causes precipitation and scaling with CaSO₄ in the strip circuit.

Role of the Liquid-Liquid Partition of the Extractable Chelates in the Solvent Extraction of Divalent Transition Metal Ions with β -Diketones

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ABSTRACT

The solvent extraction data of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with five β -diketones (HA) in carbon tetrachloride-aqueous perchlorate systems showed that the two-phase partition constants of the bis-chelates ($K_{dm} = [MA_2]_{org}[MA_2]^{-1}$) were quite different when the metal ion was different. Among these MA_2 chelates, the CuA_2 chelates gave the highest K_{dm} and the NiA_2 chelates the lowest. This was explained in terms that the latter interacted with water molecules most strongly and the former most weakly. The relation of the K_{dm} and other equilibrium constants was discussed and the role of this equilibrium in the over-all extraction equilibria was considered.

Introduction

IN THE COURSE OF A SYSTEMATIC STUDY on the solvent extraction of several divalent metal ions with β -diketones, it was found that the two-phase partition behavior of the extractable chelates was rather complicated. In the present paper, these experimental data were compiled and the equilibrium constants were compared. Then a discussion was made about the role of the liquid-liquid partition of the extractable chelate in the over-all solvent extraction equilibria of the metal ions.

Experimental

The details of the experimental procedures have been given in other papers from our laboratory⁽¹⁻⁵⁾. All the experiments were carried out in a thermostated room at 25°C. The organic phase was carbon tetrachloride, initially containing a certain amount of a β -diketone, and none or a certain amount of trioctylphosphine oxide (TOPO). The aqueous phase was 1 mol dm⁻³ sodium perchlorate solution, initially containing the metal ion (10⁻⁶ to 10⁻³ mol dm⁻³). It was usually buffered well by the extractant distributed from the organic phase but when a buffer was necessary, a small amount of sulfanilate or acetate was added. The same volume of the two phases were placed in a stoppered glass tube, agitated mechanically until the equilibrium was established, and centrifuged. The metal content in the two phases was measured by radiometry or by an atomic absorption method. The hydrogen-ion concentration was determined by potentiometry using a standard solution containing 0.99 mol dm⁻³ of sodium perchlorate and 1.00 × 10⁻² mol dm⁻³ of perchloric acid as the standard of -log [H⁺] = 2.00; thus it was in the stoichiometric units.

Statistical

In this paper, the subscript "org" and the lack of subscript denotes chemical species in the organic and aqueous phase, respectively.

The acid dissociation and two-phase partition constants of a β -diketone which is a weak acid, HA, is written as;

$$K_a = [H^+] [A^-] [HA]^{-1} \dots \dots \dots (1)$$

$$K_d = [HA]_{org}[HA]^{-1} \dots \dots \dots (2)$$

The distribution ratio of a divalent metal ion, M²⁺, in the presence of HA can be written as;

$$D = [M(II)]_{org}[M(II)]^{-1} \dots \dots \dots (3)$$

$$= [MA_2]_{org}([M^{2+}] + [MA^+] + [MA_2] + \dots)^{-1} \\ = K_{dm}\beta_2[A^-]^2 (1 + \beta_1[A^-] + \beta_2[A^-]^2 + \dots)^{-1} \dots (4)$$

where the equilibrium constants are;

$$\beta_n = [M(A_n)^{2-n}] [M^{2+}]^{-1}[A^-]^{-n} \dots \dots \dots (5)$$

$$K_{dm} = [MA_2]_{org}[MA_2]^{-1} \dots \dots \dots (6)$$

When HA is in a large excess to the metal ion and the volumes of the two phases are the same, the concentration of the β -diketonate ion in the aqueous phase, [A⁻], can be obtained from Eqs. 1 and 2 as;

$$[HA]_{org, initial} = [A^-] + [HA] + [HA]_{org} \\ = [A^-] \{1 + (1 + K_d)K_a^{-1}[H^+]\} \dots \dots \dots (7)$$

When an adduct-forming organophilic ligand, L, is added to the system, the distribution ratio may be enhanced (synergism) and the following equation is written for the distribution ratio;

$$D = ([MA_2]_{org} + [MA_2L]_{org} + [MA_2L_2]_{org} + \dots) ([M^{2+}] + [MA^+] + [MA_2] + \dots)^{-1} (8)$$

By introducing the adduct formation constants,

$$\beta_{n(org)} = [MA_2L_n]_{org}[MA_2]_{org}^{-1}[L]_{org}^{-n} \dots \dots \dots (9)$$

and the value of distribution ratio in the absence of L, but otherwise under the identical conditions, D₀, into Eq. 8, the following equations are obtained;

$$D = K_{dm}\beta_2[A^-]^2 (1 + \beta_{1(org)}[L]_{org} + \beta_{2(org)}[L]_{org}^2 + \dots) \\ \dots (1 + \beta_1[A^-] + \beta_2[A^-]^2 + \dots)^{-1} \dots \dots \dots (10)$$

$$DD_0^{-1} = 1 + \beta_{1(org)}[L]_{org} + \beta_{2(org)}[L]_{org}^2 + \dots \dots \dots (11)$$

The log D vs log [A⁻] plot in the absence of L has two asymptotes as is seen from Eq. 4 when higher chelates than MA₂ are negligible;

$$\log D ([A^-] \rightarrow \infty) = \log K_{dm} \dots \dots \dots (12)$$

$$\log D ([A^-] \rightarrow 0) = \log K_{dm2} + 2\log [A^-] \dots \dots \dots (13)$$

and by a curve-fitting method with the following family of standard curves;

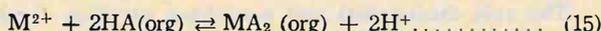
$$Y = \log(1 + pv + v^2); \quad X = \log v \dots \dots \dots (14)$$

the constants, β_1 , β_2 , and K_{dm} may be determined^(6,7).

By a similar procedure, the adduct formation constants may be determined from the $\log DD_0^{-1}$ vs $\log [L]_{org}$ plot obtained when $[A^-]$ is kept constant.

It is seen from Eqs. 10 and 11 that at a certain concentration of the adduct-forming ligand, L_1 , the distribution ratio is always higher by a factor of $1 + \beta_{1(org)}L_1 + \beta_{2(org)}L_1^2 + \dots$ than in the case of its absence. The values of the stability constants of the aqueous chelates and of $K_{dm}(1 + \beta_{1(org)}L_1 + \beta_{2(org)}L_1^2 + \dots)$ can be determined from the $\log D$ vs $\log [A^-]$ plot under such conditions, in the same way as above, and by using the values of the adduct formation constants obtained by separate experiments, the value of K_{dm} can be calculated. This provides a method for the determination of the constants, β_1 , β_2 , and K_{dm} when the distribution ratio is too low to determine accurately in the absence of L .

The extraction equilibrium of M^{2+} with HA can also be written as;



and the following extraction constant may be defined;

$$K_{ex} = [MA_2]_{org}[H^+]^2[M^{2+}]^{-1}[HA]_{org}^{-2} \dots \dots \dots (16)$$

From Eqs. 1, 2, 5, and 6, this equation can be rewritten as;

$$K_{ex} = K_{dm}\beta_2K_a^2K_d^{-2} \dots \dots \dots (17)$$

In the region where the $\log D$ vs $-\log [H^+]$ plot at a certain $[HA]_{org}$ is a straight line of a slope +2, in other words, when the distribution ratio can be represented by $D = [MA_2]_{org}[M^{2+}]^{-1}$, the following equation can be obtained;

$$D = K_{ex}[HA]_{org}^2[H^+]^{-2} \dots \dots \dots (18)$$

and the ability of reagents to extract divalent metal ions can be compared by comparing the values of K_{ex} .

Data

Since the original data have been given in other reports⁽¹⁻⁵⁾ only the final results are compiled here. Figures 1 and 2 give the extraction curves of the metal ions with benzoylacetone and benzoyltrifluoroacetone. In these systems, the extraction curve of copper(II) was a straight line of slope +2. Thus, under the conditions where the distribution ratio could be measured by the experimental technique employed, none of the constants, β_1 , β_2 , and K_{dm} could be determined on the basis of Eq. 4. Figure 3 gives the calculated extraction curves with trifluoroacetylacetone. In this case, the distribution ratio of the metal ions except copper(II) was very low. Thus the distribution ratio as a function of $[A^-]$ was determined in the presence of a certain amount of TOPO. The values of β_1 , β_2 , and $K_{dm}(1 + \beta_{1(org)}L_1 + \beta_{2(org)}L_1^2)$ were determined from these data, and from the values of the adduct formation constants obtained by separate experiments, the value of K_{dm} was calculated. The curves in Figure 3 were the calculated ones by introducing the equilibrium constants into Eq. 4. Since the value of K_{dm} for the NiA_2 chelate in this system is not very accurate, its curve in Figure 3 is only a tentative one.

The extraction of metal ions with acetylacetone and hexafluoroacetylacetone was poor except for copper(II). In the system containing the former, the β_1 and β_2 for cobalt(II) and nickel(II) could not be determined due to poor extraction of them and in the system containing the latter, the values of β_2 and K_{dm} for the bis-chelates of manganese(II) and zinc(II) could not be determined because these complexes were not stable enough to allow such an analysis.

Table 1 lists the equilibrium constants and those of the reagents⁽⁸⁾. Figure 4 compares the partition and extraction

TABLE 1. Summary of Equilibrium Constants.

Aq. phase: 1 mol dm⁻³ NaClO₄. Org. phase: CCl₄.
Adduct forming ligand: trioctylphosphine oxide (TOPO).

Extractant	Metal ion	log K_{ex}	log β_1	log β_2	log K_{dm}	log $\beta_{1(org)}$	log $\beta_{2(org)}$
Acetylacetone log $K_a = -8.99$ log $K_d = 0.40$	Mn (II)	-11.8	4.09	6.98	-1.23	2.96	4.96
	Co (II)	—	—	—	-0.94	1.46	nil
	Ni (II)	—	—	—	-2.0 to -2.5	ca 2	nil
	Cu (II)	- 3.73	7.81	14.22	0.83	1.28	nil
	Zn (II)	-11.40	4.58	7.76	-0.38	3.07	4.66
Benzoylacetone log $K_a = -8.55$ log $K_d = 2.73$	Mn (II)	- 8.4	—	—	(>3)†	3.81	5.40
	Co (II)	-13.05	4.55	8.14	1.37	3.40	nil
	Ni (II)	-12.84	4.41	9.86	-0.14	3.50	nil
	Zn (II)	-11.36	4.15	7.70	3.50	3.76	nil
Trifluoro-acetylacetone log $K_a = -6.09$ log $K_d = -0.19$	Mn (II)	-10.28	0.94	2.96	-1.44	5.43	9.16
	Co (II)	- 8.34	3.50	5.60	-2.14	5.36	7.76
	Ni (II)	ca -9	3.74	6.68	-3.0 to -3.5	ca 5	ca 8
	Cu (II)	- 1.26	4.80	9.14	1.40	2.96	nil
	Zn (II)	- 8.76	2.72	4.48	-1.44	6.70	nil
Benzoyltri-fluoroacetone log $K_a = -6.01$ log $K_d = 2.47$	Mn (II)	-12.62	0.80	2.63	1.71	—	—
	Co (II)	- 9.66	3.40	5.24	2.06	6.15	9.34
	Ni (II)	- 9.52	3.60	6.68	0.76	5.19	8.98
	Zn (II)	- 9.02	3.23	5.49	2.45	6.71	nil
Hexafluoro-acetylacetone log $K_a = -4.34$ log $K_d = - 1.74$	Mn (II)	- 5.0	1.04	—	(>-1)†	(4.9)‡	(9.4)‡
	Co (II)	- 3.90	1.56	2.32	-1.02	5.19	10.58
	Ni (II)	- 4.0	1.78	3.26	-2.1	5.8	10.5
	Cu (II)	- 0.61	2.25	3.20	1.39	5.63	9.36
	Zn (II)	- 5.2	1.0	—	(<-1)†	7.0	11.6

†Since these values could not be determined, only the lower limit is assumed.

‡These values are for adducts with tributylphosphate. The values for the adducts with TOPO should be much higher than these.

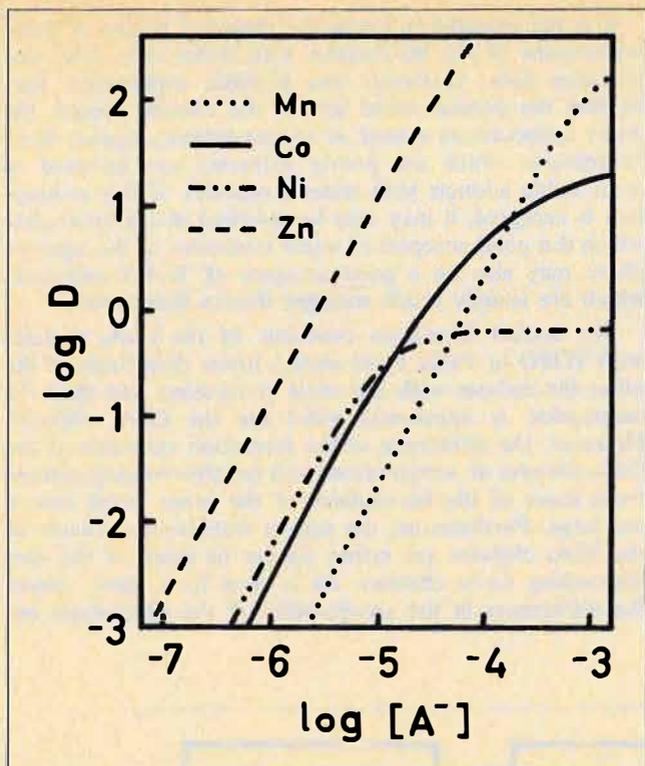


FIGURE 1. Extraction curves with benzoylacetone.

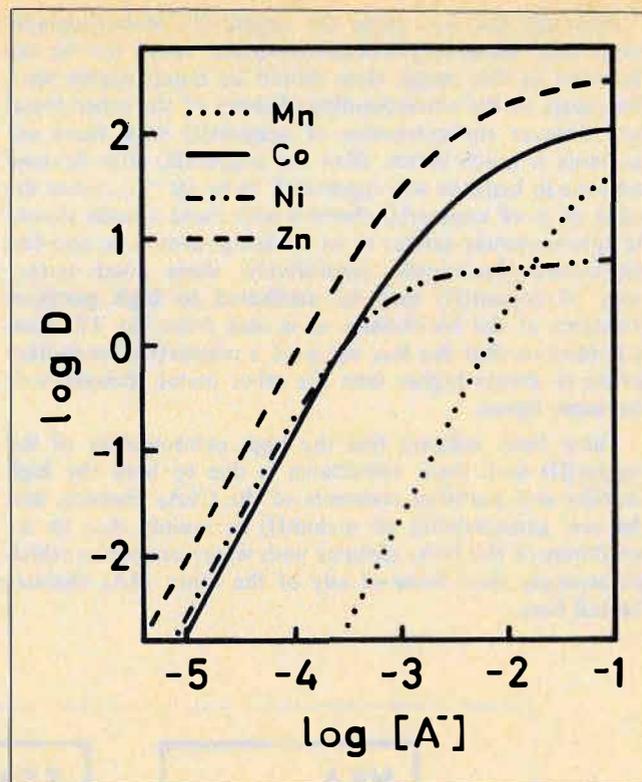


FIGURE 2. Extraction curves with benzoyltrifluoroacetone.

constants of the bis-chelates of the metal ions with each β -diketone while Figure 5 compares the partition constants of the bis-chelates of each metal ion.

Discussion

From the constants in Table 1, it is seen that the stability order of these metal chelates in aqueous solutions agrees with that usually found; Irving-Williams natural order is established among the metal complexes of the same ligand and the stability of complexes containing a certain metal ion but different ligand is higher when the pK_a of the ligand acid is higher.

The shapes of the extraction curves in Figures 1 to 3 are very complicated. The extraction curves are straight lines of a slope +2 only in the lower region of D . As is seen from Eqs. 4 and 12, the K_{am} gives the upper limit of the distribution ratio of the metal ion in that system and thus the poor extraction with trifluoroacetylacetone except copper(II) in Figure 3 is due to low partition constants of their bis-chelates. The relatively poor extraction of nickel(II) even at the maximum with the two extractants in Figures 1 and 2 is also due to the low partition constant of the NiA_2 chelates.

The partition behavior of the extractable chelates, MA_2 , between non-solvating solvents such as carbon tetrachloride and aqueous solutions containing no complex-forming ligand with them should be caused mainly by two factors in the aqueous phase, aquaphobic and aquaphilic characters. The former is dependent mainly on the volume of the molecule. However, since the number of the ligand in the bis-chelates is always two, the molar volume of the complexes with the same ligand should be rather similar and consequently, the aquaphobic tendencies of the bis-chelates should not differ very much. Thus the main reason for the great difference in the K_{am} values should be the difference in the aquaphilic tendencies; in other words, the interactions of the MA_2 chelates with water molecules.

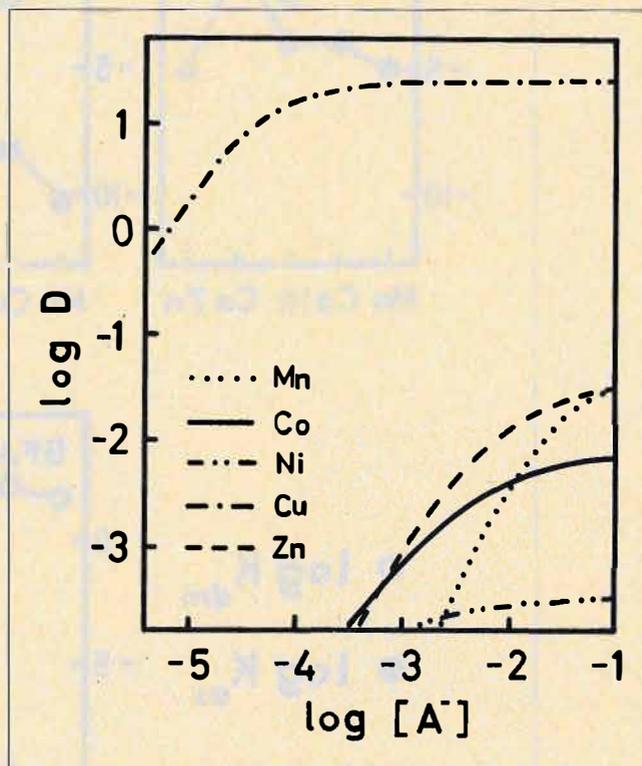


FIGURE 3. Extraction curves with trifluoroacetylacetone.

This type of rather weak solute-solvent interactions of uncharged metal complexes in aqueous solutions have not been discussed often. This is probably because an estimation of such interactions is not easy as long as the complexes are studied only in a single aqueous phase system.

Although the K_{dm} value for copper(II) bis-benzoylacetone and bis-benzoyltrifluoroacetone could not be determined in this study, they should be much higher than the values of the corresponding chelates of the other metal ions because the extraction of copper(II) with these extractants is much better, (K_{ex} for copper(II) with benzoylacetone in benzene was reported⁽⁹⁾ to be $10^{-4.17}$). Since the value of β_2 of copper(II) chelates with these ligands should be approximately similar to its bis-acetyl-acetonate and bis-trifluoroacetylacetone, respectively, these good extractions of copper(II) may be attributed to high partition constants of the bis-chelates as is seen from Eq. 17. Thus it is obvious that the K_{dm} value of a copper(II) bis- β -diketonate is always higher than the other metal chelates with the same ligand.

These facts indicate that the high extractability of the copper(II) with these extractants is due to both the high stability and partition constants of the CuA_2 chelates, and the low extractability of nickel(II) is mainly due to interactions of the NiA_2 chelates with water molecules which are stronger than those of any of the other MA_2 chelates treated here.

It is not possible to know the chemical nature of these interactions of the bis-chelates with water only from distribution data. However, one possible explanation may be that the central metal ion in the chelate accepts the water molecules as a kind of adduct-forming ligand; those bis-chelates which are poorly extracted are assumed to form stable adducts with water molecules. If this assumption is accepted, it may also be assumed that a bis-chelate which is a good acceptor of water molecules in the aqueous phase may also be a good acceptor of TOPO molecules which are usually much stronger donors than water.

The adduct formation constants of the CuA_2 chelates with TOPO in Table 1 are always lower than those of the other bis-chelates with the same β -diketonate and thus the assumption is apparently valid for the CuA_2 chelates. However, the difference of the formation constants of the CuA_2 chelates of acetylacetone and hexafluoroacetylacetone from those of the bis-chelates of the other metal ions is not large. Furthermore, the adduct formation constants of the NiA_2 chelates are rather similar to those of the corresponding CoA_2 chelates. As is seen from these values, the differences in the acceptability of the bis-chelates ob-

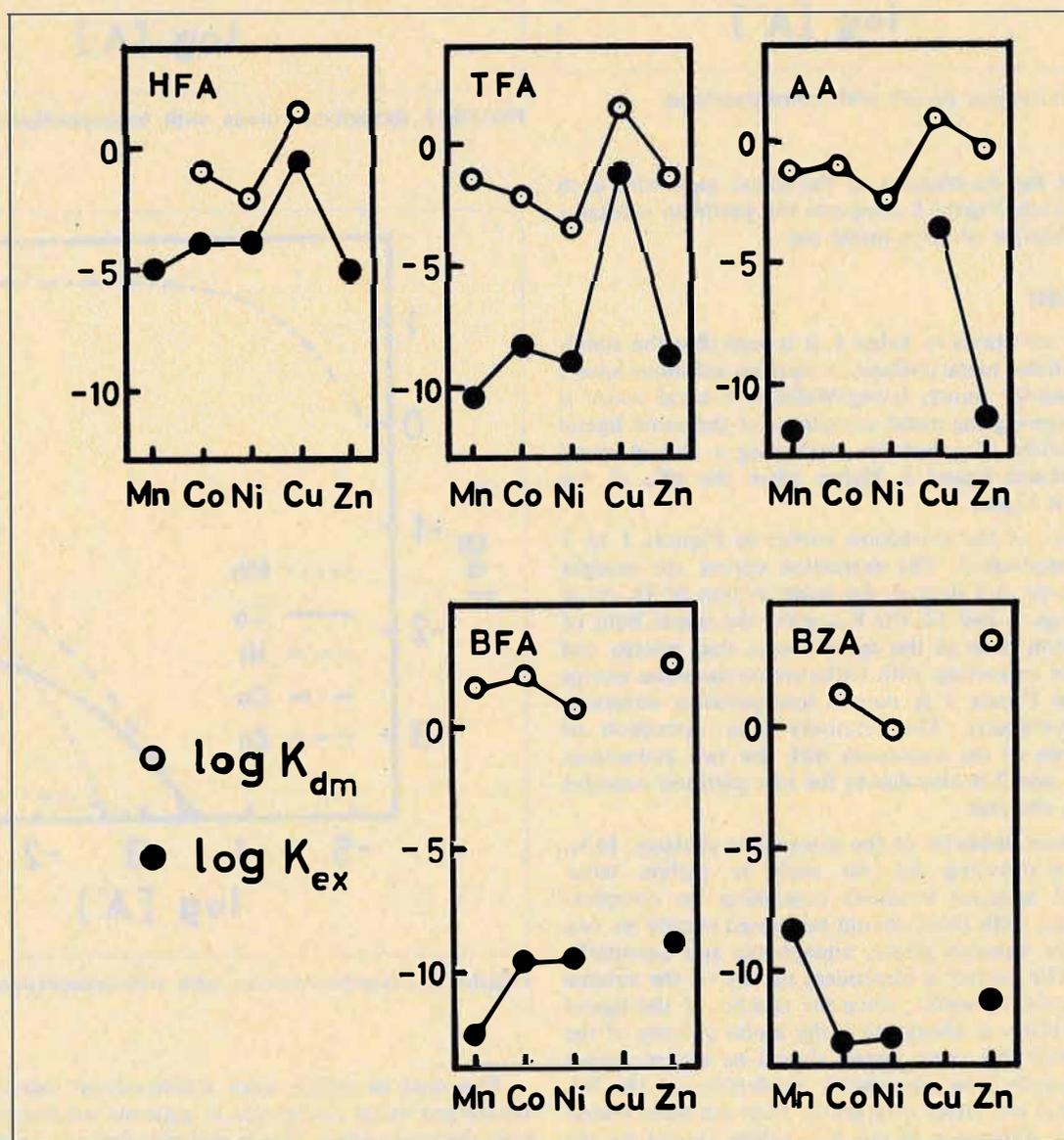


FIGURE 4. Comparison of two-phase partition constant of MA_2 chelate, K_{dm} , and extraction constant of M^{2+} , K_{ex} . The abbreviations for β -diketonate, see "Notation".

served with water molecules are thus not clear with TOPO in the organic phase.

The relation between the partition constant of the extractant in the HA form and that of the MA_2 chelates is further complicated as in seen from Figure 5. Although the K_a of hexafluoroacetylacetone is much lower than that of trifluoroacetylacetone, the K_{dm} values of the MA_2 chelates with the former are always higher than those of the latter, except the CuA_2 chelates whose values are nearly the same. (The K_{dm} for the bis-hexafluoroacetylacetonate of manganese(II) and zinc(II) could not be determined accurately but they were assumed to be higher than 10^{-1} .) Among the bis-chelates with trifluoroacetylacetone, acetylacetone, and benzoyltrifluoroacetone, the increase in the K_{dm} with the increase in the K_a appeared in a similar manner to each other except copper(II). The K_{dm} of bis-benzoylacetonates of manganese(II) (which could not be determined accurately but was assumed to be higher than 10^2) and of zinc(II) are higher than that of the corresponding benzoyltrifluoroacetonates but the cobalt(II) and nickel(II) chelates show the inverse order. Up to now, no reasonable explanation for these findings seems to be possible.

When the extraction data are analyzed from the formation of the extractable chelate and its two-phase partition, we can understand the extraction system comprehensively. This had already been pointed out in early 1950s by Rydberg⁽¹⁰⁾ and by Dyrssen and coworkers^(11,12) and has often been emphasized since then⁽¹³⁾, but not very much work studying metal chelate extraction systems from this standpoint has appeared. This is probably because experiments for this purpose are not easy; in order to determine the β_n and K_{dm} in a chelate extraction system, a greater number of experimental runs is necessary than to determine the K_{ex} in Eq. 16 or to obtain the percentage extraction curve against pH.

One of the most systematic studies from this standpoint is the extraction work of metal ions with β -isopropyltropolone⁽¹⁴⁾. The values for the β_1 , β_2 , and K_{dm} of β -isopropyltropolonates in chloroform-aqueous 0.1 mol dm^{-3} perchlorate system were reported to be $10^{5.8}$, $10^{10.8}$, and $10^{2.35}$ for cobalt(II), $10^{5.90}$, $10^{11.10}$, and $10^{2.10}$ for nickel(II) and $10^{9.55}$, $10^{18.30}$, and $10^{4.12}$ for copper(II), respectively. Thus the K_{dm} for the CuA_2 chelate is also much higher than the other two bis-chelates but the difference in the K_{dm} for the CoA_2 and NiA_2 chelates is rather small in this case.

Another interesting example of the two-phase partition behavior was found in the extraction of nickel(II) and copper(II) with dimethylglyoxime⁽¹⁵⁾. In chloroform-aqueous 0.1 mol dm^{-3} perchlorate system, the β_2 was $10^{17.24}$ for the NiA_2 chelate and $10^{19.24}$ for the CuA_2 chelate and the K_{dm} was $10^{2.51}$ for the former and $10^{-0.93}$ for the latter, and a marked synergism with quinoline and dodecylamine was observed in the latter extraction. This high partition constant of the NiA_2 chelate makes this reagent a specific extractant for nickel(II) (and also for palladium(II)⁽¹⁶⁾) although the stability of the NiA_2 chelate is lower than the CuA_2 chelate.

From the foregoing descriptions, it may be concluded that the liquid-liquid partition of the extractable chelates plays an important role in the over-all extraction equilibria of metal ions as chelate complexes; without any information about this quantity, we can not make a fundamental discussion on the extraction curves even when we know the stability of the metal chelates to be extracted or the extraction constants of the metal ions in that system.

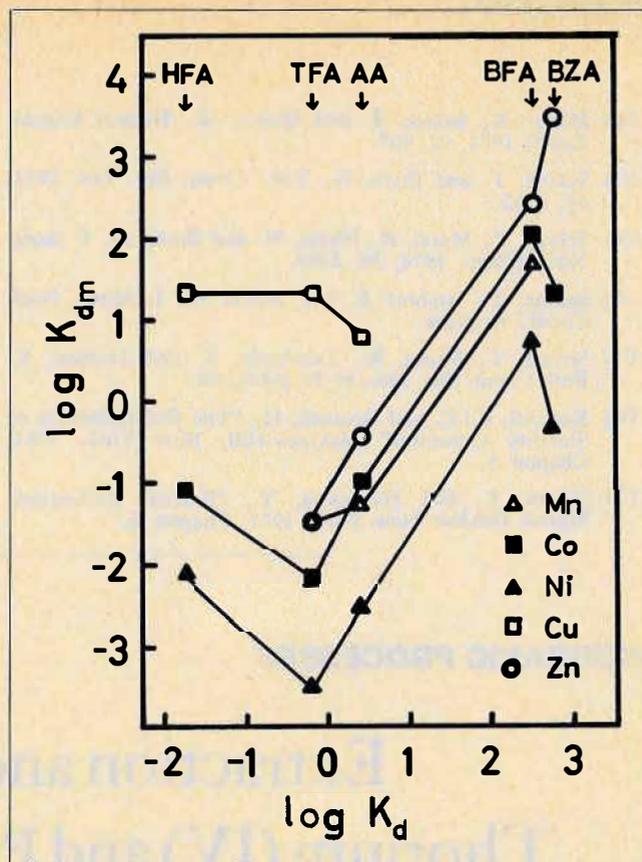


FIGURE 5. Relation between two-phase partition constant of MA_2 chelate, K_{dm} , and of β -diketone, K_d . The abbreviations for β -diketone, see "Notation".

Acknowledgement

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NOTATION

- HA and A^- = a β -diketone and a β -diketonate ion.
D = distribution ratio of M^{2+} ($= [M(II)]_{org} / [M(II)]^{-1}$).
 K_a = acid dissociation constant of HA ($= [H^+] [A^-] / [HA]^{-1}$).
 K_d = two-phase partition constant of HA ($= [HA]_{org} / [HA]^{-1}$).
 β_n = over-all stability constant of chelate in the aqueous phase ($= [MA_2^{2-n}] [M^{2+}]^{-1} [A^-]^{-n}$).
 K_{dm} = two-phase partition constant of MA_2 type uncharged chelate ($= [MA_2]_{org} / [MA_2]^{-1}$).
L = an adduct forming organophilic ligand.
 $\beta_n(ORG)$ = over-all formation constant of adduct chelate in the organic phase ($= [MA_2L_n]_{org} / [MA_2]^{-1} [L]_{org}^{-n}$).
 K_{ex} = extraction constant of M^{2+} with HA ($= [MA_2]_{org} [H^+]^2 [M^{2+}]^{-1} [HA]_{org}^{-2}$).

The β -diketones ($R-CO-CH=C(OH)R'$) are abbreviated in figures as follows.

- AA = acetylacetone ($R = CH_3, R' = CH_3$).
BZA = benzoylacetylacetone ($R = C_6H_5, R' = CH_3$).
TFA = trifluoroacetylacetone ($R = CH_3, R' = CF_3$).
BFA = benzoyltrifluoroacetone ($R = C_6H_5, R' = CF_3$).
HFA = hexafluoroacetylacetone ($R = CF_3, R' = CF_3$).

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INORGANIC PROCESSES

Extraction and Separation of Thorium (IV) and Protactinium (V) with 1-Phenyl-2-Methyl-3-Hydroxy-4-Pyridone

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ABSTRACT

The extraction of thorium(IV) from aqueous hydrochloric or nitric acid solution, and the extraction of protactinium(V) from hydrochloric acid solution by 1-phenyl-2-methyl-3-hydroxy-4-pyridone dissolved in chloroform has been studied. At pH > 4, thorium(IV) is quantitatively extracted from the hydrochloric acid solution if chloride ions are present in excess. It is also extracted at pH > 3 from nitric acid solution if nitrate ions are present in excess. Protactinium(V) is quantitatively extracted at a hydrochloric acid concentration lower than 0.5 M regardless of the chloride ion concentration. The separation of protactinium from thorium and uranium is described. The mechanism of thorium(IV) and protactinium(V) extraction has also been studied.

Introduction

IT IS KNOWN THAT PROTACTINIUM has many isotopes which are formed from uranium as natural products or can be obtained by the irradiation of uranium and thorium. Therefore, the study of the separation of protactinium from thorium and uranium is of practical and theoretical importance⁽¹⁾. This paper deals with the application of 1-phenyl-2-methyl-3-hydroxy-4-pyridone (HX) for the extraction and separation of protactinium(V) from thorium(IV) or uranium(VI). The extraction of uranium(VI) with this reagent has been described previously⁽²⁾.

Experimental

Reagents and Apparatus

Standard thorium(IV) nitrate solution (0.01 M) was prepared by dissolving Th(NO₃)₄ in 0.01 M HNO₃. Standard thorium(IV) chloride solution (0.01 M) was prepared from the nitrate solution by precipitation with aqueous ammonia, the thorium hydroxide being washed thoroughly by decantation with ammonium nitrate solution and distilled water and then dissolved in 0.1 M hydrochloric acid. Both thorium solutions were standardized by titration with EDTA using xylenol orange as an indicator⁽³⁾. The uranium solution was prepared by dissolving uranyl nitrate in distilled water. ²³³Pa was obtained from the Institute "Boris Kidrič", Vinča, Yugoslavia. HX was synthesized as described earlier⁽⁴⁾. Its solution in chloroform served as the organic phase. All chemicals used were of analytical purity. Absorbance measurements were carried out on a Perkin-Elmer Coleman 124 spectrophotometer.

Extraction Procedure

Equal volumes of the aqueous and organic phase (10ml) were equilibrated by shaking for 20 min using a mechanical shaker. Equilibrium was achieved in several minutes. Thorium concentrations in the aqueous phase were determined spectrophotometrically by thoria⁽⁵⁾, and those in the organic phase were calculated from the differences between the initial and the final aqueous values. The distribution of protactinium was followed by measuring the gamma activity of the organic and aqueous phases with a scintillation counter (NaI/Tl).

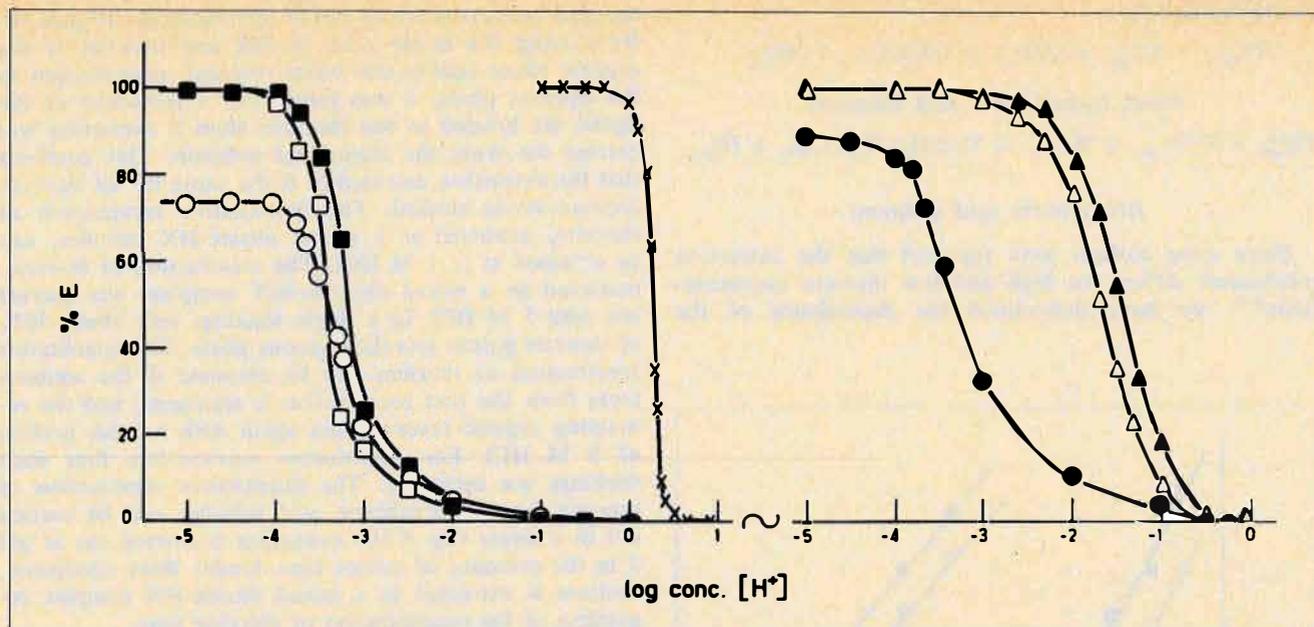


FIGURE 1. The dependence of percent extraction of thorium(IV) (\square , \square , \blacksquare) and protactinium(V) (\times) on the concentration of HCl and HNO_3 (\bullet , \triangle). ThCl_4 conc. $2 \times 10^{-4}\text{M}$, HX conc. $5 \times 10^{-3}\text{M}$, (\circ) without addition of NaCl, (\square) $(\text{H, Na})\text{Cl} = 0.5\text{M}$, (\blacksquare) $(\text{H, Na})\text{Cl} = 1.0\text{M}$. $\text{Th}(\text{NO}_3)_4$ conc. $2 \times 10^{-4}\text{M}$, HX conc. $5 \times 10^{-3}\text{M}$, (\bullet) without addition of NaNO_3 , (\triangle) $(\text{H, Na})\text{NO}_3 = 0.5\text{M}$, (\blacktriangle) $(\text{H, Na})\text{NO}_3 = 1.0\text{M}$, (\times) conc. Pa at tracer level, $(\text{H, Na})\text{Cl} = 4\text{M}$.

Results and Discussion

Extraction of Thorium(IV)

The extraction of thorium(IV) with HX dissolved in chloroform as a function of hydrochloric or nitric acid concentration is shown in Figure 1. At $\text{pH} > 4$, thorium(IV) is quantitatively extracted from the hydrochloric acid solution if chloride ions are present in excess, or at $\text{pH} > 3$ from the nitric acid solution containing an excess of nitrate ions. The dependence of the extraction on the concentration of chloride and nitrate ions is shown in Table 1. In the optimal pH range and HX concentration, thorium is quantitatively extracted if the concentration of chloride and nitrate ions is higher than 0.5 M and 0.1 M, respectively. In the optimal pH range and chloride or nitrate ion concentration, thorium is quantitatively extracted if the molar ratio of Th:HX is higher than 1:20 (Table 2).

The influence of the HX concentration in the organic phase, and the hydrogen ion concentration in the aqueous phase on the distribution ratios, D , of thorium was studied to determine the composition of the extractable complexes. The results show that D is inversely second and first-power dependent upon the hydrogen ion concentration from the varying hydrochloric or nitric acid solution (Figure 2), and second and third-power dependent upon the HX concentration in the organic phase from the aqueous hydrochloric or nitric acid solution, respectively (Figure 3). These results indicate that two protons are released on the formation of an extractable complex from the hydrochloric acid solution, and that one proton is released from the nitric acid solution, and, furthermore, that two or three molecules of the reagent are bonded to one atom of thorium. The solution of the thorium complex has a maximum absorbance at 323 nm (Figure 4) in hydrochloric and nitric acid solution. Therefore, it was possible to study the composition of the extractable thorium complex spectrophotometrically using Job's method. The results obtained (Figure 5) indicate that the molar ratio of Th : HX is 1 : 2 in the hydrochloric acid solution and

TABLE 1. The Dependence of the Extraction of Thorium on the Concentration of Chloride and Nitrate Ions.

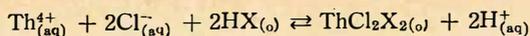
Organic phase: $5 \times 10^{-3}\text{M HX}$.			
Aqueous phase: (a) $2 \times 10^{-4}\text{M ThCl}_4$, $1 \times 10^{-4}\text{M HCl}$;			
(b) $2 \times 10^{-4}\text{M Th}(\text{NO}_3)_4$, $3.6 \times 10^{-4}\text{N HNO}_3$.			
Conc. NaCl ^(a) (M)	% E	Conc. NaNO ₃ ^(b) (M)	% E
—	73.5	—	89.0
0.04	86.0	0.05	97.5
0.06	88.0	0.1	99.0
0.08	91.0	0.2	99.5
0.1	92.0	0.4	99.8
0.2	97.0	0.5	99.8
0.3	98.0	1.0	99.8
0.4	98.2	2.0	99.8
0.5	98.5		
1.0	98.9		
2.0	98.9		

TABLE 2. The Dependence of the Extraction of Thorium on the HX Concentration.

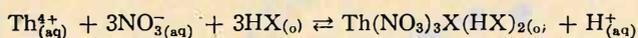
(a) $2 \times 10^{-4}\text{M ThCl}_4$, $1 \times 10^{-4}\text{M HCl}$, $(\text{H, Na})\text{Cl} = 1.0\text{M}$			
(b) $2 \times 10^{-4}\text{M Th}(\text{NO}_3)_4$, $1 \times 10^{-3}\text{M HNO}_3$, $(\text{H, Na})\text{NO}_3 = 1.0\text{M}$.			
Conc. HX $\text{M} \times 10^3$	HX:Th molar ratio	% E ^(a)	% E ^(b)
1.0	5	70.0	36.5
1.4	7	80.5	53.0
2.0	10	90.3	72.3
3.0	15	95.2	92.5
4.0	20	98.2	99.5
5.0	25	98.9	99.8
6.0	30	98.9	99.8

1:3 in the nitric acid solution. On the basis of these results and the fact that the complex containing chloride or nitrate ions is extracted, the extraction mechanism can

be represented as:



(from hydrochloric acid solution)



(from nitric acid solution)

Since some authors have reported that the extraction mechanism differs for high and low thorium concentrations⁽⁶⁻⁸⁾, we have determined the dependence of the

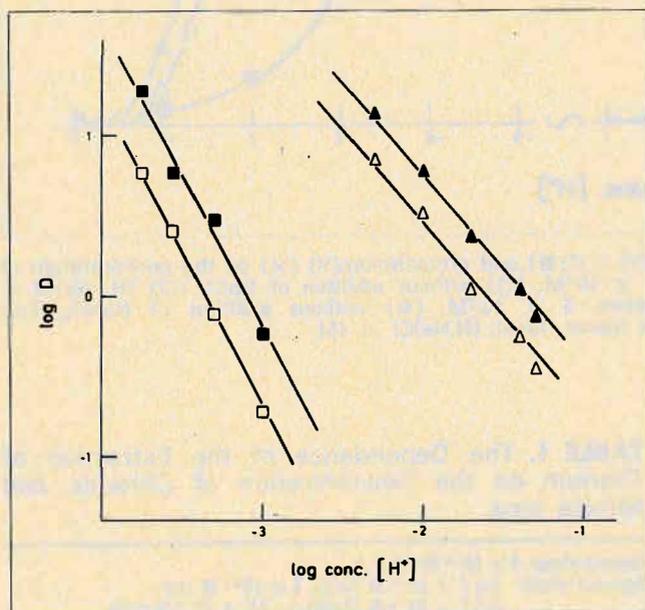


FIGURE 2. The dependence of the distribution ratio of thorium(IV) on the hydrogen ion concentration. HX conc. $5 \times 10^{-3}\text{M}$, Th(IV) conc. $2 \times 10^{-4}\text{M}$, (□) (H,Na)Cl = 0.5M, (■) (H,Na)Cl = 1.0M, (Δ) (H,Na)NO₃ = 0.5M, (▲) (H,Na)NO₃ = 1.0M.

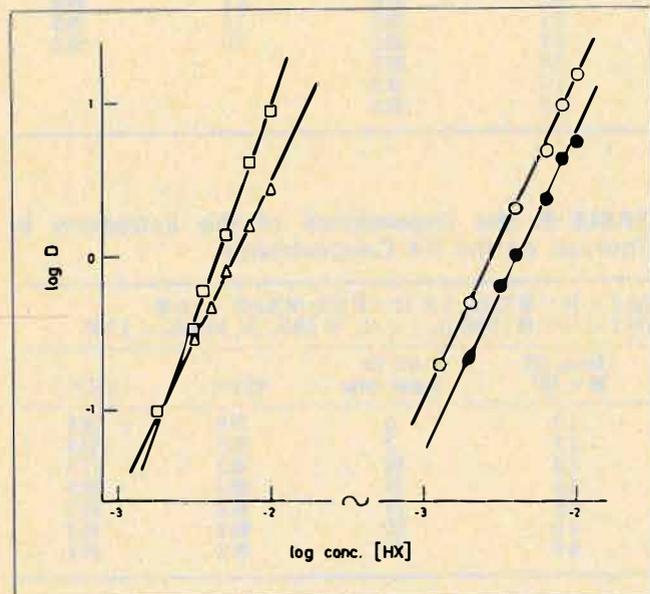


FIGURE 3. The dependence of the distribution ratio of thorium (Δ□) and protactinium (○●) on the HX concentration from $3.6 \times 10^{-4}\text{M}$ HCl, (H,Na)Cl = 1.0 M (Δ), $3.9 \times 10^{-2}\text{M}$ HNO₃, (H,Na)NO₃ = 1.0 M (□), 1.7 M HCl (○) and 1.9 M HCl (●).

thorium extraction on its initial concentration (Figure 6). By plotting the molar ratio of HX and thorium in the organic phase against the initial thorium concentration in the aqueous phase, it was found that 3 molecules of the ligand are bonded to one thorium atom if extraction was carried out from the nitric acid solution. This confirms that the extraction mechanism is the same for all thorium concentrations studied. The quantitative reextraction of thorium, extracted as a mixed nitrate-HX complex, can be obtained at $> 1\text{ M}$ HCl. The reextraction of thorium, extracted as a mixed chloride-HX complex, was carried out with 5 M HCl. In a single shaking, only about 50% of thorium passed into the aqueous phase. The quantitative reextraction of thorium can be obtained if the aqueous layer from the first reextraction is separated, and the remaining organic layer shaken again with a fresh portion of 5 M HCl. For quantitative reextraction, four such shakings are necessary. The quantitative reextraction of thorium from hydrochloric acid solution can be carried out in a single step if the extraction is carried out at pH 3 in the presence of nitrate ions. Under these conditions, thorium is extracted as a mixed nitrate-HX complex regardless of the concentration of chloride ions.

Extraction of Protactinium(V)

The extraction of protactinium(V) with HX dissolved in chloroform as a function of hydrochloric acid concentration is shown in Figure 1. At a hydrochloric acid concentration lower than 0.5 M, protactinium(V) is quantitatively extracted, and at an acidity higher than 8 M HCl, practically all the protactinium remains in the aqueous phase. The same results were obtained if the extraction was carried out from a solution of constant ionic strength, (H,Na)Cl = 4 M. Quantitative reextraction of protactinium can be achieved with $> 8\text{ M}$ HCl. The dependence of the $\log D_{\text{Pa(V)}}$ and the $\log \text{HX}_{\text{org}}$ was determined from the aqueous phase of constant acidity (1.7 and 1.9 M HCl) and is shown in Figure 3. With both acid concentrations,

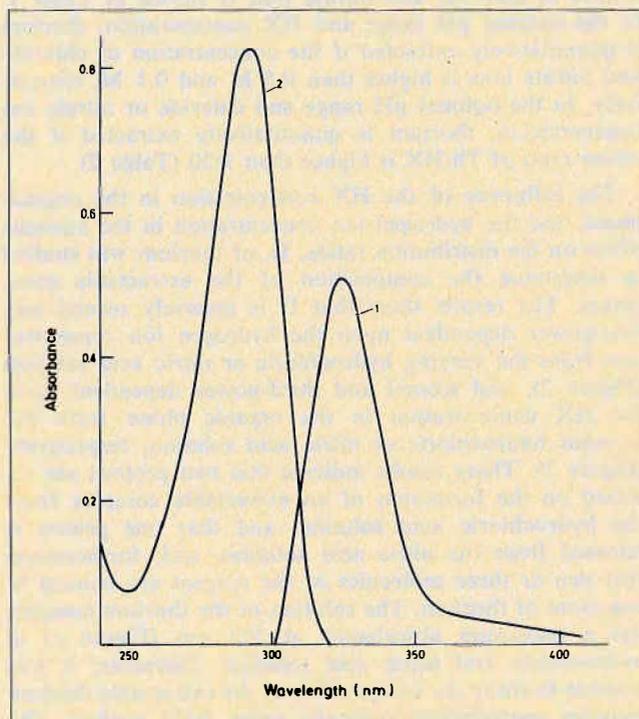


FIGURE 4. Absorption spectrum of thorium(IV) — HX complex (1) and $5 \times 10^{-5}\text{M}$ HX in chloroform (2).

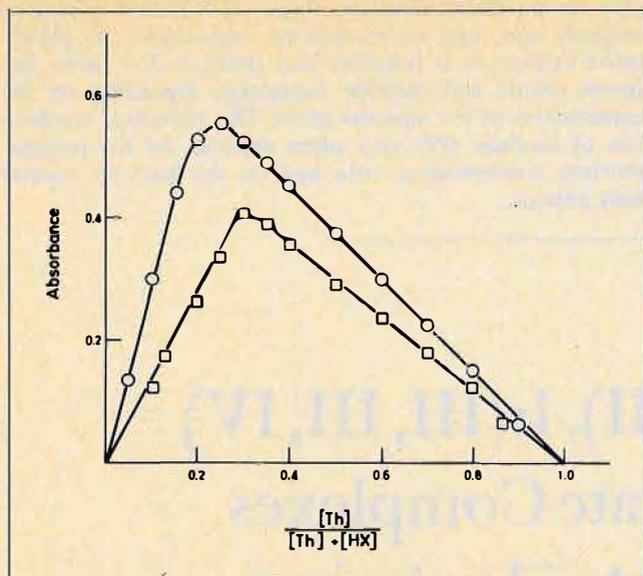


FIGURE 5. Determination of composition of the extracted thorium — HX complexes by Job's method. Conc. HCl = 3×10^{-5} M, $C_{Th} + C_{HX} = 5 \times 10^{-4}$ M, (H,Na)Cl = 1.0M (□) and conc. HNO₃ = 3×10^{-5} M, $C_{Th} + C_{HX} = 5 \times 10^{-4}$ M, (H,Na)NO₃ = 1.0M (○)

a second-power extractant dependency is found, indicating that two reagent molecules are bonded to one atom of protactinium.

Separation of Protactinium from Thorium and Uranium

The differences in the extraction properties of protactinium, thorium and uranium were utilized for their separation. From a 0.5 M hydrochloric acid concentration, protactinium is quantitatively extracted while thorium (Figure 1) and uranium⁽²⁾ remain in the aqueous phase. The ex-

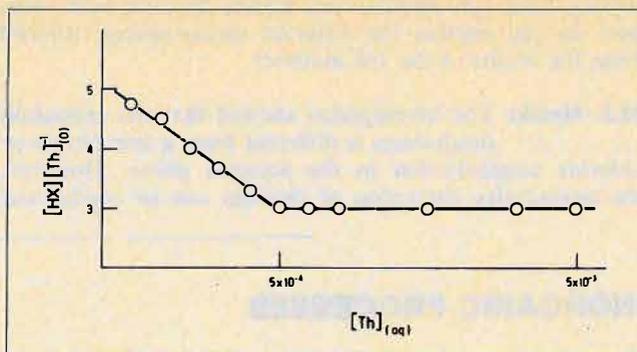


FIGURE 6. Determination of Th: HX ratio as a function of the initial thorium concentration in the aqueous phase.

traction of protactinium, present in tracer level, was unaffected by the quantity of thorium and uranium present in such a mixture. Protactinium was back-extracted from the chloroform solution into the aqueous phase by shaking with an equal volume of 8 M HCl for several minutes.

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DISCUSSION

G. Grossi: What is the solubility of the reagent in hydrocarbon-type diluents?

It is possible to separate selectively Pa from U and Th? Have you determined the composition of the Th-HX-nitrate complex?

M.J. Herak: The reagent is soluble in CHCl₃, CCl₄, petroleum ether, dioxane and ethanol. Selective separation of Pa from U and Th is possible. From a 0.5 M hydrochloric acid concentration, protactinium is quantitatively extracted while thorium and uranium remain in the aqueous phase. The investigation showed that the composition of extracted Th-NO₃-HX complex depends on concentration of nitrate ions in aqueous phase. However, the quantitative extraction of thorium can be carried out only in the presence of an excess of HX and nitrate ions and the mechanism of quantitative extraction was studied. Most probably extracted species is Th(NO₃)₃X(HX)₂.

V.A. Mikhailov: You have studied the stoichiometry of thorium extraction. What is known about the stoichiometry of protactinium extraction, especially about extraction of hydrolyzed forms of Pa(V)?

M.J. Herak: The composition of extracted Pa-HX complex was not possible to determine precisely. However, distribution studies showed that two molecules of HX are bonded to one atom of protactinium. On the

basis of this result and the fact that in acid solution protactinium can be present as Pa(OH)₃³⁺ and PaO(OH)₂²⁺, most probably extracted species are Pa(OH)₃X₂ and PaO(OH)X₂.

A. Siczek: Do you think that 1-phenyl-2 methyl-3-hydroxy-4 pyridone could be used for thorium fuel reprocessing? If yes, is this solvent stable under radiation? Can you comment on potential zirconium and ruthenium decontamination for thorium fuel? Will there be any difficulties with stripping of Th, V, Pa?

M.J. Herak: I think that this reagent could be used for the fuel reprocessing. Some of our investigations showed that the reagent is stable under radiation. Our investigations of extraction of Zr and Ru with HX showed that Zr and Ru decontamination is probably possible. Moreover, I think that there will not be any difficulties with the stripping of Th, U and Pa.

A.S. Kertes: I am somewhat puzzled by your findings that there is an order of magnitude difference in the concentration of hydrogen ions needed for a quantitative extraction of thorium from chloride and nitrate media. I would not expect the dissociation constant of your weak acid to be significantly affected by the nature of the aqueous electrolyte at the low overall ionic strength (0.1 - 0.5) used in your studies. Now, if you suggest, based on your spectral data, that the organic phase complex is

similar, both for chloride and nitrate thorium salts, then how do you explain the different stoichiometry deduced from the results of the Job method?

M.J. Herak: The investigation showed that the extraction mechanism is different from a low nitrate or chloride concentration in the aqueous phase. However, the quantitative extraction of thorium can be carried out

only in the presence of an excess of HX and nitrate or chloride ions, and we studied the mechanism of quantitative extraction. It is known that thorium (IV) forms different nitrate and chloride complexes depending on the composition of the aqueous phase. The extraction mechanism of thorium (IV) very often depends on the reagent-thorium concentration ratio and on the kind of mineral acid present.

INORGANIC PROCESSES

Extraction of Ir(III), Ir(III, III, IV) and Ir(IV) Sulphate Complexes from Sulphuric-Acid Solutions with Nitrogen-Containing Extractants

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ABSTRACT

Laws of extraction of Ir(III), Ir(IV) and Ir(III, III, IV) sulphate complexes from sulphuric-acid solutions by various classes of aliphatic amines are reported. It has been shown that a quantitative extraction is achieved at an acidity of the aqueous phase of below 2M H₂SO₄.

Complete recovery of iridium has been observed for solutions of [O.Ir₃(SO₄)₆(H₂O)₃]⁴⁻ even from a 5M-sulphuric acid. The efficiency of extraction recovery is significantly influenced by the chemical and valency states of iridium in solutions, the salt background and the nature of the diluent and extractant. Upon using protonic diluents, there is observed a growth of extraction capacity of alkyl amines in the following sequential order: tertiary < secondary < primary. Hydrolysis of starting complexes, whose velocity is in proportion with the temperature, determines the formation of hard-to-extract forms in solutions and may result in a slump of the extraction rate in the process of time down to zero level.

Iridium compounds passing into the organic phase on extraction by aliphatic amines have been isolated into individual states. The isolated compounds have been investigated using various physical and chemical methods.

Various potential extraction mechanisms are discussed.

Introduction

EXTRACTION IS SUCCESSFULLY USED for the recovery of iridium and for separating it from other platinum metals, from halide and nitrite media, by employing various classes of organic compounds⁽¹⁻⁴⁾. However, until recently the literature lacked data on extraction of iridium sulphates in fixed chemical forms. Attempts to extract iridium by salts of quaternary ammonium bases from "pure" sulphuric-acid media failed to yield any positive results⁽⁵⁾. Data on the extraction of iridium from multi-component process solutions testify to the fact that iridium

is not extractable from such solutions by alkyl amines and other classes of extractants⁽⁵⁻⁷⁾. In this context, a concept was formed of the impossibility to recover iridium by extraction from sulphuric-acid media under normal conditions. Therefore, to recover iridium from sulphate solutions, the latter are treated by organic or halide-containing reagents with a view of converting iridium into forms amenable to extraction⁽⁶⁻⁸⁾. Nevertheless, for a number of reasons, these analytical techniques proved to be hardly acceptable for extraction recovery of iridium from process solutions under real operating conditions.

In this connection, search and study of possible ways and laws of extraction of iridium in the form of its sulphate complexes acquire a large practical and theoretical significance⁽⁹⁻¹¹⁾.

This report deals with the results of a study on extraction of a number of anionic sulphate complexes wherein iridium is found at various oxidation states⁽¹²⁻¹⁴⁾:

1. Tri-nuclear iridium oxotrisulphate (III, III, IV) of the formula [O.Ir₃(SO₄)₉]¹⁰⁻ known from the literature and formed as a final product of a reaction of tri- or tetravalent iridium chlorides and hydroxides with a boiling sulphuric acid^(13,15,16). This complex is thermodynamically stable in concentrated H₂SO₄, but it is hydrolyzed in its aqueous solutions. We have found that this hydrolysis process is reversible at the first stage, wherein the structure of a tri-nuclear ring is not affected, and it is accompanied by substitution of labile monodentate sulphate groups with water molecules. As a result of this substitution, Ir(III, III, IV) oxodisulphate ion [O.Ir₃(SO₄)₆(H₂O)₃]⁴⁻ is formed⁽¹²⁾.

2. A cesium salt of tri-nuclear iridium Ir(III) sulphate [Ir₃(SO₄)₁₁H₂O]¹³⁻ prepared as an intermediate product by reacting boiling sulphuric acid with iridium hydroxide, or by reducing Ir(III, III, IV) oxotrisulphate with oxalic acid⁽¹³⁾.

3. "Sesquisulphate" of trivalent iridium of the formula [Ir₂(SO₄)₃(H₂O)₆] was isolated by salting-out Ir(III) sulphide, after oxidation, in a sulphate medium by perhydrolysis, ozone or oxygen under pressure. In equilibrium sulphuric-

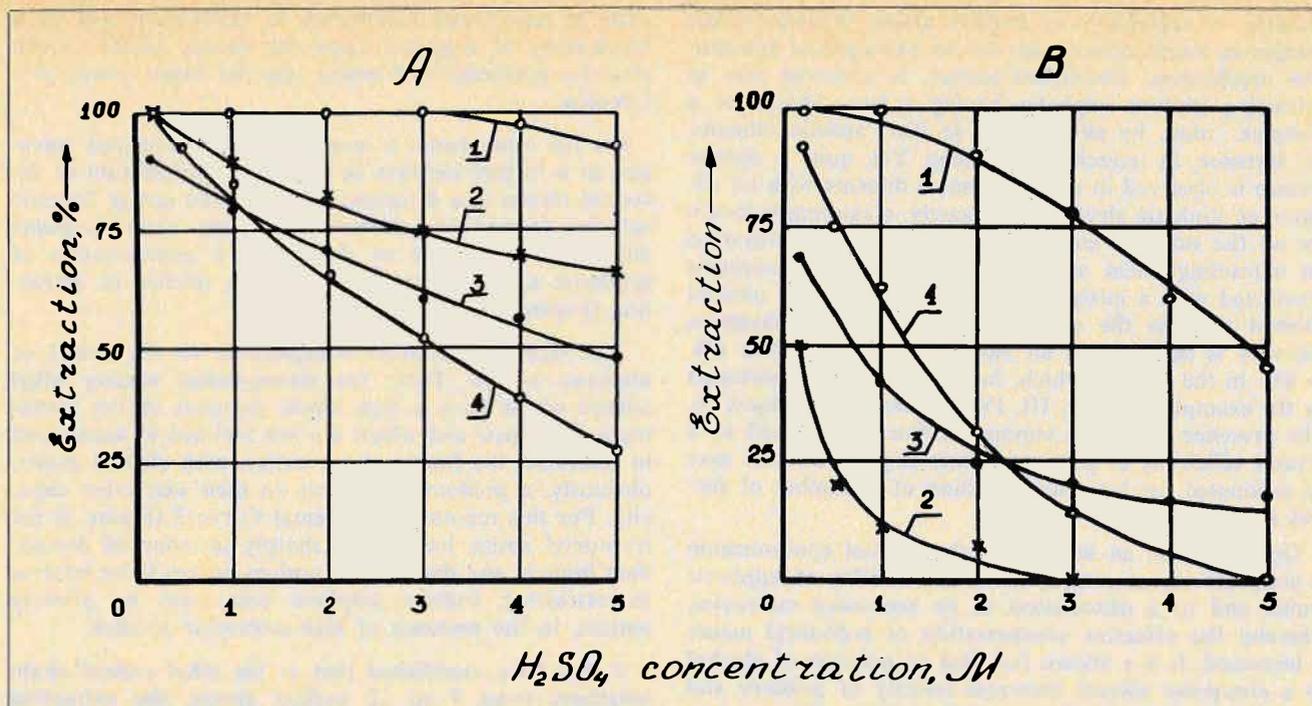
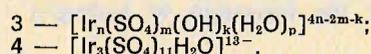
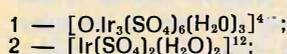


FIGURE 1. Effect of acidity of the aqueous phase on extraction of iridium sulphate complexes by 0.1 M-solutions of n-dodecyl amine (A) and tri-n-octyl amine (B) in decane, with an addition of 10 vol.% of isoamyl alcohol. Iridium concentration 0.0016 g-at./l.



acid solutions of this compound, iridium is present mainly in the form of a sufficiently stable one-charge anion $[Ir(SO_4)_2(H_2O)_2]^{1-}$ ⁽¹⁴⁾.

4. By an exothermal dissolution of Ir(IV) hydroxide in concentrated H_2SO_4 , iridium aquo hydroxo sulphate was prepared at an oxidation state of +4 which was likely to preserve the polymeric structure of the starting hydroxide (13).

The solutions of the above-listed complexes in sulphuric acid, having a required concentration, served as an aqueous phase in our study of their extraction by various classes of aliphatic amines in the form of sulphates.

Figure 1 represents experimental data illustrating the effect of acidity of the aqueous phase on extractability of iridium sulphate complexes. Thus, their maximum recovery into the organic phase is achieved within a range of from 0.1 to 0.5 M H_2SO_4 and, in the case of n-dodecyl amine, is at a level of 100%, the extraction equilibrium being practically attained after some 30 to 60 seconds of contact of equal volumes of both the phases. With an increase in the concentration of H_2SO_4 and in that of ions constituting a salt background, there is observed in the aqueous phase a gradual decline in the percentage recovery of iridium for all the extractants investigated, in particular, in the case of using strong-based ternary alkyl amines. In other words, a sulphate ion participating in the extraction process exerts a competitive effect in relation to an anion of a complex being extracted. However, Ir (III, III, IV) oxodisulphate is extracted quantitatively by trioctyl amine from a unimolar H_2SO_4 , while using dodecyl amine renders it possible even from a tetramolar solution of H_2SO_4 .

We have resorted to spectrophotometry, polarography, ion exchange and extraction to investigate the chemical conduct of sulphate complexes characterized with various oxidation rates of iridium in sulphuric-acid solution⁽¹³⁾. It

has been established that processes occurring in solutions are specific for each form and they are associated to hydrolytical polymerization and redox reactions whose velocity is directly dependent on temperature and inversely dependent on acidity of a solution.

However, all of them result ultimately in the formation of polymeric aquo hydroxo sulphates of trivalent iridium which are difficult to extract. Therefore, retention of solutions of starting sulphate complexes in the process of time leads to a decline in the percentage recovery of iridium during its subsequent extraction (Figure 2). Thus, for instance, an ion of Ir(III, III, IV) oxosulphate whose conduct is the most complicated in solutions, is kinetically stable under normal conditions in a 2.0 M H_2SO_4 for 8 days, while at a concentration of H_2SO_4 of 0.5 M this form remains fixed for some 40 to 45 hours. Any further retention of solutions as well as the effect of elevated temperatures results in an irreversible hydrolysis of a complex.

The hydrolysis process is characterized with a destruction of the main structure of a tri-nuclear anion and with a formation of tri- and tetravalent iridium sulphates in the system, the latter being unstable in sulphuric-acid solutions and passing into trivalent state even at the expense of reduction by oxygen contained in H_2O ⁽¹³⁾.

Hence, the equilibrium products of hydrolysis of sulphate complexes being investigated are not extractable. This fact, obviously, accounts for all the abortive attempts undertaken earlier to extract iridium from sulphuric-acid solutions.

In order to ascertain the effect exerted by the nature of an extractant on extraction of iridium and sulphate solutions, experiments were carried out with solutions of primary, secondary and tertiary alkyl amines in various organic diluents. Increase in extraction capacity can be proven according to the following sequential order:

primary < secondary < tertiary amine. Iridium halide complexes extractable mainly by an extraspherical substitution mechanism, established earlier, is observed also in extracting iridium sulphates having a large charge of a complex anion, by alkyl amines in inert aprotic diluents, for instance, in tetrachloro ethylene. Yet, quite a reverse picture is observed in using the same diluents with an addition of aliphatic alcohol, and namely, maximum recovery for all the sulphate complexes under study was achieved on extracting them with primary amines. Experiments conducted with a mixture of decane with isoamyl alcohol showed that, in the case of dodecyl amine, maximum recovery is observed at an alcohol content of from 6% to 8% in the system, which, in fact, is well demonstrated by the example of Ir(III, III, IV) oxodisulphate (Figure 3). The presence of the maximum on Curve 1 as well as a greater efficiency of primary amines in polar diluents may be accounted for by a superposition of a number of factors involved.

On one hand, an increase in the alcohol concentration is conducive to an improvement of solubility of sulphuric amine and to a dissociation of its associated molecules, whereby the effective concentration of n-dodecyl amine is increased. It is a known fact that an addition of alcohol to a non-polar solvent increases basicity of primary and secondary amines, but it practically had no effect on tertiary amines⁽¹⁷⁾. Ultimately, it is this factor that determines the growth of extraction (Figure 3). It has been established equally that alcohols react themselves with amines at the expense of the formation of hydrogen

bonds $R - NH_3^+ \dots O \begin{matrix} H \\ \diagup \\ R \end{matrix}$. This circumstance is a positive

factor in the case of Ir(III, III, IV) oxodisulphate, for which, unlike other sulphate complexes, a mixed intra- and extraspherical extraction mechanism is valid; this mechanism will be dealt with more in detail later. Therefore,

such an interaction contributes to labilization and to a break-away of a proton from the cation AmH^+ , which precedes penetration of amine into the inner sphere of a complex.

On the other hand, a more sharply pronounced solvation at a further increase in the IAS concentration in the system results in a screening of the amino group. Specific solvates formed by alcohols and ionic amine vapours determine a decrease in the effective concentration of sulphuric amine, and, consequently, a decline of extraction (Figure 3).

The maximum location is dependent on the nature of aliphatic amine. Thus, for strong-based tertiary alkyl amines which have a high dipole moment of the monomeric ionic pair and which are less inclined to association in solutions, the factor of a reaction with alcohol exerts, obviously, a predominant effect on their extraction capacity. For this reason, experimental Curve 2 (Figure 3) for tri-n-octyl amine has only a sharply pronounced descendant branch, and this class of amines proves to be inferior in extracting iridium sulphate complexes to primary amines, in the presence of high-molecular alcohol.

It has been established that as the alkyl radical chain lengthens from 7 to 12 carbon atoms, the extraction capacity of primary amines steps up. It is noteworthy that basicity of primary amines is almost unaffected by an increase in the chain length⁽¹⁸⁾. These data are fairly well correlated with the solubility of primary amines in sulphuric-acid solutions. The solubility declines as the number of carbon atoms in the normal chain of an alkyl radical grows⁽¹⁹⁾. Obviously, a similar dependence is valid for complexes to be extracted too.

In order to ascertain the composition, structure and properties of compounds passing into the organic phase during the extraction, we have isolated them in their individual state and investigated by various physical and chemical methods. Syntheses were carried out by saturating

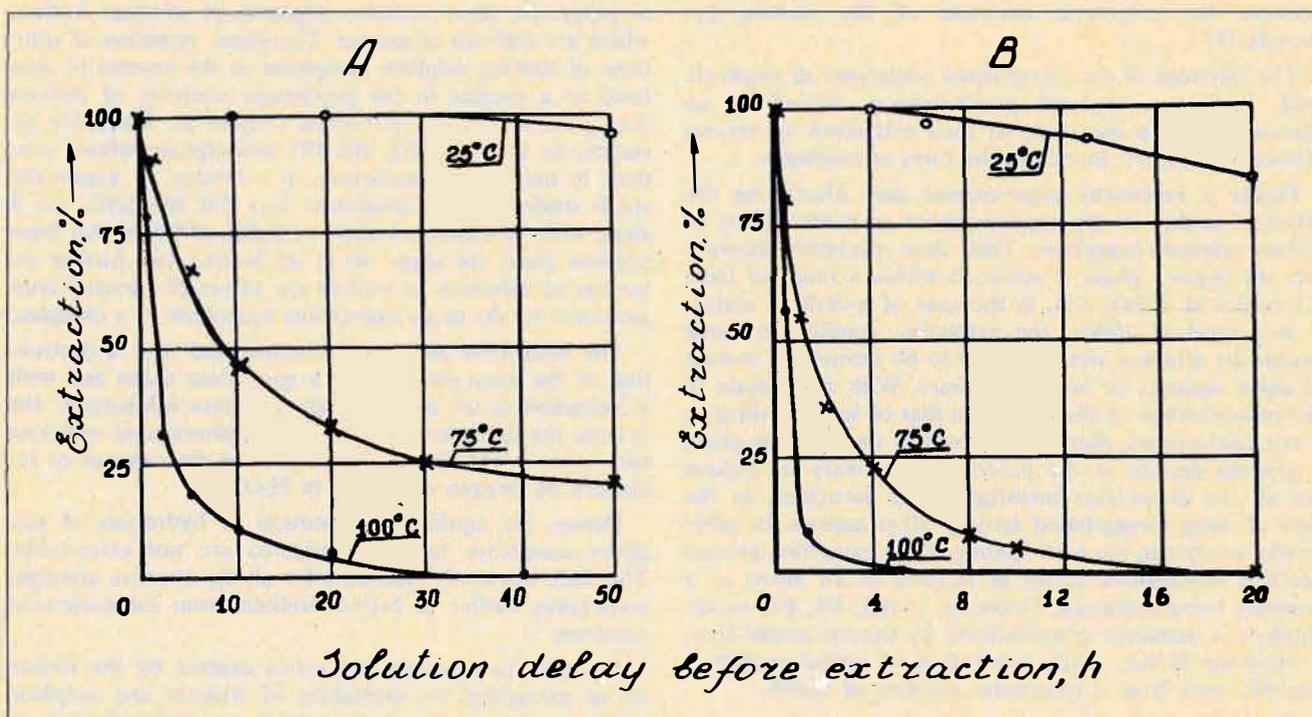


FIGURE 2. Dependence of extraction of $[O.Ir_3(SO_4)_6(H_2O)_3]^{4-}$ (A) and $[Ir_3(SO_4)_{11}H_2O]^{13-}$ (B) vs. retention time of their solutions in a 0.5 M-sulphuric acid. Iridium concentration 0.0016 g-at./l. Extractant: 0.05 M-solution of n-dodecyl amine in decane + 10 vol.% of isoamyl alcohol.

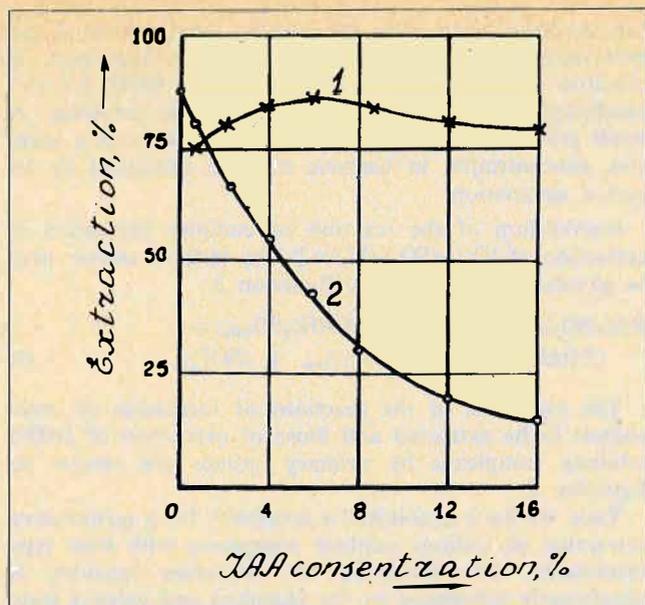


FIGURE 3. Effect of the concentration of isoamyl alcohol in the organic phase on extraction of $[O_2Ir_3(SO_4)_6(H_2O)_3]^{4-}$ from a 1.0 M-sulphuric acid. Iridium concentration 0.0018 g-at./l. Extractant: 0.01 M-solutions of n-dodecyl amine (1) and tri-n-octyl amine (2) in decane.

the organic phase. In the case of a trioctyl ammonium salt, solvent (benzene, hexane) was removed by boiling at ambient temperature, under vacuum conditions⁽¹²⁾. Complexes with dodecyl amine were isolated from an organic solution containing isoamyl alcohol by salting-out with hexane. The composition and results of a chemical analysis of compounds being extracted are reported in Table 1.

A trioctyl ammonium salt is a viscous substance, coloured blue-green, soluble in methyl reagents, characterized, as shown by measurements, by a molecular electroconductivity and dissociating preferably as per the first stage. With a decreasing dielectric constant of the diluent, the degree of dissociation of a complex declines too. Compounds with dodecyl amine are waxy substances soluble only in the presence of a high-molecular alcohol. Thermogravimetric studies showed that they melt without decomposition at 100 to 110°C.

Electronic absorption spectra of synthesized complexes (Figure 4) are similar to these of starting sulphates⁽¹²⁻¹⁴⁾ which in fact can serve as a proof as to the preservation of the basic structure of the latter in the process of their extraction. Organic phase is characterized after extraction of iridium (IV) sulphate by a significantly lower absorption in a region of 583 nm as compared to the starting aqueous phase. Moreover, its retention leads in the process of time to a complete disappearance of absorption at this wave length. That is, unlike other sulphate complexes, Ir(IV) sulphate is unstable also in organic solutions; it is reduced up to an oxidation rate of +3, which in fact constitutes an unfavourable factor for its preparation in individual state.

Table 2 represents wave numbers of the maxima of absorption bands found in IR-spectra of tri-nuclear Ir(III, III, IV) oxosulphates.

In all the complexes, the position of bands ν_3 and ν_4 related respectively to valency and deformation variations of the bond S-O, their split into three components and the presence of an intensive band $\nu_1(SO_4^{2-})$ correlates with the fact that sulphate groups belong to C_{2v} , a dotted symmetry

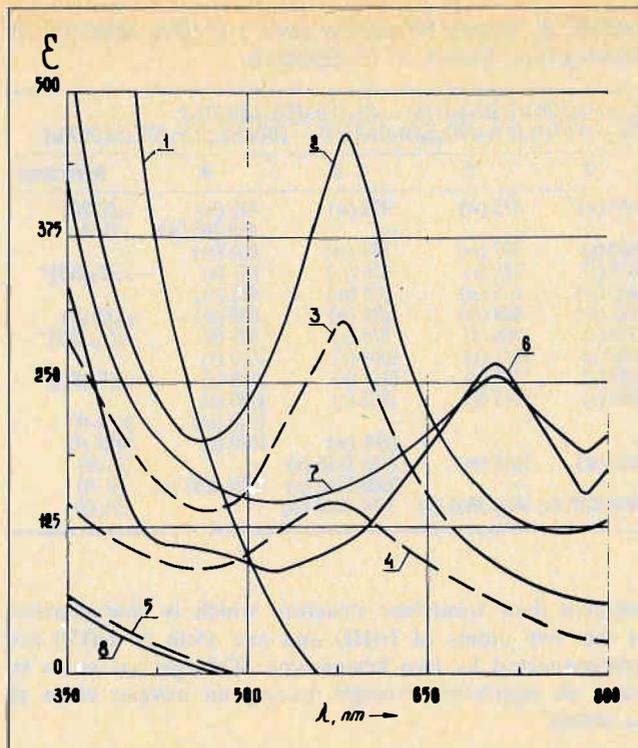


FIGURE 4. Organic phases after extraction of iridium sulphate complexes from a 0.5 M-sulphuric acid by 0.05 M-solutions of dodecyl amine (1 to 6.8) and trioctyl amine (7) and by respective alkyl ammonium salts (1.6 to 8). Solvent: decane, benzene, CCl_4 (7), hexane or decane + 10 vol.% of isoamyl alcohol.

(1) — $DDAH[Ir(SO_4)_2(H_2O)]$; (2) to (5) — organic phase after extraction of Ir(IV) aquo hydroxosulphate held at 25°C for 0(2), 2(3), 8(4) and 24(5) hours; (6) — $(DDAH)_4[O_2Ir_3(SO_4)_6(DDA)_3]$; (7) — $(TOAH)_4[O_2Ir_3(SO_4)_6(H_2O)_3]$; (8) — $(DDAH)_3[Ir_3(SO_4)_{12}H_2O]$.

TABLE 1. Results of an Elemental Chemical Analysis of Alkyl Ammonium Salts of Iridium Sulphate Complexes.

Composition	Ir	S	C	H	N
$(TOAH)_4[O_2Ir_3(SO_4)_6(H_2O)_3]$	21,4	6,95	44,8	8,43	2,45
	21,86	7,27	43,70	8,11	2,12
$(DDAH)_4[O_2Ir_3(SO_4)_6(DDA)_3]$	23,2	7,82	40,0	7,89	3,93
	23,37	7,78	40,8	7,82	3,97
$(DDAH)_3[Ir_3(SO_4)_{12}H_2O]$	13,8	8,50	46,6	9,43	4,54
	14,17	8,65	46,0	9,10	4,47
$DDAH[Ir(SO_4)_2(H_2O)_2]$	31,9	11,3	24,0	5,69	2,41
	31,71	11,06	23,75	5,28	2,31

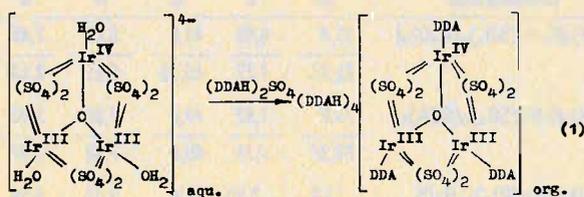
group, i.e. with the fact that they have a bridge or bidentate coordination in relation to iridium atoms. Medium-intensity bands at 687 to 690 cm^{-1} which are absent from IR-spectra of Ir(III) sulphates, are related to nonsymmetrical valency variations of the group Ir_3O which, according to references^(15,16), manifests itself in the region of 650 cm^{-1} . These data speak in favour of the fact that both inorganic and organic salts of Ir(III, III, IV) oxosulphates

TABLE 2. Wave Numbers (cm⁻¹) of the Maxima of Absorption Bands in IR-Spectra.

(1) — C ₃₀ H[O.Ir ₃ (SO ₄) ₆]; (2) — C ₃₄ [O.Ir ₃ (SO ₄) ₆ (H ₂ O) ₃]; (3) — (TOAH) ₄ [O.Ir ₃ (SO ₄) ₆ (H ₂ O) ₃]; (4) — (DDAH) ₄ [O.Ir ₃ (SO ₄) ₆ (DDA) ₃].				
1	2	3	4	Reference
440 (w)	423 (w)	425 (w)	440 (w)	$\nu_2(\text{E})\text{SO}_4^{2-}$
			490-500 (w)	$\nu(\text{Ir-N})$
590 (s)	597 (m)	597 (m)	600 (m)	
615 (s)	618 (s)	625 (m)	617 (s)	$\nu_4(\text{F}_2)\text{SO}_4^{2-}$
665 (m)	665 (w)	670 (m)	665 (m)	
687 (m)	688 (m)	690 (w)	690 (m)	$\nu_{\text{as}}(\text{Ir}_3\text{O})$
970 (s)	965 (s)	970 (s)	965 (s)	$\nu_1(\text{A}_1)\text{SO}_4^{2-}$
1038 (s)	1032 (s)	1064 (s)	1030 (s)	
1147 (s)	1139 (s)	1120 (s)	1132 (s)	$\nu_3(\text{F}_2)\text{SO}_4^{2-}$
1248 (s)	1245 (s)	1265 (s)	1235 (s)	
			1310 (m)	$\delta_{\text{s}}(\text{N-H})$
		1566 (w)	1520 (s)	$\delta_{\text{d}}(\text{N-H})$
1650 (w)	1635 (m)	1610-1655 (s)	—	$\delta(\text{H}_2\text{O})$
		3000-3100 (s)	3080-3200 (s)	$\nu(\text{N-H})$
3400-3550 (s)	3400-3500 (s)	3400-3500 (w)	—	$\nu(\text{H}_2\text{O})$

preserve their trinuclear structure which is characterized in that two atoms of Ir(III) and one atom of Ir(IV) are interconnected by two bridge-type SO₄²⁻-groups so as to form an equilateral triangle having an oxygen atom at its centre.

An IR absorption band found at 490-500 cm⁻¹ for dodecyl ammonium salt is related by us to the valency variations of the Ir-N bond. In the first place, this band is absent in the IR-spectra of other synthesized alkyl ammonium salts. In the second place, variations of the M-N bond manifest themselves in this region, in amino complexes of platinum and other transition metals⁽²⁰⁾. It should be noted that this band is absent in the spectra of other alkyl ammonium salts synthesized by us and wherein the composition of starting sulphate complex is not changed. It is worth-while noting that similar compounds are known also for Ir(III, IV, IV) nitride sulphate [N.Ir₃(SO₄)₆X₃]⁴⁻ (having a similar structure) wherein X is a nitrogen-containing ligand (NH₃, C₆H₅N)⁽²¹⁾. Hence, in the process of extraction of [O.Ir₃(SO₄)₆(H₂O)₃]⁴⁻ by n-dodecyl amine, the reaction of the complex formation is accompanied by a substitution of labile aquo groups which are in transposition with respect to the central oxygen atom by amine molecules according to Equation 1:



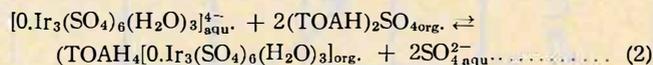
Dissociation of trioctyl ammonium Ir(III, III, IV) oxodisulphate does not take place in non-polar diluents. This fact enabled us to conduct parametric investigations of its solutions in benzene (rf. Table 3). The values of molecular masses obtained for the first time for this class of compounds are practically equal to the theoretically calculated ones in the region of low concentrations. This

TABLE 3. The Values of the Molecular Mass (TOAH)₄ [O.Ir₃(SO₄)₆ (H₂O)₃] (M.m. = 2638.6 gram)

Concentration in benzene	0,01	0,02	0,05	0,1
Molecular mass, gr.	2690	2760	2920	3020

fact confirms once more directly the composition of the synthesized complex, and, what is more important, it confirms the tri-nuclear structure of ion of Ir(III, III, IV) oxodisulphate both in aqueous and organic solutions. A small growth of the molecular mass with increasing complex concentration in benzene may be explained by its partial association.

Equilibrium of the reaction of complex formation in extraction of [O.Ir₃(SO₄)₆(H₂O)₃]⁴⁻ by tertiary amines may be generally represented by Equation 2.



The equations of the reactions of formation of compounds to be extracted and those of extraction of Ir(III) sulphate complexes by primary amines are similar to Equation 2.

Thus, we have established a possibility for a quantitative extraction of iridium sulphate complexes with base type extractants. The efficiency of extraction recovery is significantly influenced by the chemical and valency state of iridium in solutions, by the salt background and by the nature of diluents and extractants. It has been found that for all alkyl amines, complex sulphates of trivalent iridium and Ir(III, III, IV) oxodisulphate pass in the case of tertiary amines into organic phase without any change of the inner sphere, according to the extraspherical substitution mechanism. However, on using primary amines for Ir(III, III, IV) oxodisulphate, there may take place a mixed, intra- and extraspherical extraction mechanism wherein the amine molecules enter both the inner and outer spheres of a complex to be extracted.

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DISCUSSION

M. Germain: What experimental methods have you used to determine the composition of your complexes in both phases?

A.M. Orlov: Spectrophotometry, polarography, ion exchange and solvent extraction have been used to determine the composition of complexes.

L. Maya: What led to the development of these extraction systems? Are they used for metal separations? What is the evidence for a trimeric iridium complex? What is the evidence for the different oxidation states of the iridium in this trimeric complex?

A.M. Orlov: Extraction systems can be used for metal separation. The answer is given in the full text of the paper and also in the work published in the

Journal of Co-ordination Chemistry. V. 2, No. 7, 1976.

S. Dhara: (1) Under what conditions did you perform these experiments?

(2) Is it possible to separate base metals like Fe, Cu, Ni, etc. selectively by this SX technique?

(3) What was the ionic total concentration of Ir and other metals in the solution during extraction?

(4) What is the loading capacity of the solvent Wrt to Ir?

A.M. Orlov: (1) The experiments were performed under the following conditions: Ir concentration $(1.5-2.0) \cdot 10^{-3}$ g.at./l, amine concentration was 0.1 M in diluents, $t^\circ = 22^\circ\text{C}$, contact time — 3-5 min., $v_o/v_{aq} = 1$

(2) Yes, possible.

(3) See 4.

(4) In order to improve the kinetics, a large excess of solvent is used in this work.

W.R. Hatch: What is used as a reagent for stripping the IrIII and IrIV complexes from the loaded organic amine solution?

A.M. Orlov: This question was not considered in the present work.

1. The first part of the report deals with the general situation of the country and the position of the various groups of the population. It is a very interesting and detailed study of the social and economic conditions of the country and the position of the various groups of the population. It is a very interesting and detailed study of the social and economic conditions of the country and the position of the various groups of the population.

2. The second part of the report deals with the general situation of the country and the position of the various groups of the population. It is a very interesting and detailed study of the social and economic conditions of the country and the position of the various groups of the population.

CONCLUSION

The report shows that the country is in a state of economic and social development. The various groups of the population are in a state of economic and social development. The various groups of the population are in a state of economic and social development. The various groups of the population are in a state of economic and social development.

Chapter 10

Base Metals

Sessions 16 and 21



Dr. I.J. Itzkovitch



A. Van Peteghem

Session Co-Chairmen

Chapter 10

Basic Metals

Sections 17 and 18



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Section 17 and 18

Possibilities for the Use of Solvent Extraction in the Outokumpu Nickel Process

Raimo J. Leimala and Bror G. Nyman,
Outokumpu Oy, Harjavalta Works, Harjavalta, and
Metallurgical Research Centre, Pori, Finland.

Abstract

The applicability of solvent extraction to the Outokumpu nickel process has been investigated. Testwork at laboratory and pilot plant scale has shown that extraction and electrowinning of copper can be considered as an alternative to the present electrolytic copper removal system. A satisfactory copper removal was obtained with LIX 64N in two extraction stages. The suitability of solvent extraction for further catholyte purification has also been confirmed. Di-(2-ethylhexyl) phosphoric acid can be used for removal of zinc and cobalt. An increased selectivity can be achieved by a proper pH profile.

Introduction

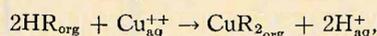
ONE OF OUTOKUMPU OY'S ACTIVITIES is the production of nickel. The process, which is a result of the company's intensive research work, is based on the use of the flash smelting method to produce high-grade matte, which then undergoes hydrometallurgical treatment to give electrolytic nickel as the final product⁽¹⁾.

The hydrometallurgical process (Figure 1) consists of grinding, leaching, solution purification, and electro-winning. The process works entirely on a sulphate basis. The purity of the final cathodes is equal to the best quality produced elsewhere in the world.

During the last five years we have been investigating the possibilities of utilizing solvent extraction in the nickel process. Three different areas of the process have been objects of more detailed studies, viz. removal of copper, zinc, and cobalt from the nickel sulphate solution.

Copper Extraction

The purpose of the copper removal in the Outokumpu nickel process is to provide an outlet for the copper content of the nickel concentrates. There is no need to produce a copper-free raffinate in the extraction step but it is necessary to remove a certain amount of copper. The solution from the copper removal stages is fed to the leaching reactors where no neutralizing agent is used because the hydrogen ions released in the extraction step, according to equation



will be useful in the leaching stage for dissolving metals. This requirement can be met with LIX reagents produced by General Mills, Inc.⁽²⁾, whereas carboxylic and phosphoric acids are not capable of extracting copper at pH values low enough.

We compared two commercial LIX reagents, LIX 64N and LIX 70 in batch tests. The properties of these reagents were very much alike with regard to extraction capacity and selectivity, but due to the ability of LIX 70 to extract

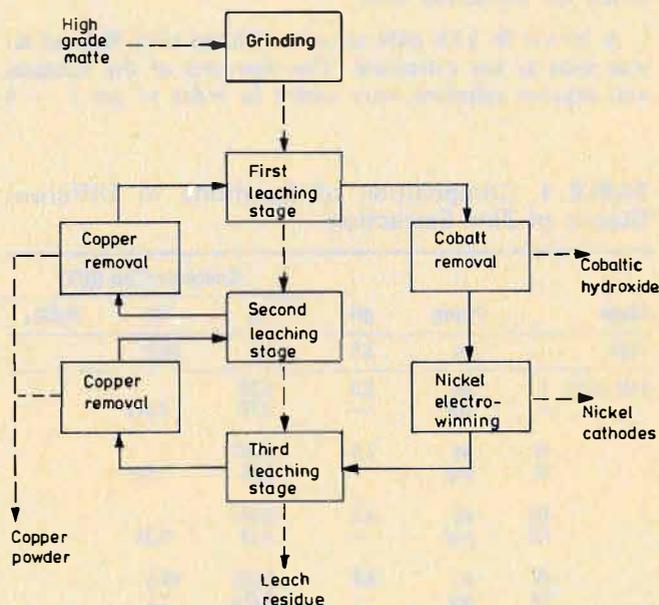


FIGURE 1. Flowsheet of the Harjavalta nickel refinery.

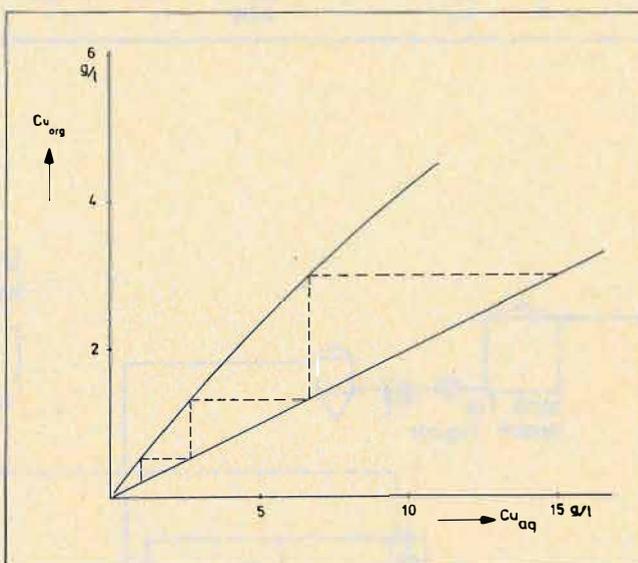


FIGURE 2. Extraction of copper by LIX 64N, McCabe-Thiele diagram.

copper at higher acidities the equilibrium curves were more favourable for LIX 70. The benefits of LIX 70 in the extraction section were, however, offset by more difficult stripping. The investigation was continued using LIX 64N because it was readily available and the batch tests showed that even with LIX 64N only two or three extraction stages were needed (Figure 2).

After the batch tests a pilot plant was run consisting of two extraction stages, two stripping stages, and an electrowinning cell (Figure 3). The pilot plant was built for an aqueous flowrate of 2 m³/h. The feed solution was taken directly from the nickel process and its composition varied within the following limits:

Ni	80 — 100 gpl,
Cu	3 — 20 gpl,
Fe	0 — 3 gpl,
Na ₂ SO ₄	150 — 200 gpl,
H ₂ SO ₄	2 — 22 gpl,

The feed solution was cooled to 50 — 55°C before entering the extraction unit.

A 20 vol % LIX 64N solution (diluted with Shellsol K) was used as the extractant. The flowrates of the aqueous and organic solutions were varied in order to get 3 — 4

gpl copper in the loaded organic phase (60 — 80% of maximum loading) and to meet the fixed capacity of the electrowinning cell. The great variations in the copper concentration of the feed solution made this task very difficult, however, and optimum conditions could not always be maintained. Nevertheless the extraction results were very good; usually more than 90% of the copper content was extracted leaving a raffinate with less than 1 gpl copper (Figure 4). At the same time, the sulphuric acid concentration in the raffinate rose to about 30 gpl. The elevated temperature was found to promote the extraction as reported by Itzkovitch et al⁽³⁾. A slight co-extraction of nickel and iron was observed. The amount of nickel extracted was 0.01% and that of iron 0.05%.

Stripping and Electrowinning of Copper

Stripping was performed in the normal way with the anolyte from the electrowinning cell. Two stripping stages were used and the stripping efficiency was about 80%. Stripping gave a pregnant electrolyte containing 40 — 60 gpl copper and 140 — 180 gpl sulphuric acid.

Electrowinning was done by using insoluble anodes of pure lead and a current density of 180 — 200 A/m². The temperature was 45-50°C without any separate adjustment. The cell voltage was 2.0 — 2.2 V and the average current efficiency was 90%. During the pilot test work a total amount of 60 ton copper was produced and the purity of the cathode was satisfactory, the greatest impurities being sulphur 45 ppm, iron 22 ppm, and nickel 15 ppm. The impurities were found to be strongly concentrated at the edges of the cathodes.

TABLE 1. Composition of Solutions in Different Stages of Zinc Extraction.

Stage	Phase	pH	Concentration (g/l)		
			Zn	Ni	H ₂ SO ₄
Feed	aq	3.5	1.3	86.2	
Extraction	I	aq	0.38		
		org	3.79	0.011	
	II	aq	0.047		
		org	1.05	0.049	
	III	aq	0.003		
		org	0.14	0.34	
	IV	aq	0.001	85.5	
		org	0.016	2.1	
Stripping	I	aq	0.84	0.004	99.8
		org	0.21		
	II	aq	16.7	0.047	84.4
		org	0.010		

Removal of Zinc

The flowsheet of Harjavalta Nickel Refinery, shown in Figure 1, does not include any particular step for removing zinc. Until lately our raw materials have contained very little zinc and the amount of zinc has been

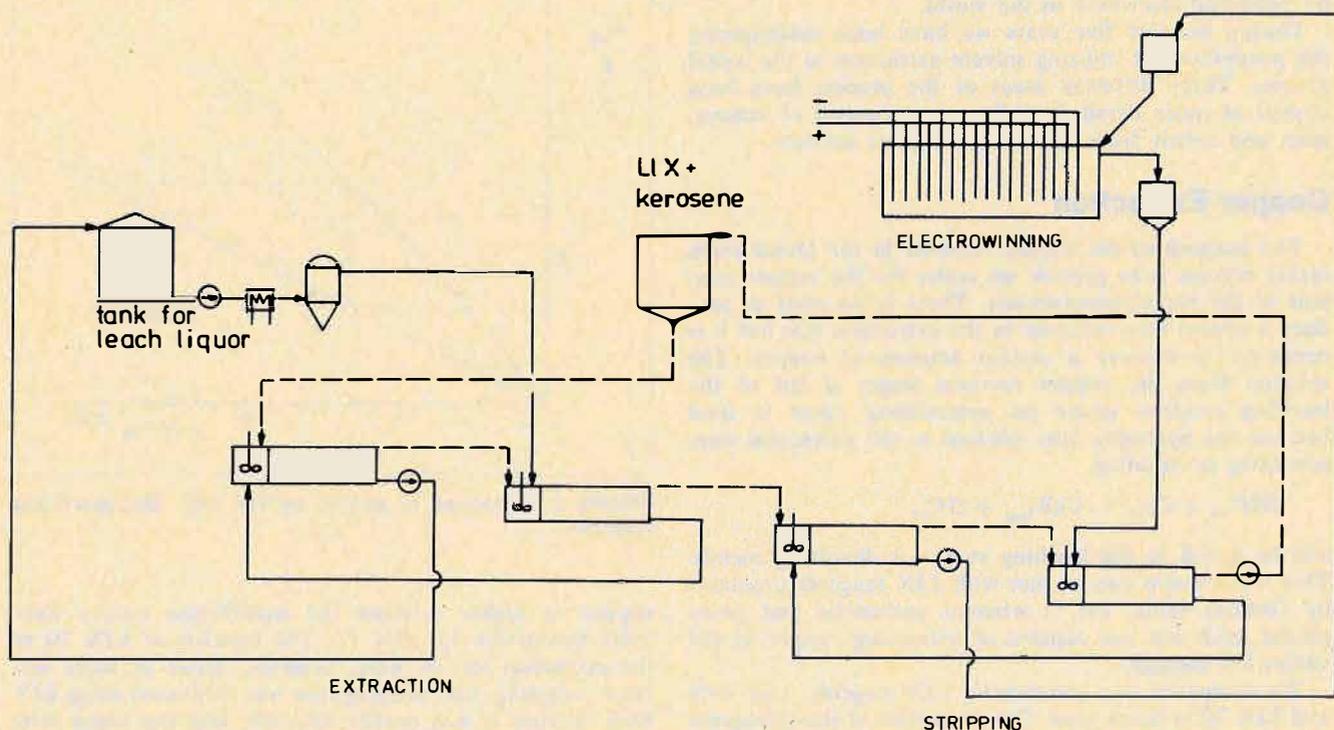


FIGURE 3. Flowsheet of copper extraction from a nickel sulphate solution.

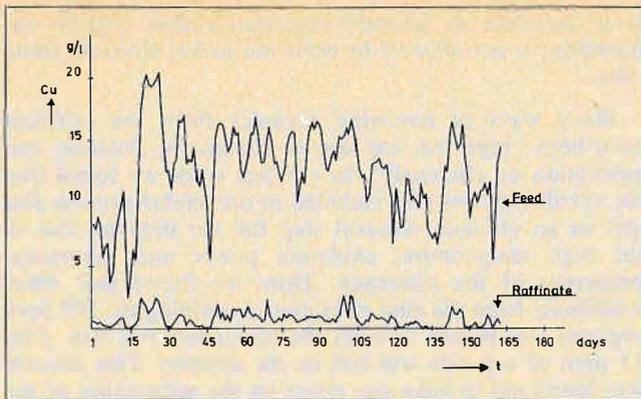


FIGURE 4. Copper contents of the feed solution and the raffinate.

further reduced during the smelter process. Small amounts of zinc can also be rejected by the leaching and cobalt removal steps. If the amount of zinc in the high-grade matte increases, a separate step for zinc removal will be needed. For this purpose we found the extraction by di-(2-ethylhexyl)phosphoric acid (HDEHP) to be very suitable.

Extraction of metals by HDEHP is highly dependent on pH (Figure 5). This figure shows that zinc can be separated from nickel at a pH of 2 — 4, especially when there is practically no iron or copper present after the leaching step. If the amount of zinc in the solution is high enough to cause a considerable decrease of pH during the extraction, advantage may be taken of the improved purification effect obtained by means of careful pH control during the extraction based on continuous measurement of pH. By this means an increased selectivity can be obtained.

Our experiments were carried out with nickel sulphate solutions containing about 90 gpl nickel. Several different zinc levels were used ranging from 10 mgpl to 2 gpl. Both bench scale and pilot plant tests were carried out. In each case it was possible to get a raffinate containing a max of 1-2 mgpl zinc using 2-4 extraction stages, when the concentration of HDEHP and the flow ratio aqueous/organic were chosen properly.

The co-extraction of nickel was found to be dependent on the zinc concentration in the organic phase and the pH values in the extraction stages (Figure 6). For example, when extracting zinc from a solution containing 1.3 gpl zinc and 90 gpl nickel, according to the flowsheet shown in Figure 7, a ratio Zn/Ni of at least 200 could easily be obtained in the strip solution, while the zinc level of the raffinate was brought down to 1 mgpl (Table 1).

Similar extraction tests were also carried out with a cobalt-nickel solution containing up to 15 gpl zinc. Even in this case it was possible to achieve a raffinate with only 1 mgpl zinc and a strip solution where the ratio Zn/Co+Ni was close to 500 or even higher.

Separation of Cobalt and Nickel by HDEHP

As reported by Ritcey et al.⁽⁴⁾, HDEHP can also be used for separation of cobalt from nickel in a sulphate solution. A high number of extraction stages are needed, however. In our test work we have found that the number of extraction stages can be reduced if the aqueous phase contains magnesium and the extraction is carried out

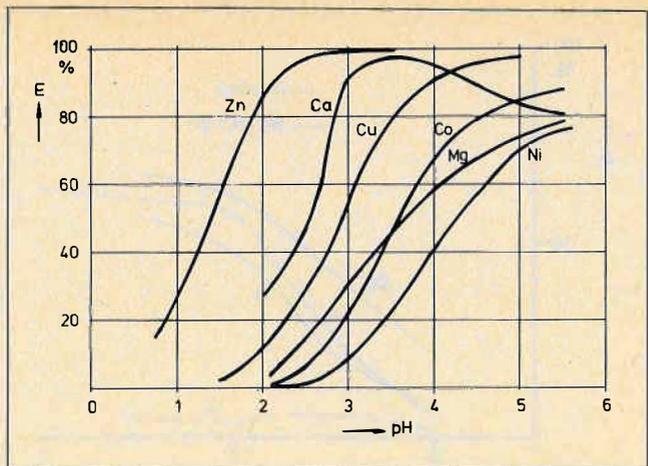


FIGURE 5. Extraction of some metals with HDEHP.

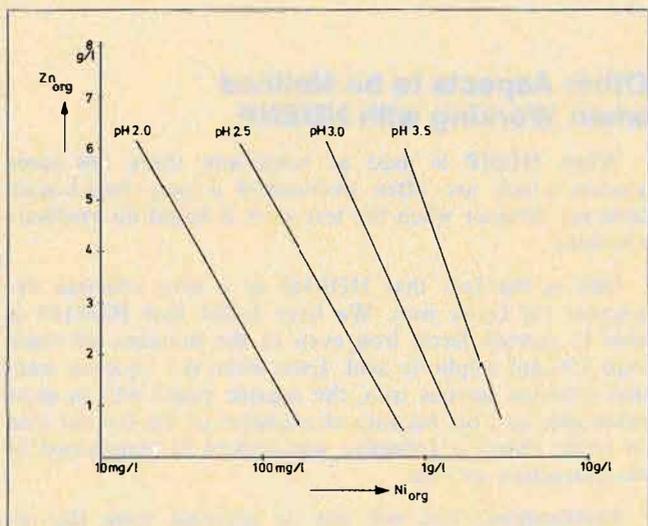


FIGURE 6. Co-extraction of nickel.

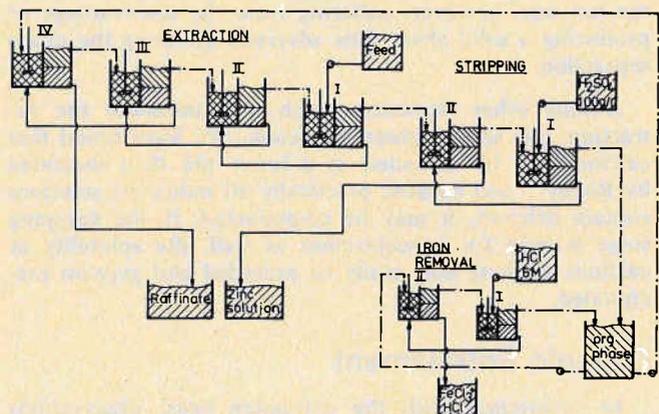


FIGURE 7. Flowsheet for zinc extraction.

at pH 4 — 7, where the extraction curve for magnesium lies between those of cobalt and nickel (Figure 8). A magnesium sulphate solution can also be used for scrubbing of nickel from the loaded organic phase.

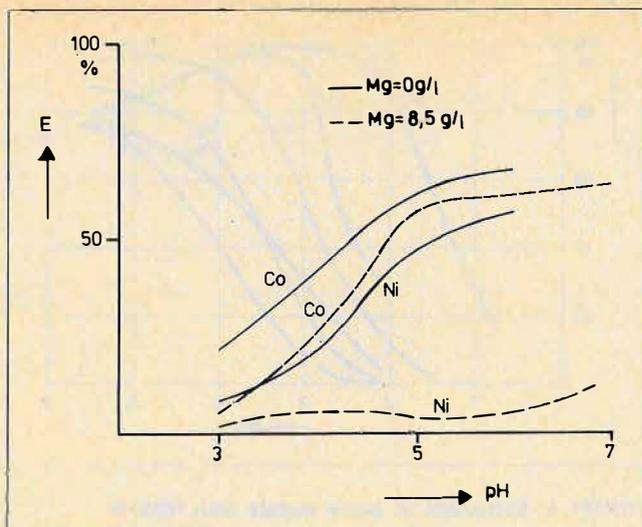


FIGURE 8. Effect of magnesium on the extraction of cobalt and nickel with HDEHP.

Other Aspects to be Noticed when Working with HDEHP

When HDHP is used as extractant, there are some aspects which are often overlooked if only bench-scale tests are done or when the test work is based on synthetic solutions.

One is the fact that HDEHP is a very efficient extractant for ferric iron. We have found that HDEHP is able to extract ferric iron even in the presence of more than 100 gpl sulphuric acid. Even when the aqueous solution contains ferrous iron, the organic phase will in most cases take up iron, because of oxidation of the ferrous iron to ferric unless a reductive atmosphere is maintained in the extraction section.

Furthermore, iron will not be removed from the organic phase during a normal stripping procedure and will accumulate in the organic phase. For an effective stripping of iron, hydrochloric acid (optimum 6 M) must be used. The use of carbohydrates⁽⁵⁾, phosphoric acid and ammonia⁽⁶⁾ has also been suggested for stripping iron — the last one, however, suffering from the disadvantage of producing a solid phase thus adversely affecting the phase separation.

Among other elements, which may influence the extraction, one should observe calcium. We have found that calcium will be extracted at a lower pH than indicated by Ritcey⁽⁷⁾ and because practically all industrial solutions contain calcium, it may be co-extracted. If the stripping stage is used for concentration as well, the solubility of calcium sulphate may easily be exceeded and gypsum precipitated.

Organic Entrainment

In connection with the extraction tests, observations were also made on the effects of organic entrainment on the succeeding process steps. In the copper extraction system the organic entrainment did not cause any special problems. During one part of the zinc extraction studies the extraction step was followed by nickel electrowinning. It was found that even relatively small amounts of organics can have a detrimental effect on the appearance of the nickel cathodes. Both the extractant and the diluent caused pitting on the cathodes at concentrations down to 50 ppm.

It is therefore of primary importance that organic entrainment is not allowed to enter the nickel electrowinning cells.

Many ways of removing organics from the raffinate have been reported, e.g. use of coalescers, flotation and adsorption on charcoal⁽⁸⁾. In our test work we found that the cobalt removal step included in our nickel process also acts as an efficient removal step for the organics due to the high temperature, oxidation power and adsorption properties of the filtercake. Thus, we found that when a raffinate from the zinc extraction containing ca. 500 ppm organics was passed through the cobalt removal step, only 11 ppm of organics was left in the solution. This amount was found not to have any effect on the appearance of the nickel cathodes.

Summary

This investigation has shown that solvent extraction can easily be introduced into the Outokumpu nickel process either to replace existing steps or as an additional step to give the process a broader region of application.

The necessary outlet for copper can advantageously be provided by solvent extraction with LIX reagents combined with copper electrowinning. The extraction can be done without neutralization and the acidity generated can be utilized in the leaching section. The copper is produced as cathodes of good quality.

For removing zinc, an extraction method has been developed and tested with several zinc levels ranging from 10 to 2000 mgpl. With a properly designed extraction system and using di-(2-ethyl hexyl) phosphoric acid as extractant, the amount of zinc can be reduced to 1 mgpl.

Entrainment of organic extractant or diluent in the nickel electrolyte was found to adversely effect the quality of the nickel cathodes. However, the cobalt removal step in the Outokumpu nickel process acts as an efficient removal step for organics. This effect could also be utilized in other processes where an extraction stage is to be followed by nickel electrowinning.

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DISCUSSION

C. Bozec: At which level of zinc content in the electrolyte do you consider that a specific zinc removal step by SX could be decided; for instance, in terms of mg/l or in terms of % in the solid concentrate feed?

R.J. Leimala: In order to make nickel cathodes of good quality the zinc concentration in the catholyte should be below 2 mg/l.

C. Bozec: The destruction, or removal, of entrained organics in the Co-removal cake—is it made by repulping this cake in the polluted solution?

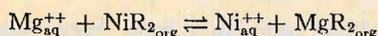
R.J. Leimala: The removal of entrained organics takes place in connection with the cobalt removal stage, where a slurry of nickelic hydroxide is added to the solution.

D.S. Flett: At Warren Spring Laboratory we have carried out extended work on the removal of zinc from nickel sulphate solution with DEHPA and would agree with the results of the present author. We have found that use of the nickel salt of DEHPA as the extractant was advantageous. Have the authors considered this in their work?

R.J. Leimala: It is possible to use the nickel salt of the extractant, but then an additional contact stage is required for conversion of the extractant to its nickel salt. Furthermore, the equilibrium between protons in the aqueous phase and nickel in the organic phase limits the choice of pH values in the extraction stages. Consequently the use of the nickel salt makes it necessary to strictly control the phase ratio in order to avoid a serious loss of selectivity. According to our experience it is easier to accomplish a sharp metal separation if the generated acid is directly neutralized in the mixers at an advantageous pH level.

D.S. Flett: The effect of $MgSO_4$ on cobalt/nickel separation is very interesting. In our work we found that increasing Na_2SO_4 concentration also depressed nickel extraction and also reduced the aqueous solubility of DEHPA. Would the authors speculate on the chemistry behind the effect of $MgSO_4$ on cobalt/nickel separation?

R.J. Leimala: In our opinion the effect of $MgSO_4$ on the cobalt/nickel separation is best explained by Figure 5 of our paper which shows that at pH values greater than about 3.5 the element which will be extracted next after cobalt is magnesium and not nickel as would be the case in the absence of magnesium. This also means that in this region the equilibrium of the reaction



is shifted to the right.

Our test work was done mainly with technical solutions from the nickel refinery and whence the Na_2SO_4 concentration was almost constant.

D.S. Flett: Finally, I would like to endorse the speaker's remarks with regard to the problems associated with ferric iron and calcium in DEHPA systems.

R.J. Leimala: Thank you for your comment.

A.J. Oliver: Comments on the question of Ca with DEHPA may be somewhat confusing and I attribute this partly to the tendency to report extraction only in terms of % extraction vs pH. When the relative concentrations in solution are considered, Ca is no more than 0.5 g/l while Ni or Co may be 10 - 80 g/l. The higher concentration clearly gives a higher driving force for the extraction of these transition metals.

Related to this point, could you tell us the loading capacity of the organic which is being utilized in the extraction of Zn and Co? When high loading capacity is used, what is the level of Ca in the organic phases?

R.J. Leimala: The way of presenting the extraction results as % extraction vs pH is not a scientific one, because different curves will be achieved depending on the concentration of the metals. For an actual separation problem, where you have a solution with relatively fixed amounts of the different metals, this presentation has many advantages, however. Figure 5 is constructed with a concentration of 0.15 moles/liter for each of the metals except for calcium where the concentration at

saturation (measured to be 0.7 g/l = 0.018 M) was used. The total concentration of metals in the solution was 0.6 M in each case.

In our experiments the metal concentration has been varied within a wide range and we have used both high and low loading capacities. The concentration of calcium in the organic phase is not a function of the loading capacity alone but depends very much on the metal in the organic phase. So as an example, when a 20% DEHPA solution was loaded to 85% of its capacity it contained 0.13 g/l calcium (extraction 19%) when the organic phase was loaded mainly with zinc, but 0.57 g/l and 0.60 g/l (extraction 84%, 88%), when the organic phase was loaded mainly with copper or cobalt and nickel, resp.

J.H. Setchfield: Have you studied the effect of temperature on the separation of cobalt and nickel with D2EHPA? In our experience the effect of temperature is considerable.

R.J. Leimala: In the case of cobalt/nickel separation we have not so far studied the effect of the temperature.

J.H. Setchfield: The use of magnesium to "crowd out" nickel from the organic phase is interesting. Whilst this may have advantages for the purity of the nickel raffinate, does it not lead to considerable contamination of the cobalt sulphate strip liquor and possibly, therefore, contamination of cobalt salts or precipitates?

R.J. Leimala: The contamination of the cobalt solution is dependent on how the scrubbing and stripping stages are performed.

H. Jedlicka: What do you make with the $FeCl_3$ -HCl-efluent from the Zn-removal system? One economic way could be the spray-roasting process to get back the HCl and produce high-grade Fe_2O_3 .

R.J. Leimala: In our cases the amount of iron removed from the organic phase has been too small to be economically recovered.

A. Georgeaux: Do you have any problem with co-extraction of Cl^- in the solvent at the stage of Iron removal?

R.J. Leimala: The coextraction of chloride is quite small especially because only 5 - 10% of the organic flow is cycled through the iron removal stage. If the coextraction of chloride is considered too big, it can be removed by adding a wash stage (pure water).

R. Georgeaux: What is the concentration of iron before and after iron removal?

R.J. Leimala: The concentration of iron both before and after the iron removal depends on the values selected for the different process variables. In our case the iron removal was usually performed at a high O/A ratio, taking only a small fraction of the total organic flow to the iron removal unit.

H. Ottertun: A process for extraction of zinc with HDEHP is described in the paper. The feed liquor contains some iron and the extraction is performed at a pH-value in the region of 2 to 4. Some extraction of iron cannot be avoided. The process contains a strong sulphuric acid stage for iron stripping. Can the process be run in the described manner without excessive accumulation of iron in the organic phase?

R. Leimala: No accumulation occurred in a pilot run, where only a bleed of the organic phase was taken to the iron stripping stage, where it was contacted with 5M H_2SO_4 . High concentrations of iron in the strip liquor were obtained.

Solvent Extraction of Base Metals Using in-Situ Neutralization with Lime

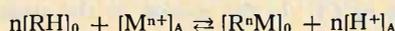
V.A. Ettel, Section Head, Electrochemistry Section
 J. Babjak, Senior Research Engineer, Electrochemistry Section
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Abstract

Solvent extraction of base metals from leach solutions was studied using in-situ neutralization with lime. The feasibility of this process was successfully demonstrated for several different systems in an integrated, continuously operating "miniplant". The advantages of this concept include very favourable extraction equilibria which permit more complete metal recovery in fewer stages, a relatively low base cost and an environmentally acceptable effluent. The organic losses in the produced gypsum were small compared to the losses due to reagent solubility in the raffinate.

Introduction

THE SELECTION OF SOLVENT EXTRACTION REAGENTS for the recovery of base metals from sulfate solutions is generally limited to two types, acidic and chelating extractants. Metal recovery with a reagent of either type involves the transfer of an equivalent quantity of hydrogen ions from the organic to the aqueous phase, as illustrated by the following reaction:



where:

- RH = acidic or chelating extractant
- Mⁿ⁺ = n - valent metal ion
- O, A = organic and aqueous phase respectively

It is obvious that the extraction equilibrium could be enhanced considerably by neutralizing the liberated acid.

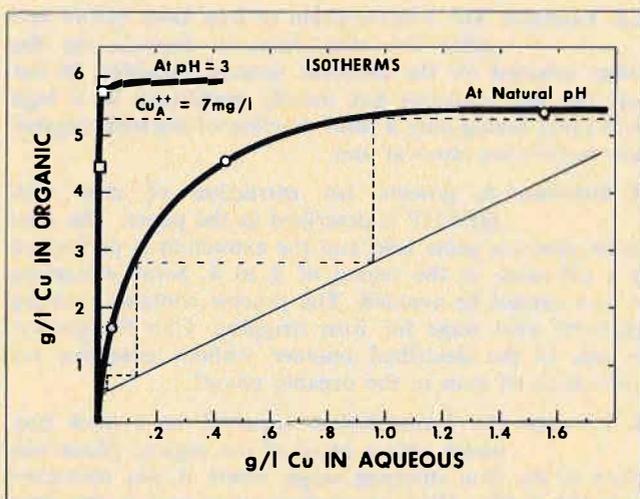


FIGURE 1. Cu — LIX65N isotherm.

For example, extracting Cu from a sulfate solution analysing 2 g/l Cu, using LIX 65N extractant (supplied by General Mills) would require 4-5 theoretical stages to produce a raffinate containing 10 mg/l Cu. On the other hand, only one theoretical stage would be needed if the pH is controlled at about 3 during the extraction (Figure 1). This is very convenient when there is no advantage in reusing the liberated acid. In fact, some commercial processes use this approach, e.g., the S.E.C. process⁽¹⁾ in which NH₃ is added during the extraction to maintain a desired pH, and the Arbiter process⁽²⁾ in which the extraction is carried out from an ammoniacal leach liquor.

The high degree of extraction achievable with pH control is particularly attractive since it allows virtually complete metal-metal separations. For example, Cu can be extracted from Cu and Ni containing solutions so selectively and completely that neither the copper containing strip liquor, nor the nickel containing raffinate, contain appreciable quantities of the other metal. In some applications, such as extracting Ni with acidic or chelating reagents, pH control is essential, otherwise the degree of extraction is impractically small.

Neutralization Techniques

Several pH controlling techniques have been recommended in the literature. Some of these methods are as follows:

- (1) Adding a base to the aqueous feed solution prior to the loading to cause the precipitation of metal hydroxides, which are then redissolved during extraction⁽³⁾ (Figure 2). An obvious disadvantage of this method is the possibility of crud formation. Also, the rate of extraction may in some cases be inadequate.
- (2) Adding a base to a recycled aqueous stream to neutralize acid generated during the extraction⁽⁴⁾ (Figure 3). This approach is obviously applicable only when using reagents capable of extracting metal values at a relatively low pH.
- (3) Contacting the organic feed with a base prior to the loading to convert an organic acid into its salt (regeneration of organic) which is then used for extracting the desired metal(s). This can be done in the presence or,

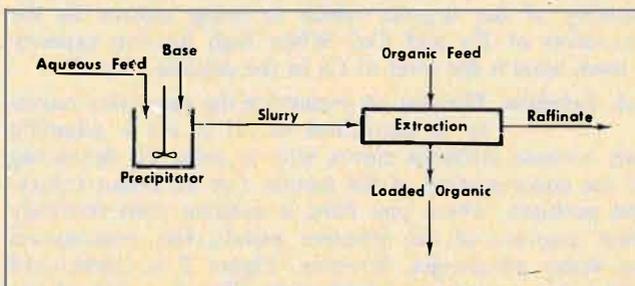


FIGURE 2. Extraction of metals from hydroxide slurry.

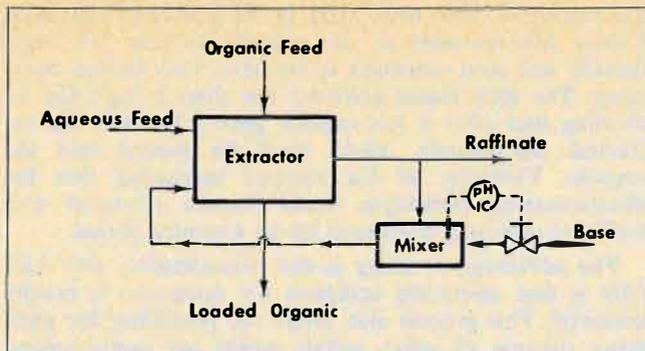
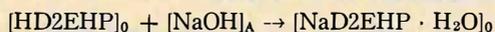


FIGURE 3. Neutralization of acid during extraction.

in some cases, even in the absence of the aqueous phase. An example of the latter is the regeneration of di-(2-ethyl-hexyl) phosphoric acid (HD2EHP) organic using concentrated NaOH⁽⁵⁾,



Water introduced with NaOH and also that produced by the reaction remains dissolved in the organic phase, so that no separate aqueous phase is present. One might expect that controlling the degree of regeneration could be difficult in this case. Surprisingly, however, we have found that ordinary pH electrodes and meters can be used for this control. The pH meter reading may not be a true indication of H⁺ activity but it is a function of degree of organic regeneration, as shown in Figure 4, and can therefore be used as a means of control. The method was tested on a continuous basis for an extended operating period with HD2EHP extractant and was found very reliable. The meter reading deviated by less than ±0.1 pH unit from the end point preset value. In general, this technique can be used conveniently for regenerating acidic extractants but is not always applicable in regenerating chelating extractants. For example, LIX reagents precipitate from the organic phase when contacted with NaOH.

(4) The method which seems most practical, however, is to add the neutralized agent directly to the mixer with pH electrodes immersed in the dispersion for control of this addition (Figure 5). Surprisingly, conventional glass electrodes perform very reliably in these dispersions. This type of operation is already used by S.E.C. Corporation⁽¹⁾ using ammonia as the base and by others^(6,7). We have studied several such systems in our laboratory using this technique, which we call extracting with in-situ neutralization, and have found it very reliable. The pH normally deviated by less than ±0.1 unit from the preset value, and the electrodes did not require frequent cleaning.

Choice of Base

Neutralizing reagents most often used in SX are NaOH, Na₂CO₃, and NH₃. These agents are not only expensive but also contribute to the problems of producing an environmentally acceptable effluent. Although NH₃ might be recovered from the raffinate stream by lime addition-boiling techniques, the cost of this operation might well exceed the cost of the SX operation. In addition, this technique alone may not be adequate to meet NH₃ pollution standards.

Lime, on the other hand, is a very desirable neutralizing reagent since it is relatively cheap and the resulting gypsum is quite acceptable environmentally. On the basis

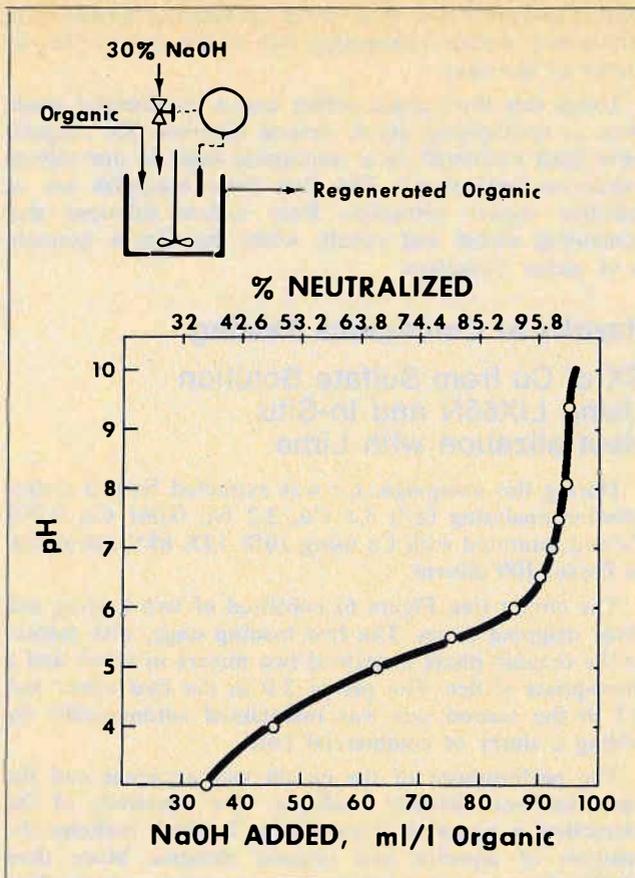


FIGURE 4. Regeneration of HD2EHP organic with 30% NaOH.

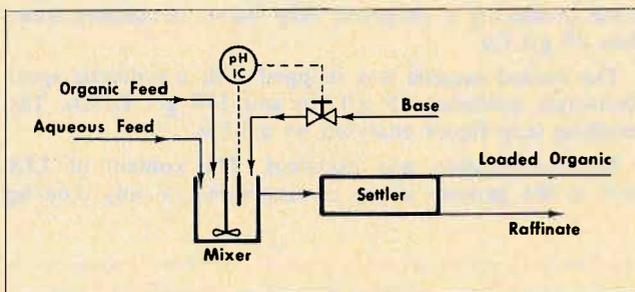


FIGURE 5. Extracting with in-situ neutralization.

of its acid neutralizing ability, lime is one sixth the price of NaOH. However, it has until now found only very limited acceptance^(8,9,10) as a neutralizing agent in SX processes, due to a generally held view that the presence of any type of solids in SX systems is detrimental and also due to the unavailability of suitable equipment to contact and separate the three phases of this system.

Neutralization with Lime

When lime is used to neutralize, a mixture of, e.g., organic containing LIX 64N extractant and copper sulfate leach liquor, a dispersion of three phases (organic, aqueous and gypsum solids) is produced. Conventional liquid-liquid settlers are not suitable for separating such dispersions since crud usually accumulates at the interface and prevents gravity separation of the dispersion. We have studied this problem extensively and succeeded in developing a simple settling apparatus capable of separating

such dispersions into their three component phases. Unfortunately details concerning this device cannot be released at this time.

Using this three-phase settler and a commercial grade lime as neutralizing agent, several common SX reagents have been evaluated on a continuous basis in our solvent extraction "mini-plant". The first three examples are of selective copper extraction from sulfate solutions also containing nickel and cobalt, while the fourth example is of nickel extraction.

Results of Continuous Testing

SX of Cu from Sulfate Solution Using LIX65N and In-Situ Neutralization with Lime

During this campaign, Cu was extracted from a sulfate solution analysing (g/l) 5.4 Cu, 2.2 Ni, 0.061 Co, 0.007 Fe and saturated with Ca using 10% LIX 65N extractant, in Escaid 100 diluent.

The circuit (see Figure 6) consisted of two loading and three stripping stages. The first loading stage, with respect to the organic phase contained two mixers in series and a three-phase settler. The pH of 2.0 in the first mixer and 2.5 in the second one was maintained automatically by adding a slurry of commercial lime.

The performance of the circuit was excellent and the operation was virtually crud-free. The selectivity of the extraction is apparent from Figure 7 which includes the analyses of aqueous and organic streams. More than 99.9% Cu was extracted in two counter-current loading stages while Ni extraction was negligible. It should be pointed out that achieving the same degree of Cu extraction without pH control would require stripping Cu from the organic to a very low value. This in turn would preclude producing a pregnant strip liquor containing more than 40 g/l Cu.

The loaded organic was stripped with a synthetic spent electrolyte analysing 45 g/l Cu and 150 g/l H₂SO₄. The resulting strip liquor analysed 64 g/l Cu.

Phase separation was excellent. The content of LIX 65N in the gypsum slurry corresponded to only 0.6¢/kg

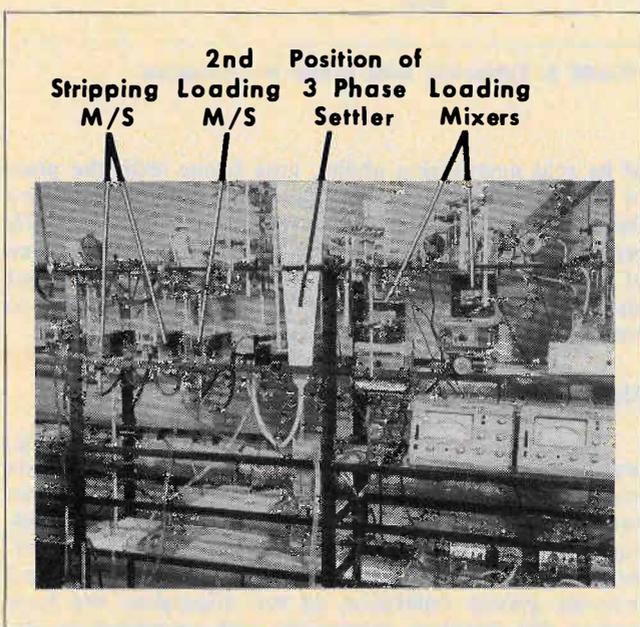


FIGURE 6. Cu — LIX65N solvent extraction circuit.

Cu extracted (LIX 65N price of \$2.5/lb was assumed). Cobalt concentration in the organic reached 5-6 mg/l initially and then remained at this level with further operating. The strip liquor analysed less than 1 mg/l Co indicating that after a few organic passes, Co was not extracted. Surprisingly, 10-15 mg/l Ca loaded into the organic. Virtually, all Ca stripped suggesting that the electrowinning electrolyte would become saturated with CaSO₄ if operating continued for an extended period.

The advantage of using in-situ neutralization with LIX 65N is that essentially complete Cu extraction is readily achieved. This process also offers the possibility for purifying streams of other metals which are contaminated with copper, e.g. Ni and Zn electrolytes. Very few stages are required as compared to conventional LIX operations and this could result in significant capital cost savings.

SX of Cu from Sulfate Solution Using D2EHP and In-Situ Neutralization with Lime

During this campaign, Cu was extracted from a sulfate leach solution assaying (g/l) 16.8 Cu, 84.9 Ni and 5.6 Co using 10% di-(ethylhexyl) phosphoric acid extractant (supplied by Union Carbide) (HD2EHP) in Shell Livestock spray base oil (SLSBO) diluent (supplied by Shell Canada Ltd.).

The circuit (Figure 8) comprised 3 loading stages, 1 stripping stage and an electrowinning cell. The first loading stage with respect to the organic phase comprised a mixer and a three-phase settler. The other two loading stages and the stripping stage were conventional mixer-settlers. Lime was added on demand to the first mixer to maintain pH <4.0-4.2>.

The results of this campaign were again most encouraging as can be seen from the analyses of the aqueous and organic streams in Figure 9. Approximately 97% Cu was extracted. Phase separation in the three-phase settler was excellent. The amount of D2EHP entrapped in the gypsum slurry corresponded to 1¢/kg Cu extracted (assuming \$1.25/lb. D2EHP). Surprisingly, the co-extraction of Ca was not significant, although D2EHP loads Ca quite readily. The loaded organic contained 2-5 mg/l Ca and the stripped organic analysed 2 mg/l Ca.

Copper can be stripped in one stage using a spent electrolyte assaying 60 g/l Cu and 150 g/l H₂SO₄ to produce a strip liquor analysing 85 g/l Cu. Electrowinning from such strip liquor reduces the size of the tankhouse considerably, relative to a conventional LIX/Cu System. However, operating at these Cu concentrations in our

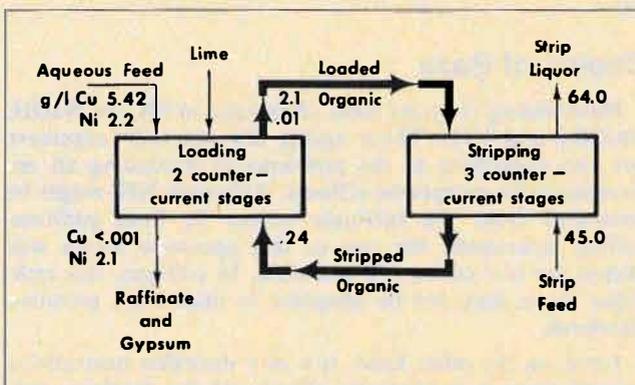


FIGURE 7. Cu — LIX65N solvent extraction flow diagram.

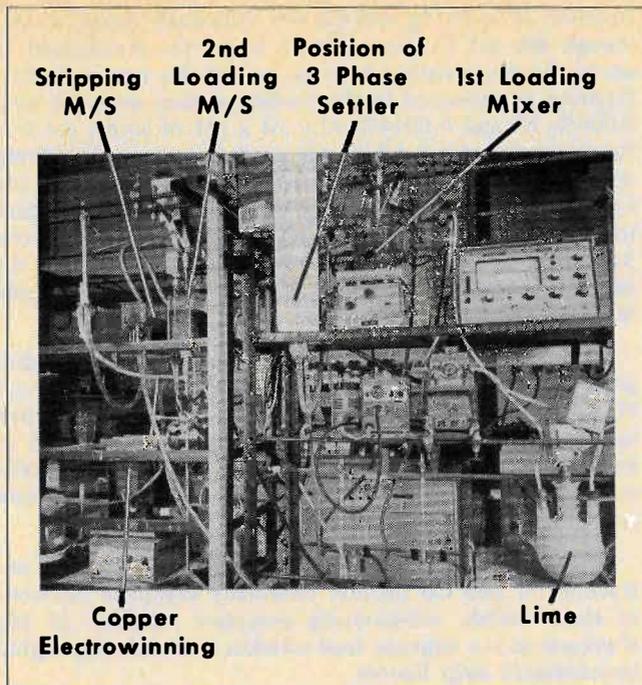


FIGURE 8. Cu — D2EHP solvent extraction circuit.

small-scale circuit was not possible due to the crystallization of CuSO_4 in the strip liquor lines overnight.

Cu was electrowon at a current density of 300 A/m^2 , from an untreated strip liquor analysing 60 g/l Cu , with the addition of Dowfax 2A0 anti-misting agent ($6\text{--}7 \text{ g/kg Cu}$ plated) and Jaguar guar gum derivative ($\sim 1.2 \text{ g/kg Cu}$ plated). No detrimental effects of these additives on the performance of the SX circuit could be detected during some 500 organic passes. Cu deposits had very good appearance and analysed (ppm) $<1 \text{ Co}$, $<1 \text{ Ni}$, $<1 \text{ Zn}$, $<1 \text{ Fe}$, $<0.5 \text{ Ca}$, $<5 \text{ S}$, $<0.5 \text{ Si}$, $\sim 0.5 \text{ Al}$, $\sim 1.5 \text{ Pb}$; P and C contents were below detectable limits.

The advantage of using D2EHP organic is the high loading capacity and the ease of stripping. It also permits treating solutions high in Co without a danger of irreversibly loading Co into the organic. The process is ideally suited to colder climates for it overcomes two major objections of a conventional LIX operation. Firstly, the large mixer-settlers must be enclosed and secondly, very large volumes of heated air must be used to ventilate the tank-house since anti-misting agents cannot be used due to their harmful effects on the LIX reagents. The high loading, fewer stages required and highly concentrated strip liquor achieved with D2EHP result in much smaller plant size requirements. Moreover the D2EHP has proved quite compatible with the most common anti-misting agent, Dowfax 2A0.

SX of Cu from Sulfate Solution Using Versatic Acid - 10 and In-Situ Neutralization with Lime

Cu was selectively extracted from a sulfate solution analysing (g/l) 15 Cu , 18 Ni and 1.3 Co using 40% Versatic acid -10 extractant (supplied by Shell Canada Ltd.) in kerosene. The circuit included loading in 2 three-phase mixer-settlers, stripping in one conventional type mixer-settler and Cu electrowinning in a 10l cell. Lime was added on demand to both loading mixers to maintain a pH of 4.2 in the first aqueous phase mixer and 4.9 — 5.0 in the second one.

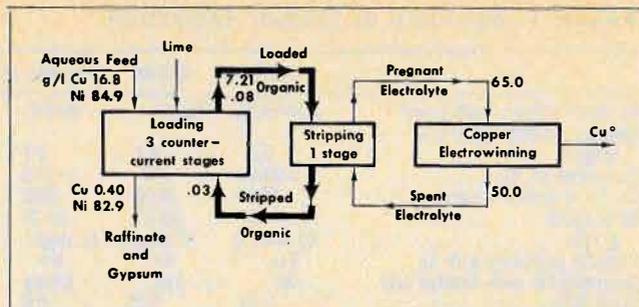


FIGURE 9. Cu — D2EHP solvent extraction flow diagram.

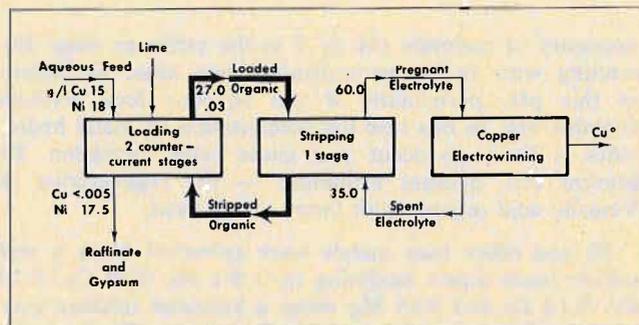


FIGURE 10. Cu — Versatic 10 solvent extraction flow diagram.

The flow diagram of the circuit and steady-state analyses of aqueous and organic streams are shown in Figure 10. More than 99.9% Cu was extracted while the co-extraction of Ni, Co and Ca was negligible. The loaded organic analysed 23-27 g/l Cu but only about 3 mg/l Ca and 30 mg/l Ni. Phase separation in the three-phase settlers was excellent. The concentration of Versatic acid in the produced gypsum slurry was the same as that in the solids-free raffinate indicating negligible entrainment of the organic in the slurry.

Copper was stripped from the loaded organic in one stage using a spent electrolyte analysing approximately 35 g/l Cu and $150 \text{ g/l H}_2\text{SO}_4$. The resulting strip liquor analysed 60 g/l Cu . It should be pointed out, however, that a strip liquor containing 80-85 g/l Cu could easily be obtained from the loaded organic, if desired.

Cu was electrowon directly from the strip liquor as produced (i.e. without any pre-treatment) at a current density of 300 A/m^2 with the addition of Jaguar ($\sim 1 \text{ g/kg Cu}$ plated). The deposits had very good appearance.

The use of Versatic acid for extracting Cu offers some advantages over previously mentioned LIX65N and HD2EHP reagents. In particular, it has much higher loading capacity than LIX65N and better selectivity than HD2EHP. A more complete comparison of these three systems is given in Table 1.

SX of Ni from Real Sulfate Leach Liquor with Ca Versatate*

Versatic acid-10 can also be used for extracting Ni and Co from sulfate solutions at pH's higher than those used for selective Cu extraction. In order to achieve essentially complete recovery of Ni using this reagent it is

*Ca salt of Versatic acid-10.

TABLE 1. Summary of Copper Extraction

	LIX65N	D2EHP	Versatic 10
Fe removal from leach liquor...	Not req'd.	Req'd.	Req'd.
Loading capacity g Cu/v/o reagent.....	0.3	0.7	0.7
Cu recovered, %.....	>99.9	97	>99.9
Cu/Ca in loaded organic.....	250	2500	9000
Strip liquor.....	64	80-85	80-85
g/l Cu.....	(3 stages)	(1 stage)	(1 stage)
Possible poisoning with Co.....	Yes	No	No
Compatibility with Dowfax 2A0.....	No	Yes	Likely
Price, \$/lb.....	2.50	1.25	0.6
Reagent losses in gypsum slurry, \$/lb Cu.....	<1	<1	<1

necessary to maintain pH ≈ 7 in the raffinate stage. Extracting with in-situ neutralization has some limitations at this pH, particularly if the aqueous feed solution contains Mg. In this case the precipitation of metal hydroxides is likely to occur and cause crud formation. To prevent this, another technique — the regeneration of Versatic acid organic with lime — was used.

Ni and other base metals were extracted from a real sulfate leach liquor analysing (g/l) 9.1 Ni, 0.28 Co, 0.20 Cu, 0.14 Zn and 0.85 Mg using a kerosene solution containing 40% Versatic acid-10 extractant. Prior to the loading contact the organic was regenerated with a slurry of commercial lime to convert the Versatic acid into its Ca salt. The regeneration of carboxylic acid extractants with lime has been described previously by Fache et al⁽⁹⁾.

The circuit (see flow diagram in Figure 11) included loading in 3 three-phase mixer-settlers, stripping in 1 conventional type mixer-settler, organic regeneration in 1 three-phase mixer-settler and an organic back-extraction from the raffinate in 1 mixer-settler. Lime was added on demand to the organic regeneration stage to maintain a desired pH. The regenerated organic was then fed to the loading on demand to maintain pH = 7.0 in the raffinate stage. The raffinate produced at this pH contained rather significant amounts of dissolved reagent and was treated by an acidification-back extraction technique as proposed by Fletcher and Wilson⁽¹¹⁾.

The performance of the circuit was very satisfactory. More than 99.5% of Ni, Co, Cu and Zn were extracted. The loaded organic analysed 25-27 g/l Ni, but less than 10 mg/l Mg and less than 30 mg/l Ca, indicating that the

rejection of both Mg and Ca was essentially complete. Although the pH in the raffinate stage was maintained at seven, the precipitation of metal hydroxides was negligible. Gypsum as produced in the loading section analysed only 0.006% Ni and 0.0014% Mg. At a pH of seven, the raffinate contained 4-5 g/l of dissolved extractant. Acidifying the raffinate to pH ≈ 3 and back-extracting into the kerosene phase reduced the soluble loss of the extractant to approximately 80 mg/l. This corresponds to about 3¢/kg Ni recovered. It is interesting to note that the reagent entrapped with the gypsum amounted to only 10% of the total reagent loss.

Nickel was stripped from the loaded organic with 100 g/l H₂SO₄ in one stage. The strip liquor analysed 55 g/l Ni and had Ni/Mg \approx Ni/Ca \approx 1000. It should be pointed out, however, that a strip liquor containing 100 g/l Ni or higher could readily be obtained in two stages using H₂SO₄ or other mineral acid strip feed solution of an appropriate strength.

The advantages of using Versatic acid-10 for extracting Ni and Co include essentially complete recovery of these metals, substantially complete rejection of Mg if present in the aqueous feed solution and achieving highly concentrated strip liquors.

Conclusions

The concept of extracting base metals from sulfate solutions using acidic and/or chelating reagents and in-situ neutralization with lime has been successfully demonstrated in a small-scale circuit on a continuous basis. Extraction under pH control results in very favourable equilibria thus permitted a very selective and complete extraction in few stages. The highly loaded organic produced in this process will also yield high-strength strip liquor for further processing such as electrowinning. Neutralizing with lime results in a low reagent cost, the production of environmentally acceptable effluent and easily disposable gypsum.

Miniplant equipment has been developed for the efficient contacting and separation of the three-phase system used in this process. The organic reagent losses in the gypsum effluent have been reduced to levels approaching those of solubility in the raffinate.

The versatility of the approach was demonstrated for the extraction of different metals using both acidic and chelating reagents.

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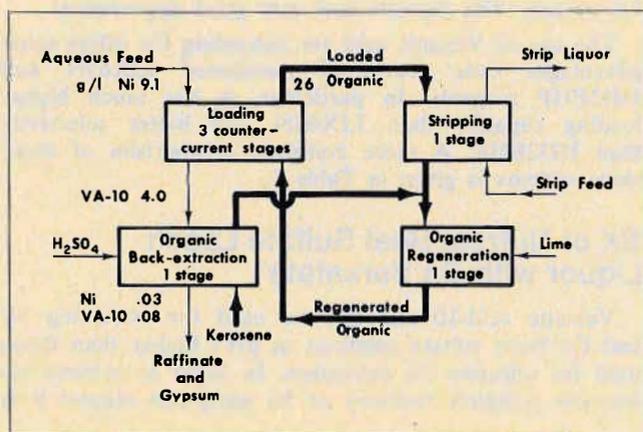


FIGURE 11. Ni — Versatic 10 solvent extraction flow diagram.

DISCUSSION

H. Jedlicka: Our problem is the leaching of serpentine ores with HCl for the production of MgO and NiO. For the neutralization during solvent extraction we use MgO. This has the important advantage that the MgCl₂-solution produced during neutralization can be recycled to the spray-roasting reactor for the production of MgO. So no special neutralization agents are needed and no unwelcomed effluents are produced, thus providing a process without any pollution problems.

J. Babjak: It is true MgO could be a very suitable neutralizing agent in some specific applications as seems to be in the case of your process. In the hydrometallurgy of nickel, however, sulfate leach liquor are generally encountered and if the feed solids are sulfidic minerals, SO₄²⁻ is usually generated during the leaching process. In this case lime is a much more desirable neutralizing agent than MgO since it is significantly cheaper and provides the rejection of SO₄²⁻ as CaSO₄·2H₂O which is fully acceptable environmentally. If MgO were used, a raffinate containing MgSO₄ would be generated and some treatment to reduce the SO₄²⁻ to below 1 g/l would be necessary before the effluent could be discarded. We believe that recycling MgSO₄ raffinate to spray-roasting is not feasible economically.

R. Blumberg: In 1965 a paper was presented by me and co-workers on *in situ* neutralization for separation of metal values e.g. Cu, Zn, Ni, Mg, Ca, also utilizing lime; our work described also e.g. an ion exchange by first preparing the Ca salt of the reagent, if desired. Similar work was done at the time by many other workers, e.g. Fletcher and Flett of Warren Spring.

Technologically this present work does not seem to contribute anything; it may well be that economics have changed and this approach is now viable. If so, this was not clear from the presentation as given (A late comment by Dr. Ettl said the economics relates to Ni recovery; if this is so, then indeed the early work is relevant as it described such separations by *in-situ* neutralization for pH control).

J. Babjak: The idea of *in situ* neutralization with lime is, of course not new and proper credit must be given to the early work of Dr. Blumberg, Dr. Fletcher, Dr. Flett and others who pioneered the idea. We don't agree with Dr. Blumberg however, that the economics of the basic concept of neutralizing the acid produced during solvent extraction have changed. It is still uneconomical to use this approach for copper recovery from leach liquors, since the costs of lime and of the neutralized acid which must be replaced will represent a disadvantage compared to acid LIX process. However the selective solvent extraction of Cu + Ni using *in-situ* neutralization with ammonia must have been economical already in 1970 for SEC Corp, who operate such a plant at El Paso, Texas. The reason for this is that the alternative nickel recovery processes would also require base stoichiometric to copper and nickel (e.g. the Sheritt Gordon H₂ reduction process would require a similar quantity of ammonia). In such a case the question is not if a base was needed, but whether a cheaper base could have been used instead of ammonia.

Lime or limestone are such inexpensive bases, but their cost advantage may well be lost if relatively small amounts of expensive SX reagents are lost with the produced solids. The attractive features of the separation process could also be lost if the phase separation is impractically difficult due to formation of metal hydroxides. E.g., US patent 3,251,646, based on Dr. Blumberg's work discourages the

use of lime with aliphatic carboxylic acid due to problems with metal hydroxide formation.

The technological contribution of our work is mainly in demonstrating that under proper operating conditions the solvent losses are tolerably small and that an efficient three-phase separation can be achieved in a continuously operating circuit even with carboxylic acids such as Versatic 10. The continuous operation, which is essential to accurately identify solvent losses, also allowed us to determine the realistic ability of a number of common solvent extraction reagents to achieve important metal separations. The data thus obtained and presented in our paper are much more reliable bases for further process development than the simple extrapolation of extraction data already available for isolated metals.

I.J. Itzkovitch: For control of pH in the mixer, is continuity of phase important, i.e. can one successfully control the pH in the mixer if the continuous phase is organic or is it necessary to ensure that the mixer is run aqueous continuous?

J. Babjak: The aqueous phase was continuous in all runs. However, at least for some systems, it is possible to control the pH in the mixer operated with the organic phase continuous.

T. Mattila: In your last figure, "Ni-Versatic Solvent Extraction Flow Diagram" you used kerosene back wash and you added this extra kerosene to the organic circuit! Do you have to remove any organic solvent out of the organic circuit to balance the system?

J. Babjak: The recovery of Versatic-10 was conducted initially in accordance with Ni-Versatic 10 Solvent Extraction Flow Diagram (Figure 11). Prior to the start-up, the organic back-extraction stage was filled with a suitable amount of kerosene. With total organic recirculation, i.e. without recovering any organic phase from this stage, we soon found that the concentration of Versatic-10 in the organic increased to 70% by volume. Even at this concentration the back-extraction of Versatic-10 was still efficient. As a result a portion of the stripped organic stream was later cycled through the organic back-extraction stage.

T. Mattila: When controlling pH by using lime in your process, have you noticed any small particles of gypsum to remain in the solvent phase after settling and have you had any difficulties when those particles precipitate on the surfaces of mixer vessels, agitators, pipes, etc?

J. Babjak: The separated loaded organic was virtually free of any gypsum. We observed some scaling of gypsum in the loading mixers, but the extent of this scale formation was not greater than that encountered ordinarily in lime neutralization operations.

D.S. Flett: I was rather surprised to hear of the very high copper to calcium ratios achieved in the organic phase for the DEHPA extraction studies. DEHPA is a remarkable extractant in many ways and one feature is its relatively high selectivity for calcium which is extracted on a pH scale very close to copper and at lower pH values than nickel. Would one author care to comment?

J. Babjak: Initially we were also surprised. However, after studying metal extraction isotherms, the reason for high copper to calcium ratios in the loaded organic became very clear. Although D2EHP loads Ca rather well at low pH values, the extraction coefficient of Ca (E_{Ca}) increases only slowly with the pH. On the other hand the extraction coefficient of Cu (E_{Cu}) increases very significantly with the pH. As a result the separation factor of Cu/Ca increases very dramatically as the pH increases.

D.S. Flett: The authors have indicated that entrained and adsorbed organic phase can be recovered by air sparging. Can this be done directly on the gypsum raffinate slurry or would a solid-liquid separation step be required prior to organic recovery?

J. Babjak: Although the organic recovery can be carried out directly from the gypsum raffinate slurry, it is preferable that a solid-liquid separation is incorporated prior to this step.

BASE METALS

LIX[®] 34 Continuous Pilot Plant Evaluations

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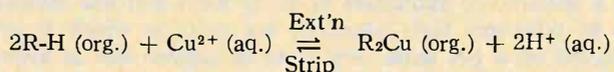
Abstract

LIX[®] 34 was piloted over a period of three months. Two circuit concepts were studied, both applicable to low copper — high iron feeds: 1. a one extraction stage-one strip stage circuit (1+1) and, 2. a new circuit concept termed parallel series (P-S) consisting of 3 extraction stages connected in parallel and one strip stage. One part of the study in the 1+1 circuit involved running a lower than normal strip acid. In addition, LIX 34, LIX[®] 64N and a LIX 34-LIX 64N mixture were compared in a conventional countercurrent 3 extraction-2 strip stage circuit on an actual commercial copper feed.

Introduction

THE NEW METAL EXTRACTANT, LIX[®] 34, was introduced by General Mills Chemicals, Inc. at the AIME Annual Meeting held in Las Vegas, February 1976⁽¹⁾. The paper reported the behavior of LIX 34 relative to a wide variety of metals with the emphasis on the LIX 34 -Cu system. Reagent development and evaluation does not always proceed smoothly nor is it problem-free. A second paper on LIX 34 pointed out some of the problems we encountered in the development and evaluation of LIX 34, how we solved or attempted to solve these problems and where these adventures led us⁽²⁾. A third paper on LIX 34 titled "Synthesis, Structure and Hydrometallurgical Properties of LIX 34" is being presented at this conference by our Dr. Michael J. Virnig, Senior Research Chemist, who first synthesized this molecule⁽³⁾.

LIX 34 operates on a hydrogen ion cycle similar to most chelating-type reagents. The equation below is representative of the extraction-stripping reaction⁽³⁾.



As has been previously reported⁽¹⁾, LIX 34 possesses those important properties needed to make it a successful solvent extraction reagent:

1. Copper extractive ability comparable to LIX 64N,
2. Total iron rejection as measured by atomic absorption,
3. Sufficient kinetics,
4. Exceptional stability,

5. Good phase separation characteristics,
6. Strippable with acid concentrations equal to or lower than needed for LIX[®] 64N.

The objectives of the pilot plant study were: (a) to make use of the above properties in new flow schemes which extend the range of feeds that can be economically treated via solvent extraction, (b) to test the reagent over a considerably longer term and on a much larger scale than is normal in a laboratory evaluation program in hopes of seeing if any long-term problems arise, and (c) to compare LIX 34 with LIX 64N on a pilot-plant scale.

New Flow Schemes

In the industry there are many low copper-high iron feeds which are now considered uneconomical to treat via solvent extraction because of the large capital investment required relative to the amount of copper recovered. A large capital investment is needed because with oxime type reagents the circuit must operate with a minimum reagent concentration to reduce iron loading, and thus staging requirements are high. However, because LIX 34 loads no iron, circuits can be run using the reagent at as high a concentration as needed to give the desired Cu recovery with minimum staging. As a way to test this concept, two pilot plant circuits were run simultaneously: a one extraction-one strip (1+1) circuit and a 3 extraction-one strip (P-S) circuit. The circuits are schematically shown in Figure 1. An individual mixer-settler unit along with its dimensions is shown in Figure 2. These mixer-settlers are of conventional design and similar to the mixer-settler units used in many existing commercial plants. The plant piping was PVC, and whereas the pipe sections performed well, the connecting pieces, elbows, T-joints and the like did develop cracks and cause some problems.

The pilot plant was set up on site at the commercial Cities Service SX-EW Plant in Miami, Arizona. The circuit feed was prepared by mixing metered quantities of Cities Service Miami Pregnant Leach Solution (PLS) and tap water. We had hoped to maintain a feed with a constant copper tenor in the range of 0.30 - 0.35 g/l at a pH of 2.6 and while we were normally successful, pressure variations in the PLS and water lines did make it very difficult to maintain the proper ratio of the two streams. The barren electrolyte for our pilot plant was tapped directly from the commercial circuit barren electrolyte line. Initially our electrolyte flows were controlled with 3/8 inch PVC gate valves which we later replaced with 1/4 inch PVC needle valves. Neither valve allowed us to control the electrolyte flow as steadily as we wanted to, and thus, the pregnant electrolyte values vary considerably from the desired 50 g/l Cu. The analyses given were normally carried out at the Cities Service laboratory.

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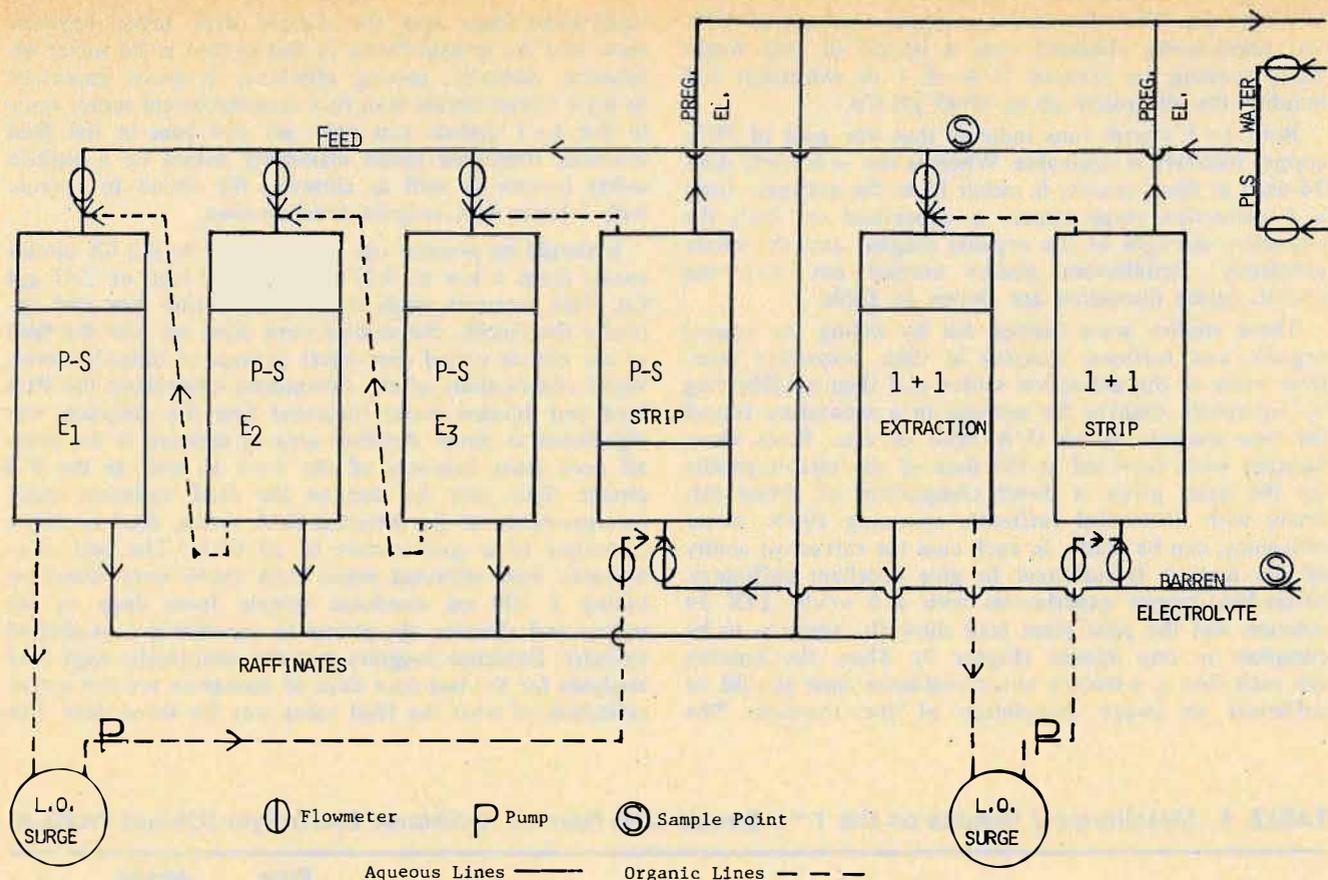


FIGURE 1. Pilot plant schematic, 1 + 1 and P-S circuits.

Our laboratory did run analyses on some of the samples, and while agreement with the Cities Service values was quite good, we normally ran slightly lower on our aqueous analysis and a little higher on the organic analyses.

Results and Discussion

The results and discussion section of this paper is divided into five parts: (A) The metallurgical results of the 1+1 circuit; (B) The metallurgical results of the P-S circuit; (C) A metallurgical comparison of LIX 34, LIX 64N and a LIX 64N-LIX 34 mixture in a 3 extraction-2 strip stage circuit; (D) The phase separation data and; (E) The entrainment data.

A. The One Extraction-One Strip Stage (1+1) Circuit

The goal of this circuit study was to define the conditions needed in order to obtain 90% copper recovery in the 1+1 circuit while building a pregnant electrolyte solution amenable to electrowinning. A second goal was to test the feasibility of stripping with a lower acid electrolyte than is normally encountered in existing commercial plants.

The results obtained from the 1+1 circuit with the normal tankhouse electrolyte (~ 30 g/l Cu, ~ 150 g/l H₂SO₄) are tabulated in Table 1. Mixer residence time was ~ 4 minutes except for 1-4-77 through 1-12-77 where the mixer residence time was ~ 5 minutes. The most interesting feature is the significant gain in extractive efficiency when operating the extraction mixer aqueous continuous rather than organic continuous. Compare for example the data of 12-3, 12-6 and 12-7-76 or that of

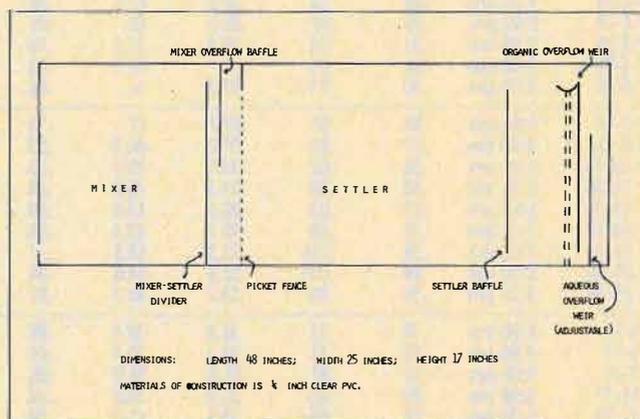


FIGURE 2. Pilot plant mixer settler unit.

12-29-76 through 1-12-77. This was an unexpected result since laboratory circuits with LIX 34 normally operate at a slightly higher extractive efficiency when running the extraction mixers organic continuous. This behavioral difference between the laboratory and pilot plant may be due to the fact that a completely organic continuous emulsion could not be maintained in the pilot plant mixers for any length of time. There was always some double phasing. The double phasing is easily detected by watching the emulsion break as it pours over the mixer-settler divider and down to the organic-aqueous interface.

Circuit data using low acid stripping is shown in Table 2. The stripping electrolyte was made by diluting normal circuit electrolyte with tap water to give a barren electrolyte containing about 115 to 120 g/l H₂SO₄ and 22

to 27 g/l Cu. With this circuit a copper recovery of 90% was consistently obtained over a period of two weeks while running an advance O/A of 1 in extraction and building the electrolyte up to 40-45 g/l Cu.

Both 1+1 circuit runs indicate that our goal of 90% copper recovery is attainable. Whereas the ~ 6 v/v% LIX 34 used in these circuits is rather high, the raffinate from a 1 extraction stage circuit is dependent on both the extractive strength of the organic reagent and the mixer efficiency. Equilibrium studies carried out with the circuits under discussion are shown in Table 3.

These studies were carried out by taking the loaded organic and raffinate samples at their respective overflow weirs of the extraction settler and then equilibrating by vigorously shaking the samples in a separatory funnel for two minutes at an O/A ratio of one. Since these samples were removed at the time of the circuit profile for the dates given, a direct comparison of actual raffinate with theoretical raffinate, assuming 100% mixer efficiency, can be made. In each case the extractive ability of the reagent is sufficient to give excellent raffinates. Mixer-box kinetic experiments with a 6 v/v% LIX 34 solution and the pilot plant feed show the reaction to be complete in one minute (Figure 3). Thus, the kinetics are such that a 4-minute mixer residence time should be sufficient to insure completion of the reaction. The

equilibrium data and the kinetic data taken together show that the crucial factor in this system is the mixer efficiency. Actually, mixing efficiency is more important in a 1+1 type circuit than in a countercurrent setup, since in the 1+1 system you only get one pass at the feed solution. Improved mixer efficiency would be a built-in safety feature as well as allowing the circuit to operate with a lower LIX reagent concentration.

It should be pointed out that the feed to the SX circuit varied from a low of 0.27 g/l Cu to a high of 0.47 g/l Cu. This variation made it difficult to fine tune and optimize the circuit. No studies were done on how the feed to our circuit varied over short periods of time; however, visual observations of the flowmeters controlling the PLS feed and dilution water indicated that the variation was significant at times. Another area of concern is the overall poor mass balances of the 1+1 as well as the P-S circuit. This may be due to the feed variation, poor measurements of the advance O/A ratios, feed sampling technique or a combination of all three. The best mass balances were obtained when O/A ratios were found by taking a 100 ml emulsion sample from deep in the mixers and allowing the phases to separate in a graduated cylinder. Evidence suggests that the abnormally high feed analyses for the last four days of operation are not a true reflection of what the feed value was for those days. For

TABLE 1. Metallurgical Results on the 1+1 Circuit with Normal Tankhouse Electrolyte (Circuit Profiles)

Date	Time	Feed	Raf.	Analyses g/l Cu				Temp °C		Phase Continuity		Advance O/A	LIX 34 v/v%
				B.E.	P.E.	S.O.	L.O.	Ext'n	Strip	Ext'n	Strip		
12-1-76	9:30 am	.39	.13	31.2	47.8	.06	.31			Org	Org	1/1	5.0
12-1-76	5:00 pm	.33	.10	30.0	49	.05	.29			Org	Org	1/1	5.0
12-2-76	5:00 pm	.31	.08	29.4	51.1	.05	.33	17.5	18	Org	Org	1/1	5.0
12-3-76	3:00 pm	.32	.05		47.5	.04	.29			Aq	Org	1/1	5.0
12-6-76	5:00 pm	.30	.13	37.3	56	.05	.25	17	19	Org	Org		5.0
12-7-76	5:00 pm	.38	.02	33.7	47	.03	.20			Aq	Aq	1.5/1	5.2
12-8-76	5:00 pm	.32	.02	35.2	46.8	.03	.23			Aq	Aq	1.3/1	5.2
12-10-76	8:30 am	.36	.02	33.6	39.2	.03	.21	16	16	Aq	Aq	1.2/1	5.5
12-14-76	8:30 am	.32	.04	29.1	45.8	.04	.29	15	14	Aq	Aq	~ 1/1	5.5
12-14-76	5:00 pm	.29	.03	26.0	43.0	.04	.31	17.5	19	Aq	Aq	1/1	5.5
12-20-76	3:00 pm	.32	.04	35.3	64.4	.08	.35	17	17	Aq	Aq	~ 1/1	5.5
12-21-76	3:00 pm	.34	.036	33.3	58.8	.07	.36	18	21	Aq	Aq		5.8
12-29-76	8:00 am	.34	.035	32.8	44.6	.08	.38	14.5	13	Aq	Aq	1/1	6.8
12-29-76	4:00 pm	.35	.03	33.7	45.2	.07	.32	14	16	Aq	Aq	1.1/1	6.8
1-4-77	4:00 pm	.30	.11	31.8	38.4	.06	.28	15	15	Org	Org		6.8
1-5-77	4:00 pm	.32	.11	31.3	39.0	.05	.26			Org	Org	1.2/1	6.8
1-7-77	9:00 am	.33	.07	31.8	38.9	.05	.24	15	14	Org	Aq	1.2/1	6.8
1-11-77	5:30 pm	.29	.06	31.0	39.6	.04	.25	15	16	Org	Aq	1/1	6.8
1-12-77	5:30 pm	.28	.02	32.5	41.9	.04	.27	17	20	Aq	Aq	1.1/1	6.6
1-13-77	4:00 pm	.33	.03	33.3	44.3	.05	.31	17	20	Aq	Aq	1.2/1	6.6
1-14-77	12:00 pm	.33	.024	28.6	38.7	.05	.31	16.5	19	Aq	Aq	1.2/1	6.6
1-18-77	9:00 am	.31	.024	31.0	45.6	.06	.26	15.5	15.5	Aq	Aq	1.2/1	6.6
1-31-77	2:00 pm	.46	.043	36.2	50.0	.05	.36	20	22	Aq	Aq	1/1	6.6

TABLE 2. Metallurgical Results on the 1+1 Circuit with Low Stripping Acid.

Feed	Time	Feed	Raf.	Analyses g/l Cu				Temp °C		Phase Continuity		Advance O/A	LIX 34 v/v%
				B.E.	P.E.	S.O.	L.O.	Ext'n	Strip	Ext'n	Strip		
1-19-77	8:30 pm	.38	.034	22.4	41.4	.10	.34	16	15	Aq	Aq	1.04	6.6
1-20-77	10:30 am	.33	.033	23.6	43.0	.10	.35	16	16	Aq	Aq	1/1	6.6
1-21-77	1:30 pm	.34	.034	24.7	46.8	.14	.40	16	16	Aq	Aq	1/1	6.6
1-24-77	7:30 pm	.30	.035	26.8	46.7	.08	.34			Aq	Aq	1/1	6.6
1-25-77	5:00 pm	.38	.031	26.8	41.5	.08	.31	16	17	Aq	Aq	1/1	6.6
1-26-77	5:00 pm	.47	.030	26.9	44.0	.09	.34	19	20	Aq	Aq	1/1	6.6
1-27-77	5:30 pm		.029	27.6	44.0	.11	.35	17	17	Aq	Aq	1.07/1	6.6
1-28-77	1:15 pm	.45	.016	26.6	41.6	.11	.31	19	20	Aq	Aq	1.1/1	6.6

TABLE 3. Aqueous Equilibrium Shakeout Values in g/l Cu

Circuit	1 + 1	P-S	P-S	P-S	Date
Stage	Ext'n	E ₃	E ₂	E ₁	
	0.001	0.005	0.002	0.008	12- 7-76
	0.006	0.004	0.006	0.012	1-24-77
	0.008	0.005	0.009	0.016	1-26-77
	0.008	0.005	0.008	0.015	1-27-77

example, the mixer O/A ratios were done by sampling the emulsion and check well with the organic and aqueous advance flows. However, the feed was sampled differently than normal. The normal procedure was to take a one liter sample from the 1/2 inch gate valve sampling tap after the sampling tap was opened wide for about ten seconds. This one liter sample was stirred well and then a small portion submitted for analysis. However, for the last four days of operation the sample submitted for analysis was obtained by opening the tap slightly and collecting the small stream directly in a test tube. If the feed stream is not well mixed at the sampling point (Figure 1), or if the sampling line contains for some reason an aqueous solution high in PLS, the method of sampling would not give a sample truly representative of the feed. Another alternative reason the sample could be high in metal is that the tap valve could have a very slow leak, some or all of the water then evaporates resulting in copper and iron sulfate salts depositing on the inside surface of the tap. These salts then redissolve when the valve is opened for sampling. Using the normal sampling procedure, where the feed is allowed to run for 10 seconds and then a large sample taken, the effect of this metal redissolution should be minimal if any. However, when the tap is opened slightly and the small stream collected immediately, the effect of redissolution should be much greater. Each mixer had a 1/2 in. gate valve for a drain; most of these had very slow leaks and salt deposits were visible on several. Thus a slow leak in the 1/2 inch gate valve sampling tap would not be unexpected.

B. The Parallel Series (P-S) Circuit

The P-S circuit was run over a two-month period with a simple goal — to define the conditions needed to get 90% copper recovery from the low-grade feed with the circuit shown in Figure 1. The metallurgical results are given in Table 4. Several things deserve mention: note that, as with the 1+1 circuit, running the mixer emulsions organic continuous results in lower mixer efficiencies. Compare for example the results of 12-21-76 with those of 12-22-76, or the results of 12-29-76 with those of 1-4-77.

Our goal of 90% copper recovery looks to be attainable, but difficult. Equilibrium studies (Table 3) and isotherm data (Figure 4) both indicate that greater than 90% copper recovery is possible with the system under discussion. For example, using only 6 v/v% LIX 34 and carrying a stripped organic of 0.07 g/l Cu, the raffinate from a feed of 0.38 g/l Cu at a pH of 2.6 should be E₃ = 0.014, E₂ = 0.035 and E₁ = 0.080 assuming 100% mixer efficiency (Figure 4). This represents an overall recovery of 88.7% Cu. Under similar conditions using 8 v/v% LIX 34, 93% recovery can theoretically result. Lower feeds will result in higher recoveries provided all other conditions remain the same. For example, a laboratory circuit using 7 v/v% LIX 34 in a P-S, 3+1 circuit on a feed containing 0.27 g/l Cu at a pH of 2.5 showed a 92% copper recovery when the circuit was run in such

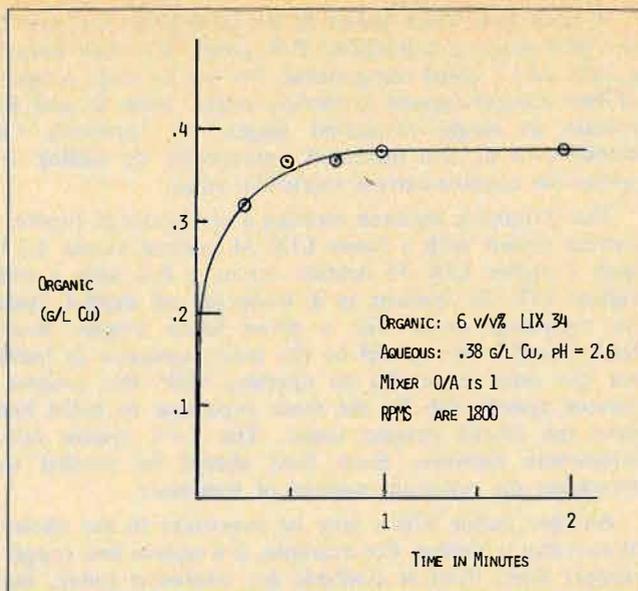


FIGURE 3. LIX 34 mixer box kinetics with synthetic pilot feed.

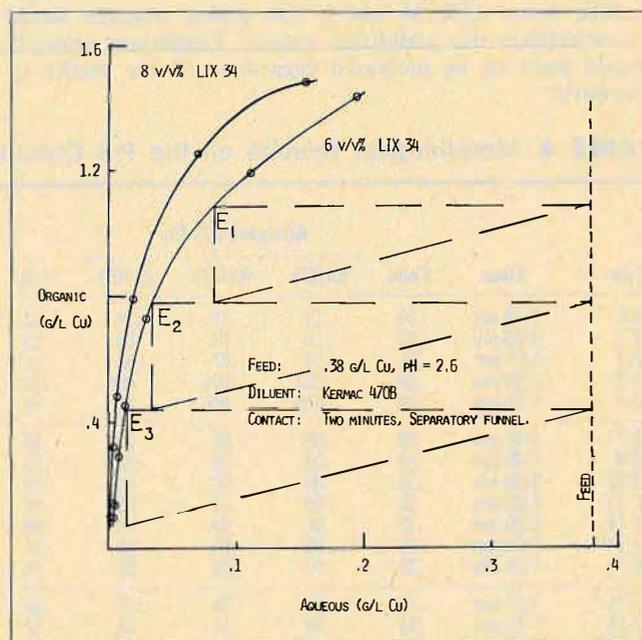


FIGURE 4. Equilibrium isotherms.

a way as to insure good mixing. This data is in agreement with the isotherm predictions and confirms the feasibility of the P-S circuit.

Copper recovery is greatest in E₃ and poorest in E₁. This is expected since the organic is loading copper as it passes from E₃ to E₂ to E₁. The labeling of the extraction stages is somewhat arbitrary, but in keeping with conventional terminology, i.e., the organic leaving E₁ is the loaded organic.

The importance of good mixer efficiency in any system, where the aqueous feed has only one contact with the organic, cannot be overemphasized. Greater reagent extractive strength and faster extraction kinetics can help overcome poor mixer efficiency. However, a reagent with greater extraction strength is necessarily more difficult to strip and the advantage of running with lower tankhouse acid is lost.

A final flow sheet tested in the laboratory, but not in the pilot plant, is a modified P-S circuit. The feed stream is split into 3 equal components, but the E₁ stage consists of two counter-current extraction stages, while E₂ and E₃ remain as single extraction stages. As expected, Cu recovery in E₁ was increased significantly by adding an additional counter-current extraction stage.

The difference between running a conventional counter-current circuit with a lower LIX 34 content versus 1+1 with a higher LIX 34 content versus a P-S with a still higher LIX 34 content is a trade off of capital costs for operating costs. For a given lower copper tenor feed, the P-S circuit will be the least expensive to build but the most expensive to operate, while the counter-current system will be the most expensive to build but have the lowest reagent losses. The 1+1 system falls somewhere between. Each feed should be studied to determine the optimum method of treatment.

Another factor which may be important in the choice of circuitry is timing. For example, if a certain low copper content dump feed is available for treatment today, but the particular company feels it will have another similar dump coming on stream in several years, the P-S concept applies nicely. A 1+1 circuit would handle the current stream; the later addition of one extraction stage, a little more LIX 34 and a few piping changes would accommodate the additional stream. Tankhouse capacity would have to be increased regardless of the choice of circuitry.

C. LIX 34 Comparison with LIX 64N

The pilot plant circuit was set up in a 3 extraction — 2 strip stage configuration employing conventional counter-current flow techniques. With this configuration we tested several LIX 34 concentrations, one LIX 64N concentration and a LIX 34-LIX 64N mixture. The results are shown in Table 5. Individual circuit data is typical of a given run and represents two or more days of circuit operation.

In general, LIX 34, LIX 64N and the LIX 34-LIX 64N mixture give comparable metallurgical results. With LIX34, a tankhouse bleed for iron control was not added to the PLS, whereas the LIX 64N circuit does include a tankhouse bleed to the PLS similar to existing commercial operations. With the LIX 34-LIX 64N mixture, the circuit was run with and without a tankhouse bleed to the PLS.

Even though analytical uncertainty in measuring iron loaded on the organic does not allow precise calculation of Cu/Fe transfer ratios, all the circuits ran very well from this point of view. With only LIX 34 as the extractant, no Fe has ever been detected on the organic whereas the LIX 34-LIX 64N mixture only loads about 1/3 to 1/2 of the iron expected based on the LIX 34-LIX 64N content. For example, with the LIX 64N circuit, iron loading normally ran 5-6 ppm, while with the mixed solvent system iron loading was only 1-2 ppm even with no tankhouse bleed back to the PLS. To develop good

TABLE 4. Metallurgical Results on the P-S Circuit.

Date	Time	Feed	Analyses g/l Cu				S.O.	L.O.	Temp °C		Phase Continuity				O/A Flow Ratio			v/v% LIX 34		
			Raf(1)	Raf(2)	Raf(3)	S.O.			Ext'n ⁽¹⁾	Strip	E ₁	E ₂	E ₃	S	E ₁	E ₂	E ₃			
12-1	9:30 am	.39	.11	.10	.12	.12	.79													
12-1	5:00 pm	.33	.10	.08	.09	.13	.71													
12-2	5:00 pm	.31	.13	.07	.08	.13	.76	16	18											
12-3	3:00 pm	.32	.051	.076	.050	.12	.66													
12-6	5:00 pm	.30	.069	.056	.12	.09	.57	17	18											
12-7	5:00 pm	.38	.06	.02	.10	.10	.52													
12-8	5:00 pm	.32	.04	.02	.07	.05	.56													
12-10	8:30 am	.36	.03	.02	.03	.04	.60													
12-13	5:00 pm	.31	.06	.03	.03	.08	.79													
12-14	8:30 am	.32	.06	.03	.03	.08	.77	15	15											
12-14 ⁽²⁾	5:00 pm	.29	.06	.03	.02	.06	.85	17	18											
12-20	3:00 pm	.32	.07	.04	.07	.08	.80	16	16											
12-21	3:00 pm	.34	.07	.04	.03	.06	.74	17	19											
12-22	7:30 am	.33	.14	.11	.13	.17	.99	14	11											
12-29 ⁽²⁾	8:00 am	.34	.064	.046	.033	.10	.94	15	13											
12-29	4:00 pm	.35	.044	.038	.015	.08	.86	14	16											
1-4 ⁽³⁾	4:00 pm	.30	.065	.065	.073	.13	.69	15	15											
1-5 ⁽³⁾	4:00 pm	.32	.07	.07	.08	.12	.64													
1-7 ⁽³⁾	9:00 am	.33	.019	.063	.076	.06	.48	15	15											
1-7 ⁽³⁾	5:30 pm	.32	.021	.010	.047	.06	.59													
1-11 ⁽³⁾	5:30 pm	.27	.03	.01	.01	.06	.59	15	15											
1-12 ⁽³⁾	4:00 pm	.28	.02	.03	.01	.06	.58	17	19											
1-13	4:00 pm	.33	.09	.03	.02	.07	.76	17	19											
1-14	12:30 pm	.33	.066	.016	.012	.08	.78	17	18											
1-17	5:00 pm	.36	.091	.023	.021	.08	.83	18	20											
1-18	5:00 pm	.31	.052	.027	.023	.08	.79	16	17											
1-19	8:30 pm	.38	.068	.038	.029	.11	.90	16	15											
1-20	10:30 pm	.33	.045	.027	.024	.08	.70	16	16											
1-21	1:30 pm	.34	.051	.026	.026	.08	.75	16	16											
1-24	5:30 pm	.30	.045	.032	.026	.10	.77													
1-25	4:30 pm	.38	.052	.028	.027	.08	.78	16	16											
1-26	5:00 pm	.47	.047	.028	.019	.09	.80	19	20											
1-27	5:30 pm	.45	.050	.033	.021	.08	.77	17	17											
1-28	1:00 pm	.45	.035	.022	.010	.09	.75	18	20											
1-31	2:00 pm	.46	.074	.050	.037	.08	.92	20	22											

Notes: ⁽¹⁾ Average temperature for the 3 extraction stages.

⁽²⁾ Materials balance excellent this day, O/A ratios, etc, carefully followed. O/A via 100 ml sample.

⁽³⁾ 4.5 minute retention time in mixers.

TABLE 5. Metallurgical Comparisons of LIX 64N, LIX 34 and a 2/1 LIX 64N — LIX 34 Mixture in a 3 Ext'n, 2 Strip Stage Pilot Plant.

Organic	Feed	pH	Analyses g/l Cu					Flow O/A Ext'n	Mixer Residence Time (min)	T° C Ext'n
			Raf	L.O.	S.O.	B.E.	P.E.			
7 v/v% LIX 34	0.99	2.1	.014	0.80	.03	34.0	46.1	1.3	3.2	23
6 v/v% LIX 34	1.03	2.1	.019	0.73	.02	31.8	44.8	1.3	3.2	26
5.3 v/v% LIX 34	0.98	2.0	.068	0.86	.01	28.4	41.8	1.0	3.0	26
6.5 v/v% LIX 64N	1.09 ¹	1.85	.13	0.97	.06	32.3	50.2	1.04	3.0	23
"	1.11 ¹	1.85	.04	0.95	.08	30.3	48.9	1.2	3.0	22
"	1.11 ¹	1.85	.04	1.06	.07	25.0	48.7	1.0	3.0	21
Reagent mixture ⁽²⁾	1.11 ¹	1.85	.10	1.14	.07	29.1	49.2	1.0	3.0	18
"	1.06 ²	1.95	.05	1.00	.07	29.4	48.1	1.0	3.0	16
"	1.01	2.1	.03	1.00	.07	29.3	51.5	1.0	3.0	23

Notes: ¹ Includes tankhouse bleed for iron control of 23 ml/min E₁.
² Includes tankhouse bleed for iron control of 5 ml/min to E₁.
³ Organic is 4.0 v/v% LIX 64N and 2.0 v/v% LIX 34.

Cu/Fe transfer ratios a long-term study including electrowinning is needed so that the iron build-up can be accurately measured. One pass of electrolyte at an O/A of 20/1 would only build 0.1 g/l Fe if the organic transferred 5 ppm. In looking at all the iron analyses which were done in conjunction with our pilot plant study, a buildup of 0.1 g/l Fe in an electrolyte already containing 3 g/l Fe could not be accurately ascertained.

Even though LIX 34 does not chemically load iron, an operating plant utilizing LIX 34 as the extractant may still need a small tankhouse bleed for iron control. Calculations on the iron transfer in existing commercial operations show that the iron transferred to the tankhouse, via entrainment and/or sludge movement, can be significant.

Our laboratory data indicates that LIX 34-LIX 64N mixtures may be slightly weaker in extractive power than either component by itself. The pilot plant study is inconclusive on this point, but if there is a loss of extraction power, the loss is very small.

D. Phase Separation

The discussion of phase separation will be concerned mainly with stripping when the mixer emulsion was running aqueous continuous. This is because phase separation in extraction when running aqueous continuous was always good, with tapered band widths from two inches and lower which seldom ran the entire length of the settler. When operating organic continuous, phase bands in both extraction and stripping were small. In fact, when phase bands were present they were of an aqueous continuous nature. This is consistent with our previous observation on the double phasing that was noted when the mixers were running organic continuous.

A sampling of the strip phase separation data for the 1+1 circuit is given in Table 6 and was chosen to show the wide range of phase bands obtained. Since we saw little if any difference in phase bands between the P-S or the 1+1 circuits when they were operated under the same conditions, the data can be considered representative for LIX 34 in our pilot plant circuit.

The data clearly shows that temperature is an important factor and the normal pattern of decreasing phase band with increasing temperature is evident. Also evident is the range of phase band widths obtained at what look to be similar conditions. For example, consider the phase bands given for the four measurements at 17°C, where the bands range from 4 to 7½ inches. Also note that the temperature range for the three days whose data is given is nearly the same yet phase bands seem to

TABLE 6. Phase Separation Data for the 1+1 Circuit. Temperature Dependence.

Date	Time	Band Width Inches	Temp °C	Mixer O/A	Flow/Area GPM/Ft ²
1-12-77	9:30 am	5 ¾	13	1.30	1.11
1-12-77	11:30 am	4	17	1.31	1.10
1-12-77	2:30 pm	2	19	1.07	1.20
1-12-77	4:00 pm	1 ½	20	1.07	1.20
1-12-77	5:30 pm	4	17	1.02	1.25
1-13-77	9:30 am	9	14	1.24	1.13
1-13-77	11:30 am	6	17	1.07	1.21
1-13-77	1:00 pm	4 ½	19	1.18	1.15
1-13-77	2:30 pm	3 ¾	20	1.24	1.13
1-13-77	4:00 pm	3 ¼	20	1.21	1.14
1-14-77	8:00 am	10 ¾	11	1.34	1.09
1-14-77	10:30 am	7 ½	17	1.26	1.12
1-14-77	12:00 pm	5	18	1.21	1.14

TABLE 7. Phase Separation Data for the 1+1 and P-S Circuit. The Effect of the O/A Ratio in the Mixer.

Date	Time	Band Width Inches	Temp °C	Mixer O/A
12-14-76	8:30 am	9 ½	14	1.46
1-13-77	9:30 am	9	14	1.24
12-21-76	8:30 am	8	14	1.16
1-19-77	9:00 am	5 ¼	14	1.13
1-26-77	9:00 am	5	14	1.04
1-7-77	9:00 am	3 ½	14	1.00
12-9-76	9:00 pm	7 ¾	15	1.30
12-9-76	10:30 pm	6	15	1.23
12-9-76	11:50 pm	5 ½	15	1.16
1-28-77	8:00 am	3 ¾	15	1.04
1-19-77	8:30 pm	3	15	1.00
1-27-77	8:30 am	3	15	1.00
1-12-77	11:30 am	4	17	1.31
1-14-77	10:30 am	7 ½	17	1.26
1-20-77	9:15 am	5 ½	17	1.15
1-13-77	11:30 am	6	17	1.07
1-27-77	5:15 pm	2 ¼	17	1.06
1-25-77	4:15 pm	3 ½	17	1.04
1-12-77	5:30 pm	4	17	1.02
12-20-76	5:30 pm	5	17	1.00

increase on a daily basis.

Another factor which appears to have some effect is the O/A mixer ratio. The data in Table 7 at 14 and 15°C indicates that the higher the O/A ratio the greater the phase band. However, the data at 17°C shows that the trends are not clear cut. Factors for which no corre-

lation to phase band could be found are impeller speeds over the range 375 to 475 rpm and the copper content of the stripped organic.

One variable which seemed to be very important was the gas trapped in the strip mixer emulsion. This gas was noticeable in both the strip mixers and in the settlers and we felt it had a detrimental effect on phase separation. In the 1+1 and P-S circuits the trapped gas can arise from only two sources: the barren electrolyte and/or vortexing in the mixer. In order to sample the barren electrolyte, a tap was installed on the upstream side of the circuit (Figure 1). When the barren electrolyte was sampled a large amount of foaming of the electrolyte was always noted, and the odor of acid mist three to four feet above the tap was strong. This suggested the electrolyte carried a large amount of dissolved gases which appeared to be liberated in the strip mixers.

As a means to test this theory, the advance electrolyte flow to the 1+1 circuit was shut down one morning. Within a few minutes the phase band had dropped several inches. Since the advance electrolyte flow was only about 1/40 to 1/60 of the electrolyte recycle flow, the drop in the phase band is not a result of a mixer O/A change nor a total flow change. This experiment was repeated on one other occasion with similar results.

Two other pieces of evidence are also consistent with the trapped gas theory. From Dec. 1 through Jan. 18 the phase bands in the 1+1 circuit and the P-S circuit averaged 5.64 and 5.66 inches respectively. However, from Jan. 19 through Jan. 28 the phase band in the 1+1 circuit averaged only 4.10 while the P-S circuit average was 7.00 inches. The difference in the two circuits from Jan. 19-28 was that the electrolyte to the 1+1 was of a lower acid content made up by mixing barren electrolyte with water in a 50 gallon container. A small chemical feed pump was used to control the advance electrolyte flow to the 1+1 strip mixer while the advance electrolyte to the P-S circuit remained a direct feed from the barren electrolyte line. By mixing electrolyte with water to reduce acid and by letting the lower acid strip electrolyte sit open to the air, much of the dissolved gas is allowed to escape before the electrolyte is pumped into the strip mixer. The reduced acid content of the 1+1 strip solution may also have a positive effect on phase band, and the improvement noted may be a combination of less trapped gas and lower strip acid.

The second piece of evidence was noted when the LIX 34- LIX 64N mixture was run in the 3 ext'n — 2 strip stage pilot plant. The phase band in S₂ was running high at 10 inches (3-2-77, 8:30 am.) and the operator noted that air was being pumped into the mixer via the organic line from S₁. After the pumping of air was stopped, the phase band fell to 4-5 inches within minutes and stayed at 4 inches or lower for the duration of the run, even at temperatures as low as 13°C (Table 8).

To prevent air from becoming trapped in the emulsion via vortexing, a thin PVC plate was used as an emulsion cover in the mixer. Whereas the vortexing decreased dramatically, the amount of gas trapped in the emulsion did not decrease and the emulsion band remained the same.

Overall, phase separation in the pilot plant strip mixers was poorer with LIX 34 than with LIX 64N. Even if trapped gas is the cause of the problem, the same sort of problem is not evident with LIX 64N under similar conditions. However, laboratory data on phase separation with LIX 34 shows it to have phase separation properties similar to LIX 64N or perhaps slightly better. For example, a 20 v/v% LIX 34 solution showed phase bands of 3 to 5 inches at a flow of 2.4 gpm/ft² when run against a synthetic tankhouse electrolyte carrying 150 g/l H₂SO₄ and 30 g/l Cu at 20-22°C. These results are significantly better than those obtained in the pilot plant. However, in the laboratory study mixer O/A ratios were always one and no air was trapped in the emulsions.

One variable which has been found to be very important in laboratory evaluations of phase separation is static electricity. For example, we have observed that simply running ones fingers over the outside of a PVC mixer box will greatly aid phase separation. In addition, grounding the emulsion in a dynamic laboratory phase separation test will often cause the phase band to collapse. In our pilot plant experiments this potential problem was not studied nor were any precautions taken to reduce or eliminate the problem if it was present.

E. Entrainment

Entrainment was measured using calibrated centrifuge tubes. Samples were normally 100 ml and were removed from the circuit at the settler overflow weir for the respective phase in question. The samples were taken in a

TABLE 8. Phase Separation Data for the 3+2 Circuit.

Date	Time	Band Width (in.)		Temp °C.		O/A		v/v% Reagent		Continuous Phase	
		S ₁	S ₂	S ₁	S ₂	S ₁	S ₂	LIX 34	LIX 64	S ₁	S ₂
2-3-77	9:00 am	7	9 ¼	16	14	.98	1.16	7	None	A	A
2-3-77	10:00 am	5	8	21	19	1.20	1.20	7	None	A	A
2-3-77	1:30 pm	3 ½	3 ½	23	23	1.30	1.09	7	None	A	A
2-3-77	5:00 pm	2 ¾	3	24	24	1.05	1.07	7	None	A	A
2-10-77	4:00 pm	2 ½	2	27	28	2.83	1.09	5.3	None	A	A
2-11-77	11:30 am	2 ½	2 ¼	26	25	3.00	1.13	5.3	None	A	A
2-22-77	Noon	2 ½	2 ¾	20	20	1.21	1.09	None	6.5	O	A
2-22-77	3:00 pm	1 ¾	2	23	23	1.17	1.13	None	6.5	O	A
2-23-77	9:30 am	2 ½	3	20	18	1.27	1.15	None	6.5	O	A
2-23-77	Noon	1 ½	2 ½	24	24	1.56	1.18	None	6.5	O	A
2-25-77	10:30 am	1 ¼	1 ½	20	18	1.15	1.10	None	6.5	O	A
3-1-77	9:00 am	2	10	16	16	1.00	1.00	2.1	4.0	A	A
3-1-77	9:00 am	1 ½	5	16	16	1.00	1.00	2.1	4.0	A	A
3-2-77	8:30 am	2	10	16	16	1.00	1.00	2.1	4.0	A	A
3-2-77	4:30 pm	1 ½	4	13	13	1.00	1.00	2.1	4.0	A	A
3-3-77	4:30 pm	2 ¼	3 ¼	21	21	1.00	1.00	2.1	4.0	A	A
3-4-77	9:00 am	2	4 ½	15	15	1.00	1.00	2.1	4.0	A	A
3-4-77	1:00 pm	2	2 ¾	23	23	1.00	1.00	2.1	4.0	A	A
3-7-77	1:00 pm	1 ½	2	26	26	1.00	1.00	2.1	4.0	A	A

TABLE 9. Entrainment in PPM, 1+1 and P-S Circuits.

Date	Time	1 + 1 Circuit				P - S Circuit					
		L.O.	S.O.	P.E.	Raf.	L.O.	S.O.	P.E.	E ₁	E ₂	E ₃
1-6-77	10:50 am	3000		500	< 10	1000		600		40	40
1-7-77	10:20 am	1800		< 10		500		<10		75	30
1-12-77	1:00 pm	600		200	100	1600		0	10	50	30
1-13-77	10:00 am	300		200	130	2000		80	100 ^a	100	40
1-13-77	1:00 pm	200			10	400			250 ^a		
1-13-77	2:30 pm	1200			80	1800			250 ^a		
1-14-77	9:00 am	700		50	80	2100		> 800	300 ^a	80	50
1-14-77	Noon	400		80	125	1000		> 800	400 ^a	30	80
1-17-77	3:00 pm					900	30		160 ^a	20	20
1-18-77	9:30 am	300	20	20	20	1000	30	20	20	25	25
1-19-77	10:30 am		400	20	80	1000	40	30	30		60
1-20-77	11:30 am	500	30	25	40	300	40	25	50	30	30
1-21-77	9:30 am	500	40	20	30	300	30	20	20	20	20
1-25-77	9:45 am	200	< 50	< 10	10	<50	<50	< 10	< 10	0	<10
1-26-77	9:15 am	200	< 10	20	10	75	<50	< 10	20	20	20
1-27-77	8:30 am	2000	< 50	< 20	350		<50	30	250	250	300
1-28-77	8:30 am	800				1400					
1-28-77	9:30 am	1800 ^b									
1-28-77	9:30 am	300 ^b									

a Mixer purposely run at O/A = 1/2, E₂ and E₃ at O/A ~ 1/1

b Organic sampled twice at same time and place

TABLE 10. Entrainment in PPM, 3 Ext'n and 2 Strip Circuit.

Date	Time	Entrainment in PPM								
		Aqueous in			Organic in					
		L.O.	S.O.	E ₁	E ₂	Raf	P.E.	S ₂	LIX 34	LIX 64N
2-8-77	12:55 pm	400 ^a		0	0	50	0	40	6	
	12:55 pm	1200 ^a							6	
2-9-77	1:15 pm	750		20	20	250	30	30	6	
2-10-77	11:45 am				20	30	<10	<10	5.3	
2-22-77	1:00 pm	2600				50				6.5
2-23-77	9:00 am	1700				30	30			6.5
	1:00 pm	1600				10	70			6.5
2-24-77	9:00 am	3400				<10	<20			6.5
	1:15 pm	400 ^b				<10	50			6.5
2-25-77	9:00 am	800 ^b				<10	70			6.5
3-2-77	4:30 pm	200	500			10		20	2.1	4.0
3-3-77	9:00 am	250	500			10		10	2.1	4.0

(a) Organic sampled twice at the same time and place.

(b) Second picket fence inserted into E₁ settler after 9:00 am sample.

container that would not be wetted by the entrained phase, i.e., organic phases were sampled with plastic containers, and aqueous phases were sampled with glass containers.

The entrainment measuring portions of the centrifuge tubes used in this study are calibrated in 50 ppm sections. Thus, values under 50 ppm were estimated with the aid of a magnifying glass. Suffice to say that entrainment values of 20 ppm or less are quite low and difficult to measure accurately.

Several things in the entrainment data stand out (Tables 9 and 10). For example, consider the entrainment values for the loaded organic (L.O.) on 1-28-77, Table 9 and 2-8-77, Table 10. Note that on each day two samples were taken at the same time and that the entrainment values differ markedly. The problem seems to be caused by the crud which was at the organic-aqueous interface. At times some of the crud made its way over the organic overflow weir and moved into the loaded organic surge tank. A second thing to note is that aqueous entrainment in the loaded organic is fairly high overall, averaging 700 ppm in 1+1 circuit and 1000 ppm in the P-S circuit over the period 1-12-77 to 1-28-77 when the extraction mixers were running aqueous continuous. It is difficult to explain why the entrainment in the P-S circuit is 300 ppm higher

than in the 1+1 circuit. The difference in organic concentrations is only 1-2 v/v%, O/A ratios are about the same, and settler times are the same. Perhaps aqueous entrainment builds a little in each stage as the organic passes from E₃ to E₂ to E₁.

As a way to crudely check the aqueous entrainment in the loaded organic stream, we monitored the aqueous drained from the bottom of the loaded organic surge tank in the P-S circuit over different periods of time. These studies confirmed that aqueous entrainment of about 1000 ppm in the loaded organic was normal in our system. However, these studies also showed that the pilot plant would sometimes run for one or two days with very little aqueous collecting in the loaded organic surge tank, and at other times, a large amount of aqueous would collect just running over half a day. It looked like surges of entrainment took place perhaps similar to sludge runs in a commercial circuit.

In order to determine the residence time required in a loaded organic surge tank to reduce the aqueous entrainment below 100 ppm the following study was carried out: about a liter of organic was collected in a plastic container at the inlet pipe to the respective loaded organic surge tank. The organic in the containers was then sampled at the indicated times and entrainment

measured (Table 11). Both organic streams had less than 50 ppm aqueous entrainment after ten minutes in the plastic container indicating that much of the aqueous entrainment will settle to the bottom of a loaded organic surge tank.

TABLE II. Aqueous Entrainment as a Function of Loaded Organic Surge Tank Residence Time

Time	Aqueous in Loaded Organic (ppm)	
	S-P	1 + 1
0.....	2000	1500
3 min.....	500	200
5 min.....	200	75
10 min.....	50	50

It is interesting to note that aqueous entrainment in the loaded organic was also quite high when LIX 64N was running in the 3+2 circuit, but that this entrainment was reduced significantly by adding an extra PVC picket fence into the E₁ settler (Table 9, 2-24-77). The LIX 34-LIX 64N mixture also showed relatively low aqueous entrainment in the loaded organic with the extra PVC picket fence in the E₁ settler. Presumably, the second picket fence would have benefited the LIX 34 circuits previously run, but time was not available to verify this.

Low organic entrainment in pregnant electrolyte is crucial since cathode quality is adversely affected by large amounts of organic in the tank-house. As can be seen from the data, LIX 34 performs well from this point of view. There are several instances where the organic entrainment values were very high, 1-6-77 (Table 9) is an example; however, we do not believe these values are typical and result from poor sampling technique. In order to get enough electrolyte recycle to the strip mixers, an electrolyte head had to be built in the aqueous compartment at the rear of the settler. If by spillage, entrainment, or the like, organic got to the surface of this electrolyte it was trapped since the aqueous exit was at the bottom of this rear compartment. Since the head was built up to the level of the aqueous overflow weir, sampling the aqueous in such a way as to minimize extraneous organic from the sample was tricky. Once all the operators became fully aware of the problem, the entrainment values settled down to about 20 ppm in the circuits using LIX 34. The values for LIX 64N were somewhat higher, averaging about 50 ppm for five determinations.

An important operating cost for solvent extraction is the organic loss via entrainment in raffinate. In the 1+1 and P-S circuits the entrainment values for LIX 34 in raffinate streams were a little higher than we would like to see, but during the last two weeks of operation they had settled down to much more acceptable levels, averaging 30 ppm (Table 9). Why the reported raffinate values are extraordinarily high for 1-28-77 is not known.

From an entrainment standpoint the LIX 34-LIX 64N mixture appears to behave very well (Table 10). However, to draw conclusions on only two sets of entrainment data is tenuous.

No definite conclusions about the effects of impeller speed or temperature on entrainment could be drawn from the data we collected. It is expected that both should have some influence on entrainment, but the temperature range of comparative samples (about 5°C) or the range of impeller speeds (425 - 475 rpms) may be too narrow to reflect the expected results. The 1+1 and P-S circuits were run at 375 rpms for the weekend of 1-21-77, and

the entrainment values for 1-24-77 are quite low; but again, drawing conclusions on one set of entrainment values is speculative.

One variable we did find which significantly altered the organic entrainment in the raffinate stream was the O/A ratio in the mixer. Consider the organic entrainment in E₁ of the P-S circuit for 1-13-77 through 1-17-77 (Table 9) where the values are very high; averaging about 250 ppm. This mixer was run at an O/A of ½ compared to the normal ratio of about 1-1.3/1. Laboratory studies on entrainment confirm the observation that mixer O/A ratios significantly less than one have an adverse effect on organic entrainment in the raffinate exit stream, and that the phenomenon is much more pronounced with LIX 34 than with LIX 64N.

Crud buildup in SX settlers will have an influence on both entrainment and phase separation when it is not controlled. As a result, the tendency for a reagent to cause or increase crud buildup in an operating circuit must be considered in reagent evaluation. Within two days after startup crud was noted in the extraction settlers of the pilot plant and remained for the entire pilot plant study. The crud was always more visible in the extraction settlers than in the strip settlers but seemed to reach a steady-state level in both settlers. Samples of the crud were analyzed in our research laboratories and shown to be the same as the crud which was collected from the pilot plant when LIX 64N was used as the reagent. In both instances the solid portion of the crud was shown to be silicates and sulfates of many metals, primarily Fe, K and Cu. This solid portion, when wetted, has film-like properties which trap aqueous and organic resulting in the formation of crud. The organic should be recoverable by centrifuging. It is interesting that crud formation has been observed with an SX feed and kerosene even without the addition of an SX reagent⁽⁴⁾.

Long Term Effects

Over the course of the pilot plant run no long-term or potential long-term problems were seen. As predicted from laboratory studies⁽³⁾ no reagent degradation was observed, and normal reagent criteria such as kinetics, extraction power and phase separation showed no changes over the extent of the 2-month 1+1 and P-S pilot plant runs.

Conclusion

The major goals of the pilot plant study were met. Both the 1+1 and P-S circuit concepts, teamed with a selective reagent like LIX 34, have the potential of extending the solvent extraction process to the treatment of low copper — high iron feeds. In addition, the results of the lower strip acid circuit run are encouraging. For the situations where a 1+1 or perhaps even a 2+1 circuit is needed, the ability to strip effectively with lower acid offers the operator a tankhouse which should be easier to maintain and from which better copper can be produced.

An area which offers exciting potential is the mixing of LIX 34 and LIX 64N in a circuit. Because iron loading decreases much faster on a LIX 34-LIX 64N mixture than is predicted based on the per cent of each reagent present, successful circuits, even from high iron feeds, may very well be possible using a mixture of the two reagents. This type of a circuit has the potential to offer cost savings over a circuit using an oxime extractant, where the tankhouse bleed requirement may be high, or

over a LIX 34 circuit, where the reagent cost may be higher. Each individual case will have to be analyzed as to the best method of treatment; however, if the circuit using an oxime as the extractant is borderline because of iron transfer to the tankhouse, then consider LIX 34.

We had hoped to be able to crosscheck reagent loss by inventory measurement, but the many spills due to joints cracking, elbows breaking, etc. prevented this crosscheck. Only a certain type of PVC fitting gave us problems and these problems were equally shared by organic and aqueous lines. Therefore, these mechanical failures were not reagent related.

Acknowledgement

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Chemicals, Inc. A special thank you is extended to Mr. Wayne Jensen, now with the Criterion Corporation, Casa Grande, Arizona, under whose direction the major portion of this study was carried out. Finally, we acknowledge the many people of Cities Service Copper Company without whose efforts this project could not and would not have taken place. These people not only made this study possible; they also made it pleasurable.

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DISCUSSION

D. Spink: The stability of LIX-34 has been emphasized in your paper. How does LIX-34 hold up in acidic nitrate solutions?

G. Kordosky: Degradation in nitrate systems can be via 3 mechanisms: a) hydrolysis, b) oxidation or c) nitration of the aromatic ring. LIX® 34, as already discussed, is chemically stable to hydrolysis. Furthermore, it should be far less susceptible to oxidation and nitration than the oxime type reagents.

A. Georgeaux: Have you comparative data about stability of LIX 34 and LIX 64N?

G. Kordosky: LIX® 34 is very stable when stirred against a solution of 30 g/l Cu and 150 g/l H₂SO₄ at 81°C. Little or no degradation is seen after nearly 200 days contact. For actual data see the paper "Synthesis, Structure and Hydrometallurgical Properties of LIX 34" by M.J. Virnig given at ISEC '77.

D. Todd: What are the relative kinetic rates of copper loading between LIX 34 and LIX 64N?

G. Kordosky: In a standard, closed box kinetics test, using a feed solution patterned after copper leach solutions, LIX 34 will load in 45 seconds what LIX 64N loads in 40 seconds. Tests with a wide variety of other feed solutions also show that LIX 34 kinetics are only slightly slower than those of LIX 64N. One note of caution would be that in normal mixers used in the industry, short-circuiting can magnify differences in kinetics.

Copper Extraction with an Alkylated 8-Hydroxy-Quinoline: Modifier, Effects and Kinetics in Mixed Copper-Iron Solutions

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SUMMARY

From equilibrium and kinetic measurements on copper solvent extraction with an alkylated 8-hydroxy-quinoline (Kelex 100), it has been found that addition of nonyl phenol as a diluent modifier increases the equilibrium distribution of copper between the two phases but reduces the rate of copper extraction. The fall in the rate of copper extraction with nonyl phenol concentration is paralleled by an increase in the interfacial tension of the systems, which may be indicative of a H-bonded interaction between nonyl phenol and Kelex 100. The addition of Fe^{3+} to the aqueous phase reduces the rate of copper extraction by nearly an order of magnitude. The presence of iron in both the organic and aqueous phases does not affect the rate of stripping copper from the organic phase, however.

Introduction

SINCE KELEX 100 (an alkylate 8-hydroxy-quinoline, Ashland Chemical Co.) was first introduced as a selective extractant for copper⁽¹⁾ there have been several papers describing the hydrometallurgical behaviour of this extractant⁽²⁻⁵⁾, its behaviour with metal ions other than copper^(6,7) and the factors of importance in design of a Kelex 100 solvent extraction plant⁽⁸⁾. A review of the properties of Kelex 100 has recently been given⁽⁹⁾. The selectivity of this reagent for copper over ferric iron was found to be due to kinetic factors^(6,10). In view of this finding, it is perhaps surprising that relatively few papers have reported on the fundamental equilibrium and kinetic behaviour of this extractant although Spink and Okuhara⁽¹¹⁾ have compared equilibrium and kinetic data for LIX 65N (β hydroxy-benzophenone oxime, General Mills Inc.) and Kelex 100, and Flett et al⁽¹²⁾ have reported results of a basic study of the equilibrium and kinetics of the extraction of copper by Kelex 100. This latter study suggested that the slow step in the extraction of copper by this reagent was the formation of the 1:2 complex at the interface and this conclusion has also recently been reached by Fleming⁽¹³⁾.

To be able to use Kelex 100 in aliphatic diluents, it is necessary to avoid third phase formation by addition of a diluent modifier. The manufacturers recommend nonyl phenol and offer a modified product for sale, Kelex 120, which is 20% Kelex 100, 80% nonyl phenol. Ritcey⁽²⁾ has compared the effects of nonyl phenol, tributylphosphate and isodecanol as modifiers in the extraction of metal ions by Kelex 100. While TBP reduces the degree of copper extraction, isodecanol has only a slight effect on the extraction properties of the system. Nonyl phenol

on the other hand initially increases the degree of extraction up to a concentration of 10 v/o of modifier whereafter a further increase in nonyl phenol concentration causes a steep decrease in degree of extraction of copper. Spink and Okuhara⁽¹¹⁾ presented data for several diluents which showed a variability of copper distribution with nonyl phenol concentration depending on the nature of the diluent and Kelex 100 concentration. Some kinetic work on the effect of nonyl phenol on the rate of copper extraction was included in this study but gave rather ambiguous results. Recently it has been shown⁽¹⁴⁾ that nonyl phenol addition depresses both the extraction equilibrium and the rate of copper extraction by the hydroxyoxime reagent LIX 64N and a straight line relationship was found between the initial copper extraction rate, measured using a falling drop technique, and the nonyl phenol concentration. A limited interfacial tension study showed that nonyl phenol was less interfacially active than LIX 64N but no measurements were reported on the mixed nonyl phenol — LIX 64N solution. Preferential solvation of unionised β -hydroxyoxime molecules by nonyl phenol is concluded to give rise to the observed rate effect. This effect has been put to commercial use in the development of the P5000 series of reagents produced by Acorga Ltd⁽¹⁵⁾. It is therefore of considerable interest to see whether more quantitative examination of the effects of nonyl phenol on the extraction of copper by Kelex 100 shows the same trends as for the hydroxyoxime compounds.

Although the high selectivity shown by Kelex 100 for copper over ferric iron is now well known to be kinetic in origin, no systematic study of the relative rates of copper and iron extraction has been carried out. A limited amount of data on the effect of time of mixing on the copper:iron ratio in the organic phase has been presented by Ritcey⁽⁶⁾ which suggests that the rates of iron extraction and perhaps of copper-iron exchange are very slow. A preliminary study by Fleming⁽¹³⁾ on the extraction of copper in the presence of other metal ions by Kelex 100 and LIX 64N showed that a considerable decrease in the rate constant resulted, due to the effect of small amounts of ferric ion. In this study the first stage of reaction of Kelex 100 with Fe^{3+} was found to be rapid formation of a green intermediate species in the aqueous phase followed by a slow reaction, possibly at the interface, which gives rise to the maroon complex FeR_3 in the organic phase. For mixtures of copper and ferric ions, copper is extracted first which shows, the author suggests, that a metal exchange reaction occurs at the interface as the slow step of the process.

This paper, therefore, reports the results of investigation into the effect of nonyl phenol on the equilibrium and kinetic behaviour of the Kelex 100 — copper extraction system and some data on kinetic behaviour of the Kelex 120 — copper — iron system.

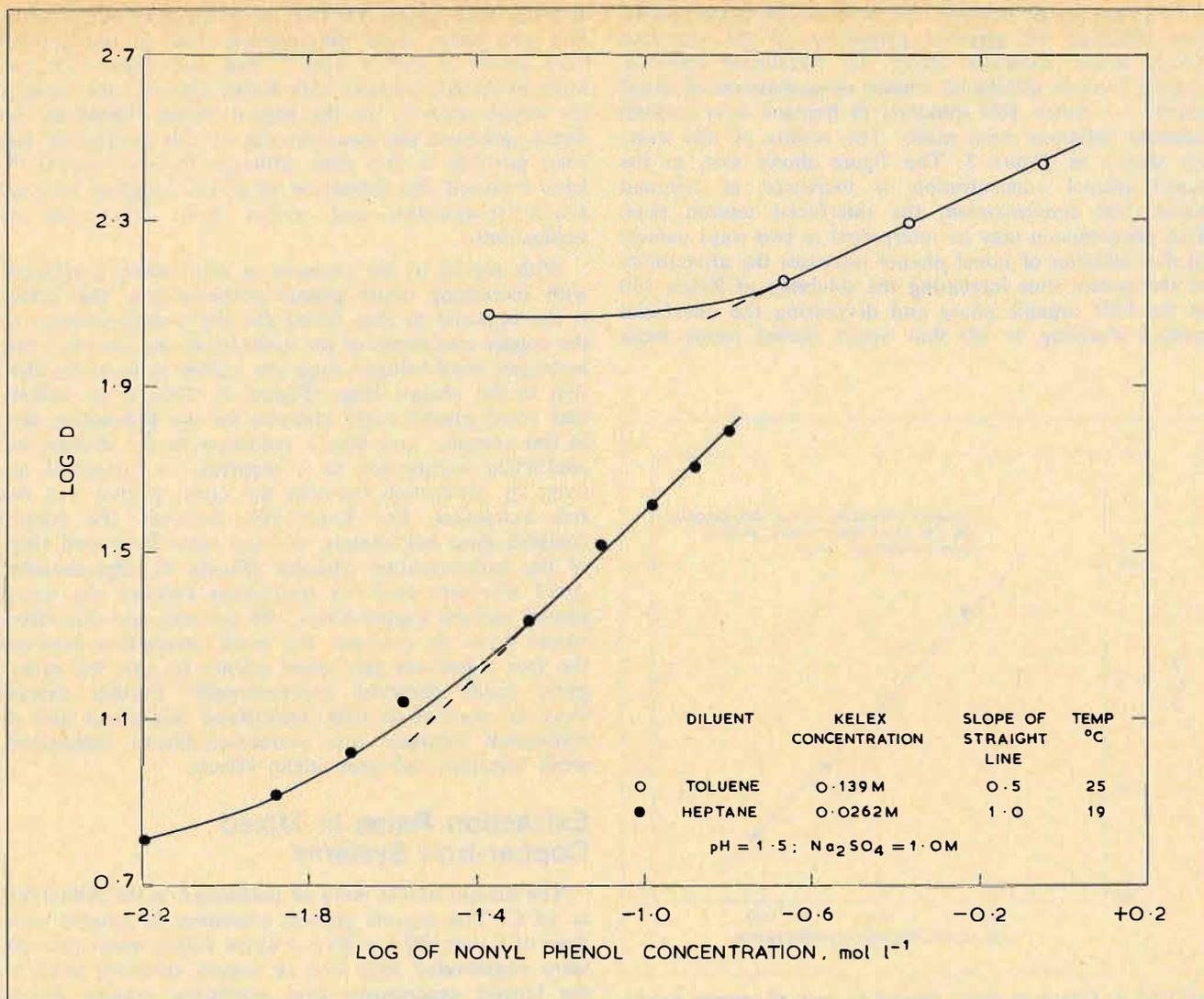


FIGURE 1. Extraction of copper with Kelex 100: variation of log D with nonyl phenol concentration.

Experimental

The Kelex 100, Kelex 120 and nonyl phenol were first conditioned by acid and water washing cycles before dilution, as required, with either AnalaR heptane or toluene. Copper sulphate, ferric sulphate and sodium sulphate of BDH AnalaR grade were used throughout and pH adjustments were made with sulphuric acid and sodium hydroxide solutions prepared from BDH standard solutions.

For both equilibrium and kinetic studies an AKUFVE apparatus as described by Rydberg⁽¹⁶⁾ was used with ancillary data logging and control systems as described previously⁽¹⁷⁾. For tracer work, pure copper was irradiated in a neutron flux to produce ⁶⁴Cu. Copper sulphate solutions were prepared from this irradiated metal as previously described⁽¹⁸⁾. The iron tracer used was ⁵¹Fe. The techniques for generation and treatment of equilibrium and kinetic data were as previously described⁽¹⁸⁾.

The interfacial tension data were obtained using a Du Nuoy ring tensiometer. The experimental techniques employed here have also been described in a previous publication⁽¹⁹⁾.

Results and Discussion

Equilibrium and Kinetic Effects of Nonyl Phenol Addition

The effect of nonyl phenol on the distribution of copper between heptane and toluene solutions of Kelex 100 and a 1M solution of sodium sulphate is shown in Figure 1. The figure shows that log D increases with increasing nonyl phenol concentration for both diluents. The data are seen to tend towards a straight line of slope unity for the heptane diluent and 0.5 for the toluene diluent which might indicate a direct interaction between nonyl phenol and the copper complex thus providing the basis for the observed synergism in this extractant — modifier system.

The corresponding effect on extraction rate is shown in Figure 2. The figure shows that addition of nonyl phenol to the system depresses the rate of copper extraction. Although the few data points available are seen to lie on a straight line of slope 0.115, no physical significance can be given to this slope and the effect is quite small.

In order to see whether the addition of nonyl phenol was affecting the physical properties of the interface which would naturally affect the interfacial rate-controlling process, interfacial tension measurements of nonyl phenol — Kelex 100 solutions in heptane over sodium sulphate solutions were made. The results of this study are shown in Figure 3. The figure shows that, as the nonyl phenol concentration is increased at constant Kelex 100 concentration, the interfacial tension rises. This phenomenon may be interpreted in two ways namely (i) that addition of nonyl phenol increases the aromaticity of the system thus increasing the solubility of Kelex 100 in the bulk organic phase and decreasing the interfacial tension lowering or (ii) that nonyl phenol forms weak

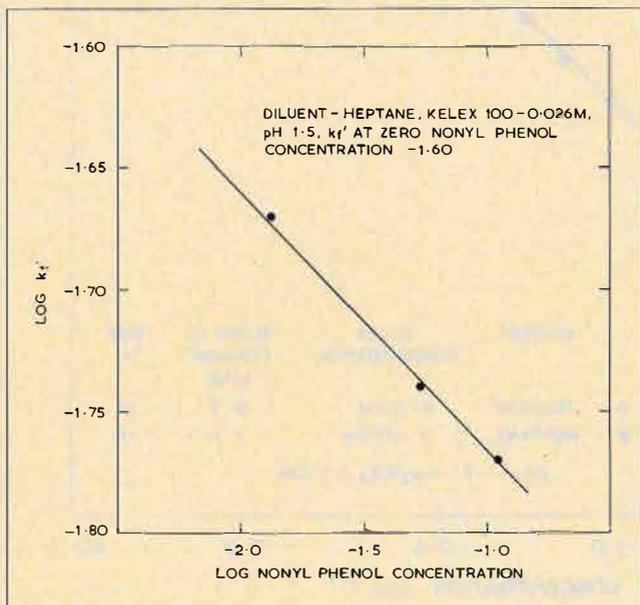


FIGURE 2. Effect of nonyl phenol on rate of copper extraction with Kelex 100.

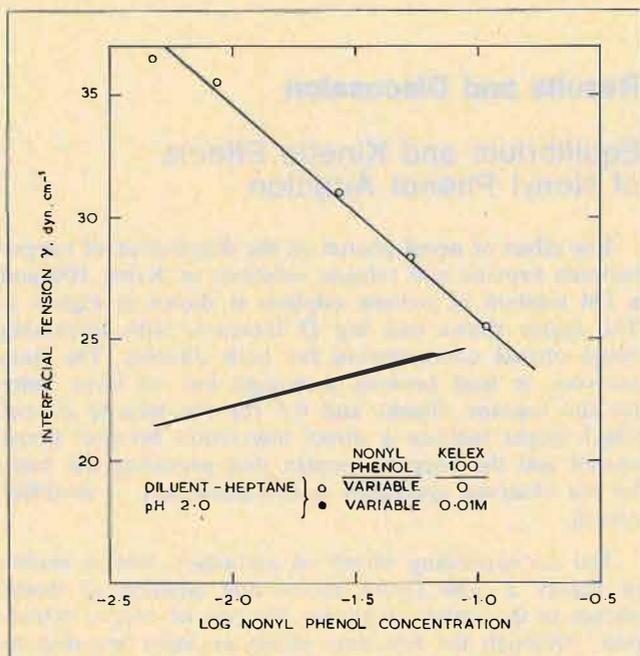


FIGURE 3. Effect of nonyl phenol on interfacial tension of Kelex 100.

H-bonds with Kelex 100 thus removing it from the interface and hence from the reaction zone. It has already been shown in earlier work⁽¹⁹⁾ that carboxylic acids can form H-bonded adducts with Kelex 100 and thus option (ii) would seem to be the logical choice. However, no direct spectroscopic measurement of this interaction has been possible in this case although Russian workers⁽²⁰⁾ have reported the formation of a 1:2 complex between 8-hydroxy-quinoline and phenol from cryoscopic investigations.

With regard to the increase in distribution coefficient with increasing nonyl phenol concentration, this effect is the opposite to that found for the hydroxyoximes. In the copper complexes of the hydroxyoximes, however, two hydrogen bond bridged rings are known to form in addition to the chelate rings (Figure 4). Thus it is unlikely that nonyl phenol could compete for the H-bonding sites in this complex and thus a reduction in the distribution coefficient occurs due to a reduction in extractant activity by interaction between the nonyl phenol and the free extractant. For Kelex 100, however, the copper complex does not contain the two extra H-bonded rings of the hydroxyoxime complex (Figure 4). Opportunities could therefore exist for interaction between the nonyl phenol and the copper-Kelex 100 complex and this effect would have to override the weak interaction between the free extractant and nonyl phenol to give the synergistic result observed experimentally. Further careful work is required to fully understand this effect and to distinguish between true extractant/diluent interaction, weak solvation and aromaticity effects.

Extraction Rates in Mixed Copper-Iron Systems

The kinetic studies were all performed in the AKUFVE at 18°C. The organic phases, consisting of toluene solutions of Kelex 120 (i.e. 20 v/o Kelex 100 in nonyl phenol), were equilibrated with iron or copper solutions prior to the kinetic experiments thus producing organic phases containing considerable amounts of metal but not achieving total conversion of the Kelex to either the copper or iron forms. The radiotracer of the metal under study was then added to the aqueous phase and the rate of extraction studied in presence of macro quantities of each metal ion. The results are given in Table 1.

The table shows that the rate of iron extraction is very much slower than copper by almost two orders of magnitude. It is interesting, although perhaps not significant, to note that the rate ratio between copper and iron is constant for the two different pH and extractant concentration values presented in the table. The rate of

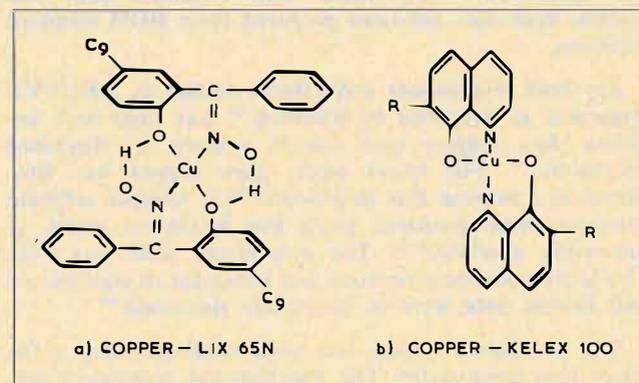


FIGURE 4. The copper-LIX and copper-Kelex complexes.

copper extraction by 0.0019 molar Kelex 100 can be compared with that predicted from Figure 17 (reference 11). The predicted value for $\log k'_r$ of -1.20 min^{-1} compares very well with the experimental value of -1.17 min^{-1} recorded in Table 1. As it has been shown⁽¹¹⁾ that $\log k'_r$ is a linear function of $\log [\text{Kelex 120}] + \text{pH}$, it can be predicted that, on changing from pH 1.80 and 0.0019M free Kelex 100 to pH 1.44 and 0.0069M Kelex 100, the rate of copper extraction should increase to $\log k'_r \approx -1.00$. However, Table 1 shows that the rate of copper extraction has fallen by nearly an order of magnitude. This effect may be attributed to the presence of iron in agreement with Fleming⁽¹³⁾ who found the presence of iron reduced the copper extraction rate by just over an order of magnitude. The rate of iron extraction also decreases on changing from the higher pH and low Kelex 120 concentration to the lower pH and higher Kelex 100 concentration system. Since nothing is known of the mechanism of iron extraction by Kelex 100 or of the dependency of k'_r on pH and Kelex 120 concentration, no further comment can be made on the iron rate measurements. The results, however, show no evidence for copper-iron exchange reactions and in any event such reactions must be very slow as neither metal complex is interfacially active. Thus the rate controlling step in such an exchange would need to be the rate of stripping of the metal in the organic phase under the pH conditions prevailing which at the pH values of the present work would be very slow indeed.

It was, therefore, also of interest to measure the rate of stripping of copper and iron from Kelex 120 and to examine the effect of each ion on the rate of stripping of the other. The results of the stripping rate tests are shown in Table 2.

The table shows that neither copper nor iron interferes in any way with the strip kinetics of the other metal in contrast to the effect of iron on the rate of copper extraction. As expected from the extraction rate data, iron strips much more slowly than copper although the rate difference is about an order of magnitude less under the given strip conditions than that found for the extraction rates. Nothing of significance can really be deduced from this observation because a different diluent was used and, as stated earlier, nothing is known about the mechanism of iron extraction.

Conclusions

The addition of nonyl phenol to Kelex 100 increases the distribution coefficient of copper in both heptane and toluene diluents. The presence of nonyl phenol reduces the rate of copper extraction which is paralleled by an increase in interfacial tension suggesting direct interaction between nonyl phenol and Kelex 100. The rate of iron extraction by Kelex 120 is two orders of magnitude slower than the copper extraction rate. The presence of iron reduces the rate of copper extraction by about a factor of ten. However, neither metal affects the rate of stripping of the other from loaded Kelex 120. To fully understand the rate effects on extraction from mixed copper-iron solution, some knowledge of the iron extraction mechanism is necessary.

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TABLE 1. Extraction Rates in Mixed Copper-Iron Systems.

Total Kelex 100 concentration = 5 v/o = 9.678 g l^{-1} = 0.0317M,
Nonyl phenol concentration = 4 v/o = 0.146M, Na_2SO_4 concentration = 1.0 M.

Initial inactive Fe^{3+} concentration prior to equilibration = 6.936 g l^{-1} ,
Initial inactive Cu^{2+} concentration prior to equilibration = 1.728 g l^{-1} ,
Phase ratio O/A = 0.99

Tracer Added	Final pH Value	Equilibrium Metal Concentration in the Aqueous Phase		Concentration of Free Kelex 100 at Equilibrium moles l^{-1}	Rate of Metal Extraction $\log k'_r \text{ min}^{-1}$
		Fe g l^{-1}	Cu g l^{-1}		
Fe	1.42	6.478	—	0.0069	-3.76
Cu	1.44	6.478	0.010*	0.0069	-1.81
Fe	1.77	N.D.	0.791	0.0019	-3.11
Cu	1.80	—	0.791	0.0019	-1.17

*Initial tracer copper concentration 0.011 g l^{-1} .

TABLE 2. Stripping Rates of Copper and Iron from Kelex 120.

H_2SO_4 concentration = 150 g l^{-1} , Aqueous iron concentration = 2 g l^{-1} ,
Aqueous copper concentration = 40 g l^{-1} , Temperature = 18°C , Diluent = Napoleum 470.

Kelex 120 Concentration		Stripping Rate	
Copper Form Vol. %	Iron Form Vol. %	Cu^{2+} $\log k_b \text{ min}^{-1}$	Fe^{3+} $\log k_b \text{ min}^{-1}$
2.982	0	0.14	—
2.790	2.790	0.14	-1.08
0	2.985	—	-1.08

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DISCUSSION

J.E. Barnes: I believe that the current obsession with modifier effects shows a basically unsound philosophy. I think that, from a practical point of view, we should be aiming at simplifying the solvent system

rather than complicating it by the use of modifiers. For example, in the separation of cobalt & nickel with D2EHPA it is common practice to add TBP to the organic phase as a modifier. We have found that by operating at the correct temperature TBP can be omitted from the organic phase with advantages such as greater selectivity and ease of maintaining a consistent organic phase composition.

D.S. Flett: We completely agree with Dr. Barnes concerning the practicality of simplifying the solvent system by aiming to avoid the use of diluent modifiers. However, our aim was rather different. We were concerned with showing further examples of the relationship between changes in the interfacial behaviour of the system, the kinetics of the system and interactions, in particular weak H-bond interactions between the extractant, the complex and diluent additives. From such studies we believe that a deeper understanding of the chemistry of the extraction process will arise leading in time to the kind of goals envisaged by Dr. Barnes. However it is worthwhile at this point to remind Dr. Barnes that Acorga Ltd are staking their future as reagent manufacturers on such modifier-extractant interaction in the production of their P5000 series.

M.A. Hughes: Your work describes the use of the AKUFVE to measure kinetics. In this technique I understand that you use a constant power input into the stirred cell. Is it possible that when all other variables are held constant but the organic phase is varied in diluent type and modifier type (e.g. nonylphenol) that the possible alteration to the interfacial tension in the system leads to smaller (or larger) drops? Thus some changes in the kinetics may be due to a change in effective interfacial area. Also, changes in

- (1) coalescence phenomena and/or
- (2) diffusional film thickness around the drop might account for some of the observed phenomena.

Do the authors consider that there are no local temperature changes in the centrifuge where the phases are under high shear stress? Such temperature changes would affect kinetics.

D.S. Flett: Dr. Hughes is of course quite right that changes in the organic phase composition cause changes in the interfacial tension of the system. It is, therefore, possible that under conditions of constant power input, changes in the interfacial area generated in the AKUFVE mixer can occur which will affect the observed extraction rate. At present, however, there are no known means of estimating this change in interfacial area and thus no estimate of the effect on the observed extraction rate can be made. As the measured change in interfacial tension with nonylphenol concentration is quite small, we have assumed that a kinetic contribution from the physical consequences of this effect would be small and have ignored it.

We certainly do not believe that changes in diffusional film thickness around the drops in any way contribute to the observed change of extraction rate in our system.

With regard to temperature changes in the AKUFVE centrifuge we do not believe these to be of importance as the residence time in the centrifuge is so short. Temperature control in the system is achieved via a cooling coil located in the mixer.

A. Leveque: From our own experience in fields other than copper, the purity of Kelex may have some influence on the kinetic of extraction and interfacial properties. Have the authors any comments on that?

D.S. Flett: The differences in purity, etc., of different batches of Kelex and the probable effect on kinetics were discussed with respect to the extraction of gallium (discussion on paper 14a). In our study of the effect of nonyl phenol on the extraction equilibrium and kinetics we have used the same batch of Kelex 100 throughout at constant Kelex 100 concentration and thus constant impurity concentration. We must also point out that the Kelex 100 was thoroughly washed with acid and water before use. Therefore, unless the nonyl phenol is preferentially interacting with the impurities (and no evidence whatsoever for this exists) then the data do reflect the effects of interaction between nonyl phenol and Kelex 100.

Solvent Extraction of Vanadium (IV) with Di-(2-ethyl-hexyl) phosphoric Acid and Tributylphosphate

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E. Strandell, Mineralprojet Ranstad Project group of LKAB, AB Atomenergi and Vattenfall AB, Stockholm, Sweden.

ABSTRACT

Solvent extraction of fourvalent vanadium with a mixture of di-(2-ethylhexyl) phosphoric acid and tributylphosphate from two different leach solutions is discussed. One of these solutions is linked to the proposed uranium production plant at Ranstad in Sweden. The other solution is related to the recovery of vanadium from ash and soot residues from oil-fired power stations. A special emphasis is put on the kinetic effects involved in competitive extraction of other metals such as iron.

Introduction

RECOVERY OF VANADIUM BY MEANS OF SOLVENT EXTRACTION was first considered in connection with the basic work on uranium extraction at Oak Ridge National Laboratory (ORNL) in the fifties. This was a consequence of the fact that liquors from the uranium mills contained the valuable metal in concentrations comparable to that of uranium.

Up to now several solvent extraction plants for vanadium production, both alone and in combination with uranium plants, have been put in operation. In several cases amines have been used as extraction reagents⁽¹⁾. This reagent class extracts anionic species of pentavalent vanadium from moderately acid solutions. To attain the pentavalent state in acid solution, a relatively high oxidation potential must be kept. Depending on the raw material and its pretreatment before the leaching procedure, strong and expensive oxidation chemicals may have to be used.

Tetravalent vanadium can be extracted by acidic organophosphorous reagents, e.g. di-(2-ethylhexyl) phosphoric acid (HDEHP). This extractant was used by ORNL in the s.c. Dapex process^(2,3) and is also practised in a plant newly brought in operation⁽⁴⁾.

The purpose of this paper is to evaluate the conditions for solvent extraction of vanadium with HDEHP from leach solutions emanating from two different projects.

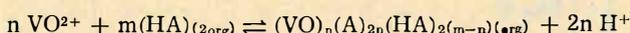
One of these solutions is linked to the proposed uranium production plant of Ranstad in Sweden under the direction of the Swedish iron mining company LKAB, Lousavaara — Kiirunavaara AB. This plant will be based on the uranium-bearing alum slate deposit in the middle of Sweden (Mineral project Ranstad). The deposit contains about 10^6 tons of uranium of which at least 0.3×10^6 is considered to be extractable. The projected mining of slate is at present 10^6 tons annually corresponding to a production of 200 tons of uranium. This production is to constitute the base for a continuous development work,

aiming at a full exploitation of the valuable components of the slate and minimizing environmental changes. The flowsheet contains a direct sulphuric acid leach and a recovery of the uranium with amine extraction. The possibility of extraction of vanadium from the uranium-barren raffinate is discussed in this paper.

The other solution is produced in a process for recovery of vanadium from ash and soot residues from oil-fired power stations. An extraction plant with a capacity of 2000 tons of ash per year, corresponding to about 100 tons of vanadium (5% content) is presently in the engineering stage. The flowsheet contains an acid leach in two steps and a solvent extraction step to recover vanadium from the leach solution. A full-scale plant is to be built by the Swedish company SOTEX AB. The project has been supported by the Swedish Board of Technical Development (STU) and the Environmental Protection Agency of Sweden.

Extraction of Vanadium(IV) with HDEHP

The extraction of vanadium in its fourvalent state from a weakly acidic solution by HDEP (HA) may be represented by the following cation exchange reaction:



It is not the intention here to discuss the stoichiometry of this reaction. However, it may be commented that data by Crouse et al.⁽²⁾ indicate that some polynuclear complexation ($N > 1$) is taking place. Thus, at constant pH the distribution factor increases with the metal concentration at a moderate loading of the organic phase. The dependence of extraction on pH and reagent concentration is positive as indicated by the given reaction.

Provided that acidity and reagent concentrations are suitable, the *equilibrium* conditions for the reaction are such that a high extraction yield is obtainable in a multi-stage system. However, experiences from the Ranstad project mentioned above have highlighted the importance of the *kinetic* conditions involved when competitive extraction of other metals is taking place.

Tributylphosphate (TBP) has been added to the organic phase as a diluent modifier in all tests throughout this work to improve phase separation characteristics. Chemical effects of TBP on the extraction of vanadium are negative but small in magnitude⁽²⁾.

Recovery of Vanadium from a Uranium-barren Raffinate Solution

According to the flowsheet for the Ranstad process uranium is extracted from the sulphuric acid leach liquor with a tertiary amine at moderate acidity. The composition of the raffinate with respect to the most important metals is shown in Table 1.

The liquor has a pH value of 0.5 to 1. This must be raised above at least 1.0 to obtain a significant extraction of vanadium. The oxidation potential is approximately +300 to 350 mV relative to a saturated calomel electrode. Assuming that chemical equilibrium with respect to potential oxidation/reduction reactions is prevailing, the ratios between various oxidation states for vanadium and iron at a potential of +350 mV, pH 1 and an absolute temperature of 298°K can be calculated from

TABLE 1. Composition of the Uranium-Barren Raffinate.

Metal	Me g/l
U.....	0.003
V.....	0.04
Mo.....	0.01
Fe.....	15
Al.....	10
Ni.....	0.3
Zn.....	0.2

TABLE 2. Valence State Ratios for Vanadium and Iron.

Valence state, ratio	Normal potential (V)	Ratio value
V(V)/V(IV).....	+1.00	$10^{-4.5}$
V(IV)/V(III).....	+0.337	$10^{6.8}$
Fe(III)/Fe(II).....	+0.770	$10^{-2.6}$

normal potentials⁽⁵⁾ according to Table 2 (the normal potential for the calomel electrode is +0.268 V).

It should be pointed out that the given ratios refer to free metal ion concentrations. Thus if no metal complexing agents are present, essentially all the vanadium should be fourvalent and all the iron twovalent. However, ligands forming complexes with Fe³⁺ may raise the total concentration of Fe(III). Chemical analysis of Fe(III) indicate values between 0.1 and 1 g/l, corresponding to a ratio of Fe(III)/Fe(II) between 1/100 and 1/10. It is well-known that Fe(III) is extracted fairly well by HDEHP. At equilibrium the distribution factor is higher than that of V(IV). However, the kinetics is slow. The extraction of Fe(II) is very low. Thus, provided the extraction kinetics for the four-valent vanadium is fast enough, a selective separation from iron in the leach solution with HDEHP-extraction might be possible.

Preliminary attempts, by the staff at Ranstad, to extract vanadium with HDEHP were negative. A close investigation at MX-Processer showed that this was due to the kinetic conditions in the system involving competitive extraction of iron and aluminium.

Extraction Kinetics

The extraction kinetics for the actual system was studied by means of the AKUFVE-technique⁽⁶⁾. Calculated volumes of leach liquor with adjusted pH and kerosene diluent were added to the AKUFVE. The system was put in operation with a high energy input to the mixing chamber to produce a homogeneous mixture of the phases. After separation in the centrifuge the liquids were returned to the mixing chamber. Adjustments were

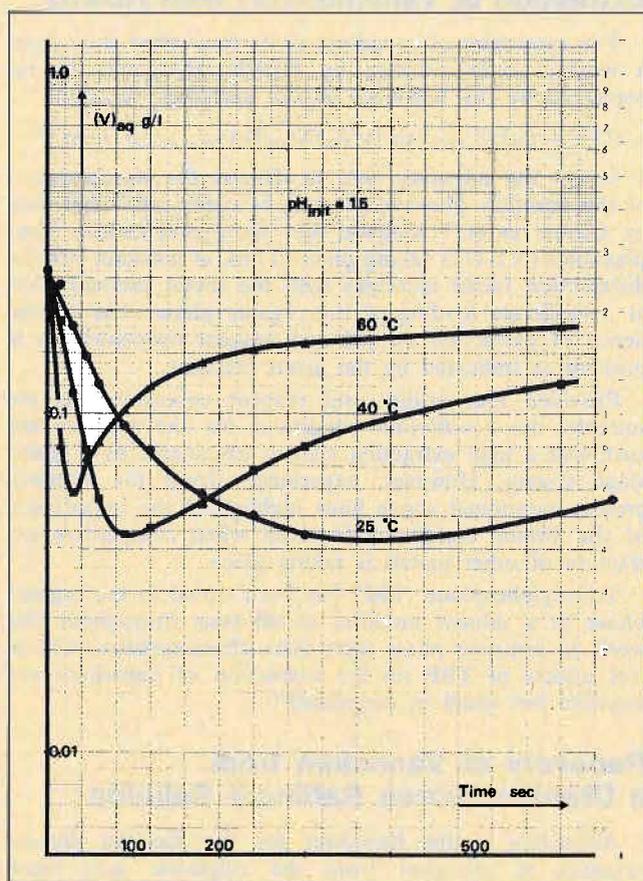


FIGURE 1. Extraction of vanadium with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 1.5.

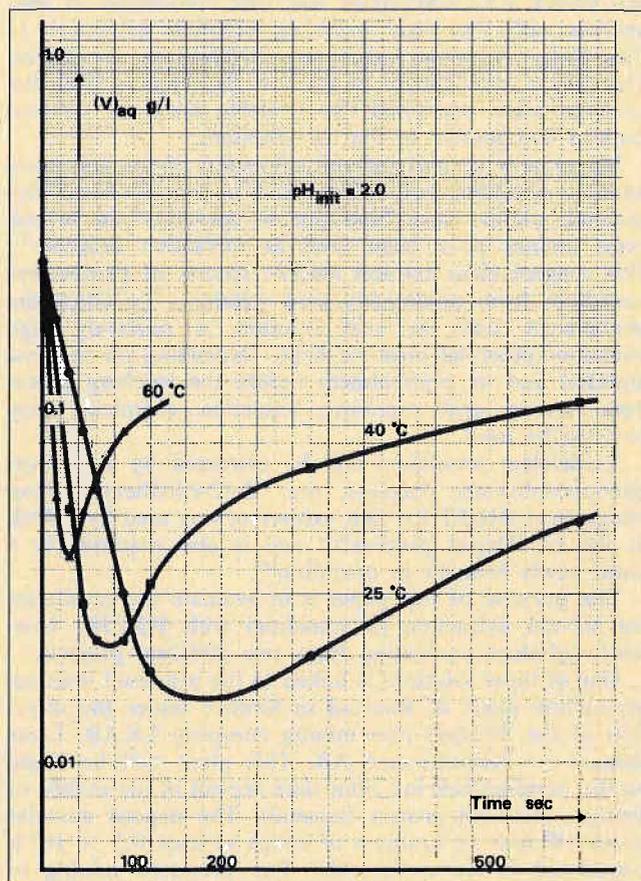


FIGURE 2. Extraction of vanadium with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 2.0.

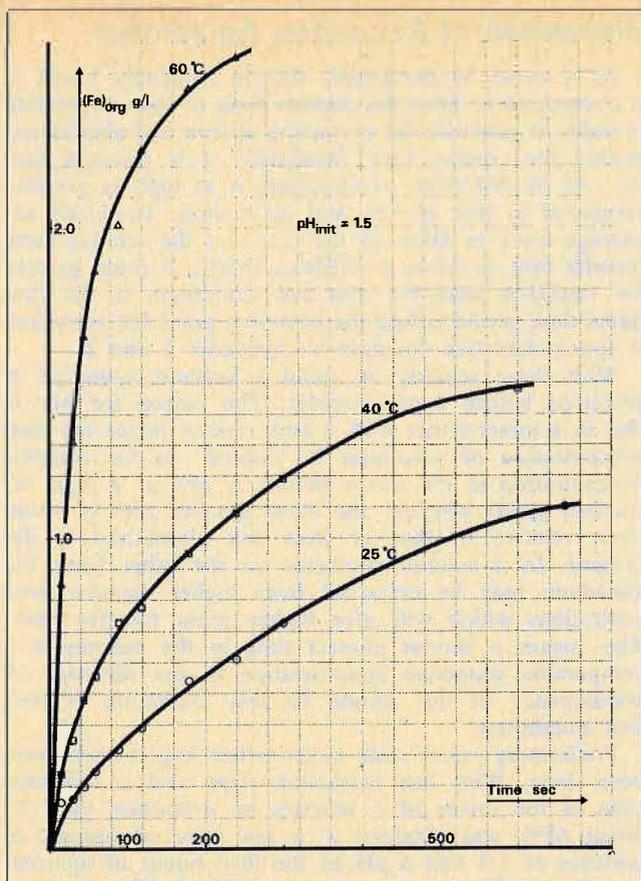


FIGURE 3. Extraction of iron with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 1.5.

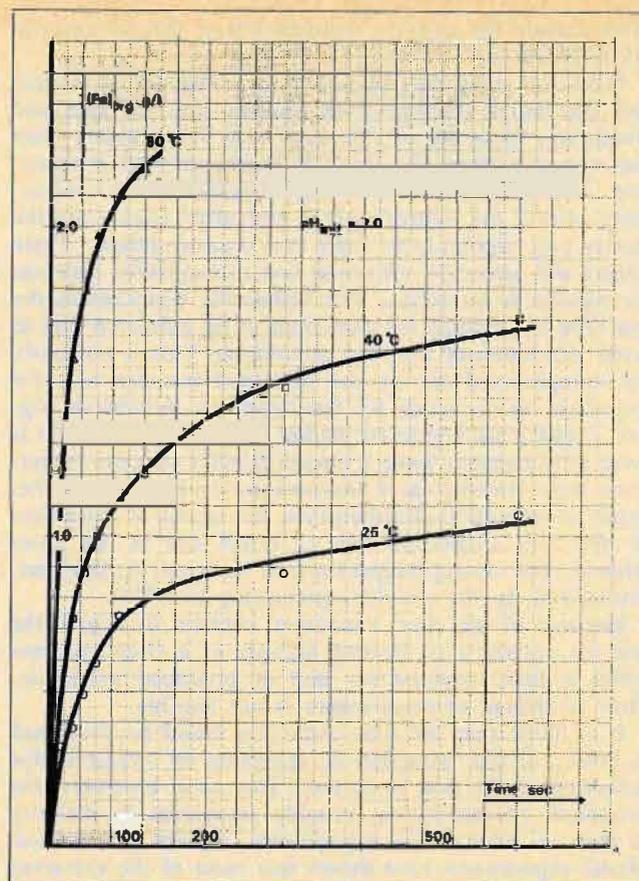


FIGURE 4. Extraction of iron with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 2.0.

made to obtain a complete phase separation and a stable dynamic state at a predetermined temperature. HDEHP and TBP in amounts corresponding to a composition of 20% (v/v) and 15% (v/v) respectively and at the same temperature as the AKUFVE-system were added to the mixing chamber at a given point of time. After 10 seconds two valves connected to sampling by-passes were opened, one for each phase, allowing small flows of the pure separated phases to pass through nozzles producing free jets from which samples could be withdrawn. Samples of 3 ml volume were collected within 2 seconds. The liquids passing continuously through the nozzles were returned to the mixing chamber.

In the centrifuge a fast phase separation is achieved and the solution volumes in the centrifuge may be considered as mainly separated. Because of this, the mass transfer between the phases in the centrifuge is supposed to be small in magnitude. The time delay from the mixing chamber through the centrifuge to the sampling points is about 5 seconds, which time should be subtracted from the sampling times counted from the addition of reagents to get the true contact times.

Since the separated liquids are recirculated to the mixing chamber in the AKUFVE each addition of a chemical will cause a transient state with a certain time period before a constant concentration of the said chemical has been obtained throughout the liquid system. The liquid system consists of a turbulent volume (V_{turb}) in the mixing chamber (to which the reagents are added) and a laminar volume (V_{lamin}) in the tubings. The time period of the transient equals the ratio between V_{lamin} and the flow through the centrifuge (F). The amplitude of the transient increases with $V_{\text{lamin}}/V_{\text{turb}}$.

To minimize the effect of the transient on the experimental conditions the values of V_{lamin}/F and $V_{\text{lamin}}/V_{\text{turb}}$ should be as small as possible. Transient state processes in connection with the AKUFVE have been discussed by Rydberg⁽⁵⁾. The mathematical correlations, documented in this work, give for the used experimental values of V_{lamin}/F and $V_{\text{lamin}}/V_{\text{turb}}$ a deviation of the reagent concentration in the mixing chamber from its infinity value of less than 0.5% after one time period and less than 0.1% after two time periods. The time period was about 8 seconds. Because of the small magnitude of the transient, its disturbing effect on the system is of minor importance.

The parameters studied were the initial pH value (1.5 and 2.0) and the temperature (25, 40 and 60°C). The obtained data is presented in Appendices 1 and 2. In Figures 1 and 2 the vanadium concentration in the aqueous phase is plotted logarithmically against time. From these figures it can be seen that the vanadium concentration passes through a minimum. The back extraction phenomenon is caused by competitive extraction of iron and aluminium. The simultaneous extraction of these metals is shown in Figures 3 and 4, 5 and 6 respectively, in terms of the metal concentration in the organic phase as a function of time.

A quantitative evaluation of the kinetic data given is difficult because of the complexity of the system and the conditions under which the experiments were performed. However, the linearity of the logarithmic plots of the aqueous vanadium concentration in Figures 1 and 2 (see especially the curve for 25°C in Figure 2) indicates that the rate of extraction is first order with respect to the vanadium concentration in the aqueous phase. For all

three metals the positive dependence of the kinetics on pH is observed.

From the given data in Appendix 1 and 2 it is evident that the initial absolute mass transfer rate for iron and aluminium in terms of $\partial[\text{Me}]_{\text{org}}/\partial t$ is much higher than that for vanadium and strongly increases with temperature. The extraction of iron and aluminium will continuously acidify the aqueous phase and after some time the metals will significantly load the organic phase. These effects will adversely influence and subsequently decrease the vanadium extraction. The higher the temperature the less time is available for vanadium to be extracted due to faster extraction of iron and aluminium. This is obviously not compensated for by the increased transfer rate for vanadium, as the levels for the respective minima in Figures 1 and 2 are higher for higher temperature. Thus, it is more advantageous from a chemical point of view to perform the extraction at a temperature in the interval between 25 and 40°C. Furthermore, the extent of extraction of iron and aluminium will be much less in the given interval. The design temperature in the plant is, however, determined by the uranium processing to 50°C.

Because of the low vanadium content (0.3 g/l) the cost for cooling (and heating because of a closed process cycle) is high, counted per unit of produced vanadium. Thus, a change of temperature is not feasible.

It is likely that the iron extraction could be decreased in favour of the extraction of vanadium by a quantitative reduction of the iron to its divalent state. However, the extraction of aluminium, roughly equivalent in molarity to that of iron in the experiments, cannot be avoided. Model experiments have shown that most of the extracted aluminium is stripped together with vanadium by a dilute sulphuric acid strip solution.

Discussion of Extraction Equipment

As is shown by the kinetic data in Appendix 1 and 2, it is essential to keep the contact time as low as possible in order to minimize the extraction of iron and aluminium. Within the contact time "available" it is essential that the rate of extraction of vanadium is as high as possible compared to that of iron and aluminium. Therefore advantage must be taken of the fact that the relative mass transfer rate, in terms of $\partial[\text{Me}]_{\text{org}}/[\text{Me}]_{\text{aq}}$, is much greater for vanadium than for iron and aluminium in the first initial time period before the turn-over point for vanadium is approached (see the data in Appendix 1 and 2).

With these remarks in mind a column contactor is preferred before a mixer-settler. The reason for this is that in a mixer-settler with a tank reactor mixer the feed concentration of vanadium is "diluted" to the aqueous concentration in the mixer (which is low at a high extraction yield) whereby the mass transfer rate of vanadium relative to that of iron and aluminium is decreased. In a column contactor on the other hand the vanadium may be extracted from higher aqueous concentrations which will give higher mass transfer rates. This means a shorter contact time in the column at a comparable vanadium concentration in the raffinate. A consequence of this should be less extraction of iron and aluminium.

Preliminary small scale mixer-settler experiments have been done. With one extraction stage and a residence time in the mixer of 5 minutes an extraction yield of about 65% was obtained at a low ratio of organic to aqueous of 1:1 and a pH of the feed liquor of approximately 1.6. The temperature was 25°C. The result is roughly in agreement with calculations from the batch

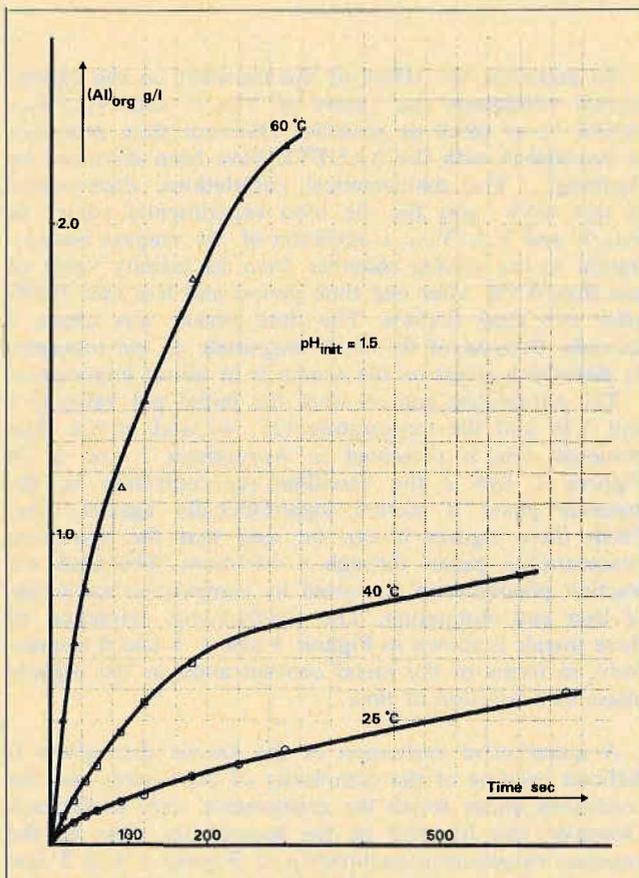


FIGURE 5. Extraction of aluminium with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 1.5.

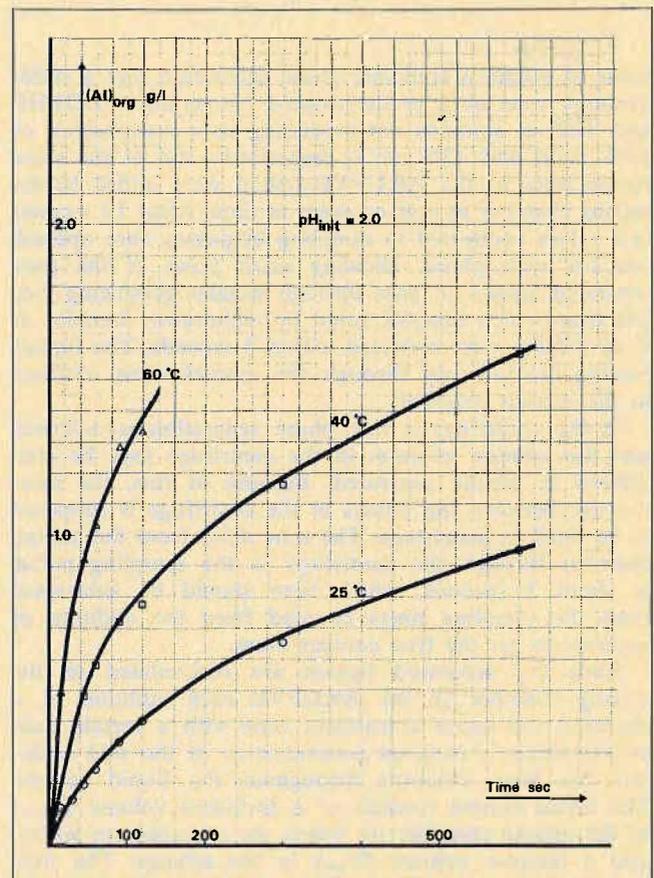


FIGURE 6. Extraction of aluminium with 20% HDEHP + 15% TBP from the Ranstad feed liquor as a function of time and temperature. Initial feed pH is 2.0.

kinetic data. More extraction stages with a proportionally increased total residence time did not increase the vanadium extraction yield substantially as was expected due to increased extraction of iron and aluminium.

New Process Conditions

At present, development work has begun on a new process with the purpose of a total exploitation of the valuable constituents of the slate deposit. Thus the content of carbonaceous matter is utilized for energy or gas production in a roasting or gasifying stage before a strong acid leach of the metal content.

This process technique will give a much higher yield of metals such as uranium, molybdenum, vanadium and aluminium. Because of the altered leach procedure the conditions for the recovery of these metals will change completely. LKAB has given a commission to MX-Processor to investigate the solvent-extraction flowsheet in the total process.

Recovery of Vanadium from Ash and Soot Residues from Oil-fired Power Station

The most abundant metals in crude oil are vanadium, nickel and iron and these are also the dominating metal constituents together with sodium and magnesium in the ash and soot residues from oil-fired power stations. The relatively high content of vanadium and nickel converts the waste product to an interesting raw material for production of these metals.

The flow sheet for a process producing 100 ton vanadium per year from this material is shown in Figure 7. The valuable metals, vanadium and nickel, are leached by a moderately acid sulfate solution. The leach residue, containing carbon as its main component, is burnt and released in a second stage whereby the total yield of metals is increased. In the same operation the concentration of iron is diminished by precipitation of jarosite. During leaching, vanadium is kept in its fourvalent state by feeding SO_2 to the solution to obtain a suitable redox-potential. Solvent extraction of vanadium is performed with 20% HDEHP and 15% TBP in three mixer-settler stages with a yield of about 80%. The raffinate, now with increased acidity, is returned to the primary leach stage after bleeding about 10% to control the build-up of sodium and magnesium sulfates.

Vanadium is stripped with 1.5 M sulphuric acid to a concentration of 50 g/l in three stages. After that, extracted iron is stripped with 6 M H_2SO_4 . After a water washing stage the organic phase is recycled. Vanadium may be precipitated directly with sodium carbonate or ammonia from the strip solution. Precipitation as red cake after oxidation is another alternative.

Work is presently being carried out to find a solvent extraction process to recover nickel from the leach solution. Such a step will be needed to control build-up of nickel. The process is now in the engineering phase and a solvent extraction pilot is being tested. A full-scale plant is to be built and operated by the Swedish company SOTEX AB at a power station at Stenungsund in Sweden, owned by the Swedish company Vattenfall AB.

Leaching Circuit

The ash and soot materials from the power stations have a complex structure varying with conditions in the combustion process. Thus, the valence number of vanadium may be four or five, depending on the amount of excess air in the flue gases. Sulfur present in the fuel reacts to sulfur dioxide, which may participate in redox-

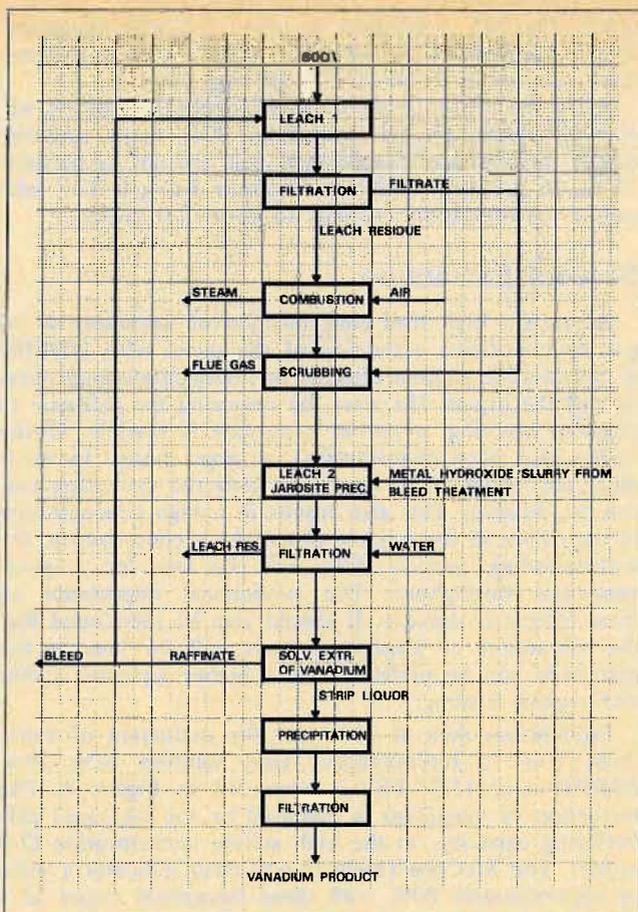


FIGURE 7. Principal flow sheet for the SOTEX Process.

reactions with vanadium and change its valence state. The metals in the soot are forthcoming as oxides and/or sulfates.

The feed material (2000 tons/year) is leached with raffinate solution from the solvent extraction unit. During leaching the pH value is kept at about 1 and the redox-potential of the solution is adjusted to keep vanadium reduced to its fourvalent state. This is important not only for the following extraction with HDEHP but also because of limited solubility of fivevalent vanadium at the prevailing acidity. Experimental studies of leaching of many feed materials from different power stations have shown a great variation in the leaching characteristics of vanadium. Generally the vanadium is more quickly leached from materials containing the metal in its fourvalent state, whereas materials with fivevalent vanadium may require several days of leaching time for a 90% yield. The mass transfer rate in the latter case could be controlled by diffusion in the solid phase and/or the liquid phase trapped in narrow pores in the solid particles. The leaching is promoted by higher temperature and acidity. Addition of reducing agents such as SO_2 to reduce vanadium in solution do not increase the leaching rate. To achieve highest possible yield of vanadium in the first leach stage the temperature will be kept between 50 and 100°C.

After filtration and washing of the filter cake, the leach residue, containing mostly carbon, is burnt in an oven in a fluidized bed to reduce the weight and volume. The flue gases, carrying the ashes, are scrubbed with leach solution from the first leach stage to retain the ashes. In the scrub solution more vanadium will be leached and iron being mostly threevalent will precipitate as jarosite as the temperature is kept near the boiling

point. The pH is adjusted to about 1.2 with limestone. The redox-potential is controlled with SO_2 to keep vanadium reduced as in the first leach stage.

After the second leach stage the pregnant solution will contain about 25 g/l vanadium. The main impurity metals, sodium and magnesium, will amount to between 20 to 25 g/l each and iron to about 3-5 g/l. The total sulfate concentration amounts to about 2.0 molar.

Solvent Extraction

At such a high feed concentration of vanadium as 25 g/l, a quantitative extraction of the metal with HDEHP is not possible without dilution or intermediate neutralization of the liquor. However, by returning the raffinate to renewed leaching, a partial extraction is feasible. Owing to the high feed concentration, a large change in vanadium concentration in the liquor over the extraction unit can be obtained. This also results in a high concentration of vanadium in the organic phase. As a consequence, the corresponding process flows will be less for a given vanadium throughput. The economical importance of these effects is decisive. It should also be mentioned that the extraction of impurity metals will be less as the extraction can be performed at a higher aqueous acidity and organic loading.

Equilibrium data at 25°C for the extraction of vanadium from a representative feed solution with 20% HDEHP and 15% TBP is presented in Figure 8. The extraction of vanadium is favoured by the increased pH-buffering capacity at the high sulfate concentration (2.0 molar). The McCabe-Thiele construction indicates a yield of approximately 80% with three theoretical stages at a flow ratio of 3.3:1 (organic to aqueous).

Concerning the *kinetic* conditions for vanadium extraction, the given batch kinetic data in Figures 1 and 2 indicate that equilibrium, with respect to the vanadium distribution, is reached within five to seven minutes at 25°C. Continuous pilot-plant experiments with mixer-settlers at 25°C have given about 90% efficiency in the extraction stages with a residence time in the mixer of about 10 minutes. With three extraction stages, a flow ratio of 4:1 and the given residence time, a total extraction yield of 80% for vanadium has been obtained.

In contrast to the Ranstad project the choice of temperature in the extraction unit has little economic effect because of the high vanadium concentration and may be set at convenience, probably between 25 and 40°C. This fact and the relatively low pH value during extraction (pH approx. 1) will contribute to the decrease in the rate of extraction of iron, part of which will be trivalent. Reduction of all iron to the twovalent state in order to decrease its extraction is not believed to be necessary.

Vanadium is stripped under moderately acid conditions with 1.5 M H_2SO_4 . With three mixer-settler stages, a vanadium concentration in the strip liquor of 50 g/l is obtainable. The kinetic conditions at 25°C are such that equilibrium is reached in 10 to 15 minutes in a batch experiment. Somewhat longer residence time in the mixer is therefore needed than in the extraction section.

The kinetics for iron stripping with sulphuric acid is much slower compared to vanadium. To ensure sufficient stripping capacity to match the extraction rate and prevent accumulation of iron in the organic phase, a high residence time in the mixer will be used. The mass transfer rate increases with acid concentration, which will be about 6 molar.

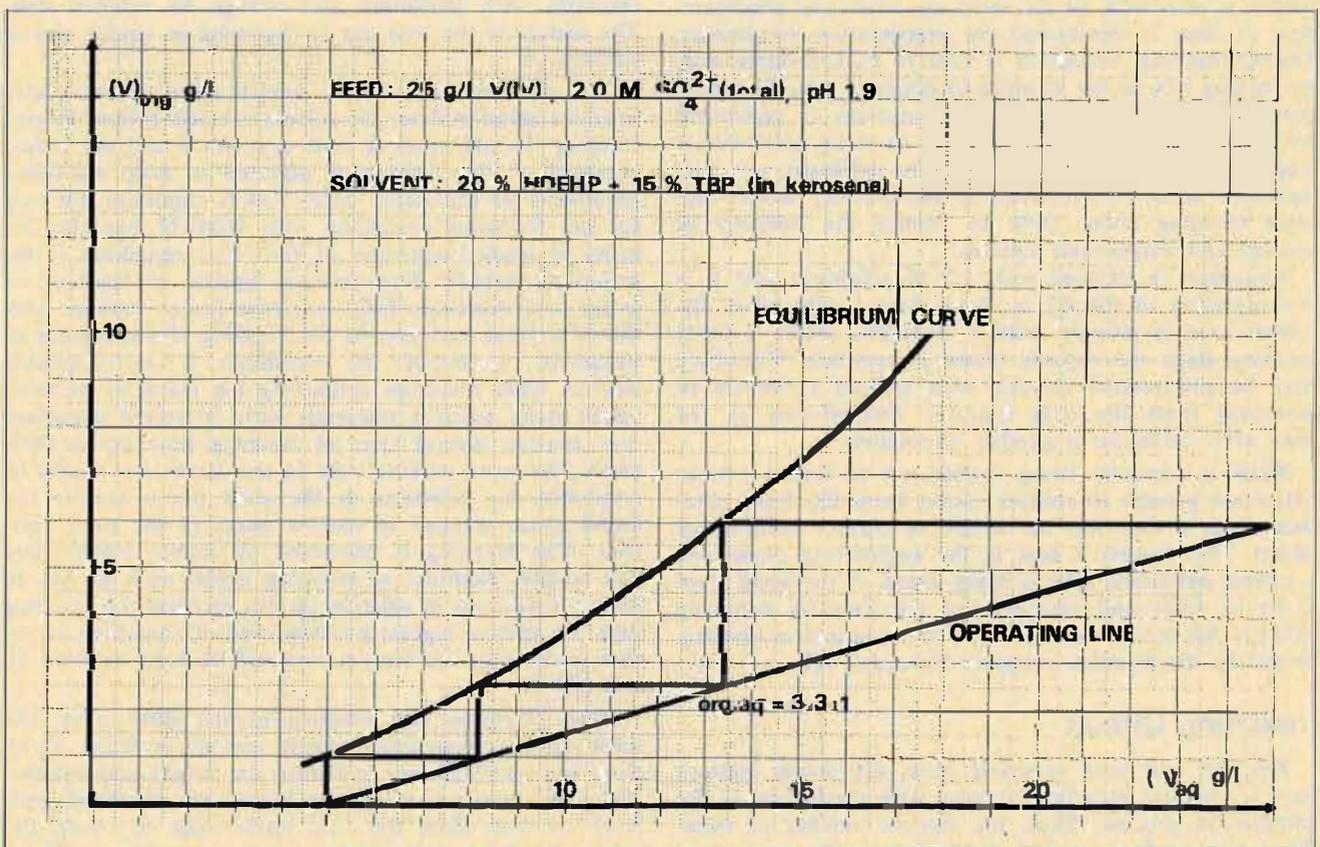


FIGURE 8. McCabe Thiele diagram for extraction of vanadium with 20% HDEP + 15% TBP from a vanadium rich feed liquor.

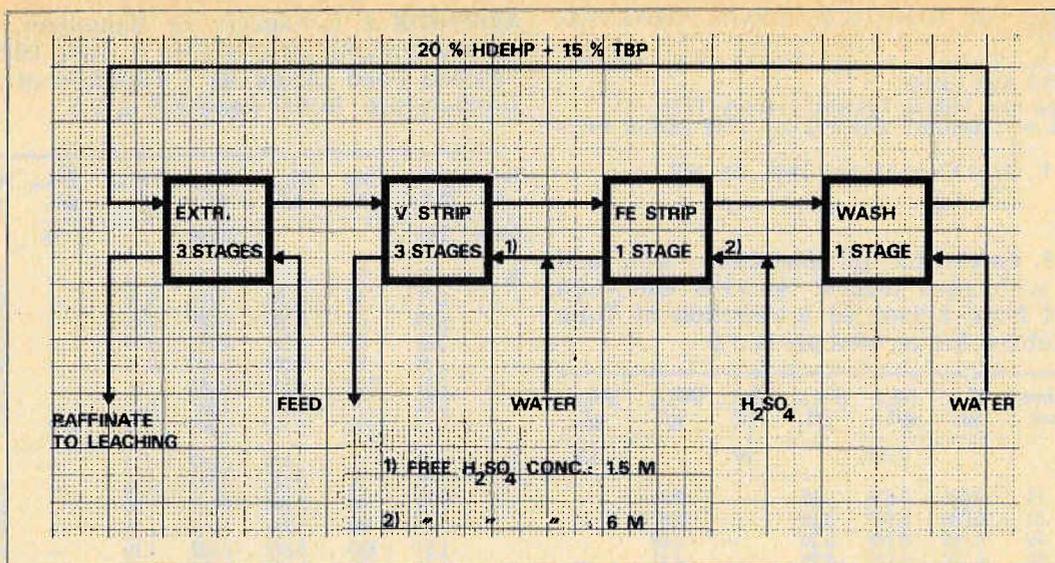


FIGURE 9. Solvent extraction flow sheet for the SOTEX process.

Estimations from both batch bench-scale tests and small-scale mixer-settler experiments indicate that the maximum amount of iron extracted per unit of vanadium will be 5%. This is not more than can be tolerated without penalty in a commercial product. With this in mind, a flowsheet with stripping of vanadium and iron to the same solution according to Figure 9 is being tested. Here most of the vanadium is stripped in three stages with a solution made from dilution of the strong acid solution from the following stage for stripping of iron. The organic solution is then washed with water to recover extracted and entrained sulfuric acid. The wash solution is taken to the iron stripping stage. One condition for this flow sheet is that the ratio of extracted iron to vanadium does not exceed a certain upper limit because of a limited obtainable iron concentration in the strong acid solution and acid balance conditions.

Bleed Treatment

To control build-up of impurities in the leach circuit, a bleed of about 10% is taken out from the raffinate solution from the extraction unit. The bleed is neutralized to precipitate the heavy metals as hydroxides. After thickening the mother liquor containing the alkali metals, sodium and magnesium and corresponding sulfate is taken out of the process. The hydroxide slurry is returned to the second leach/jarosite stage, whereby nickel and vanadium are recycled.

Product Precipitation

Vanadium may be precipitated directly in its fourvalent state from the pregnant strip solution at a pH of 6 to 7 with sodium carbonate or ammonia. Iron will also precipitate under these conditions. A sodium carbonate precipitate sample made from a strip solution from a small scale mixer-settler experiment had a composition after thorough washing and drying according to Table 3:

Precipitation with ammonia may be more favourable if problems with too high a sulfate content arise. Any occluded ammonium sulfate may be eliminated by calcination. Direct oxidation and precipitation in acid medium will yield a purer product (less iron impurity) with better filtering characteristics.

TABLE 3. Composition of Vanadium Precipitate.

Component	%
V	53.8
V ₂ O ₅	96.0
Fe	0.09
SiO ₂	0.02
Na ₂ O	0.72
K ₂ O	0.01
N	0.004
S	0.08

Economy

The proposed plant with a capacity of 100 tons of vanadium per year is intended to be a full-scale test of the process. The operating cost is balanced by the product value, which is about US \$6 per kilogram vanadium. The investment cost is estimated to be less than US \$2 million. The process is economically favourable at a level of 250 tons of vanadium per year.

General Conclusions

When judging the possibilities of using HDEHP/TBP as a solvent for vanadium in acid sulfate media the following items should be considered:

1. Vanadium should be fourvalent. Reduction if necessary, is most suitably done with sulfur dioxide.
2. The iron content of the solution should be as low as possible. If the iron is threevalent, its concentration may be decreased through precipitation of jarosite. If necessary, the iron may be reduced before the extraction unit to minimize its extraction.
3. The temperature in the extraction unit may be between 25 and 40°C. However, too high a temperature is negative because of excessive iron extraction.
4. If possible, a closed process cycle permitting a partial extraction of vanadium at a higher acidity, should be considered. Extraction of impurities will be less.

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APPENDIX 1. Extraction of Vanadium, Iron and Aluminium with 20% HDEHP + 15% TBP from the Ranstad Feed Liquor as a Function of Time and Temperature. Initial feed pH is 1.5.

Temp. °C	pH 25°C	Time sec	[V] _{org} g/l	[V] _{aq} g/l	[Fe] _{org} g/l	[Fe] _{aq} g/l	[Al] _{org} g/l	[Al] _{aq} g/l
Feed:	1.50			0.260		20		6.5
25	1.48	15	0.038	0.238	0.15	—	0.05	—
	1.46	30	0.080	0.180	0.16	—	0.07	—
	1.45	45	0.106	0.146	0.20	—	0.09	—
	1.46	60	0.126	0.122	0.25	—	0.11	—
	1.44	90	0.152	0.092	0.32	—	0.14	—
	1.43	120	0.170	0.078	0.39	—	0.16	—
	1.43	180	0.190	0.058	0.54	—	0.22	—
	1.42	240	0.200	0.050	0.61	—	0.26	—
	1.41	300	0.204	0.044	0.73	—	0.31	—
	1.37	660	0.192	0.056	1.10	18.4	0.49	6.1
40	1.44	15	0.102	0.186	0.24	—	0.09	—
	1.42	30	0.163	0.114	0.35	—	0.14	—
	1.39	45	0.189	0.078	0.48	—	0.20	—
	1.37	60	0.197	0.056	0.56	—	0.25	—
	1.34	90	0.208	0.044	0.73	—	0.36	—
	1.33	120	0.210	0.046	0.78	—	0.46	—
	1.33	180	0.202	0.054	0.95	—	0.59	—
	1.29	240	0.186	0.068	1.08	—	—	—
	1.27	300	0.175	0.080	1.19	—	—	—
	1.23	600	0.135	0.122	1.48	16.6	0.87	5.9
60	1.33	15	0.168	0.080	0.85	—	0.40	—
	1.27	30	0.174	0.058	1.31	—	0.65	—
	1.23	45	0.166	0.074	1.65	—	0.82	—
	1.21	60	0.156	0.082	1.86	—	1.00	—
	1.19	90	0.140	0.102	2.01	—	1.15	—
	1.16	120	0.134	0.120	2.25	—	1.43	—
	1.13	180	0.108	0.140	2.45	—	1.82	—
	1.11	240	0.096	0.152	2.55	—	2.08	—
	1.11	300	0.088	0.158	2.58	—	2.25	—
	1.08	600	0.074	0.178	2.74	17.4	2.64	5.2

APPENDIX 2. Extraction of Vanadium, Iron and Aluminium with 20% HDEHP + 15% TBP from the Ranstad Feed Liquor as a Function of Time and Temperature. Initial Feed pH is 2.0.

Temp. °C	pH 25°C	Time sec	[V] _{org} g/l	[V] _{aq} g/l	[Fe] _{org} g/l	[Fe] _{aq} g/l	[Al] _{org} g/l	[Al] _{aq} g/l
Feed:	2.01			0.260		18		6.5
25	1.76	15	0.103	0.178	0.32	—	0.12	—
	1.71	30	0.153	0.126	0.38	—	0.15	—
	1.69	45	0.189	0.086	0.49	—	0.20	—
	1.66	60	0.212	0.059	0.59	—	0.24	—
	1.68	90	0.242	0.030	0.74	—	0.33	—
	1.61	120	0.248	0.018	—	—	0.40	—
	1.54	300	0.194	0.020	0.88	—	0.66	—
	1.47	600	0.170	0.048	1.07	17.2	0.95	6.1
40	1.64	40	0.225	0.052	0.73	—	—	—
	1.59	45	0.240	0.028	0.88	—	0.48	—
	1.55	60	0.240	0.022	1.00	—	0.58	—
	1.52	90	0.245	0.022	1.11	—	0.72	—
	1.51	120	0.242	0.032	1.19	—	0.78	—
	1.41	300	0.190	0.068	1.48	—	1.16	—
	1.34	600	0.156	0.104	1.70	17.0	1.58	5.7
60	—	15	0.220	0.056	1.22	—	0.49	—
	—	30	0.227	0.038	1.57	—	0.75	—
	—	45	0.210	0.051	1.79	—	0.92	—
	—	60	0.189	0.063	1.97	—	1.03	—
	1.32	90	0.162	0.086	2.10	—	1.28	—
	1.30	120	0.157	0.098	2.18	15.6	1.33	5.6

DISCUSSION

A. Van Peteghem: As you have tested the stripping of iron from HDEP-TBP organic for longer periods, did you notice any iron accumulation and/or changes in physical properties?

H. Ottertun: After four weeks of continuous operation of a small-scale pilot plant, the iron reached a concentration in the organic phase of about 0.6 g/l after the iron stripping stage. Before steady state conditions are reached, the iron is expected to accumulate to about 2 g/l. No changes in physical properties were observed during the pilot run.

Liquid-Liquid Extraction of Nickel (II) by Dialkylphosphorodithioic Acids

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ABSTRACT

Separation of nickel in sulphuric acid medium by liquid-liquid extraction with dialkylphosphorodithioic acids (HL) has been studied. Nickel(II) and cobalt(II) species may be represented by the simplest formulas NiL_2 and CoL_2 . The extractant capacity for nickel(II) is particularly high and may be 1 mole of nickel(II) per liter of solvent. The stripping reaction of nickel is slow but its kinetics are enhanced by addition of octanol to the organic phase. The influence of the extractant alkyl group is discussed. Countercurrent nickel(II) extractions have been performed. It is possible to extract nickel with a yield close to 100 per cent from a leaching liquor, 5 g.l^{-1} in nickel(II) and 20 g.l^{-1} in sulphuric acid. Nickel concentration in organic phase is 12 g.l^{-1} . Stripping of nickel(II) can be achieved by 9 M chlorhydric acid with a yield close to 100 per cent. A yield of 50 per cent may be preferred; then nickel concentration in aqueous phase is close to 100 g.l^{-1} .

Introduction

LIQUID-LIQUID EXTRACTION OF NICKEL (II) has recently been reviewed by Flett^(1,2) and Warshawsky⁽³⁾. Solvent extraction is often proposed as a means of separating nickel(II) from its impurities for various hydro-metallurgical purposes. Two alternative routes may be proposed:

First, all the impurities are removed from the nickel(II) solution by solvent extraction in order to obtain a raffinate of a pure nickel(II) salt solution. This way is intended only for solutions of high initial nickel(II) concentration.

Second, the nickel(II) is extracted, as selectively as possible, with the impurities remaining in the raffinate. Stripping of the organic is achieved with an appropriate aqueous solution to give a pure nickel(II) salt solution. This process presents a real advantage over the preceding one, when operating on dilute nickel solutions. In addition to nickel(II) separation from its impurities, nickel(II) concentration in solution is greatly increased. This allows the treatment of solutions obtained by leaching of low-grade ores which in the future will constitute the main sources of nickel.

In the first case, separations by solvation with tributylphosphate^(4,5) or by ion-pair formation with long chain amines⁽⁶⁾ have been widely used.

In the second case, acidic extractants and particularly chelating agents are proposed: carboxylic acids⁽⁷⁻⁹⁾, dioximes⁽¹⁰⁾, hydroxyoximes^(11,12), 8-hydroxyquinoline and its derivatives⁽¹³⁾, β -diketones⁽¹⁴⁾, hydroxamic acids⁽¹⁵⁾, dithiocarbamates⁽¹⁶⁾, xanthates⁽¹⁷⁾; chelating agents-LIX or KELEX- and carboxylic acids mixtures⁽¹⁸⁻²²⁾ may be proposed.

However, none of the above extractants shows an expansion in nickel hydrometallurgy as comparable to the hydroxyoximes with regard to the commercial copper

TABLE 1. Leaching Solution Composition.

Component	Concentration, g.l ⁻¹
Ni.....	5
Al.....	3
Mg.....	2
Mn.....	2
Fe.....	1
Co.....	0.5
Cr.....	0.3
Zn.....	0.2
Cu.....	0.05
free H ₂ SO ₄	20

solvent extraction plants⁽²⁾. Moreover, some extractants mentioned before are suitable for ammoniacal leach-liquor treatment, but there are none for treatment of acid leach liquors.

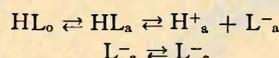
Now, sulphuric acid leaching is considered economically the best way for the treatment of low-grade lateritic ores; sulphuric acid is a cheap reagent and the leaching is selective when carried out in an autoclave at high temperature and pressure⁽²³⁾. Such a sulphuric acid leaching process of nickel ores has been carried out at Moa Bay, Cuba. Applied to a typical ore of New Caledonia, it would give a solution the composition of which is indicated in Table 1⁽²⁴⁾. The high concentrations of some impurities, especially Al(III) and Mg(II) and the high acidity of the solution, must be pointed out.

Nickel(II) being a soft acid⁽²⁵⁾, and thiophosphoryl group being a typical soft base⁽²⁶⁾, dialkylphosphorodithioic acids seem to suit particularly well for the treatment of nickel ores' sulphuric leaching liquors⁽²⁷⁾.

Reaction Mechanisms

For extraction of a metal ion, M^{n+} by an acidic chelating extractant HL, the following reactions occur.

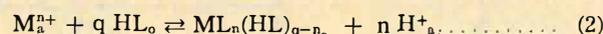
Distribution of Extractant



In a non-dissociating solvent, L^- exists as ion pair. If P_{HL} and P_{L^-} are the partition constants of the extractant (HL) and its conjugated base (L^-), K_A the acidity constant of the extractant in aqueous phase, the distribution coefficient D_{HL} of the extractant is:

$$D_{HL} = \frac{P_{HL}}{1 + \frac{K_A}{|H^+_a|}} + \frac{P_{L^-}}{1 + \frac{|H^+_a|}{K_A}} \dots \dots \dots (1)$$

Distribution of the Metal M^{n+}



the distribution coefficient D_M of the metal M^{n+} is expressed by:

$$\log D_M = \log K_{ex} + n pH + q \log |HL|_o \dots \dots \dots (3)$$

where K_{ex} is the extraction constant of the above reaction. This expression is used for the determination of the extracted species formulae.

Extractant Capacity

The extractant capacity with respect to the metal, M^{n+} , is defined as the ratio of the number of metal moles in organic phase per initial mole of extractant. According to equation (2), the theoretical value of extractant capacity is $1/q$.

Experimental

Reagents

All aqueous solutions are prepared from reagent-grade metallic salts. Di-n-butylphosphorodithioic acid is synthesized from pure n-butanol (Hopkin and Williams) and pure phosphorpentasulfid (Fluka)⁽²⁸⁾; the extractant is purified by two successive treatments, each consisting in a neutralization by sodium hydroxide followed by sulphuric acid addition to the dibutylphosphorodithioate solution. Other dialkylphosphorodithioic acids have not been purified considering that in all cases synthesis yield is close to 90 - 95 per cent. The extractant is dissolved in an appropriate diluent. Except for contrary indications, the diluent consists of Solvesso 150 and 1-octanol, the concentration of which is 160 g.l^{-1} .

Extraction Procedure

Equal volumes (20.0 ml) of organic and aqueous phases are introduced in 250 ml thermostated separatory funnels. Shake-out tests are carried out with an Agitelec equipment (Sté Jean Toulemonde et Cie, Paris) which allows shaking of several separatory funnels under identical and reproducible conditions.

The countercurrent extractor consists of glass mixer-settler equipment. Each mixer compartment is fitted with a mechanical stirrer operated by an electric motor, the

speed of which can be adjusted. In the settling compartment it is possible to precisely adjust the interface level. The circulation of liquids is achieved by the stirrers pumping action.

Analytical

The extractant in aqueous phase is titrated by iodine⁽²⁹⁾. The extractant in organic phase is determined by potentiometric titration with silver nitrate⁽³⁰⁾. Nickel(II) and zinc(II) titrations in aqueous phase are carried out by complex formation with EDTA⁽³¹⁾. Cobalt(II) is determined by potentiometric titration with potassium ferricyanide⁽³²⁾. Nickel(II)-zinc(II) mixtures and nickel(II)-cobalt(II) mixtures are determined by pulse polarography (TACUSSEL PRG 5 polarograph) in ammoniacal⁽³³⁾ and pyridinium⁽³⁴⁾ medium respectively. Nickel(II) concentration in organic phase is determined by atomic absorption spectrophotometry (VARIAN AA6 Atomic spectrophotometer) when countercurrent extractions are performed.

Results and Discussion

Distribution of di-n-butylphosphorodithioic Acid

Preliminary tests were performed with several aliphatic and aromatic diluents. Solvesso 150 with a 97 per cent aromatic content gave the highest extractant partition constant value and was the preferred diluent. Modifiers, such as octanol, must be added to the diluent to avoid stable emulsion formation. Moreover, the influence of octanol on nickel stripping kinetics is shown hereafter and kinetics of the nickel(II) extraction reaction with the single drop experiment is being investigated⁽³⁵⁾. This study shows that presence of octanol inorganic phase improves nickel extraction rate. This method has been described in the literature⁽³⁶⁾.

The extractant distribution between an organic phase of Solvesso 150 and various concentrations of octanol and an aqueous phase of various sulphuric acid concentrations (Figure 1), corresponds to relation (1) and shows high P_{HL} and low P_{L-} values. In this case, relation (1) becomes simplified:

$$\log D_{HL} = \log P_{HL} - \text{pH} - \log (|\text{H}^+|_a - K_A) \dots \dots (4)$$

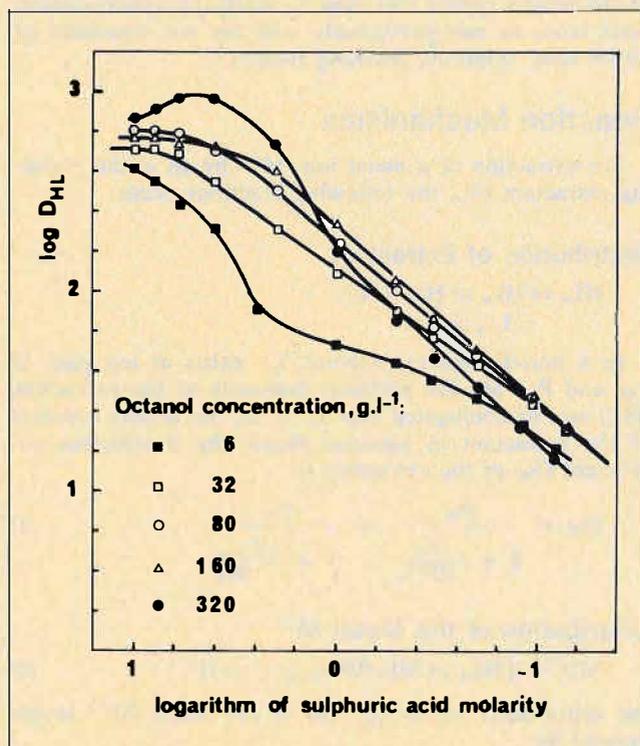


FIGURE 1. Dibutylphosphorodithioic acid distribution.

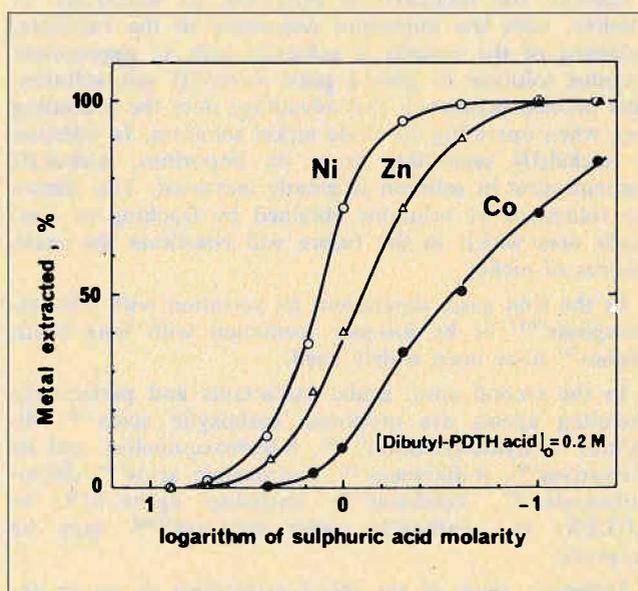


FIGURE 2. Percentage extraction of Ni(II), Zn(II) and Co(II) (10^{-2} M) as a function of H_2SO_4 concentration.

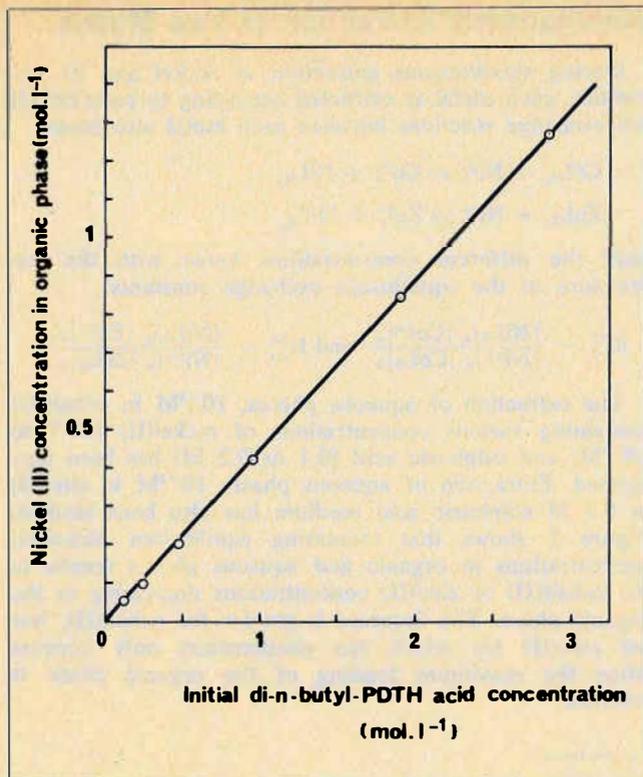


FIGURE 3. The Ni(II) concentration in the organic phase as a function of extractant concentration.

However, at low sulphuric acid concentrations, the slope of the linear part of the curve is -0.88 , that is to say lower than the theoretical value -1.0 , from equation (4). This difference may be attributable to the limited solubility of the di-n-butyl PDT⁻ anion in aqueous phase and the fact that variation of $\log D_{HL}$ is plotted versus logarithm of sulphuric acid concentration instead of pH which is not determined for high sulphuric acid concentrations. The influence of octanol on extractant distribution must be underlined; a low content as well as a too high content have disturbing effects on distribution coefficient variations. Octanol concentration of 160 g.l^{-1} has been chosen for the following tests. The influence of octanol concentration on nickel stripping kinetics is responsible for this choice.

Nickel(II), cobalt(II) and zinc(II) extraction

The extraction of different metals from the leaching solution, after copper cementation and iron(III) reduction to iron(II) shows a good selectivity with respect to nickel(II). Indeed cobalt(II) and zinc(II) are the only metals which are coextracted with nickel(II) in 0.2 M sulphuric acid medium (Figure 2). Selectivity of nickel(II) separation will be fairly satisfactory towards cobalt(II), poor towards zinc(II).

During extraction of various volumes of an aqueous solution, 0.17 M in nickel(II) and 0.19 M in sulphuric acid by 20 ml of di-n-butyl PDTH solutions of various concentrations (Figure 3), solvent capacity is proportional to extractant concentration: capacity is 0.44 mole of nickel(II) per mole of extractant. This value is very high, considering that the theoretical value is 0.5 for a ML_2 complex. On that account, di-n-butyl PDTH acid is a powerful extractant.

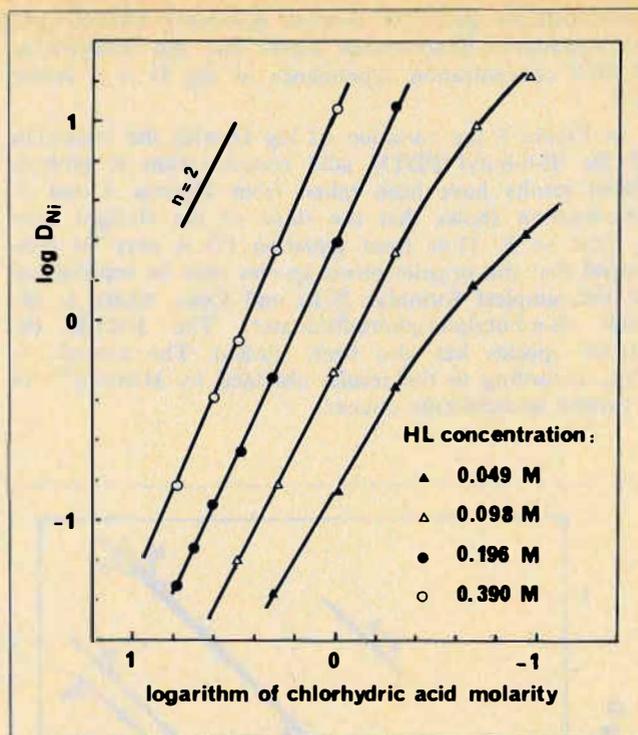


FIGURE 4. The distribution of Ni(II) as a function of HCl concentration for different dibutyl — PDTH acid (HL) concentrations.

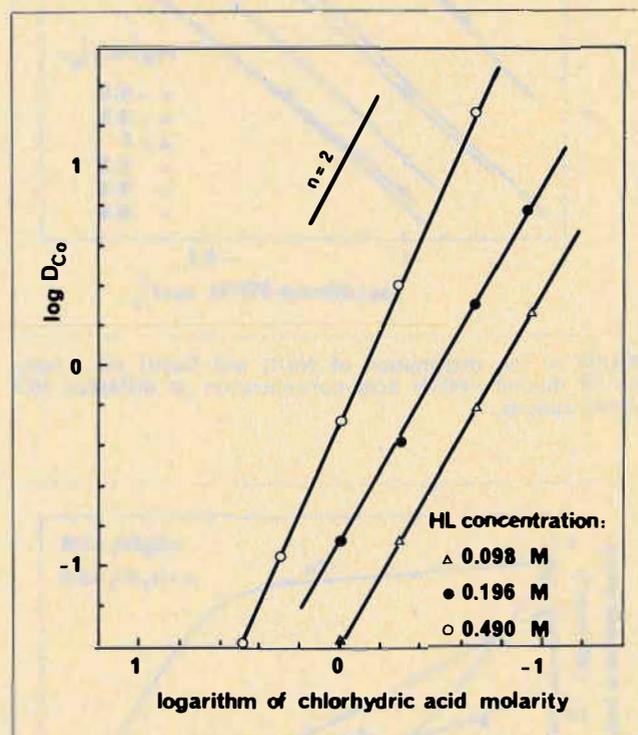


FIGURE 5. The distribution of Co(II) as a function of HCl concentration for different dibutyl — PDTH acid (HL) concentrations.

Determination of extracted species formulas

In Figures 4 and 5 the equilibrium results for extraction of nickel(II) and cobalt(II) by di-n-butyl PDTH acid in Solvesso 150 are shown as $\log D/\text{cologarithm of HCl}$

concentrations plots for several di-n-butyl PDTH acid concentrations. Examination shows that the cologarithm of HCl concentration dependence of log D is a factor of 2.

In Figure 6 the variation of log D with the logarithm of the di-n-butyl PDTH acid concentration is plotted. These results have been taken from Figures 4 and 5. Examination shows that the slope of the straight lines is close to 2. Thus from equation (3) it may be concluded that the organic phase species may be represented by the simplest formulas NiL_2 and CoL_2 where L denotes di-n-butylphosphorodithioate*. The zinc(II) extracted species has also been studied. The formula is ZnL_2 according to the results obtained by Handley⁽³⁷⁾ in a carbon tetrachloride diluent.

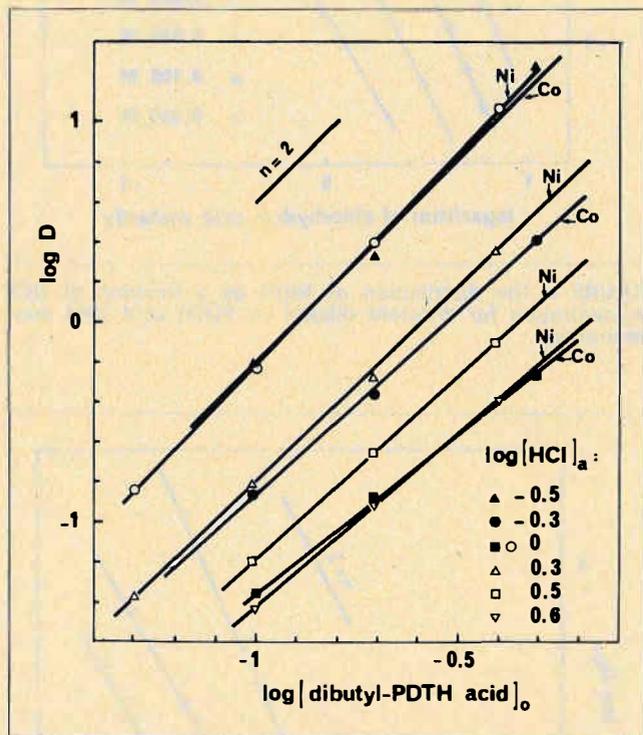


FIGURE 6. The distribution of Ni(II) and Co(II) as a function of dibutyl-PDTH acid concentration at different HCl concentrations.

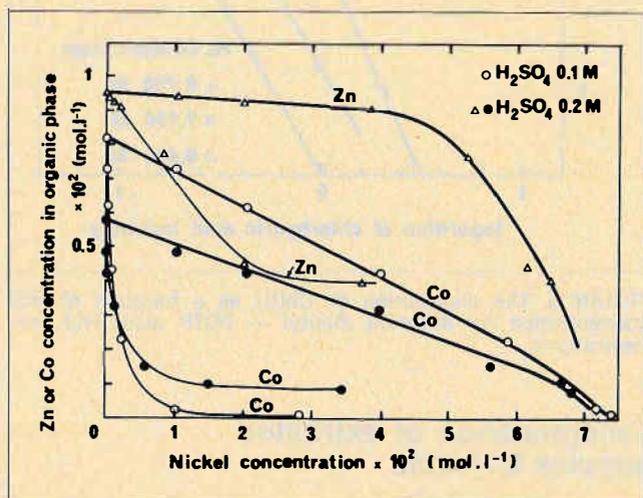
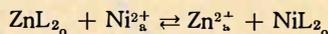
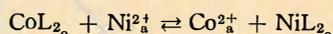


FIGURE 7. Cobalt or zinc concentration in organic phase as a function of nickel concentration in organic (—) or aqueous (---) phase.

Simultaneous Extraction of Two Metals

During simultaneous extraction of nickel and its impurities, each metal is extracted according to reaction (2) but exchange reactions between each metal also occur:



until the different concentrations agree with the expressions of the equilibrium exchange constants:

$$K_{Co}^{Ni} = \frac{|NiL_2|_o |Co^{2+}|_a}{|Ni^{2+}|_a |CoL_2|_o} \text{ and } K_{Zn}^{Ni} = \frac{|NiL_2|_o |Zn^{2+}|_a}{|Ni^{2+}|_a |ZnL_2|_o}$$

The extraction of aqueous phases, $10^{-2}M$ in cobalt(II) containing various concentrations of nickel(II) (10^{-2} to $10^{-4}M$) and sulphuric acid (0.1 or 0.2 M) has been performed. Extraction of aqueous phases $10^{-2}M$ in zinc(II) in 0.2 M sulphuric acid medium has also been studied. Figure 7 shows that increasing equilibrium nickel(II) concentrations in organic and aqueous phases results in the cobalt(II) or zinc(II) concentrations decreasing in the organic phase. The decrease is greater for cobalt(II), less for zinc(II) for which the phenomenon only appears when the maximum loading of the organic phase is reached.

*The blue cobalt complex CoL_2 evolves in the organic phase after extraction and gives a yellow complex, the formula of which is CoL_3 . This reaction is very slow and our results concern the initial cobalt(II) complex.

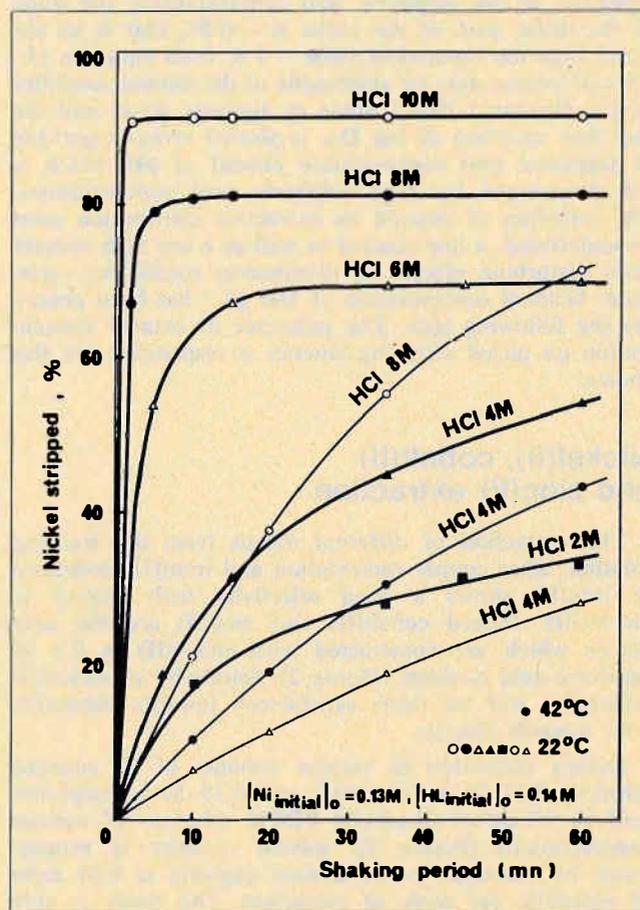


FIGURE 8. Percentage stripping of Ni(II) as a function of shaking period. (—) octanol $160 g.l^{-1}$, (---) without modifier.

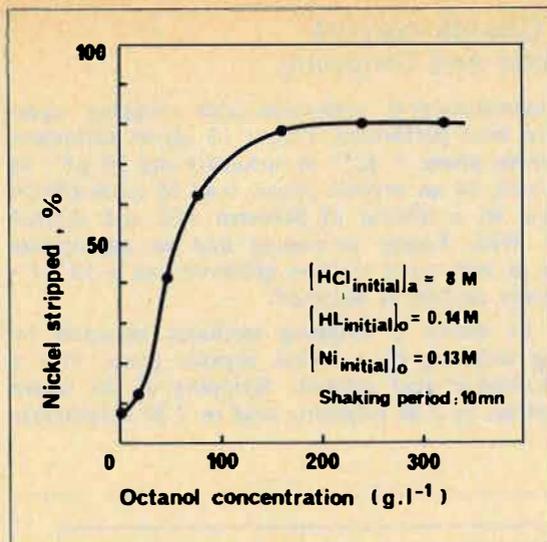


FIGURE 9. Percentage stripping of Ni(II) as a function of octanol concentration in the organic phase.

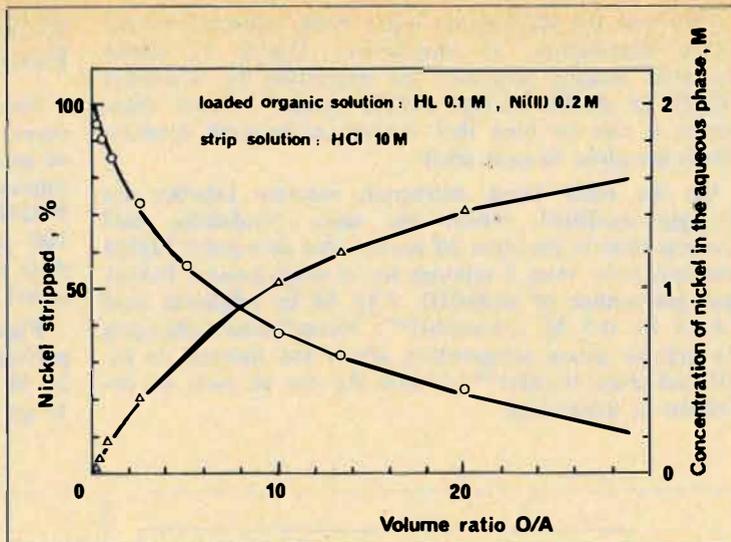


FIGURE 10. The effect of the volume ratio of organic and aqueous phase on percentage stripping and concentration of stripped nickel.

However, during countercurrent extractions, the extract has been previously equilibrated with the aqueous phase feed so that the extracted cobalt quantity is minimized without deleterious effect on the nickel(II) extraction yield.

Nickel stripping

Eventual chloride complex formation results in lower metal distribution coefficients so that stripping yield is increased. In addition, the chlorhydric medium is amenable to a later treatment to eliminate several impurities: cobalt(II), zinc(II) and eventual traces of copper(II) and iron(III). Such a treatment may be performed by ion-exchange⁽³⁸⁾ or by liquid-liquid extraction with tributylphosphate^(4,5). For the above reasons chlorhydric acid stripping solutions are preferred.

In Figure 8, the influence of chlorhydric acid concentration and temperature on stripping kinetics is shown. In the absence of a modifier, stripping reaction is very slow at ambient temperature. Increasing both temperature and chlorhydric acid concentration enhances stripping reaction rate. However, another factor may be considered: the addition of a modifier greatly increases stripping rate. 1-octanol has been preferred. Stripping of an organic phase initially containing 0.13 M nickel(II) in the presence of free extractant (0.14 M), by a 8 M chlorhydric acid solution, at 22°C, has been performed (Figure 9). Increasing octanol concentration in the organic phase increases stripping yield for a constant shaking period (10 min). For octanol concentrations higher than 160 g.l⁻¹, the stripping yield does not increase; that is why this value has been kept. Nevertheless, the influence of chlorhydric acid concentration is significant (Figure 8). Stripping by a 10 M chlorhydric acid solution reaches equilibrium within 2 minutes but stripping by 2-4 M solutions is very slow. So a concentration higher than 6 M is all the more necessary, so that an important concentration gain can be achieved during stripping operations by increasing volume ratio or flow rate ratio (counter current operations) of organic and aqueous phases.

In Figure 10, the variation of both stripping reaction yield and stripped nickel(II) concentration versus the volume ratio O/A of organic and aqueous phases is plotted. For low values of the O/A ratio, stripping yield is close to 100 per cent but stripped nickel concentration

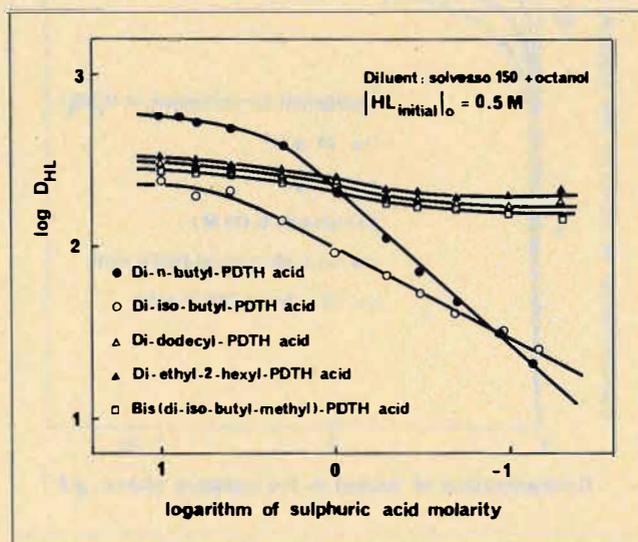


FIGURE 11. The distribution of several dialky-PDTH acids.

in the aqueous phase is very low. If the O/A ratio is increased, stripping yield decreases but nickel(II) concentration in the aqueous phase increases and may be higher than 1.5 M.

Influence of the Extractant Alkyl Group

In dilute acid solutions, di-n-butyl PDTH acid presents a low distribution coefficient value which is not very favourable for hydrometallurgical applications. Several dialkylphosphorodithioic acids have been synthesized and tested.

The alkyl group plays an important part as far as extractant distribution is concerned (Figure 11); di-n-butyl PDT⁻ and di-isobutyl PDT⁻ anions are soluble in aqueous phase. Then, extractant distribution is strongly dependent on pH of the aqueous phase, according to relation (4). Di-n-dodecyl PDTH, diethyl-2-hexyl PDTH and bis(diisobutylmethyl) PDTH acids distribution is practically independent of the aqueous phase acidity. In fact their conjugated bases are almost insoluble in the aqueous phase.

However, the alkyl group has a weak influence on the nickel distribution, at equilibrium. Figure 12 shows nickel(II) loading isotherms for extraction by di-n-butyl PDTH or diethyl-2-hexyl PDTH acids⁽³⁹⁾. From these curves it can be seen that extraction reaction constant values are close to each other.

On the other hand, extraction reaction kinetics are strongly modified. Under the same conditions, half reaction time is less than 30 seconds for di-n-butyl PDTH acid and more than 5 minutes for di-ethyl-2-hexyl PDTH acid (extraction of nickel(II), 0.15 M in sulphuric acid 0.2 M by 0.5 M extractant)⁽³⁹⁾. Nevertheless, changing the organic phase composition allows the increase in interfacial mass transfer⁽³⁵⁾ so that the use of such an extractant is interesting.

Nickel Countercurrent Extraction and Stripping

Some countercurrent extraction and stripping operations have been performed. Figure 13 shows extraction of an aqueous phase, 5 g.l⁻¹ in nickel(II) and 20 g.l⁻¹ in sulphuric acid, by an organic phase, 0.48 M in di-n-butyl PDTH acid in a diluent of Solvesso 150 and octanol 160 g.l⁻¹. With 4-stage processing and an appropriate A/O ratio, a very good yield is achieved and a 12 g.l⁻¹ nickel organic content is obtained.

Figure 14 shows a stripping isotherm obtained by performing stripping of a nickel organic phase with a 10 M chlorhydric acid solution. Stripping of the above 12 g.l⁻¹ extract by 5 M sulphuric acid or 9 M chlorhydric

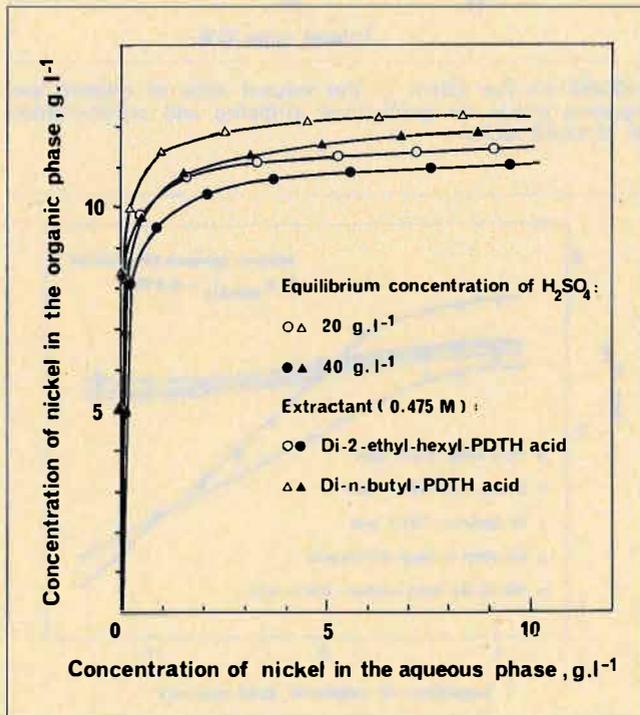


FIGURE 12. Loading isotherm for Ni(II) in a solvent containing a dialkyl-PDTH acid.

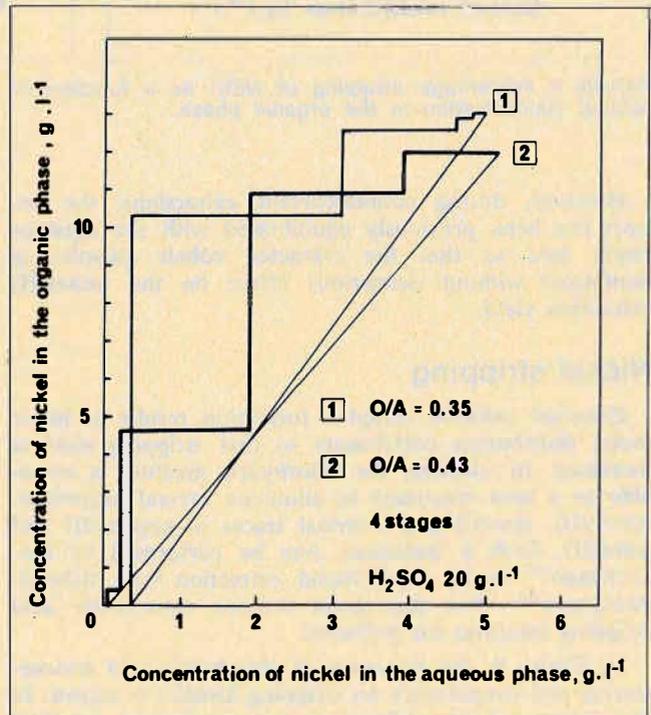


FIGURE 13. Countercurrent extraction of nickel by dibutyl-PDTH Acid 0.48 M.

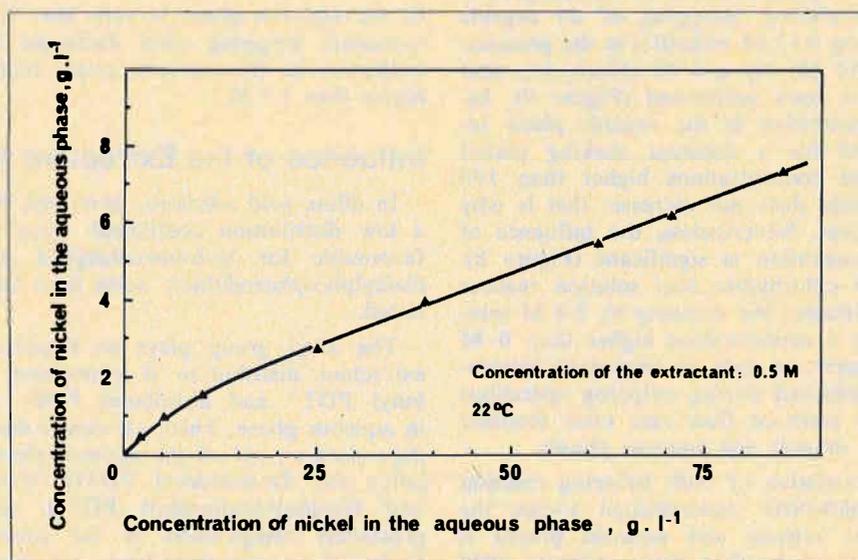


FIGURE 14. Stripping isotherm for Ni(II) with a 10M strip solution.

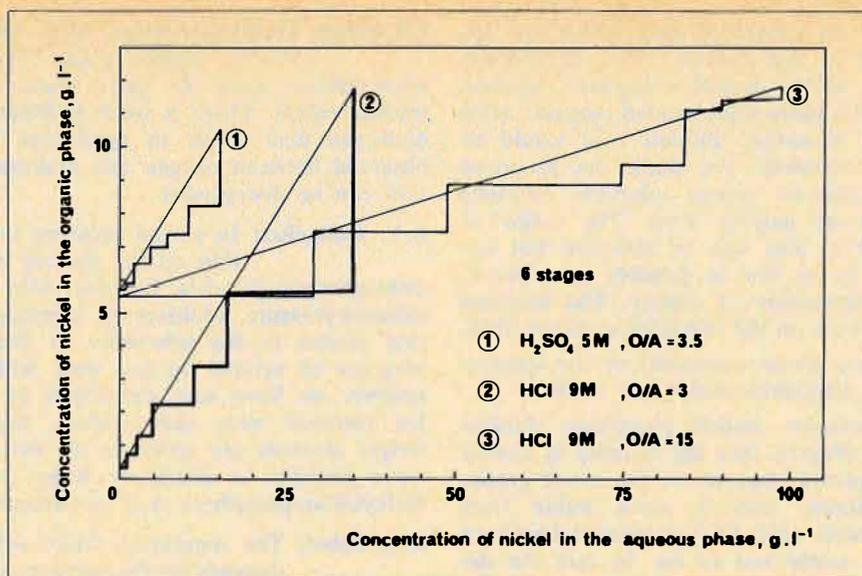


FIGURE 15. Countercurrent stripping of nickel.

acid (Figure 15) with 6-stage processing is achieved with a good yield in chlorhydric medium. Thus a 35 g.l⁻¹ nickel(II) solution is obtained with a 95 per cent yield (O/A = 3). Higher nickel(II) concentration in aqueous phase can be obtained: with a higher O/A ratio (15) a 100 g.l⁻¹ nickel aqueous solution is obtained but stripping yield is close to 50 per cent.

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DISCUSSION

D. Marcus: For an estimation of industrial application of this new extractant for Ni and Co, some information regarding economics, reagent cost, loss by volatilization, decomposition or solubilization are very useful. Only in this way is it possible to make an estimation on this new extractant as a commercial application (assuming the cost of equipment is the same or very close to the actual industrial processes).

The paper refers to a special liquor obtained from New Caledonia ores. Are there any data referring to the applicability of this process to other liquors having completely different ratios of iron to nickel (or other metals)?

This new type of extractant may be a "key" for nickel-cobalt sulfuric solution processing. More work and development in this direction should be encouraged, to get new results in solvent-extraction of non-ferrous metals.

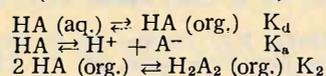
J.-L. Sabot: We have no economic data about the applicability of this process. Now we propose an extraction system using dialkyl phosphoro dithioic acids but we think that a more sophisticated reagent, more powerful than dibutyl phosphoro dithioic acid would be suitable for such a treatment. We think the proposed process can be applicable to various sulphuric solutions obtained by leaching of lateritic ores. The ratios of nickel to iron, cobalt or zinc can be different but the copper content must be as low as possible in order to minimize the prior elimination of copper. The leaching performance itself depends on the nickel/magnesium ratio.

H. Reinhardt: Will you please comment on the stability of the alkyldithiophosphoric acids.

J.-L. Sabot: If we consider dialkyl phosphoro dithioic acid, we observe that the stability is closely related to the hydrophobic feature of the alkyl group. Dibutyl phosphorodithioic acid is more stable than diethyl phosphoro dithioic acid. Di-2-ethylhexylphosphoro dithioic acid is more stable and so on. In fact the degradation of the extractant occurs in aqueous phase and the stability of the extractant depends on its solubility in water.

D.H. Liem: Dialkylphosphorodithioic acids may be expected to form dimeric and even polymeric species in the organic phase by hydrogen bonding. This may be compared with dialkylphosphoric acid which has been shown to have these properties.

My question is whether you have data on the distribution equilibria of your extractant, i.e. value of K_d , K_a and $K_2 =$ (dimerization constant)?



J.-L. Sabot: Dialkylphosphoric acids form dimeric species in the organic phase but with dialkylphosphorodithioic acids the same phenomenon occurs at a smaller extent. There is weak hydrogen bonding between hydrogen acid sulfur in apposition to the interactions observed between oxygen and hydrogen. Here, dimerization can be disregarded.

L.V. Gallacher: In partial response to the previous question on the toxicity and uses of dialkyl-dithiophosphoric acids, the zinc salts are widely used as extreme-pressure additives in lubricating oils. My question relates to the selectivity of these reagents in the presence of octanol. In our work with several extractant systems we have seen reductions in separation factors, for instance with nickel/cobalt, when high-molecular-weight alcohols are added to the extractant. Do you observe changes in selectivity when octanol is added to dialkyldithiophosphoric acid extractants?

J.-L. Sabot: The separation factor for nickel and cobalt depends on the polarity of the diluent. When alcohols or tributylphosphate are added to the organic phase, we observe an enhancement of the cobalt distribution so that both cobalt and nickel may be quantitatively extracted.

A.J.M. Schepper: Is there a specific reason why you have done most of your stripping tests with HCl solutions?

J.-L. Sabot: The specific reason why we chose hydrochloric acid medium to perform the stripping is that elimination of residual impurities from the stripped aqueous phase is made easier, for example, by extraction of chloride complexes by solvation (with TBP for instance).

BASE METALS

The Complex Utilization of Red Mud or Low Grade Bauxite by Solvent Extraction

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University of Zagreb, Yugoslavia.

ABSTRACT

The commercial success of smelting prepared red mud or low grade bauxite depends on complete utilization of the slag obtained by smelting. The paper describes a process based on leaching this slag with sulphuric acid. The undissolved residue is separated and mixed with raw phosphate to give a new synthetic fertilizer. From the filtered solution compounds of Ti, Zr, U, Th and lanthanides are extracted by di-2-ethylhexyl-phosphoric acid and 2-ethyl-hexanol dissolved in kerosene. From the solution, after extraction of titanium and other elements mentioned above, iron compounds and aluminium sulphate or alumina are recovered.

Introduction

IT IS WELL KNOWN that there are large occurrences of bauxite characterized by high SiO_2 content which are not suitable for alumina extraction treatment by Bayer process. A major part of these bauxites contain also considerable amounts of iron compounds, so that they simultaneously represent some type of poor iron ore.

At same time, the red mud produced as a waste in the leaching of bauxite in the Bayer process contains almost all elements from the Mendelejeff periodic system. Red mud, a silt-like mixture of iron oxides, titanium dioxide, silica, alumina, caustic soda and various impurities, has for many years been the subject of various approaches to its utilization as a very unconventional "iron ore". It includes also most of the alloy and minor elements as well as the rare earths, contained in the bauxite. The continuous research toward developing economical technologies for processing of red mud as well as bauxite not suitable for the Bayer process, led in Yugoslavia to developing a complex process suitable for

the exploitation of almost all ingredients of these materials, as follows^(1,2).

Practical Work

This work consisted of the large-scale smelting of the bauxite or red mud burden in the blast and electric furnaces, to produce an alloy or high-quality pig iron and the slag, different than by the Pedersen process⁽³⁾. The solutions to the slag processing problem developed earlier could not satisfy us for reasons of economy, so we tried to solve the problem by working out complex methods for the most complete utilization of slag constituents. The slag was leached in a pilot plant with dilute sulphuric acid, and then the undissolved part of the slag was converted to a synthetic fertiliser. Finally, the large laboratory-scale solvent extraction equipment was used for the extraction of the useful ingredients from the pregnant acid leach solution.

The Smelting of Bauxite or Red Mud

The briquetted, pelletized or sintered red mud or low-grade bauxite burden, enriched with the purple ore, or with iron scrap, was smelted in both the blast furnace and electric arc furnace on an industrial scale. The smelting process had to be carried out in such a way that alumina and titania went into slag, as well as almost all minor and rare-earth elements, while the alloy elements were mostly reduced to pig iron. Particular attention was paid to the reduction of titanium since for the proper functioning of the furnace the Ti-content of the iron should not exceed 0.3 percent.

The qualities of the pig iron produced with acid and basic slag were identical, except for the fact that the sulphur content in the basic practice was lower than 0.03 percent while the acid pig iron had to be desulphurised. Otherwise the pig iron was of high quality and in chemical composition similar to the well known "VANTIT" pig iron⁽⁹⁾. The silicon content varied depending on the smelting schedule, from approximately 3 percent in foundry pig iron to less than 0.5 percent in basic pig iron. Reduction of alloying elements greatly depended on basicity of manufactured slag.

Figure 1 shows the flow sheet for red mud smelting in a Tysland-Holle electric furnace — very similar to smelting of ferruginous bauxite. The slag composition produced during smelting had an important role in the process, especially in the earlier days of our work when this was similar to the work in the other countries over the world. The slag produced in the smelting work was used for production of alumina, as in Pedersen process⁽³⁾ and as was done in the USSR, France, Germany, Hungary, USA and other countries^(4,6,7,8). Besides that, the slag was used in titanium ferroalloys production and also for the production of high-quality cement and lightweight construction aggregate.

Later, because of economical reasons, we found that the commercial success of the red mud as well as of the ferruginous bauxite depended on finding a better solution for the utilization of the slag produced by the smelting process other than the solutions mentioned above.

Distribution of Elements During Smelting

Neutron activation analyses of the pig iron and slag produced by the smelting of red mud in the electric arc furnace at the Iron and Steel Works, Sisak, in 1972, were carried out in the Netherlands Reactor Centre (RCN), Petten, by Dr. H.A. Das. Table 1 shows the following

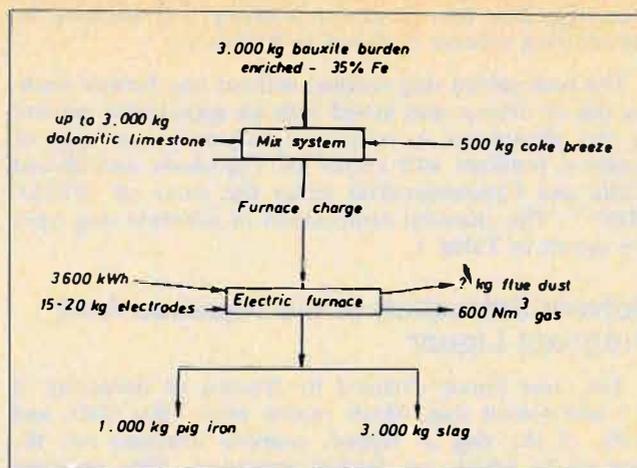


FIGURE 1. Flowsheet of electric furnace smelting process.

TABLE 1. Distribution of Elements in Slag and Pig Iron.

	Sr	Pb	Th	U	La	Sc	Hf	Eu	Sm
Slag I	276	<200	133	7	103	13	35	11	40
Pig Iron I	< 2	< 50	< 5	<0.5	3	< 0.1	< 1	< 2	≤ 2
Slag II	230	200	61	3	34	8	43	6	50
Pig iron II	< 2	<50	< 5	<0,5	3	< 0,1	< 1	< 2	≤ 2
	Ni	Co	Nb	Ce	Sb	Rb	Cs	Cr	
Pig iron I	1110	132	600	200	143	<50	< 1	5330	
Slag I	< 100	3	< 100	257	3	<50	< 1	600	
Pig iron II	1700	177	530	283	145	<50	< 1	7130	
Slag II	< 100	1	< 100	124	1	<50	< 1	1620	

contents of trace elements in ppm (analyses made in October 1974)⁽¹⁰⁾.

As is seen from Table 1, the minor elements, including thorium and uranium as well as the rare earths except cerium, almost completely passed into the slag. These elements concentrated in the zirconia concentrate obtained after the production of titania concentrate by solvent extraction of the pregnant solution from the slag leaching with sulphuric acid. Table 1 shows the alloy metals which passed into the pig iron. Here also rubidium and caesium are included, with a similar reduction to that for the reduction of cerium.

The composition of the resulting pig iron is as follows:

C	3.8 ... 4.5%	Ni	0.2 ... 0.3%
Si	0.5 ... 3.0%	Co	0.02 ... 0.03%
Mn	0.3 ... 0.8%	Mo	0.02 ... 0.03%
Ti	0.1 ... 0.3%	Nb	0.05 ... 0.06%
V	0.2 ... 0.3%	Ce	0.02 ... 0.03%
Cr	0.2 ... 0.4%		

The degree of reduction of the alloy metals depends on the temperature of smelting as well as on the slag basicity, and is shown in Table 2. Regarding the % reduction of nickel, cobalt and molybdenum into the pig iron, all three alloy metals reduce almost completely.

Leaching of the Slag

The leaching of the granulated slag, formed during the smelting process, is carried out in a suitable tank where it is vigorously agitated with 30 percent sulphuric acid, for 30 to 60 minutes, at the temperature of 80 to 90°C. After the leaching, undissolved slag is separated by

decanting. The flow sheet for leaching slag obtained by the smelting process is shown in Figure 2.

The undissolved slag residue, without any further washing out or drying, was mixed with an appropriate amount of raw phosphates in order to produce a new type of synthetic fertilizer well known in Yugoslavia and abroad (India and Czechoslovakia) under the name of "PELOFOS"⁽¹¹⁾. The chemical composition of different slag types are shown in Table 3.

Solvent Extraction of the Aqueous Acid Pregnant Liquor

The clear liquor obtained by filtering or decanting of the undissolved slag, which retains most TiO₂, ZrO₂ and Al₂O₃ of the slag as tapped, contains uranium and the rare earths which are further processed. This pregnant liquor must be diluted with water so that it then contains: 6 - 8 g/l Al₂O₃, 3 - 5 g/l Fe₂O₃, 0.5 - 1 g/l TiO₂. The further operation proceeds favourably when the aqueous-

TABLE 2. The Reduction Grade of the Alloyed Metals.

	Basic slag	Acid slag
Vanadium.....	77 %	95%
Chromium.....	83.9	94
Titanium.....	11.3	
Niobium.....	90.0	
Cerium.....	50.0	

TABLE 3. Chemical Composition of Slags Produced by Smelting of Red Mud and Bauxite.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	CaO	MgO	S	CaO	SiO
Red mud	1.	7,85	10,30	34,70	3,47	31,64	10,20		0,98
	2.	8,50	8,70	33,20	2,96	40,10	4,80		1,08
	3.	10,20	9,20	34,43	3,21	29,38	11,19		0,90
	4.	16,40	5,12	18,70	3,54	37,52	18,36		1,68
	5.	16,67	8,34	31,20	1,72	31,27	8,72		0,83
	6.	16,77	8,07	34,19	1,57	29,58	7,94		0,73
Bauxite	1.	14,68	2,59	47,28	1,14	31,89	1,43	1,15	
	2.	14,02	1,78	49,68	1,18	31,00	1,68	1,02	
	3.	19,32	2,77	41,11	2,00	30,93	1,95	1,11	
	4.	19,73	1,82	35,12	1,17	38,89	1,11	1,04	

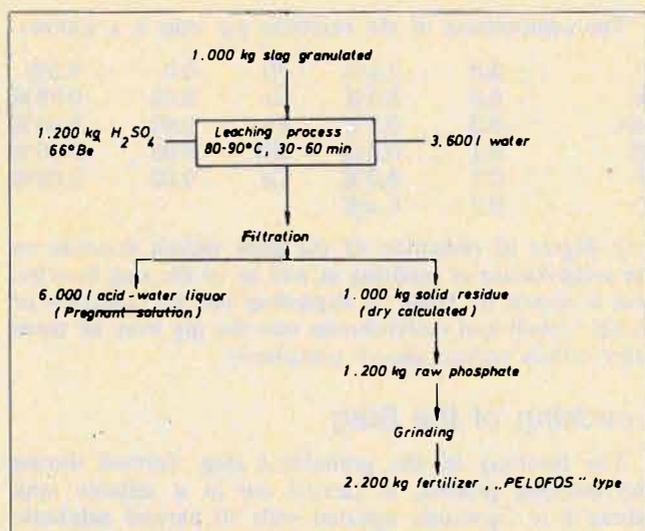


FIGURE 2. Flowsheet of leaching process.

acid liquor is treated with organic solvent by hand-shaking in large-scale trials in mixer-settler units of 50 l volume each, four-stage Denver Laboratory Solvent-Extraction System.

The above-mentioned elements, as well as ZrO₂, uranium, thoria and the rare earths are separated from the aqueous — acid solution by the application of solvent extraction in the flow sheet which is shown in Figure 3.

The extraction itself was done by means of organic solution composed of kerosene containing 5 percent of di-2-ethylhexyl-phosphoric acid (DEHPA) with 2 percent 2-ethylhexanol. The phase ratio between the diluted aqueous acid solution, and the organic solution, was 1.6. The loss of the active organic solvent in our work was 0.02 percent, whereas according to the available literature, the loss of up to 0.05 percent is considered to be tolerable.

The first stage of solvent extraction was carried out with a pH value slightly below 1.0 and with phase contact time of 3 minutes. After the extraction had been completed, the primary aqueous acid solution contained only traces of titanium, zirconium, uranium, thorium and rare earths. Distribution coefficient, D, for titanium of 159.1 was reached with 99.5 percent of extraction.

The organic solvent was then stripped with 10 percent Na₂CO₃ solution, the ratio being 2 to 1, in order to obtain the useful constituents mentioned above. After that, the organic phase was reused in the solvent extraction process, with practically no losses. Hydrolyzed Ti(OH)₃ precipitate was separated from the Na₂CO₃ solution using a normal vacuum filter, and was washed and purified because during the process of extraction a part of Fe(III) also precipitated. The purified Ti(OH)₃ is then calcined into TiO₂⁽⁹⁾.

Because the process of purification includes dissolving of Ti(OH)₃ in sulphuric acid and the reducing of this solution to Fe(II) prior to the solvent extraction of titanium, we decided that this purification is excessive and that Ti(OH)₃ obtained in such a way with some iron is suitable for the production of titanium ferroalloys.

The filtered Na₂CO₃ solution was recycled to the stripping process until its contents of zirconia, uranium, thoria and lanthanides attained concentration levels allowing their commercial recovery. The pregnant Na₂CO₃ solution was then replaced by fresh solution, usually after 2 to 3 successive reextractions.

Our work has proved that this reextraction procedure extracted 52 percent of titanium contained in the organic solvent. From pregnant Na₂CO₃ solution we produced a mixture which, after drying, contained up to 84 percent ZrO₂ with the remainder being compounds of rare earths, thoria and uranium.

Titanium which could not be reextracted with Na₂CO₃ solution was completely reextracted from organic phase with hydrochloric acid, producing quite white titanium salts.

The aqueous acid solution, after the first stage of solvent extraction containing almost unchanged amounts of Fe₂O₃ and Al₂O₃ but only traces of TiO₂, ZrO₂, ThO₂, uranium and other elements, was sent to desilication at atmospheric pressure, after raising its pH value to approximately 2.5 by adding NaOH. The desilication operation took about two hours, after which it was possible to separate by filtration a mud consisting of sodium aluminium silicate, with about 4% percentage of Al₂O₃. It is more convenient to do the desilication operation before solvent extraction of titanium at pH value below 1.0. Of course the silica gel precipitate then absorbs titanium, rare elements and rare earths, usually in very small

quantities, depending on the temperature and the leaching time of the slag.

The aluminate solution so obtained contained iron(III) — 1.145 g/l, iron(II) — 0.588 g/l, aluminium — 2.351 g/l and silicon(IV) — 0.065 g/l. In order to turn iron(II) into iron(III), oxidation of this solution was done by adding hydrogen superoxide. After that the same organic solvent separated iron(III). The highest percentage of iron(III) extraction was reached at pH value of 2.5. Simultaneously, aluminium was co-extracted with iron(III) in the range between 10 to 25 percent, whereas silicon was not co-extracted. Distribution coefficient for iron(III) of 89.357 was reached with 98 percent of the iron extracted mixed with an appreciable amount of aluminium as mentioned above⁽¹³⁾.

With further addition of NaOH, pH just below 5.0 was reached where aluminium compounds in the form of aluminium sulphate or alumina were extracted. The extraction yield of alumina compared to that in the initial slag amounted to between 85 - 90 percent and will yield 100 kg of alumina or at least 500 kg of aluminium sulphate per ton of pig iron produced.

If cheap steam is available, the remaining waste liquid after the extraction and filtration of Al-precipitate can be vaporized with the purpose of obtaining sodium compounds in the form of sodium sulphates.

Conclusion

The extensive long-term laboratory and industrial-scale investigation in Yugoslavia described here, is in our opinion an interesting way of red mud or low-grade bauxite processing, the more so as all constituents of these raw materials can be recovered. This complex processing of red mud or low-grade bauxite involves smelting of these materials, usually enriched with the purple ore sinter or pellets or iron scrap, in the electric arc furnace in order to produce high quality pig iron and slag. From this slag constituent elements, primarily TiO₂, ZrO₂ and Al₂O₃ the uranium and rare earths, are obtained by means of solvent extraction.

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DISCUSSION

T. Sato: (1) I think that the concentration of alkali in red mud is high. What method do you use to take off alkali from red mud before the solvent extraction process if you apply this extraction technique to red mud?

(2) What is the temperature dependency of this extraction?

V.G. Logomerac: The content of alkali in red mud depends on the washing process in the alumina plants. Usually this content is about 5-7%, most of that is bound with SiO₂, TiO₂ and other constituents of red mud, and only 0.2% is as NaOH.

The alkali content is removed from the red mud during the melting process, partly in the slag produced and partly

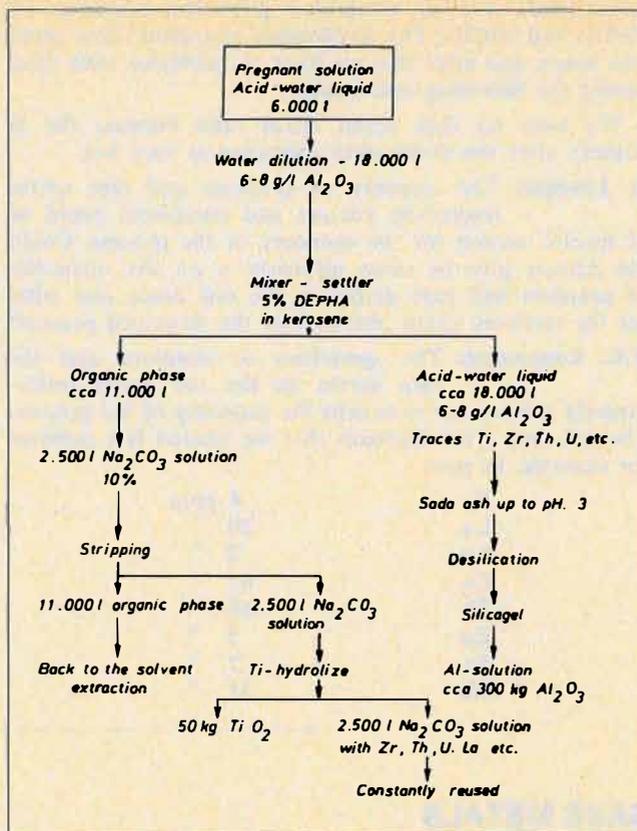


FIGURE 3. Flowsheet of solvent extraction process.

- (4) Vorwerk, O., Verein Deutscher Eisenhuettenleute in NSBDT, Vertraulicher Bericht No. 50, 1943.
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in the form of fume or flue dust. The melting process is shown on the Figure 1 (Flowsheet).

Solvent extraction of the solution from the leaching of the slag, produced by melting of red mud, is carried out from room temperature up to a maximum of 30°C, at pH 1, for Ti, Zr and the rare earths, as well as for U and Th. This is the same temperature we have had during extraction of Fe and Al.

G. Ritcey: In your flowsheet you show a desilication stage prior to aluminum recovery. Can you state the amount of Si at that stage, what was the process you used and what was the final Al/Si ratio achieved?

V.G. Logomerac: The aqueous — acid solution contains 0.028 to 0.061 g/l Si(IV), and therefore we use a desilication operation at atmospheric pressure prior to solvent extraction of titanium at pH

value below 1.0, or sometimes prior the extraction of Fe(III) and Al(III). The desilication operation takes about two hours, and after that we have no problems with silica during the following extractions.

We have no data about Al/Si ratio because the Si content after the desilication operation is very low.

A. Leveque: The recovery of uranium and rare earths (especially yttrium and europium) could be of special interest for the economy of the process. Could the Author give us some information on the quantities of uranium and rare earths in the red muds and what are the recovery yields obtained by the described process?

V.G. Logomerac: The quantities of uranium and the rare earths in the red muds unfortunately are too low to benefit the economy of the process. The red mud from Surinam that we treated last contains for example, in ppm:

U	4 ppm
La	20 "
Sm	2 "
Ce	62 "
Th	66 "
Eu	3 "
Sc	7 "
Hf	31 "

Most of these elements were concentrated by the smelting process in the slag, and during the leaching process into the sulphuric acid solution. By the first stage of solvent extraction below pH 1.0, titanium and zirconium, as well as the elements mentioned above, concentrate in the organic solvent and are stripped with Na₂CO₃ solution. After obtaining titanium, the clear Na₂CO₃ solution is recycled to the stripping process until its content of zirconia, uranium, thorium and rare earths attains a concentration level allowing their commercial recovery. From pregnant Na₂CO₃ solution we produced, after drying, a precipitate containing around 84% ZrO₂, whereas the rest were compounds of uranium, thorium and rare earths.

Of course, by this way of obtaining titanium, simultaneously and without any additional expenses, we produced a very interesting concentrate. Up to date we investigated on the laboratory scale the possibilities of obtaining zirconia only, the recovery yields of Zr being about 67% of the Zr content in the red mud.

I.J. Itzkovitch: In your solvent extraction circuit did you experience any difficulties with loading of silica in the organic? Was crud formation an operating difficulty?

V.G. Logomerac: None.

BASE METALS

Recovery of Chromium and Vanadium from Alkaline Solutions Produced by an Alkaline Roast-Leach of Titaniferous Magnetite

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CANMET, Dept. E.M.R., Ottawa, Canada.

ABSTRACT

Large orebodies of titaniferous magnetite containing Ti, V, Cr and Al are located in eastern Quebec. The Quebec Mining Exploration Company (SOQUEM) considered that the recovery of Al, V and Cr from a Na₂CO₃ roast-leach of a magnetic concentrate might generate sufficient revenue to defray the costs of mining and transporting the iron ore to a steel production facility. The present paper briefly describes the integrated circuit, and in more detail that part of the circuit that was developed following the alkaline roasting-leaching sequence.

Quaternary amines were used for the stagewise extraction and separate recovery of chromium and vanadium from the alkaline leach liquor at pH 13. Seven stages of mixer settlers achieved 99.9% extraction of chromium, which was further purified by scrubbing with a sodium chromate solution. Sodium chloride effectively stripped the chromium, which was recovered by crystallization to produce Na₂CrO₄·4H₂O. Vanadium was similarly extracted with a quaternary amine, scrubbed with sodium vanadate, and stripped with an ammoniacal ammonium chloride solution. The NH₄VO₃ product was dried and calcined to V₂O₅. Estimated capital and operating costs are shown for the process.

Introduction

THE QUEBEC MINING EXPLORATION COMPANY (SOQUEM) acquired in 1968 an interest in four titaniferous magnetite orebodies located in Eastern Quebec, 85 miles north of Mingan on the north shore of the St. Lawrence River. The Mingan deposit, with an estimated tonnage of one billion tons, has a reported average grade of 43% Fe, 6.3% Ti, 1.60% Cr, 0.19% V plus minor amounts of nickel. SOQUEM, on the basis of previous bench scale data, believed that the recovery of chromium, vanadium and alumina by alkaline roasting would generate sufficient revenue to defray the mining costs and the costs of transporting the ore to a steel production facility on the coast. One of the approaches selected by SOQUEM for beneficiation of the ore consisted of a combination of magnetic concentration followed by alkaline roasting of the calcine.

The development of such resources as the Mingan deposit would make Canada a major supplier of chromium and vanadium besides adding a non-bauxitic source of aluminum. Canada at present imports all its chromite ores, i.e., about 75,000 tons/yr. The Mingan operation would provide around 100,000 tons/yr., thus making Canada an exporter of chromium. Although vanadium is a minor constituent of the Mingan concentrate it would be produced in sufficient quantities to cause an oversupply on the world markets. An integrated processing plant

TABLE 1. Summary of Possible Treatment Routes.

Route	Remarks
1. Precipitation of Al with CO ₂ and recovery of V by ppt'n and Cr by crystallization.	Excessive Co-ppt'n of vanadium occurs, Na ₂ CO ₃ recovered by evaporation. Costly to produce pure products.
2. Bulk ppt'n of Cr, Al & V. Dissolution and separate recovery of metals.	High neutralization costs and no recovery of Na ₂ CO ₃ for recycle to process. Possibly expensive to produce pure products.
3. Ppt'n of Al by pH adjustment and extraction of and sep'n of Cr and V from acidic solutions.	Co-ppt'n losses of vanadium in aluminum ppt. No recovery of Na ₂ CO ₃ . Possibly expensive to produce pure products.
4. Alter the prior roasting conditions to solubilize only Cr and V. Recovery by SX.	Low costs but no Al recovery. The Al in the iron residue makes it less desirable to steel-making. Na ₂ CO ₃ recovered.
5. Stagewise recovery of Cr and V by SX followed by ppt'n of Al.	Good recovery of metals and possibly of high-purity final products. Na ₂ CO ₃ would be recovered for recycle.

that could provide a suitable feed to iron processing, while at the same time recovering Cr, V and Al as valuable by-products would be a valuable asset to an area such as Mangan. Such a process could enable the processing of low grade iron ores and the opening-up of some remote areas of Canada, thus increasing employment in those areas, and more important, the conservation and best utilization of our mineral resources would be maintained. The scope of the work included bench-scale and pilot plant tests, and the objective was to develop and optimize a roast-leach technique. Because very little was known regarding the treatment of the resultant solution for the separate extraction and recovery of soluble products of chromium, vanadium and aluminium, the bulk of the program was in those areas.

With respect to the alkaline solution treatment aspects, there were many possible alternatives such as precipitation and crystallization, and from acidic media separations by precipitation or solvent extraction are well known. Some of the possible treatment routes that were considered are shown in Table 1. Each of these had certain advantages, but after careful examination and some preliminary testing, Route 5 was considered to warrant a complete investigation. Because the solution from leaching the calcine would be alkaline, and because the process could not tolerate much additional operating expense to adjust the pH with acid, it was decided to attempt the separation and recovery of the values from the alkaline medium. Reagent costs, as well as operating costs, would be decreased, and the treated solution would be amenable to recycle to the leaching stage. The studies on the separation of the metals from the alkaline solution therefore consisted of solvent extraction and precipitation. The research program was directed towards the development and optimization of such a process flowsheet.

The work describing the alkaline roast-leach circuit and the plant economics was recently reported⁽¹⁾.

A search of the literature and patents revealed very little with respect to solvent extraction separation of the three metals. From acidic liquors, vanadium was extracted at pH 1.4-3.0 range, at 90-120°C, using DEHPA⁽²⁾. In the pH 0-4 range, LIX 64N was reported useful for vanadium⁽³⁾. Solutions resulting from a salt roast, and in the pH 5.5-7.0 range, were contacted with a long chain amine for the extraction of vanadium⁽⁴⁾. General Mills described in their literature⁽⁵⁾ data showing that maximum extraction of 98.5% vanadium occurred at pH 5.1, compared to 25% at pH 11.3 using 0.1M Aliquat 336 in contact with 2 g V₂O₅/l at an aqueous organic ratio of 5. Recovery of vanadium by direct precipitation from the organic phase has been reported using gaseous ammonia⁽⁶⁾ or ammonia plus ammonium chloride at pH 8.0⁽⁴⁾.

General Mills also have reported on the extraction of chromium⁽⁷⁾ or of Cr⁺, in the presence of V⁵⁺ using

TABLE 2. Screen Analysis of Mangan Concentrate.

Fraction	Weight %
65 mesh.....	0.5
-65 + 100.....	1.0
-100 + 150.....	14.3
-150 + 200.....	22.1
-200 + 270.....	10.0
-270 + 325.....	8.7
-325.....	32.6

TABLE 3 Typical Analyses of Concentrate and Leach Filtrate.

	pH	Fe	Ti	Si	V	Al	Cr
Concentrate, (%)		51.6	6.99	0.65	0.22	4.78	1.86
Leach Filtrate, (g/l)	13.5				0.9	12.5	7.0
	Mg	Ca	Na	Mn	P	S	Ni
Concentrate (%)	2.06	0.090	0.047	0.28	0.054	0.092	0.13

Aliquat 336⁽⁵⁾. Preferential extraction of vanadium occurred at pH 9, but at pH 5 chromium was preferentially extracted. At pH 12, although very low loading occurred, chromium was preferentially extracted.

Hughes and Leaver's investigation⁽⁸⁾ of a chromate system was not considered pertinent because their data were obtained from tests on solutions at a lower pH with essentially no aluminium present.

The literature and patent search revealed no separation technique using solvent extraction for recovery of aluminium from alkaline solution. DEHPA has been shown to be useful for extraction from acidic solutions at pH 3.0⁽⁹⁾.

Feed Analysis

The screen analysis on the titaniferous magnetite concentrate is shown in Table 2.

The typical analysis of the concentrate, and the filtered leach solution feed to the solvent extraction circuit are shown in Table 3.

Roast-Leach Operation

The feed concentrate was ground to 51% minus 200 mesh. A lignosol binder was added to the concentrate which was mixed with 22.5 wt% Na₂CO₃, and -3/8" + 10 mesh pellets were produced using a balling disc. The pellets were fed, in the pilot plant operation, to two Bartlett-Snow rotary calciners, operated in parallel. The feed rate to a calciner was 1200 g/hr of pellets at a temperature of 1025°C, in an air atmosphere for a 3-hour period. The calcine was leached in one stage, at 90°C for two hours at a liquid/solid (L/S) ratio of 5. Caustic was

added to the leach at the rate of 65 lb/ton calcine. Overall extraction, in per cent, was 91.1 V, 84.2 Cr, 74.7 Al. The addition of caustic increased the vanadium extraction from 85% and the aluminium from 69%. There was little effect on chromium extraction by the addition of extra caustic. Following thickening and liquid-solids separation, and filtration on drum filters, the solution was clarified before being sent to a surge tank for feed to purification by solvent extraction.

Solution Purification

Bench Tests

Preliminary Extraction Tests for Chromium and Vanadium

Because it was desirable to recover Cr, V and Al as pure products it was decided to use solvent extraction wherever possible. Early tests showed that aluminium began to precipitate at pH 11.5, and so the solution could not be adjusted over a wide range of pH to test and evaluate various solvent extraction reagents, without the aluminium being first removed from the liquor.

Fourteen extractants were made up at 5 volume percent (v/o) strength in kerosene and pre-equilibrated with H₂SO₄, and then contacted with the leach liquor at a volumetric ratio, aqueous/organic (A/O) of 1. The feed pH of the leach liquor was adjusted to 4, 6, 8, 10 and 12 after prior removal of aluminium by precipitation. The leach liquor at pH 13.2, containing Al, was also contacted with the solvents.

The feed solution used for the tests, prior to removal of aluminium by precipitation with CO₂ down to pH 8, and prior to pH adjustment, analysed in g/l: 0.86 V, 7.02 Cr, 12.5 Al.

The results of exploratory screening tests on a number of extractants indicated Adogen 464 and Aliquat 336, quaternary amines, to be the most effective in both the alkaline and acidic pH ranges. The data are shown in Table 4.

However, although the loading from alkaline solutions was less than from acidic solutions, no neutralization costs between metal recovery stages would be incurred using alkaline solutions. This could be an important advantage in the overall economics. Also, as the pH was increased from 4 to 13, the V/Cr separation factor decreased (Cr/V increased). That is, the quaternary amines were selective for vanadium from the acidic solutions, and selective for chromium from highly alkaline solutions. The metal loading was decreased with increasing pH. These results are shown graphically in Figure 1.

Extraction Data for Chromium

Because of the immediate quantity of reagent on hand, and the fact that the Aliquat 336 was several years old, Adogen 464 was initially selected for the extraction and separation of chromium from vanadium. Equilibrium data were obtained by contact of the leach liquor with 10 v/o Adogen 464 at a feed pH 13.5. Contact time was for 5 minutes, at A/O ratios of 1/5, 1/2, 1/1, 2/1, and 5/1.

The data from the leach liquor, at a feed pH 13.5, are shown in Figure 2 for Cr, indicating a loading of 2.7 g Cr/l at an equilibrium pH of 13.4. The McCabe Thiele diagram, from data obtained at an equilibrium pH of 13.4, is shown in Figure 3, indicating that 7 stages are necessary for the extraction of chromium from a liquor containing 7.2 g Cr/l and to obtain a raffinate of < 0.02 g Cr/l.

With respect to the kinetics of Cr extraction, tests performed at a temperature of 50°C over a period of 15 seconds to 2 hours indicated maximum extraction occurred

TABLE 4. Screening of Extractants for Metals Separation.

Extractant	Amine Type	pH		Extraction %			E		SF			
		Feed	Equil.	V	Cr	Al	V	Cr	Al	Cr/Al	Cr/V	V/Cr
Adogen 464.....	Quat	4.0	2.35	94.4	74.5	—	21.2	2.92	—	—	—	7.3
Aliquat 336.....	Quat	—	2.15	96.5	74.9	—	28.6	2.99	—	—	—	9.6
A1 336.....	Tert	—	2.10	89.7	75.0	—	8.9	3.00	—	—	—	3.0
LA -2.....	Sec	—	2.17	32.5	81.0	—	0.48	4.29	—	—	8.9	—
Primene JMT.....	Prim	—	2.27	81.5	75.7	—	4.4	3.11	—	—	—	1.41
Adogen 464.....	—	6.0	2.65	94.0	72.9	—	16.0	2.0	—	—	—	8.0
Aliquat 336.....	—	—	2.60	95.1	71.5	—	20.2	1.89	—	—	—	10.7
A1 336.....	—	—	2.50	74.0	73.4	—	2.86	2.04	—	—	—	1.4
LA -2.....	—	—	2.35	50.5	89.4	—	1.0	4.5	—	—	4.5	—
Primene JMT.....	—	—	3.01	93.9	75.0	—	5.3	3.0	—	—	—	5.1
Adogen 464.....	—	8.0	8.00	65.5	41.0	—	1.90	0.70	—	—	—	2.7
Aliquat 336.....	—	—	8.02	70.0	41.4	—	2.33	0.71	—	—	—	3.3
A1 336.....	—	—	7.60	0.0	1.8	—	—	—	—	—	—	—
LA -2.....	—	—	7.70	0.0	0.9	—	0.0	0.01	—	—	—	—
Primene JMT.....	—	—	7.85	0.0	0.0	—	0.0	0.0	—	—	—	—
Adogen 464.....	—	10.0	9.83	32.2	26.2	—	0.47	0.36	—	—	—	1.3
Aliquat 336.....	—	—	9.83	34.4	28.2	—	0.50	0.39	—	—	—	1.3
A1 336.....	—	—	9.52	0.0	0.0	—	—	—	—	—	—	—
LA -2.....	—	—	9.53	0.0	0.0	—	—	—	—	—	—	—
Primene JMT.....	—	—	9.45	0.0	0.0	—	—	—	—	—	—	—
Adogen 464.....	—	12.0	10.63	1.0	29.3	—	0.01	0.42	—	—	38.0	—
Aliquat 336.....	—	—	10.53	2.2	35.1	—	0.02	0.54	—	—	23.5	—
A1 336.....	—	—	9.98	—	2.0	—	—	0.02	—	—	—	—
LA -2.....	—	—	9.85	—	—	—	—	—	—	—	—	—
Primene JMT.....	—	—	9.85	—	—	—	—	—	—	—	—	—
Adogen 464.....	—	13.2	13.10	0.0	26.5	0.9	0.0	0.36	0.01	36.0	α	—
Aliquat 336.....	—	—	13.12	0.0	30.0	2.2	0.0	0.43	0.02	21.5	α	—
A1 336.....	—	—	13.00	0.0	0.0	2.6	0.0	—	0.03	—	—	—
LA -2.....	—	—	12.90	0.0	0.0	3.7	—	—	0.04	—	—	—
Primene JMT.....	—	—	12.85	0.0	0.0	0.0	—	—	—	—	—	—

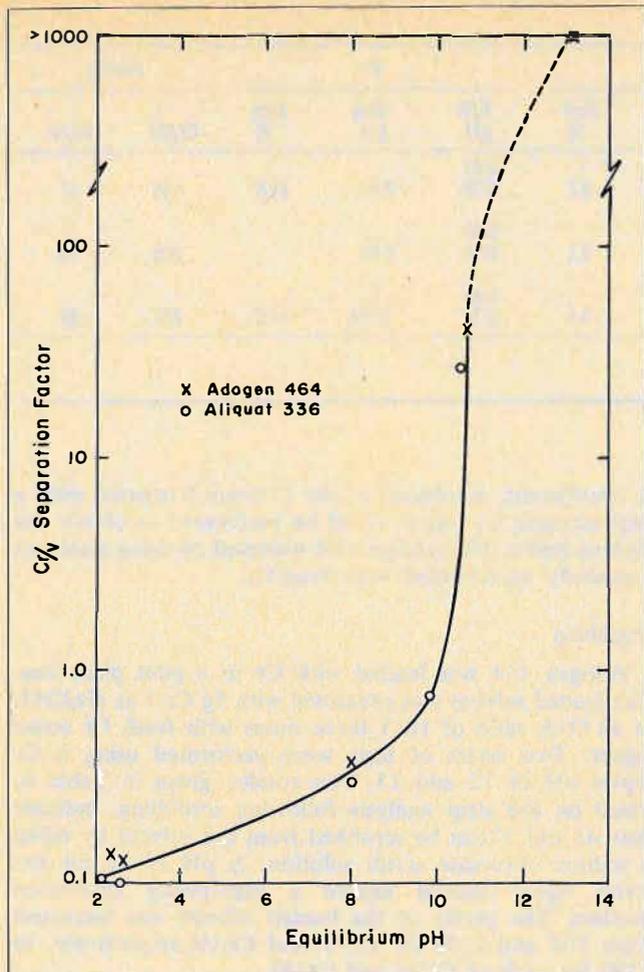


FIGURE 1. Change of Cr/V separation factor with equilibrium pH.

in less than 1 minute. Closely-controlled experiments, perhaps in an AKUFVE apparatus, would be required to clearly define this.

Extraction Data for Vanadium

The screening tests in Table 4 showed that V could be extracted by a quaternary amine at pH 2-3 quite satisfactorily, and with good loadings. However, to achieve pH 2-3, the neutralization would produce a co-precipitation of aluminium and vanadium. Such a precipitate would require acid dissolution, followed by solvent extraction separation of vanadium. This route was considered expensive, and would destroy the Na_2CO_3 solution which would be advantageous to recycle in the process to the roasting stage.

Tests were carried out at feed pH 13.3 using a synthetic as well as actual leach liquor. Using 10 v/o amine, the vanadium loaded to 0.84 g/l from the synthetic solution, compared to only 0.29 g V/l from the leach liquor.

The data from the equilibrium tests on the leach liquor, at a pH of 13.3, are shown in Figure 4 for vanadium, indicating a loading of 0.29 g V/l at an equilibrium pH of 13.2. The McCabe Thiele plot of this data is shown in Figure 5, indicating that 6 stages of extraction are required for the extraction of vanadium in order to obtain a raffinate of 0.05 g V/l.

Pilot Testing

The next stage in the investigation was to pilot test the stagewise separation of chromium followed by vanadium,

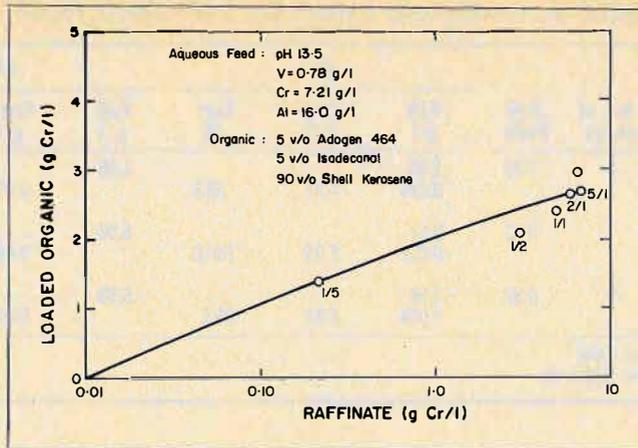


FIGURE 2. Equilibrium curve for Cr from leach liquor.

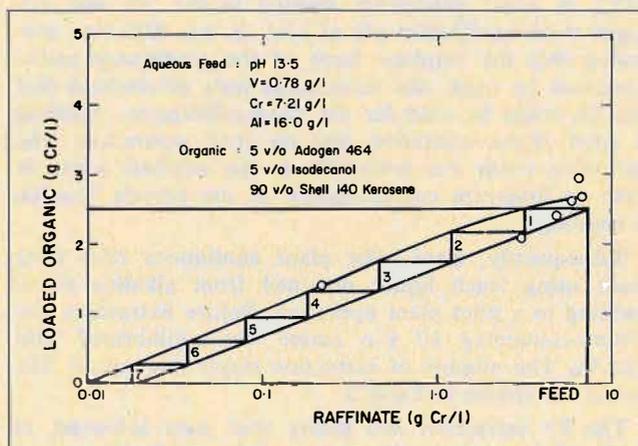


FIGURE 3. McCabe-Thiele diagram for Cr from leach liquor.

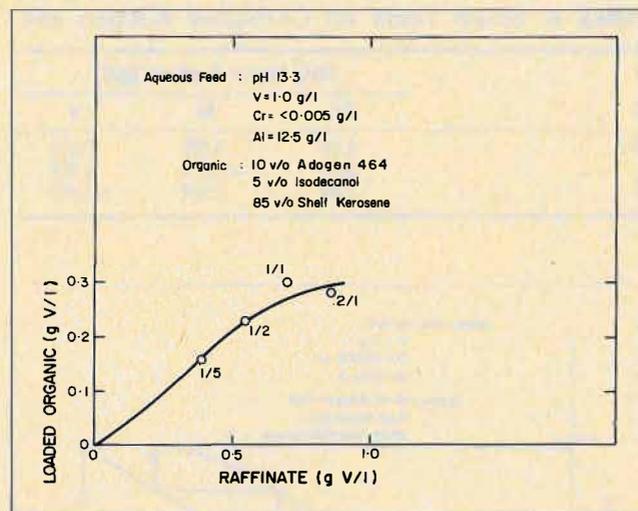


FIGURE 4. Equilibrium curve for V from leach liquor.

from the alkaline leach solution using a quaternary amine in a solvent extraction process.

Chromium

Extraction

Ten per cent Adogen 464 in the sulphate form was used with 5% isodecanol in kerosene. Eight stages of mixer-

TABLE 5. Cr Solvent Extraction Pilot Plant Runs.

No. of stages	A/O Ratio	Cr			Al			V			Purity	
		F/R g/l	Org g/l	Extr %	F/R g/l	Org g/l	Extr %	F/R g/l	Org g/l	Extr %	Cr/Al	Cr/V
5	0.82	3.58 0.026	2.91	99.3	6.98	0.014	0.2	0.43 0.38	0.04	11.6	188	87
7	0.82	3.58 0.001	2.93	100.0	6.98	0.007	0.1	0.43 0.46	0.03		605	96
9	0.82	3.58 0.004	2.93	99.9	6.98	0.017	0.1	0.43 0.37	0.031	14.0	251	89

F = Feed
R = Raffinate

settlers were used, with a 2 minute retention time for mixing the aqueous feed at pH 13.3, which was heated to 80°C. A white precipitate formed in the 7th and 8th stages at an equilibrium pH of 13.1. It was therefore concluded that the sulphate form of the quaternary amine could not be used, and subsequent tests determined that Na₂CO₃ could be used for the pre-equilibration, resulting in good phase separation and no crud separation. The carbonate anion was preferable to the sulphate anion in order to minimize contamination of the recycle Na₂CO₃ to roasting.

Subsequently, three pilot plant continuous runs were made using leach liquor obtained from alkaline roast-leaching in a pilot plant operation. Before extraction, the solvent-containing 10 v/o amine was equilibrated with Na₂CO₃. The number of extraction stages was varied. The results are shown in Table 5.

The Cr extraction and purity that were achieved, at an equilibrium pH 13.05, were optimum in 7 stages, confirming the earlier bench studies. If the purity of the Cr

is insufficient, scrubbing of the Cr-loaded organic with a high-strength Cr liquor could be performed to obtain the desired purity. No precipitation occurred by using a solvent previously equilibrated with Na₂CO₃.

Scrubbing

Adogen 464 was loaded with Cr in a pilot plant run. The loaded solvent was contacted with 5g Cr/l as Na₂CrO₄ at an O/A ratio of 10/1 three times with fresh Cr scrub liquor. Two series of tests were performed using a Cr liquor pH of 12 and 13. The results, given in Table 6, based on the strip analysis following scrubbing, indicate that Al and V can be scrubbed from the solvent by using a sodium chromate scrub solution. A pH of 12 for the scrub liquor should ensure a high-purity chromium product. The purity of the loaded solvent was increased from 100 and 1500 for Cr/V and Cr/Al respectively, to 3700 for each of Cr/V and Cr/Al.

Stripping

It would be desirable to recover the Cr from the organic phase with a carbonate salt so that the solvent would be left in the carbonate form, and thus a process step to convert the organic from the Cl⁻ or SO₄⁼ form would be eliminated. Preliminary results indicated that the carbonate salts could not be used, but that NaCl could be effective.

In subsequent continuous testing, a Cr-loaded solvent was stripped with 1M NaCl. The number of stages and the O/A ratio were varied. The results are given in Table 7.

The data indicated that 5 or 6 stages are required and an O/A ratio of 7 can be used resulting in a strip liquor containing 18.4 g Cr/l.

NaCl solution was further investigated as a stripping reagent for Cr. Retention time and pH had little or no effect on Cr stripping. However by increasing the NaCl molarity from 1 to 5 the concentration of Cr was increased from 16.8 to 66.4 g Cr/l (Table 8).

Chromium Product

Because no particular final product specification had been set, NaCl was arbitrarily selected as the stripping medium, but may not be the best reagent to obtain the desired final product. This process stage was not optimized further due to time constraints.

Such a strip liquor was evaporated to a first-stage saturation. NaCl was crystallized from solution and was removed prior to further evaporation and chromate crystallization. The chromate crystals were identified as Na₂CrO₄•4H₂O. The V, Al and Cl impurities in the crystals analysed, in per cent, were 0.02, 0.08, and 0.5 respectively.

TABLE 6. Scrub Tests on Cr-loaded Adogen 464.

pH	Strip Liquor Analysis (g/l)		
	Cr	Al	V
Feed.....	3.14	0.002	0.031
12.....	3.71	< 0.001	0.001
13.....	3.59	0.004	< 0.001

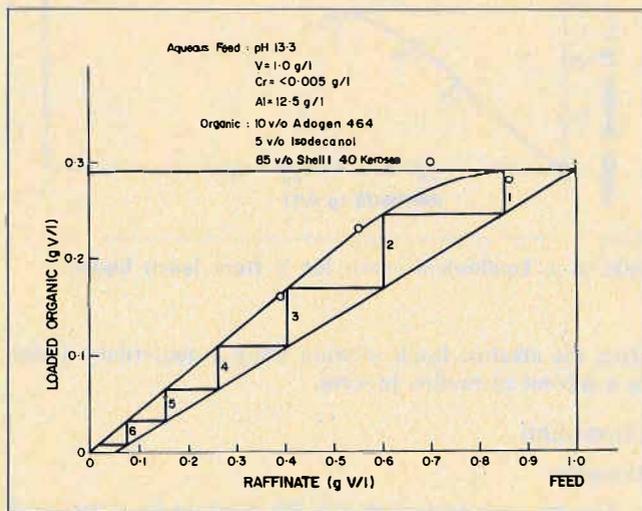


FIGURE 5. McCabe-Thiele diagram for V from leach liquor.

TABLE 7. Use of NaCl for Cr Stripping — Pilot Plant Tests.

No. Stages	O/A Ratio	Cr(g/l)			Al (g/l)			V (g/l)		
		Loaded org	Strip	Stripped org	Loaded org	Strip	Stripped org	Loaded org	Strip	Stripped org
4	7	3.06	18.2	0.33	0.002	0.027	< 0.001	0.032	0.19	< 0.001
6	7	3.06	18.4	0.037	0.002	0.022	< 0.001	0.032	0.12	0.002
6	9	3.06	17.5	1.11	0.002	0.049	< 0.001	0.032	0.43	0.004

TABLE 8 NaCl Stripping of Cr (Loaded Solvent 3.14 g Cr/l).

NaCl Mol.	O/A Ratio	pH	Retent. Time (min)	Strip liquor g Cr/l
1	25	6.5	1	16.8
2	25	7.0	1	31.4
5	25	7.7	1	66.4

Vanadium

Extraction

Because of the problem of co-precipitation of vanadium with aluminium, when the feed liquor was neutralized, it was decided to remove the vanadium by solvent extraction prior to aluminium purification. The bench data for vanadium extraction indicated a relatively low loading of 0.3 g V/l on 10 v/o Adogen 464, and that the equilibrium was also poor unless an excess of solvent was present. That is, a raffinate as low as 0.006 g V/l could be achieved in seven stages at an O/A ratio of 1.2. That data was verified in continuous pilot testing. Pilot plant data also confirmed the earlier data on the McCabe Thiele plot, (Figure 5), where 0.05 g V/l was achieved at an O/A of 1.0 in seven stages, with a loading of 0.29 g V/l.

Scrubbing

Because of the relatively impure vanadium product produced without a scrub treatment, scrub tests were carried out to determine the purity that could be obtained.

Vanadium-loaded Adogen 464 from the pilot plant, containing essentially no chrome because of the efficiency of the prior extraction stage, was scrubbed three times with 5 g V/l as NaVO₃. The O/A ratio was 10/l, and the pH was varied. The results in Table 9 indicated that the V/Al purity ratio could be increased from 3.5 to > 800. Although Al was removed, it was not known from those tests if Cr could be scrubbed. The V scrub liquor should contain less than 5g V/l, and at a pH of 13, to minimize increased V loading which would increase the subsequent stripping costs. These data indicate that in the absence of salts and/or high alkalinity, the loading of vanadium was considerably increased.

To test chromium scrubbing, a six-hour pilot plant scrub test on V-loaded Adogen 464, also containing added Cr, was carried out, using four stages at an O/A of 9/1 with a scrub solution containing 5 g V/l, as sodium vanadate, at pH 12. The results given in Table 10 indicate the possibility of removal of aluminium and chromium by the scrubbing operation.

Stripping

The scrubbed organic was then stripped with 10 g NH₃/l and 140 g/l NH₄Cl. The O/A ratio was 2/1. The contact time was arbitrarily 50 minutes and separation time was 2 hours. The stripping efficiency was greater than 99.5% in a single stage. Any chrome present on the solvent, although stripped, was not precipitated with the vanadium. The results are shown in Table 11.

TABLE 9. Scrubbing of V-loaded Adogen 464.

Scrub Solution 5 g V/l as NaVO₃, 3 stages, O/A 10/l

pH	Organic Analyses (g/l)		
	Al	Cr	V
Feed.....	0.052	< 0.0001	0.18
10.....	0.002	< 0.0001	1.39
11.....	< 0.001	< 0.0001	1.13
12.....	< 0.001	< 0.0001	0.89
13.....	< 0.001	< 0.0001	0.80

TABLE 10. Scrubbing of V-loaded Adogen 464.

	Analyses (g/l)				
	V	Cr	Al	V/Cr	V/Al
Scrub liquor	4.50				
Scrub Raff	0.12	0.002	0.30		
Feed Solvent	0.22	0.042	0.012	5.2	18.3
Scrubbed Solvent	0.68	0.020	< 0.001	34.0	> 680

TABLE 11. Stripping of V with NH₃-NH₄Cl.

	Analyses (g/l)		
	V	Cr	Al
Solvent Feed.....	0.68	0.020	< 0.001
Stripped Solvent.....	0.004	< 0.001	< 0.001
Strip Sol'n.....	0.096	0.048	< 0.0003

TABLE 12. V₂O₅ Product.

	Analyses (%)
V.....	54.49
Al.....	0.08
Cr.....	0.03
Na.....	0.02
Cl.....	0.02
LOI*.....	0.12

*Loss on ignition at 110°C

The resultant ammonium metavanadate precipitate was dried and roasted at 690°C for 3 hours. The V₂O₅ product analyses are shown in Table 12.

Aluminium Precipitation

Concurrent with the bench-scale and pilot plant programs for solution treatment for recovery of chromium and vanadium, tests were also conducted on recovery of aluminium. No satisfactory solvent extraction or ion exchange process was found for its recovery from such an alkaline leach solution. Therefore the tests were directed towards precipitation of aluminium by CO₂, after a pre-treatment to remove the silica contaminant. At the time of the pilot plant work on chromium and vanadium, because no satisfactory separation of the silica from

aluminium was achieved, no pilot plant work was directed towards producing an aluminium product.

The leach liquor averaged 0.035 g Si/l in its original dilute state. At such a low level of Si, lime addition did not reduce the silica to a desirable level. Therefore, by evaporating the liquor, the silica was concentrated to 0.57 g/l.

By using an autoclave, at 200°C and 200 psig, and adding 20 g CaO/l, the silica was reduced to 0.007 g/l. The initial Al/Si wt ratio was 92 and was increased by desilication to 6980.

The work on that portion of the flowsheet is not yet completed.

Integrated Flowsheet and Processing Steps

The flowsheets shown in Figures 6, 7, 8 are the results of testwork in the laboratory and in pilot plant operations for the treatment of Mangan titaniferous magnetite. The metallurgical balance and sizing of the equipment are based on an assumed throughput of 5,000,000 tons per year. For convenience, the hourly concentrate rate was rounded off at 600 t/hr while the leach liquor flow rate was simplified at 11,000 igpm. These rates were used for the sizing of equipment.

The concentrate analysis was averaged at 0.22% V, 1.86% Cr and 4.78% Al. The extraction values were taken as 90% V, 85% Cr and 75% Al. Metal production estimates were calculated from the above figures.

The details of only the chromium and vanadium purification steps are given in this paper. The basis of the reagent costs are given in Appendix A. The complete roast-leach plant was recently described⁽¹⁾.

Leach Solution Storage

Solution from leaching amounts to 3290 tons of liquor per hour, or approximately 11,000 gal/min total flow. This is split into 4 streams of 2750 gal/min. A storage

hold-up capacity of about 16 hours was allowed, or 4-2.5 million gal capacity storage tanks are required, each at an estimated cost of \$280,000 giving a total cost of \$1,120,000. The leach liquor analyses were calculated as follows: V = 0.38 g/l, Cr = 3.03 g/l, Al = 6.87 g/l, pH = 13.5.

Chromium Circuit Sizing and Estimated Equipment Costs

Extraction

The solution is adjusted to pH 13 with CO₂. The solvent extraction circuit is composed of 4 parallel circuits, each with a throughput of 2750 gal/min of leach solution. Extraction is in 7 stages of mixer-settlers using 0.2 M Adogen 464 in an aliphatic diluent, such as Shell 140, and containing 5-10% isodecanol. At an O/A phase ratio of 1.03, the solvent will load to 2.9 g Cr/l. The retention time in the mixer is 1 minute and the settler is designed at 0.5 gal/min/ft². It should be noted that this design is based on extremely small-scale continuous equipment, and therefore the area of the settler design would have to be optimized in a subsequent larger pilot plant. If this design is in fact too large, the solvent inventory will also be decreased in a subsequent design.

Although it may well be feasible to use a two-parallel streams system, a four-parallel design was selected because of the remainder of the circuit, such as the four-parallel roasters. Such a plant would provide advantages where isolation of a circuit might be necessary due to a breakdown in the front-end of the process, or where maintenance is required in the overall circuit. Naturally the four-parallel stream design will be more expensive compared to the two-parallel stream design.

Therefore, the dimension of each mixer settler would be as follows:

Mixer: 1117 cu ft or equivalent to 12 foot diam × 10 foot high. Seven mixers are required.

Settlers: At the capacity noted above, the requirement would be a conventional 50 ft x 200 ft x 4 ft deep

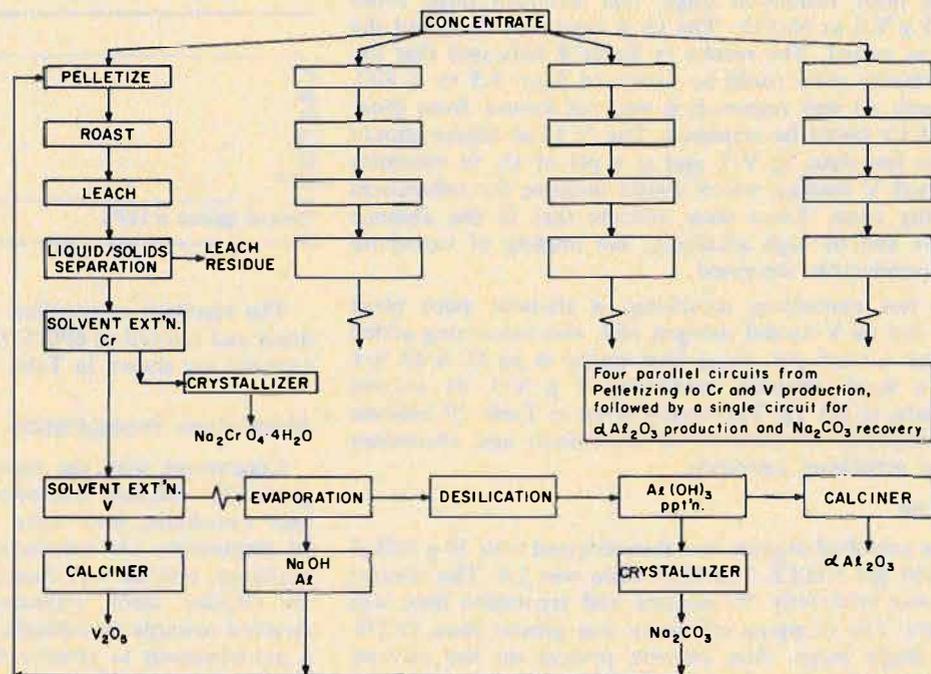


FIGURE 6. Schematic flowsheet of plant.

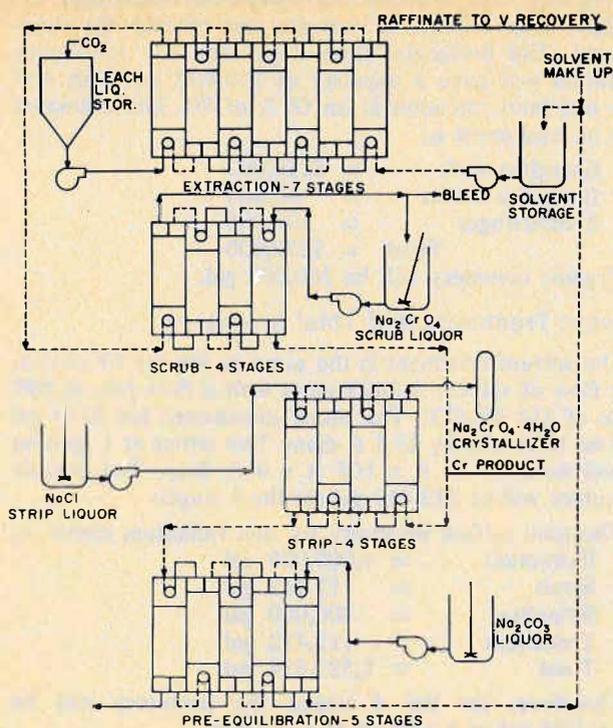


FIGURE 7. Chromium recovery circuit- 1 of 4 trains.

settlers. However, improved settler design (such as Israeli Mining, Lurgi, Power Gas) could decrease this cost by a factor of at least 4. The 7 settlers for each extraction circuit, with a 9-inch organic interface would each contain 47,000 gallons of the mixed solvent or 328,125 gal per train.

The solvent throughput at an O/A ratio of 1.03, is equivalent to 2833 gallons, that is $2833 \times 7 = 19,831$ gallons for mixers or a total mixer-settler requirement of approximately 350,000 gallons ($328,125 + 19,831$). In addition to filling the system, a storage of 3 times this was taken, giving a total of 1,400,000 gal.

Scrubbing with Na_2CrO_4

A design of 1 gal/min/ft² was assumed in the settlers because the phase separation is much better than in extraction. At an O/A ratio of 5 the requirement for each of the 4 scrub circuits would be $2833 + 567$ or 3400 gal/min. At 1 min retention time in the mixer stage, a volume of $3400 + 25\%$ freeboard or 4250 gal is needed. Requirements for each scrub circuit is 4×4250 gal tank (mixers), or dimensions of 8 ft high x 10 ft diam.

At a settling rate of 1 gal/min/ft² the requirement is 3400 sq ft or 40 ft x 85 ft x 4 ft deep settlers. With organic at 9 inch depth in the settlers, the solvent inventory is:

$$\begin{aligned} \text{mixer (mx)} &= 2,833 \text{ gal} \\ \text{settler (s)} &= 15,938 \text{ gal} \end{aligned}$$

$$\text{Total for each Mx S} = 18,771 \text{ gal}$$

The volume for a 4 stage train is 75,082 gal.

Stripping

Stripping is with 5M NaCl in 4 stages to achieve a loading of 66.4 g Cr/l at O/A of 22.5/1. Total flow is 2833 gpm solvent plus 126 gpm NaCl. Retention time is one minute. The mixer size will be $2959 + 25\%$ freeboard or 3699 gal which is equivalent to an 8 ft high by 10 ft diam. tank. Settling is at 1 gal/min/ft² giving a

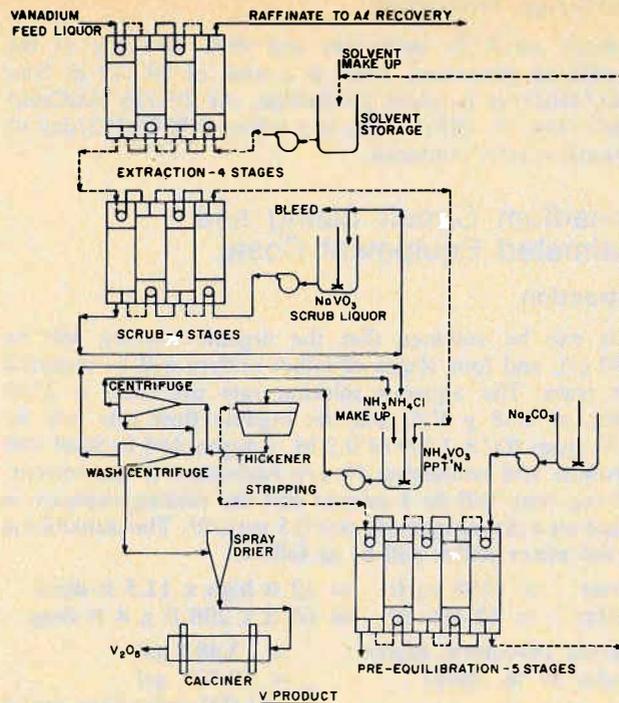


FIGURE 8. Vanadium recovery circuit- 1 of 4 trains.

4 ft deep x 40 ft x 75 ft long settler. The solvent inventory is as follows:

$$\begin{aligned} \text{Solvent flow} &= 2,833 \text{ gal} \\ \text{Settler (9 in. deep)} &= 13,870 \text{ gal} \\ \text{Total} &= 16,703 \text{ gal/stage} \end{aligned}$$

The resulting solvent for 4 stages will be 66,813 gal.

Solvent Treatment and Total Inventory

Five stages of treatment with 1M Na_2CO_3 are needed. Organic feed rate is 2833 gpm at an O/A of 5 giving a flow rate of 567 igpm of Na_2CO_3 . Retention time is one minute. The mixer size will be 8 ft high x 10 ft diam for 3400 gpm flow. The settler at 1 gal/ft²/min will be 40 ft x 85 ft x 4 ft. The solvent inventory will be:

$$\begin{aligned} \text{Mixer} &= 2,833 \text{ gal} \\ \text{Settler (9 in.)} &= 15,938 \text{ gal} \\ \text{Total} &= 18,771 \text{ gal} \end{aligned}$$

Total solvent inventory for 5 stages will be 93,855 gal.

The total solvent inventory for the Cr circuit will be:

$$\begin{aligned} \text{Extraction} &= 1,400,000 \text{ gal} \\ \text{Scrub} &= 75,082 \text{ gal} \\ \text{Stripping} &= 66,813 \text{ gal} \\ \text{Solv. treatment} &= 93,855 \text{ gal} \\ \text{Total} &= 1,635,750 \text{ gal} \end{aligned}$$

The total inventory for the 4 circuits is 6,543,000 gal.

Unit Cost:

$$\begin{aligned} 10\% \text{ amine} & 0.1 \text{ gal @ } \$1.25/\text{lb} = 1.25 \\ 10\% \text{ isodecanol} & 0.1 \text{ gal @ } 50\text{¢}/\text{lb} = 0.50 \\ 80\% \text{ kerosene} & 0.8 \text{ gal @ } 60\text{¢}/\text{gal} = 0.48 \\ \text{Total estimated cost per gal} & \$ = 2.23 \end{aligned}$$

We require 6,543,000 gal at \$2.25 for a total solvent cost of around \$14.7 million.

Evaporation of Cr Strip Liquor

There is a total flow of $126 \text{ gpm} \times 4 = 504 \text{ gal/min}$; at 1,014 tons of $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ per day. The approximate cost is \$1,000,000 for the evaporator equipment.

Chromium Production

Based on 85% extraction and 99% recovery of the solubilized chromium, there is a total of 84,519 lb $\text{Na}_2\text{-CrO}_4 \cdot 4\text{H}_2\text{O}$ /hr in plant production. At 29¢/lb $\text{Na}_2\text{-CrO}_4 \cdot 4\text{H}_2\text{O}$ (June 9, 1975), there is a value of \$588,252/day of chromium salts produced.

Vanadium Circuit Sizing and Estimated Equipment Costs

Extraction

It can be assumed that the organic loading will be 0.30 g/l, and four stages of mixer settlers will be required per train. The aqueous solution rate per train is 2750 igpm, at 0.38 g V/l, and the organic flow rate will be 3493 igpm (O/A 1.27) of 0.2 M. Adogen 464 in Shell 140 kerosene and containing 10 v/o isodecanol is the solvent. Mixing time will be 1 minute and the settling capacity is based on a disengagement rate 0.5 gpm/ft². The dimensions of the mixer settler will be as follows:

Mixer = 1250 cu ft = 12 ft high x 11.5 ft diam.
 Settler = 12,486 ft² = 60 ft x 208 ft x 4 ft deep
 Solvent Inventory: Mixer = 3,493 gal
 Settler (9 in. deep) = 58,500 gal
 61,993 gal/mixer settler

Therefore the vanadium extraction circuit will require 248,000 gal plus 750,000 gal storage or 1,000,000 gal per train.

Scrubbing with NaVO_3

At an O/A of 5 the flow to each scrub circuit will be 3493 + 699 or 4192 gal. At one minute retention time in the mixer and 25% excess volume, 5240 gal volume is needed. Each scrub circuit will need four stages, each of 5240 gal volume, or 10 ft high x 10.5 ft diameter. At a settling rate of 1 gpm/sq ft each settler will measure 50 ft x 105 ft x 4 ft deep. The organic inventory is:

Mixer = 3,493 gal
 Settler (9 in.) = 24,610 gal
 Total = 28,103 gal/mixer settler

The total volume per train is 112,412 gal.

Stripping

Stripping is accomplished with a solution composed of 10 g NH_3 /l and 140 g NH_4Cl /l. The vanadium will form an ammonium metavanadate precipitate. Therefore a

TABLE 13. Capital Costs for Chromium Circuit

Circuit	Unit	Size (gal)	No. Units	Unit Cost \$	Total Cost \$
Extraction.....	Mixer	7,000	28	22,000	616,000
	Settler	250,000	28	72,000	2,016,000
Scrubbing	Mixer	4,250	16	17,000	272,000
	Settler	85,000	16	40,000	640,000
Stripping.....	Mixer	3,700	16	16,000	256,000
	Settler	75,000	16	40,000	640,000
Solvent.....	Mixer	4,250	20	17,000	340,000
	Settler	85,000	20	40,000	800,000
$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$	Crystallizer		1		1,000,000
Solvent Inventory.					14,700,000
			Total		21,280,000

mixing tank, a settler and two continuous centrifuges are needed in the circuit to separate and recover the three streams. The horizontal three-stage tank for continuous operation will have a capacity of 250,000 gal. This will give one hour retention at an O/A of 70. The estimated cost of equipment is:

fiberglass tank = \$110,000
 fiberglass settler = 60,000
 2 centrifuges = 100,000
 Total = \$270,000

Organic inventory will be 300,000 gal.

Solvent Treatment and Total Inventory

The solvent treatment is the same as for the Cr circuit. The flow of solvent is 3493 igpm with a flow rate of 699 igpm of 1M Na_2CO_3 . The mixer dimensions for 5240 gal will be 10 ft high by 10.5 ft diam. The settler at 1 gpm/sq ft will measure 50 ft x 105 ft x 4 ft deep. The organic inventory will be 112,412 gal for the 5 stages.

The total solvent inventory for one vanadium circuit is:

Extraction = 1,000,000 gal
 Scrub = 112,412 gal
 Stripping = 300,000 gal
 Treatment = 112,412 gal
 Total = 1,525,824 gal

Therefore, for the 4 trains, the inventory will be 6,100,000 gal at a cost of \$13,725,000.

Vanadium Production

Production will be at the rate of 28.7 tons vanadium/day or 51 tons V_2O_5 /day. Two 1000 gal repulp tanks will be required together with a continuous centrifuge. The wet cake will be dried in a continuous oven and then calcined to V_2O_5 at a temperature of about 700°C.

The size of the equipment will be:

- Repulp tanks = 1000 gal polyester glassfibre
- Centrifuge = est 5HP — stainless steel
- Spray dryer = 14 ft diam.
- Calciner = 1.5 x 10⁶ btu/hr

Based on 99% recovery of the solubilized vanadium, there is a total of 2382 lb V/hr in plant production. This is equivalent to 4250 lb V_2O_5 /hr. At \$3.06/lb V_2O_5 (June 9, 1975) there is a value of \$312,120/day of V_2O_5 produced.

Estimated Costs

Based on the assumed throughput rate of 5,000,000 tons of concentrate per year, and the equipment-sizing estimates as outlined above, the plant cost estimates are given below. All estimates are based on June, 1975 prices.

Capital Costs

In Tables 13 and 14 are shown the estimated capital requirements of the chromium and vanadium circuits. To that total is added the cost of solution feed storage tanks of \$1,120,000, resulting in a total estimated purchase cost of \$41,241,000. The total solvent extraction plant fixed capital costs are shown in Table 15 as \$160,901,761.

Based on an amortization of \$160,901,761 on a 10-year straight line depreciation and 350 days per year, a capital cost of \$3.22/ton of concentrate treated is estimated for the recovery of vanadium and chromium products.

Operating Costs

The estimated labor, maintenance and administration requirements for such a plant are shown in Table 16. The

TABLE 14. Capital Costs for Vanadium Circuit.

Circuit	Unit	Size (gal)	No. Units	Unit Cost \$	Total Cost \$
Extraction	Mixer	7,800	16	25,000	400,000
	Settler	312,150	16	90,000	1,440,000
Scrubbing	Mixer	5,240	16	21,000	336,000
	Settler	131,250	16	62,000	992,000
Stripping	Tank	250,000	1	110,000	110,000
	Settler	125,000	1	60,000	60,000
	Centrifuge		2	50,000	100,000
Solvent Treatment	Mixer	5,240	20	21,000	420,000
	Settler	131,250	20	62,000	1,124,000
V ₂ O ₅ Prod'n.	Tank	1,000	2	3,500	7,000
	Centrifuge		1	25,000	25,000
	Spray drier	14 ft	1	22,000	22,000
	Calciner		1	80,000	80,000
Solvent Inventory.					13,725,000
Total Cost =					18,841,000

rates were arbitrarily taken as \$5.00 and \$8.00 per hour respectively for hourly, staff and administration. The cost of labor for the vanadium and chromium production is equivalent to \$1.82/ton of concentrate processed.

The power requirements are estimated at 15130 and 11455 hp respectively, or a total of 19,824 kW which is equivalent to 33 kWh/ton concentrate at a feed rate of 600 tons conc./hour. At a unit power cost of 1¢/kWh, the power cost is equivalent to \$0.33/ton of concentrate.

The heat requirements are estimated at 174,129 and 11,667 btu/ton conc. for the chromium and vanadium circuits respectively, or a total of 185,736 btu. The unit heat cost was estimated at \$1.00/10⁶ btu from 10,000 btu coal delivered at \$20/ton. The heat cost is therefore estimated at \$0.19/ton concentrate treated. This cost was based on 1975 estimates, and with the present energy situation, the heat cost could be doubled.

Reagent costs are shown in Table 17. Unit costs for reagents, based on June 9, 1975, are given in Appendix A. The reagent cost is estimated at \$4.93/ ton of concentrate treated.

The total operating cost per ton of concentrate treated for the recovery of chromium and vanadium is estimated at \$10.49 and is summarized in Table 18.

Income

The value of daily production is shown in Table 19. Obviously the aluminium value is small compared to the chromium and vanadium. The total daily value of the chromium and vanadium is \$900,372.

Daily operating cost for the entire roast-leach-purification plant was estimated at \$701,856⁽¹⁾. Therefore, the daily gross profit will be \$333,647. It is estimated therefore, that this plant, to produce by-product chromium, vanadium and alumina, can operate at a gross profit of around \$117,000,000 per annum.

Discussion and Conclusions

The work that has been described indicates the technical feasibility of treating the Mingan titaniferous magnetite concentrate by a roast-leach-solvent extraction process for the separation and recovery of chromium and vanadium. No attempt was made, in the work reported here, to optimize any of the equipment used.

TABLE 15. Total Solvent Extraction Plants Fixed Capital Costs.

Total Est. Purchase Costs	41,241,000
Installed Equip. Costs (× 1.43)	58,974,630
Piping (20% of Installed Cost)	11,794,926
Instrumentation (10% of Installed Cost)	5,897,463
Buildings & Site (15% of TEPC)	6,186,150
Auxiliaries (e.g. electric power) 10% of IEC	5,897,463
Outside Lines (10%)	5,897,463
Total physical plant costs	94,648,095
Engineering & Construction (55% of total phys. plant costs)	52,056,452
Contingencies (15% of PPC)	14,197,214
Total Plant fixed Capital Costs	160,901,761

TABLE 16. Labour Requirements for Chromium and Vanadium.

Operation	Number		\$/ton treated
	Tech.	Labour	
Cr and V Purification Circuit...	6	48	0.48
Tech. Support & Maintenance..	37	30	0.74
Admin. & Other Support Services.....	21	38	0.60
Cost \$/ton treated			\$1.82

TABLE 17. Reagent Requirements.

	Requirement lb/ton conc.	Cost \$/ton conc.
Cr — Solvent.....	0.33	0.75
NaCl.....	70	1.40
Na ₂ CO ₃	36	0.75
V — Solvent.....	0.33	0.74
NH ₄ Cl.....	4.2	0.40
Na ₂ CO ₃	36	0.76
NH ₃	1.4	0.13
Total Cost/ton conc.		\$4.93

TABLE 18. Operating Costs*.

	\$/ton throughput concentrate
Labor, Maintenance and Admin.....	1.82
Amortization.....	3.22
Reagents.....	4.93
Power.....	0.33
Heat.....	0.19
Total.....	\$10.49

*The operating costs for the entire roast-leach-purification plant were estimated at \$48.74/ton concentrate⁽¹⁾.

TABLE 19. Daily Production and Value.

	Production t/d	Value \$
Na ₂ CrO ₄ ·4H ₂ O @ 29c/lb.....	1014	588,252
V ₂ O ₅ @ 3.06/lb.....	51	312,120
Al ₂ O ₃ @ 7c/lb.....	966	135,131
		1,035,503

Because of the difficulty of pH adjustment, due to the presence of the high concentration of aluminium, the solvent extraction had to be carried out under alkaline conditions. Such extraction conditions were not truly favorable, with respect to solvent loading, when compared to the extraction from acidic solutions. By direct extraction from the alkaline solution, the Na_2CO_3 could be recovered for recycle to the roast-leach plant.

Part of the reagent costs are due to solvent losses and solvent treatment. Soluble amine losses were estimated at 30 ppm. However, it is known that although this figure is common on the acid side, it is much lower on the basic side for Alamine 336. It has been observed that considerable solvent is released in evaporation of leach liquor prior to aluminium extraction. Treatment for solvent recovery should reduce this figure considerably. It has been considered that the solvent must be pre-equilibrated with Na_2CO_3 to allow the solvent extraction to function without a precipitate forming in the settlers. A caustic addition to the proper stage may overcome this problem. Using chloride forms of stripping agents would leave the solvent ready for re-use, thus eliminating solvent pre-equilibration. It may then be possible to separate NaCl and Na_2CO_3 in the crystallizer thus reducing or eliminating chloride recycle to the roaster which is undesirable.

It was mentioned that the settler capacity used in this design is at a maximum and could possibly be reduced by adoption of one of the latest settler designs. This would reduce the solvent extraction equipment costs. Although we realize that the large copper solvent extraction plants use large equipment and split flows to solvent extraction, the flowsheet described in this paper, by comparison, has probably been overdesigned. That is, instead of four parallel streams it would probably be necessary to consider a two-stream process. The vanadium and chromium circuits have not had the advantage of the copper circuits, where the large plants have resulted in high confidence in the design and scale-up.

The recovery of Na_2CO_3 is essential since it would cost \$11.62/ton concentrate to replace the Na_2CO_3 . The liquor evaporation costs are realized in adjusting the aluminium feed liquor to a proper composition, to recover aluminium, and then the cost to recover Na_2CO_3 is comparatively small.

With respect to further work, pilot plant investigation should be done on the entire process. Although the throughput used at CANMET (approx. 2400 grams concentrate/hour) would be a useful size for some of the work, nevertheless it would still be necessary to further scale-up in order to provide all the necessary information to assist in the decision to build a plant. Such a pilot plant should be sufficient size to:

- Provide reliable scale-up data for the plant,
- Provide corrosion data and sufficient information for equipment selection,
- Test, evaluate and size various types of equipment,
- Test, confirm and optimize variables, and determine where the circuit can be automated and controlled and possibly improve on the flowsheet,
- Set up a sampling and analysis program to assess all solutions, residues, and products, and determine whether onstream analyses would be of a cost-saving benefit.
- Study and analyse solvent losses and vary the circuit to minimize entrainment, crud or volatile losses, (Not much can be done regarding soluble losses, except to obtain good reliable analyses of soluble losses). (The effect of recycling the solvent should be studied as to degradation effects.)

- Provide approximate costs for the plant and the process,
- Assess the reagent costs for the total process and the energy requirements,
- Determine manpower requirements, (Such a pilot plant also provides an opportunity for the training of personnel for the ultimate plant.)
- Determine possible environmental problems and provide an opportunity for the solving of such problems.

A good-sized pilot-plant operation, in order to provide sufficient solution for reasonable solvent extraction and purification, would be capable of throughput of 5-20 tons/day of the magnetic concentrate. The wide range is stated because of confidence levels of the information established prior to piloting as well as the amount of funds available for such a project. Although a smaller, continuous pilot plant operation could achieve much information, nevertheless reliable scale-up data, and energy requirements, costs and solvent losses, for example, would not be accurately collected. Naturally, if many types of equipment are to be evaluated, or problems arise during the testing, the pilot plant should be run for a much longer period.

Acknowledgements

The authors gratefully acknowledge the work of K. Price, J. Kearns, P. Prudhomme, G. Wallingford and L. Carter of the Hydrometallurgy Section who carried out the numerous tests, and also the work of R. Guest, D. MacPherson and R. Pugliese of the Chemical Laboratory for the chemical analysis.

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APPENDIX A

(1) Reagent Unit Costs:

Na_2CO_3	— Bulk Lots
NaOH	— \$42.00/ton*
Isodecanol	— 7c/lb*
Adogen 464	— 50c/lb
Kerosene	— \$1.25/lb
NaCl	— 60c/gal
NH_3	— 2c/lb*
NH_4Cl	— \$190/ton*
CaO	— 9.5c/lb*
	— 2c/lb*

- *From Chemical Marketing Reports — June 9, 1975.
 (2) Specific Heat of Concentrate = 0.29 BTU/lb/°F
 (3) Power = 1c/KW hr.
 (4) Heat Source — Coal — 10,000 btu/lb @ \$20.00/ton.

DISCUSSION

A. Van Peteghem: Can the chromium scrub be operated industrially; because there seems to be more V extracted from the scrub liquor than the amount originally present?

G. Ritcey: The use of a scrub solution containing the metal to be subsequently purified is indeed becoming established practice. By using a chromium solution to scrub a solvent containing chromium plus co-extracted impurities, the presence of the high concentration of chrome relative to the impurities results in the replacement of the impurities with chrome. The amount of chrome exchanged for the impurities is however very small as the results show. As the amount of impurities are built up in concentration in the scrub solution and the chrome concentration is decreased, a bleed stream will be necessary for treatment. The bleed would be replaced by some chrome strip solution. Thus, a relatively minor quantity of chrome is being used for scrubbing, and being replaced. That quantity is insignificant compared to the feed chromium concentration. Such a process step should be economically viable.

G.A. Kordosky: Economics of the process were somewhat dependent upon the revenue from vanadium, i.e. ~ 35% of the total revenue. However, if you produce an amount of vanadium equal to the world demand, either you will not be able to sell the total vanadium production or only probably at a much lower price than current price. Would it be economical to just forget about the vanadium altogether?

G. Ritcey: At today's market price and demand for vanadium, such a plant producing such a quantity of vanadium would certainly have a problem disposing of the product at a profit. That is on the assumption that the plant was actually in production today. However, the process that has been described is really to be considered as technology for the future, where the economics with respect to the demand and price of the product will undoubtedly be considerably different. As the ore grade to be processed becomes lower and more complex, technology considered economically marginal today could probably be considered viable perhaps as early as 10 years hence. As to whether the process would be economical if vanadium recovery was neglected altogether, we believe that such an operation would still be profitable, even for the recovery of chrome. Because chrome is one of the world's strategic metals, one would anticipate an increase in the demand and in the selling price to occur in the future.

M.A. Hughes: One of my PhD students (T. Leaver 1974) published a thesis on the use of ALIQUAT 336 to extract chromium and vanadium. (1) Extensive equilibria data were published which showed that vanadium could be extracted along with chromium and then the vanadium could be separated by scrubbing the organic phase with pure vanadate solution.

We noted some problems with a system involving a leach liquor from the alkaline roast of the ferrous chrome spinel. Although aluminium, as aluminate, was not extracted when excess chromate or vanadate was present it did contribute to interfacial crud by hydrolysis-complexing reactions. Have you noted similar problems with aluminium in your system?

We note high viscosities when the organic phase became saturated with chromium or vanadium — presumably this is avoided in your process by not allowing the system to approach maximum load?

Why is your circuit a chloride one? Are there disadvantages in the use of a sulphate circuit?

Could you use a pH lower than 13 but then work up the separation by scrubbing? Our own work would suggest that in the range pH 9-10 fewer stages would be needed. Ref 1: see Hughes and Leaver, ISEC 1974.

G. Ritcey: Your work to which you refer, was performed on solutions in the pH range of 9 where the extraction favoured vanadium. I agree that such a co-extraction of the two metals would be feasible as we indicate in Figure 1. Also, if vanadium is preferentially extracted to chromium, any chromium that is co-extracted should be scrubbed off with a vanadium solution. The problems you noted with aluminium were not experienced in our work, which was at considerably higher alkalinity, at pH 13. Because of such a high pH, the metal saturation loadings are decreased. Although we operated at saturation conditions, viscosity was not a problem. As the equilibrium pH for extraction is increased from 9 to 13, the extraction loading is not only decreased, but also the equilibrium is affected in that more stages are required at the higher pH. It would be more economical to operate at a lower pH and selectively scrub to affect metal separation, but in the treatment of a high alkaline solution, at pH 13, the economics do not favour such a neutralization prior to extraction, particularly if aluminium is present which could hydrolyse. We note this in the text. Also, to ensure economic viability of the process, the sodium carbonate leach solution must not be destroyed, but must be recycled to the process.

We use a carbonate roast — not a chloride or sulphate attack. You are probably referring to the use of chloride for stripping of the chromium. The use of chloride was an arbitrary selection due to no real product specifications having been set at the time when the research was performed. However, such a chloride strip was effective and a relatively pure sodium chromate was produced. Sodium chloride was recovered for recycle to the strip circuit.

Thus, to help make such a circuit as we describe economically feasible, the various chemicals used in the process must be recycled. Such was the case with the leaching medium (Na_2CO_3), the NaCl for stripping, as well as the scrub solutions in both the chromium and vanadium circuits.

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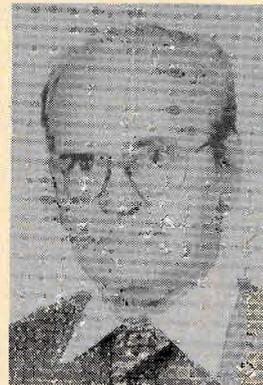
Chapter 11

Copper Processing

**Session 23 — Plenary
and
Panel Discussion**



Dr. J.C. Agerwal



J. Dasher

Session Co-Chairmen

Chapter 11

Copper Processing

Section 11-1 Introduction

11-1

Section 11-2



Figure 11-1

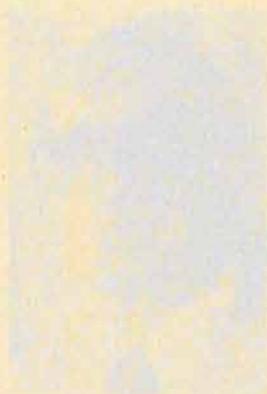


Figure 11-2

Section 11-3

Synthesis, Structure, and Hydrometallurgical Properties of Lix[®] 34

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ABSTRACT

The active component in LIX[®] 34 ion exchange reagent is an 8-(alkarylsulfonamido) quinoline. The synthesis involves coupling an alkarylsulfonyl chloride with 8-aminoquinoline in the presence of an organic base. The reagent forms a two-to-one ligand to metal ion chelate. Electronic factors alone do not appear to offer an adequate explanation for the observed changes in extractive power with changes in substituents on the quinoline system of the reagent. A complex mixture of steric and electronic factors may be required to explain the observed trends. In addition, the behaviour of LIX 34 with regard to important hydrometallurgical properties, such as extraction and stripping kinetics, sulfuric acid loading, hydrolytic stability and toxicity, was examined.

Introduction

SLIGHTLY OVER A DECADE AGO, General Mills Chemicals, Inc., introduced LIX[®] 63, the first chelating extractant available for use in commercial solvent extraction processes, to the mining industry^(1,2). This announcement was quickly followed by the development of LIX 64^(3,4), which offered significant advantages over LIX 63 in terms of extractive power and selectivity for copper. The intervening period of time has been one of growing interest and activity in the use of solvent extraction for the recovery of nonferrous metals^(5,6,7).

During February, 1976 at the AIME Annual Meeting held in Las Vegas, Nevada, General Mills Chemicals, Inc. introduced a new liquid ion exchange reagent under its LIX trademark to the metals industry⁽⁸⁾. At that time, it was pointed out that the reagent designated LIX 34 was a member of a totally new class of commercial metal extractants. The circuit performance characteristics of the reagent were discussed with regard to kinetics, attained minimum raffinate, and copper (II) selectivity. In addition, preliminary extraction data for cobalt, nickel, lead, zinc, cadmium, mercury and silver were presented. Additional data from the evaluation of several pilot plant production lots of LIX 34 were discussed at the Spring Meeting of the Arizona Section of the AIME, Hydrometallurgical Division⁽⁹⁾.

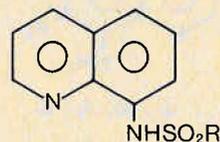
In this paper, the structure and synthesis of LIX 34 will be discussed. In addition, extensive laboratory evaluation of LIX 34 with regard to criteria⁽¹⁰⁾, such as pH functionality, stripping and extraction kinetics, sulfuric acid loading, and hydrolytic stability has revealed some novel behaviour which will be examined in terms of electronic and steric factors. Toxicity data for LIX 34 will also be presented.

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Experimental Results and Discussion

Structure and Synthesis

The active component in LIX 34 is an 8-(alkarylsulfonamido) quinoline having an average molecular weight of 438 with the structure given below:



R = ALKARYL (Mixed Isomers)

The general synthetic route to the 8-sulfonamidoquinolines involves coupling 8-aminoquinoline with the appropriate sulfonyl chloride in the presence of an organic base, such as pyridine or triethylamine.

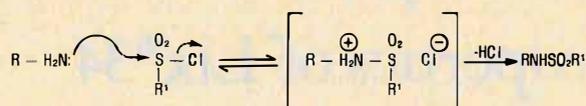
The 8-aminoquinolines were obtained in the following fashion. Both 8-aminoquinoline⁽¹¹⁾ and 8-amino-6-methoxyquinoline⁽¹²⁾ were commercially available. Conversion of 8-hydroxyquinoline⁽¹²⁾ to 8-amino-2-methylquinoline was accomplished by the method of Wöröschtzow and Kogan⁽¹³⁾. The approach of Hurdis⁽¹⁴⁾ was employed to obtain 8-amino-6-methylquinoline and 8-amino-6-chloroquinoline. Chlorination of 8-aminoquinoline led to 8-amino-5,7-dichloroquinoline⁽¹⁵⁾. Reaction of hydroxylamine and 5-nitroquinoline produced 8-amino-5-nitroquinoline⁽¹⁶⁾. Purity was verified by melting point, IR, and NMR.

The desired alkarylsulfonyl chlorides were prepared by conversion of the appropriate alkylated benzene to the sulfonic acid with chlorosulfonic acid. Once the sulfonic acid was obtained, it was easily converted to the alkarylsulfonyl chloride by treatment with thionyl chloride or phosphorus pentachloride. Purification was accomplished by wiped-film distillation at reduced pressure. An alkane-sulfonyl chloride was prepared by converting the alkylbromide to a mercaptan and then oxidizing the mercaptan with chlorine in acetic acid⁽¹⁷⁾. It was used without further purification.

The sulfonyl chlorides were added neat to a stirred solution of the 8-aminoquinoline in pyridine or triethylamine. The resultant 8-sulfonamidoquinolines were purified by pouring the reaction mixture into water, extracting the product with Skelly C, washing the organic alternately with a methanolic sodium bicarbonate solution and a 50 gpl sulfuric acid solution, and then stripping off the solvent in vacuo after drying over anhydrous sodium sulfate.

With the exception of two cases, the coupling reaction was essentially complete after several hours at room temperature. The preparations of 8-alkarylsulfonamido-5-nitroquinoline and 8-alkarylsulfonamido-5,7-dichloroquinoline required extended reaction periods at temperatures of 80-100°C in the presence of a minimum amount

of pyridine. The coupling reaction is believed to involve nucleophilic attack of the amine group's free electron pair on the sulfur atom of the sulfonyl chloride, coupled with displacement of the chloride. Loss of a proton then leads to the sulfonamide.



The nitro and chloro substituents present in the starting amines; 8-amino-5-nitroquinoline, I, and 8-amino-5,7-dichloroquinoline, II, are efficient electron-withdrawing groups. The presence of these groups effectively reduces the availability of the electron pair on the amino group for attack on the sulfonyl sulfur atom.



- I R₁ = NO₂; R₂ = H
- II R₁ = R₂ = Cl

An additional factor may play a role in determining the behaviour of II. In II, the chloro group in the seven position (R₂) is thought to hinder the coupling reaction by exerting a significant steric effect on the course of the reaction. The cumulative electron withdrawing and/or steric effects of the substituents in I and II necessitate

TABLE 1. Slopes of Log D vs. pH for LIX 34 at Various Concentrations

[RH] [*] _(o) (M)	Slope
0.01	1.0
0.03	1.6
0.10	1.5
0.30	1.6

*The reagent was dissolved in KerMac 470b.

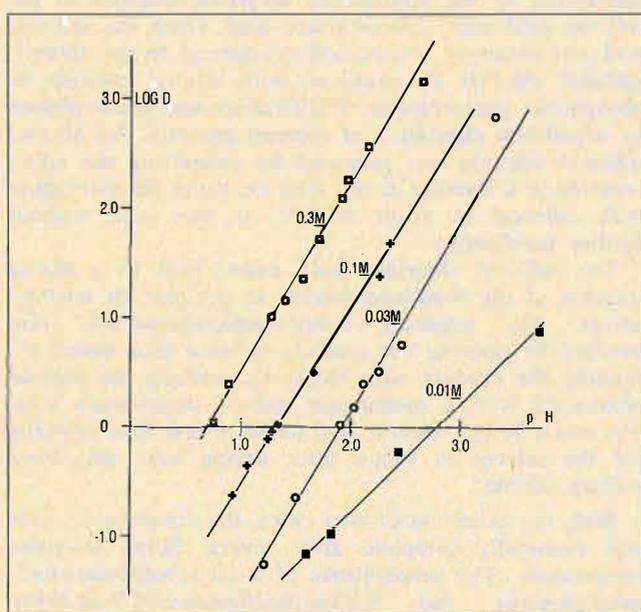


FIGURE 1. Dependence of the distribution coefficient on pH at various concentrations of LIX® 34.

the use of much harsher conditions to promote the coupling reaction.

Stoichiometry of Extraction

The extraction of a metal ion from an aqueous solution by a chelating reagent may be represented by the following equation:



The extraction constant, K_{ex} , is defined as:

$$K_{ex} = \frac{[MR_n]_{(o)} [H^+]^n_{(a)}}{[M^{n+}]_{(a)} [HR]^n_{(o)}} \dots \dots \dots (2)$$

The distribution coefficient, D , may be defined under certain conditions as:

$$D = \frac{[MR_n]_{(o)}}{[M^{n+}]_{(a)}} \dots \dots \dots (3)$$

For equation 3 to be valid, the formation of intermediate complexes with the reagent, metal hydrolysis products, and complexes with any other extraneous substances in the aqueous phase must be negligible over the pH range under consideration. The concentration of MR_n in the aqueous phase must also be negligible.

Substituting D into equation 2 and rearranging terms, one derives¹⁸:

$$\text{Log } D = \text{Log } K_{ex} + n\text{pH} + n \text{Log } [HR]_{(o)} \dots \dots \dots (4)$$

Equation 4 states that we should obtain a straight line of slope n if we plot $\log D$ vs. pH provided the free reagent concentration is maintained constant. A family of $\log D$ vs. pH plots for LIX 34 at various concentrations is shown in Figure 1. The slopes of these plots are presented in Table 1.

The distribution coefficients and equilibrium pH values were determined in the following fashion. A sample of the organic was contacted with an equal volume of an aqueous solution by shaking for one hour. The aqueous solution was prepared by mixing equal volumes of a 0.600 gpl copper(II) solution containing 1.0M of sodium sulfate ($\text{pH} = 1$) and a pH adjusting solution. The pH adjusting solutions contained various concentrations of sodium hydroxide or sulfuric acid. All reagents were AR grade. The phases were separated after one hour. The pH of the aqueous raffinate was determined with a Sargent-Welch Model NX pH meter and the concentration of copper in the aqueous was measured with an Instrumentation Laboratory, Inc. Atomic Absorption-Emission Spectrophotometer Model 353. The concentration of copper in the organic was then determined by difference.

The observed slopes (Table 1) all differ significantly from the predicted value of two. The extreme deviation of the slope observed for 0.01M reagent concentration is quite easily discounted. At the higher pH values, approximately one-half of the total reagent concentration is actually bound to copper. The assumption that the free reagent concentration is constant over the pH range investigated is no longer valid.

A possible explanation for the deviations at higher reagent concentrations might be significant complexation of the metal ion with sulfate and/or bisulfate in the aqueous phase. In the presence of interfering ions: e.g. sulfate or bisulfate, the total metal ion concentration might be better represented as⁽¹⁸⁾:

$$[M^{n+}]_{\text{tot}(a)} = [M^{n+}] + [MSO_4^{n-2}] + [M(SO_4)_2^{n-4}] + \dots \dots \dots + [M(HSO_4)^{n-1}] + [M(HSO_4)_2^{n-2}] + \dots \dots \dots (5)$$

The overall formation constants for the ion association reactions, β_i and β_i^1 , may be defined as:

$$\beta_i = \frac{[M(SO_4)_i^{n-2i}]}{[M^{+n}][SO_4^{-2}]^i} \dots \dots \dots (6)$$

$$\beta_i^1 = \frac{[M(HSO_4)_i^{n-1}]}{[M^{+n}][HSO_4^{-1}]^i} \dots \dots \dots (7)$$

Upon redefining D in terms of equation 5, substituting from equation 2, and rearranging terms, one obtains⁽¹⁸⁾:

$$\log D = \log K_{ex} + npH + n \log [RH]_{(o)} - \log \left\{ \sum_0^i \beta_i [SO_4^{-2}]^i + \sum_0^i \beta_i^1 [HSO_4^{-1}]^i \right\} \dots \dots \dots (8)$$

where $\beta_0 = 1$ and $\beta_0^1 = 0$.

The second acid dissociation constant, K^{11} , for sulfuric acid is defined as:

$$K^{11} = [H^+][SO_4^{-2}]/[HSO_4^{-1}] \dots \dots \dots (9)$$

Rearranging equation 9 and substituting into equation 8, one arrives at:

$$\log D = \log K_{ex} + npH + n \log [RH]_{(o)} - \log \left\{ \sum_0^i \beta_i \left(K^{11} \frac{[HSO_4^{-1}]}{[H^+]} \right)^i + \sum_0^i \beta_i^1 [HSO_4^{-1}]^i \right\} \dots \dots \dots (10)$$

Equation 10 points out that the slope of a log D vs. pH plot will depend not only on n but also upon contributions from the last term in the equation, which is also acid dependent.

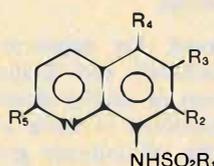
Identical experiments with LIX 65N led to log D vs. pH plots having slopes nearly identical to those for LIX 34 at 0.3M, 0.1M, 0.03M, and 0.01M⁽¹⁹⁾. Since Eccles and co-workers⁽²⁰⁾ have reported that increasing the sulfate ion concentration hinders the extraction of copper(II) by LIX 64N, some dependence of log D on sulfate ion concentration for LIX 34 does not seem unreasonable.

If one holds the pH constant, equation 10 may be reduced to:

$$\log D = K + n \log [RH]_{(o)} \dots \dots \dots (11)$$

Thus if one extrapolates the values for log D at the various concentrations at a chosen pH value from the plots in Figure 1, one can then plot log D vs. log [RH] (Figure 2). The value of the free reagent concentration must be calculated for the data determined at 0.01M. The slopes of the lines in Figure 2 are summarized in Table 2. The value of n closely approximates two. Therefore, the metal to ligand ratio is 1:2 for copper and LIX 34.

Effects of Substituents on Copper pH Isotherms



The pH isotherms of the following 8-sulfonamidoquinolines were determined:

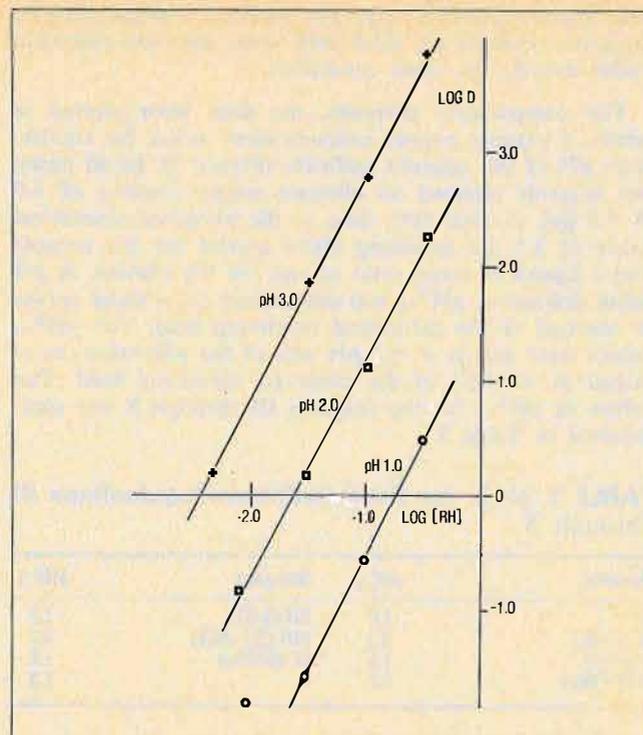


FIGURE 2. Dependence of the distribution coefficient on LIX® 34 concentration at various pH's.

TABLE 2. Slopes of Log D vs. [LIX 34] at Constant pH

pH	Slope
1.0	2.08
2.0	2.00
3.0	2.15

- III $R_1 = alkaryl ; R_2 = R_3 = R_4 = R_5 = H$
- IV $R_1 = alkaryl ; R_2 = R_3 = R_4 = H ; R_5 = CH_3$
- V $R_1 = alkaryl ; R_2 = R_4 = R_5 = H ; R_3 = CH_3$
- VI $R_1 = alkaryl ; R_2 = R_4 = R_5 = H ; R_3 = OCH_3$
- VII $R_1 = alkaryl ; R_2 = R_4 = R_5 = H ; R_3 = Cl$
- VIII $R_1 = alkaryl ; R_3 = R_5 = H ; R_2 = R_4 = Cl$
- IX $R_1 = alkaryl ; R_2 = R_3 = R_5 = H ; R_4 = NO_2$
- X $R_1 = C_{10}H_{21} (Mixed Isomers) ; R_2 = R_3 = R_4 = R_5 = H$

The isotherm determination involved shaking a 0.1M solution of the reagent in Exxon Aromatic 150 with an equal volume of an aqueous copper(II) solution. The aqueous solution was prepared by mixing equal volumes of a 0.2M copper sulfate solution and an aqueous pH adjusting solution. The pH adjusting solutions were composed of various concentrations of sulfuric acid or sodium hydroxide. The desired equilibrium pH for the aqueous raffinate determined which pH adjusting solution was selected. The phases were separated after one hour, the organic was filtered to remove aqueous entrainment, and the pH of the aqueous raffinate was measured. The organic copper concentration was obtained by atomic absorption spectroscopy. The pH isotherms were evaluated under these conditions in order to obtain some measure of their behaviour under practical conditions.

One must remember that pH isotherm comparisons of different reagents are valid only when they are evaluated under exactly the same conditions.

For comparative purposes, the data were plotted in terms of organic copper concentration versus the equilibrium pH of the aqueous raffinate (Figure 3). In all cases, the reagents attained an ultimate copper loading of 3.0 ± 0.2 gpl, a value very close to the predicted theoretical value of 3.1 gpl assuming 100% purity for the reagent and a ligand to metal ratio of two for the chelate. A pH value defined as $\text{pH}^*_{0.5}$ was determined from these curves at one-half of the theoretical maximum load. The $\text{pH}^*_{0.5}$ values were within ± 0.1 pH unit of the pH value determined at one-half of the observed maximum load. The values of $\text{pH}^*_{0.5}$ for the reagents III through X are summarized in Table 3.

TABLE 3. $\text{pH}^*_{0.5}$ for the 8-Sulfonamidoquinolines III Through X

Reagent	$\text{pH}^*_{0.5}$	Reagent	$\text{pH}^*_{0.5}$
III	1.0	VII (6-Cl)	1.7
IV (2-Me)	3.3	VIII (5,7-diCl)	3.3
V (6-Me)	1.5	IX (5-NO ₂)	1.6
VI (6-OMe)	1.6	X	1.3

The reagents may be ranked in order of apparent extractive strengths based on $\text{pH}^*_{0.5}$ as follows:



The trends illustrated by the data in Table 3 were very surprising. Introduction of electron withdrawing substituents, such as nitro and chloro, was expected to increase the acidity of the sulfonamide group and thus lower the observed value of $\text{pH}^*_{0.5}$. Investigations carried out in our laboratories have shown that introduction of an electron withdrawing group into the 3-position of the 2-hydroxybenzophenone oxime system produced a much stronger extractant than the parent compound⁽²¹⁾. Similarly, Parish observed that incorporating a 3-nitro substituent into 5-dodecyl-2-hydroxybenzophenone oxime resulted in a 1.2 pH unit decrease in the observed $\text{pH}^*_{0.5}$ value⁽²²⁾.

Substituents exert an influence on the acid dissociation constant, K_{HR} , of the reagent. They also will have a direct influence on the metal to ligand sigma bonds and pi backbonding, which will be reflected in the overall stability constant, β_n , for the chelate⁽²³⁾.

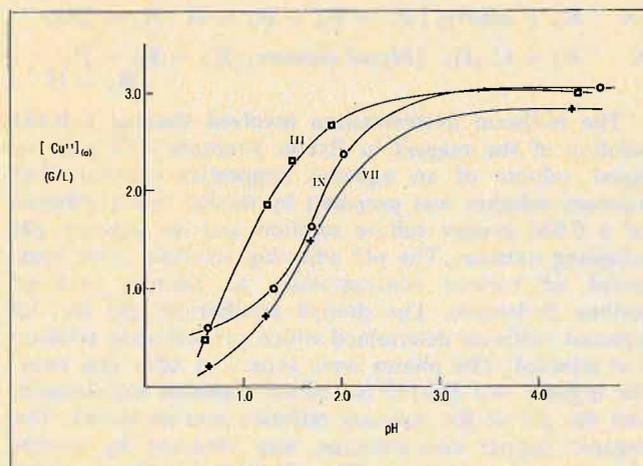


FIGURE 3. Cu pH isotherm comparison of reagents III, VII and IX.

Burger and Egyed have studied a series of 5-substituted salicylaldoximes with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II). They showed that the acidity increased in the expected order:



and β_n increased in the reverse order⁽²⁴⁾. Steger and Corsini⁽²⁵⁾ investigated a series of 5-substituted oximes. Their data demonstrated similar trends to that of Burger and Egyed.

The dependence of the distribution coefficient, D, on K_{HR} and β_n can be described as follows⁽¹⁸⁾:

$$\log D = \log \beta_n + n \log K_{HR} + npH + n \log [RH] + \log K_{exc} - n \log K_{exR} \dots \dots \dots (11)$$

$$K_{exc} = \frac{[MR_n]_{(o)}}{[MR_n]_{(a)}} \dots \dots \dots (12)$$

$$K_{exR} = \frac{[RH]_{(o)}}{[RH]_{(a)}} \dots \dots \dots (13)$$

In comparing the data for the phenolic oximes^(21,22) and the 8-sulfonamidoquinolines, the changes in K_{exc} and K_{exR} with changes in the substituent should be negligible and may be assumed to have a negligible influence on changes in log D. In the case of the phenolic oximes⁽²¹⁾, the increase in K_{HR} must overwhelm the effects of the decrease in β_n . In the 8-sulfonamidoquinoline case, the situation appears to be much more complex.

No information concerning the values of K_{HR} for the 8-sulfonamidoquinolines is currently available. Comparison of the $\text{p}K_{HR}$ data for phenols with that for benzenesulfonanilides (Table 4) suggests that the relative changes in $\text{p}K_{HR}$ with change in substituent are of the same order of magnitude for both systems.

TABLE 4. Values of $\text{p}K_{HR}$ for Substituted Phenols and Benzenesulfonanilides in Water

X	X-C ₆ H ₄ -OH ²⁶ 25°C	C ₆ H ₅ SO ₂ NH-C ₆ H ₄ -X ²⁹ 20°C; $\mu = 0.1$
H	9.99	8.31
p-CH ₃	10.28	8.64
p-CH ₃ O	10.20	8.70
p-Cl	9.42	7.93
p-NO ₂	7.15	6.20

Based on the comparison of the $\text{p}K_{HR}$ data for both systems, one would suggest that the electronic perturbations introduced by substituents would be of the same order of magnitude in phenolic and sulfonamide type systems. The effects on β_n should therefore be in the same direction and IX (5-NO₂) should be a substantially stronger reagent than its parent compound, III.

Since III is a more powerful extractant than IX, the observed results do not appear to be attributable to differences in electronic behaviour between phenolic systems and sulfonamide systems. Substantiation of this point must await the availability of $\text{p}K_{HR}$ data for the 8-sulfonamidoquinolines.

On the other hand, the apparent relative extractive strengths of (III (alkaryl) and X(alkyl) may be readily explained on the basis of acidity alone. The phenyl group in III would be expected to have a net electron withdrawing effect on the sulfonamide group, while the alkyl group in X would be a net electron donor. On this basis, III would be expected to be a slightly stronger acid than X and therefore a slightly stronger extractant.

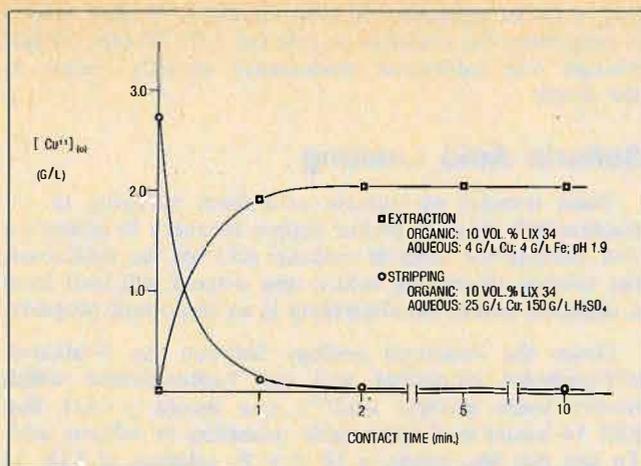


FIGURE 4. Extraction and stripping rates for LIX® 34.

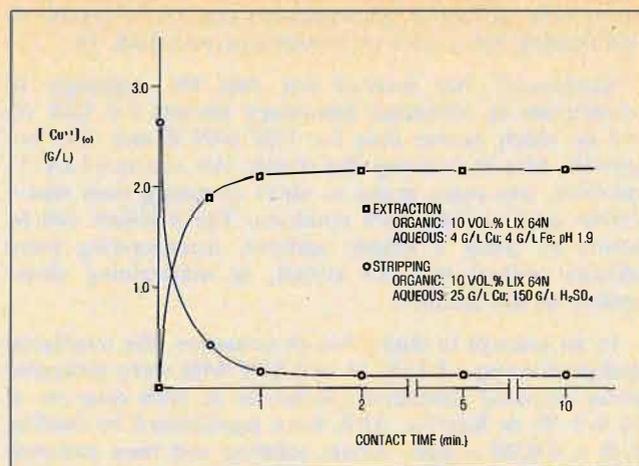


FIGURE 5. Extraction and stripping rates for LIX® 64N.

Rationalization of the differences between III and the reagents V, VI, VII, and IX is much more complicated. There are a number of potential interactions which are unique to this system. These interactions would be predicted to have a significant effect on β_n .

Secondary and tertiary silver(I)-amine complexes have been shown to be less stable than one might have predicted based on consideration of the relative base strengths of the ligands⁽²⁸⁾. The differences have been rationalized on the basis of steric crowding. Brown examined the base strengths of various amines when compared with Lewis acids of various sizes and found that the usual order of basicity could be inverted by using a large enough acid⁽²⁹⁾. The results were explained in terms of "F-strain" and "B-strain", "F-strain" is defined as due to face-to-face interference between the incoming Lewis acid and the ligand. "B-strain" is believed to come from enforced crowding on the back side of the molecule. Such effects should be minimal in a phenolic system; such as LIX 65N, but could have a significant effect on β_n for the 8-sulfonamidoquinolines.

An additional steric factor which might have a bearing on β_n arises from packing a second 8-(alkarylsulfonamido)quinoline around a central copper(II) ion. Steric interactions between the two ligands appears to be very real on the basis of space filling models; however, the magnitude of this effect is difficult to assess.

The anomalous position of IV (2-Me) and VIII (5,7-diCl) in the proposed order of extractive strengths can be rationalized on the basis of the steric factors discussed previously. In IV, the two-methyl function should result in increased strain in packing two ligands about the central ion similar to that observed for 8-hydroxyquinoline⁽³⁰⁾. In VIII, steric interactions and electrostatic repulsions between the seven-chloro group and the oxygens of the sulfonyl group should contribute to a decrease in chelate stability by increasing "B-strain". This hypothesis is strengthened by consideration of space filling models.

A complete rationalization of the observed effects must await extensive experimental investigation. The various electronic effects, steric effects, and their interactions are difficult to qualitatively assess. Prediction of substituent effects on chelating systems would appear to be a relatively difficult task.

Extraction and Stripping Kinetics

In addition to the novel behaviour exhibited by the 8-(alkarylsulfonamido)-quinolines with regard to substituent effects on $\text{pH}^*_{0.5}$, the extraction and stripping

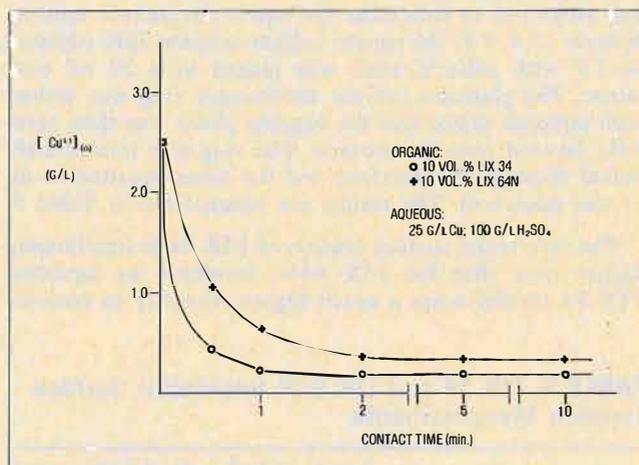


FIGURE 6. Comparison of stripping rates for LIX® 34 and LIX® 64N with 100 g/l H_2SO_4 .

kinetics of LIX 34 have been extensively investigated. Static mixer box kinetics of extraction and stripping were measured for LIX 34 and LIX 64N (Figures 4, 5 and 6). Equal volumes of the appropriate organic and aqueous feeds were stirred at 2000 rpm in a static mixer box (I.D. $2\frac{1}{4} \times 2\frac{1}{4} \times 4$ inches) at 25°C with a 1.25 inch diameter impeller positioned so that aqueous continuous mixing is obtained. For extraction kinetics, 10 v/v % solutions of the reagents in KerMac 470b were the organic feeds and the aqueous feed contained 4.0 g/l of copper(II) and 4.0 gpl of iron(III) at an initial pH of 1.9 (The pH was adjusted with sulfuric acid.). The organic feed for the stripping experiments was prepared by maximum loading a 10 v/v % solution of the reagent in KerMac 470b with copper(II) from the aqueous extraction feed while maintaining the pH at 1.9 with dilute sodium hydroxide solution.

Two aqueous stripping solutions were employed. Both aqueous stripping feeds contained 25 gpl of copper(II). One contained 100 gpl of sulfuric acid and the other contained 150 gpl sulfuric acid. Samples of the emulsion were withdrawn at various time intervals and the organic was analyzed for copper by atomic absorption spectroscopy.

Comparison of the curves in Figures 4 and 5 indicate that the kinetic behaviour of LIX 34 was very similar to that of LIX 64N under these conditions. A significant advantage for LIX 34 is indicated by the data in Figure 6.

Acceptable stripping performance can be obtained at significantly lower acid concentrations with LIX 34.

Kordosky⁽⁹⁾ has pointed out that the approach to equilibrium in miniature laboratory circuits for LIX 34 can be much poorer than for LIX 64N if one does not exercise care in running the circuit. An aqueous-LIX 34 emulsion was more prone to short circuiting than was a similar aqueous-LIX 64N emulsion. The problem can be solved by using a kinetic additive, incorporating more efficient mixers into the circuit, or maintaining closer control of the circuit⁽⁹⁾.

In an attempt to study this phenomenon, the interfacial surface tensions of LIX 34 and LIX 64N were measured under identical conditions. Solutions of both reagents at 14 v/v % in KerMac 470b were equilibrated by loading with a 0.03M copper sulfate solution and then stripping with a 150 gpl sulfuric acid solution. The final concentration of copper(II) on the organic was 0.51 gpl for LIX 34 and 0.7 gpl for LIX 64N. The deNouy method was employed to determine the interfacial surface tension. A layer of a 0.015M copper sulfate solution (pH adjusted to 1.9 with sulfuric acid) was placed in a 50 ml container. The platinum-iridium tensiometer ring was wetted with aqueous phase and the organic phase was then carefully layered onto the surface. The ring was immediately pulled through the interface and the force required to do so was measured. The results are summarized in Table 5.

The interfacial surface tension of LIX 34 is significantly higher than that for LIX 64N, therefore an aqueous-LIX 34 emulsion has a much higher tendency to coalesce

TABLE 5. LIX 34 and LIX 64N Interfacial Surface Tension Measurements

RUN	Interfacial Surface Tension (dynes/cm)	
	LIX 34	LIX 64N
1	29.8	18.6
2	31.0	18.3
3	30.5	18.4
Av. Val.	30.4	18.4

TABLE 6. Summary of H₂SO₄ Loading Data for LIX 34

Aqueous Feed (H ₂ SO ₄) (gpl)	Aqueous Scrub Raffinate pH
100	5.4
150	5.8
200	4.9
250	4.4

TABLE 7. Hydrolytic Stability Data for LIX 34 (11 v/v %) at 80°C

Time (Days)	Cu ^{II} Maximum Load (gpl)	% Active Component
0	3.34	100 (By Definition)
10	3.41	93
40	3.20	94
61	3.21	94
108	3.21	95
140	3.12	96
195	3.14	96
261 ¹	4.00	112

¹The test was terminated after 261 days because kerosene losses due to evaporation were becoming appreciable.

than does an aqueous-LIX 64N emulsion. If poor mixing is occurring, the coalescence rate for LIX 34 may be fast enough that substantial coalescence actually occurs in the mixer.

Sulfuric Acid Loading

Since transfer of sulfuric acid from stripping to extraction will result in poorer copper recovery in extraction and increase the costs of makeup acid for the tankhouse, the amount of sulfuric acid a new reagent will load from a standard tankhouse electrolyte is an important property.

Given the structural analogy between the 8-(alkaryl-sulfonamido) quinolines and the 7-alkenyloxine which readily loads sulfuric acid⁽³¹⁾, one would predict that LIX 34 would load appreciable quantities of sulfuric acid. To test this hypothesis, a 10 v/v % solution of LIX 34 in KerMac 470b was contacted with an equal volume of a sulfuric acid solution by shaking for one hour at ambient temperature. The organic was filtered to remove aqueous entrainment and then contacted with an equal volume of deionized water (pH = 6.8) by shaking for one hour. The pH of the aqueous scrub raffinate was then determined. The results are summarized in Table 6. No appreciable amounts of sulfuric acid are loaded by LIX 34 over a wide range of sulphuric acid concentrations.

A plausible explanation of the observed differences between the 8-(alkarylsulfonamido) quinolines and 7-alkenyloxine might be derived from consideration of steric factors and hydrogen bonding effects. In 7-alkenyloxine, approach of a hydronium ion to the basic quinoline nitrogen appears to be unhindered. Once protonation occurs, the hydroxyl group in the 8-position is available for stabilization of the bisulfate salt by hydrogen bonding. In the 8-(alkarylsulfonamido) quinolines, approach to the quinoline nitrogen and stabilization of the bisulfate salt by hydrogen bonding might be physically hindered by the alkarylsulfonyl group. Unfavorable electrostatic interactions between the sulfonyl group and the bisulfate anion might also destabilize the bisulfate salt of the reagent. Alternatively, there might be a substantial difference in the basicity of the two quinoline nitrogen atoms. A study of pK_{NH} in both systems would quickly answer this question.

Stability

For recovery of metal values by solvent ion exchange to be economically viable, the multiple reuse of the reagent is mandatory. During each pass through the circuit, the value of the metal transferred is only a small fraction of the value of the reagent. For a reagent to be economically feasible, it must demonstrate sufficient stability so that degradation of the reagent is not a significant factor in the overall cost of operation.

TABLE 8. Hydrolytic Stability Data for LIX 34 (11 v/v %) in the Presence of DNNSA (0.5 w/v%) at 80°C

Time (Days)	Cu ^{II} Maximum Load (gpl)	% Active Component
0	3.52	100 (By Definition)
7	3.47	96
20	3.57	95
71	3.26	91
118	3.48	92
150	3.30	94
187	3.43	96

The excellent hydrolytic stability of the 8-(alkarylsulfonamido) quinolines is documented by the data in Tables 7 and 8.

The stability data was accumulated in the following fashion. A solution of the reagent in KerMac 470b was placed in a round bottom flask fitted with a mechanical stirrer and condenser containing an aqueous solution composed of 30 gpl of copper(II) and 150 gpl of sulfuric acid. The mixture was continuously agitated at 80°C and aliquots of the organic were removed periodically. The organic was completely stripped of copper by repeated contacts with 150 gpl sulfuric acid. A portion of the organic was then maximum loaded by contacting with an equal volume of a 4.0 gpl copper(II) and 4.0 gpl iron(III) aqueous feed while maintaining the pH at 1.9 by addition of a sodium hydroxide solution. The concentration of the copper in the organic phase was then determined by atomic absorption spectroscopy. The percent active component was determined by IR analysis.

Table 7 shows that after extended periods in continuous contact with a typical tankhouse electrolyte at 80°C, LIX 34 still shows no signs of appreciable degradation. The excellent hydrolytic stability of LIX 34 is further underscored by the data in Table 8. Dinonylnaphthalene-sulfonic acid (DNNSA) is a very strong organic acid and would be expected to promote hydrolysis of the reagent. Under the conditions of this study, the presence of DNNSA does not promote the degradation of LIX 34 even after several months at 80°C.

Toxicity

The toxicity of a reagent is a very important consideration in its development. The results of short-term toxicity tests performed by Industrial Bio-Test Laboratories, Inc. are summarized in Table 9.

It should be noted that these tests covered periods of several days. Long term effects such as would develop over years of exposure are still unknown.

Summary

The active component in LIX 34 is an 8-(alkarylsulfonamido) quinoline. The synthesis involves coupling an alkarylsulfonyl chloride with 8-aminoquinoline in the presence of an organic base. This synthetic route may also be used to prepare various substituted derivatives of the reagent.

Plots of log D versus the log of the free reagent concentration at a constant pH establish that the copper chelate involves two ligand molecules per copper ion.

Electronic factors alone do not appear to offer an adequate explanation for the observed changes in extractive power with changes in substituents, such as methyl, chloro, methoxy, or nitro. Steric factors may play a significant role in explaining the observed trends. In addition steric effects may hinder sulfuric acid loading on LIX 34.

Copper extraction and stripping kinetic measurements illustrate the excellent kinetic behaviour of LIX 34. These experiments also show the lower acid requirement for stripping LIX 34.

The excellent hydrolytic stability of LIX 34 is also underscored along with its relatively nontoxic nature based on the results of short-term toxicity data.

Acknowledgments

I would like to thank R. L. Jensen, L. M. Komula, A. W. Olson, and E. Young for their assistance with the

TABLE 9. Short Term Toxicity Results for LIX 34¹

Acute Dermal Toxicity (Albino rabbits)	LD ₅₀ > 3,000 mg/Kg. (Practically non-toxic)
Primary Skin Irritation (Albino rabbits)	Minimally Irritating
Acute Oral Toxicity (Albino rabbits)	LD ₅₀ > 15,380 mg/Kg. (Relatively harmless)

¹Tests were carried out with 100% active solids.

experimental work. I would also like to thank R. Fisher and J. Mahlberg for their assistance with spectral analysis. I am also indebted to L. T. Ditsch, G. A. Kordosky, K. D. MacKay, P. L. Mattison, E. B. Spitzner and R. R. Swanson for helpful discussions and suggestions.

NOTATIONS

β	= overall stability constant of the complex component
D	= distribution coefficient of the metal ion
K^{11}	= second acid dissociation constant of sulfuric acid (see eq. 9)
K_{ex}	= defined by eq. 2
K_{exC}	= defined by eq. 12
K_{exR}	= defined by eq. 13
K_{HR}	= acid dissociation constant of the chelating reagent
M^{+n}	= metal ion of charge n
MRs	= metal chelate
RH	= chelating reagent

Subscripts

(a)	= aqueous phase
(o)	= organic phase

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DISCUSSION

G.A. Kordosky: The LIX — 34 system is a much simpler system than the LIX 64N system. There is no kinetic modifier and the stoichiometry of the extraction equation over the pH range 1 - 3 is constant. The same is not true for the LIX 64N system. Thus mechanistic studies on the LIX 34 system might prove to be an excellent starting point in trying to unravel the mysteries of copper extraction with chelating extractants.

M.J. Virnig: I agree with my colleague, Dr. Kordosky. Our investigations suggest that the LIX 34 system is a much simpler system than the LIX 64N system. Studies of the LIX 34 system might lead to insights into the more complicated LIX 64N system.

COPPER PROCESSING

The ACORGA P-5000 Series in the Solvent Extraction of Copper: Performance Characteristics and Implications for Plant Economics

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ABSTRACT

The paper describes the ACORGA P-5000 SERIES, a unique and comprehensive range of solvent extraction reagents for copper, developed from a parent salicylaldoxime, P-1, and a formulation technique involving 4-nonyl phenol. The properties and characteristics of the reagents forming the Series are discussed along with the large financial savings in plant capital and running costs that can accrue from their usage in new or existing SX facilities. To illustrate the application of the Series, two prime members, P-5100 and P-5300, are compared and contrasted with reference to present generation products where possible, in order to highlight differences.

Introduction

NEARLY A DECADE HAS NOW PASSED since solvent extraction as a means of recovering cathode quality copper was introduced at the Bluebird Mine, Miami, Arizona by Ranchers Exploration and Development Corporation. It represented a major step forward in the economic treatment of low-grade ores. The extractants involved, LIX® 64 and LIX® 64N, were until recently the only oxime products available.

Since 1968 many organizations have employed solvent extraction and a further growth in its use seemed inevitable. In 1977, however, inflationary pressures coupled with low copper prices have eroded the economic ad-

vantages. It is therefore necessary to restore the economic benefits presented by solvent extraction and make the application of the technique significantly more cost effective. These economic constraints acted as a catalyst in the development and commercial production of the ACORGA P-5000 Series. The concept behind the Series was to present to the user a comprehensive range of technically advanced extractants capable of reducing overall costs and removing artificial constraints in the use of solvent extraction.

Properties and Performance Characteristics

Earlier papers^(1,3) discussed in detail the chemical composition of the ACORGA P-5000 Series, including the novel ability of controlling the distribution characteristics of the anti-isomer of 5-nonyl-salicylaldoxime, P-1, by selective formulation with 4-nonyl phenol. Research work, by ICI in the UK, had shown that P-1 possessed the most desirable properties required of a selective reagent⁽⁴⁾ not least that it lent itself to low cost, high purity manufacture, a property so far unique on a commercial scale.

The strength of an extractant is measured in terms of the distribution of the copper (or other metal) between the organic and the aqueous phases and is represented by a distribution isotherm. In extraction we see that for one of the strongest members of the P-5000 Series — P-5100, this is steep and sharply bowed (Figure 1), an essential property for achieving a high degree of extraction in a minimum number of contacting stages. By comparison, a first generation extractant under identical feed conditions is shown (Figure 2). In the stripping stage the distribution must be effectively reversed under conditions

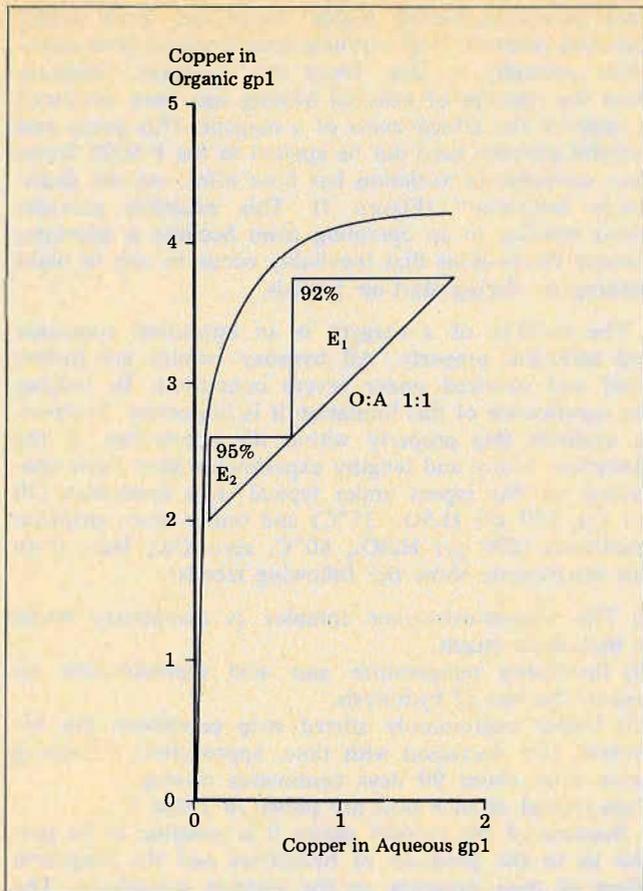


FIGURE 1. Extraction isotherm 8 v/o P-5100 in Escaid 100. 1.8 gpl Cu^{2+} , pH 2.0.

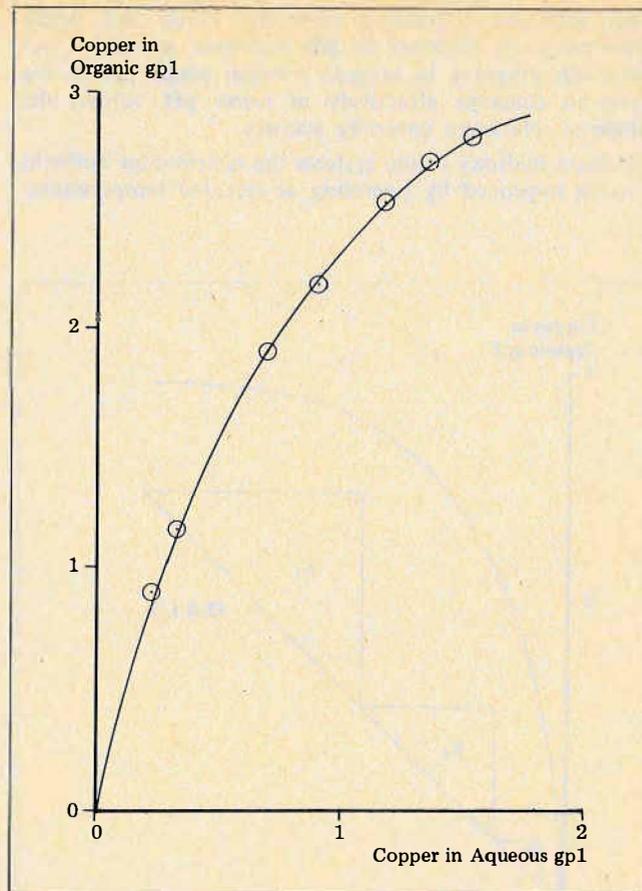


FIGURE 2. Extraction isotherm first generation extractant. 1.8 gpl Cu^+ pH 2.0.

compatible with electrowinning. Usually 30 g/l copper and 150 g/l acid is available and the strip isotherm (Figure 3) shows that a stripped organic value commensurate with $> 50\%$ transfer capacity is readily available. The need for a strong reagent does not apply in some circuits such as those dump leach operations with low copper and acid tenors. In these cases a weaker extractant such as P-5300 can be used (Figure 4). The illustrated isotherm is produced under the same conditions as those shown in Figures 1-3 in order that a direct comparison of relative strengths can be made.

The rate at which chemical equilibrium is approached either in the extraction or stripping processes is of vital importance since it dictates energy input, mixer size and overall recovery. Conventionally the rate processes have been slow in copper solvent extraction. As a result, most commercial copper circuits use 3-minute mixers to produce relatively modest stage efficiencies, usually of the order of 85%. P-5000 Series extractants are exceptionally fast both in extraction and strip^(1,2).

The variation in phase disengagement rate for two prime P-5000 Series members, P-5100 and P-5300 is shown in Figure 5 based on a static test method, described by Birch⁽⁵⁾. Reagent concentrations are such that they show the same transfer capacity. By way of comparison the data also show a present generation extractant under identical conditions.

Selectivity data have been described in earlier papers⁽¹⁻²⁾ showing virtually total rejection of cobalt and nickel under acid conditions and high rejection of ferric iron. An 'S-curve' for a 10V/o P-5100 solution in Escaid 100® shows the pH functionality of the reagent to copper and ferric iron (Figure 6). The curves were generated from

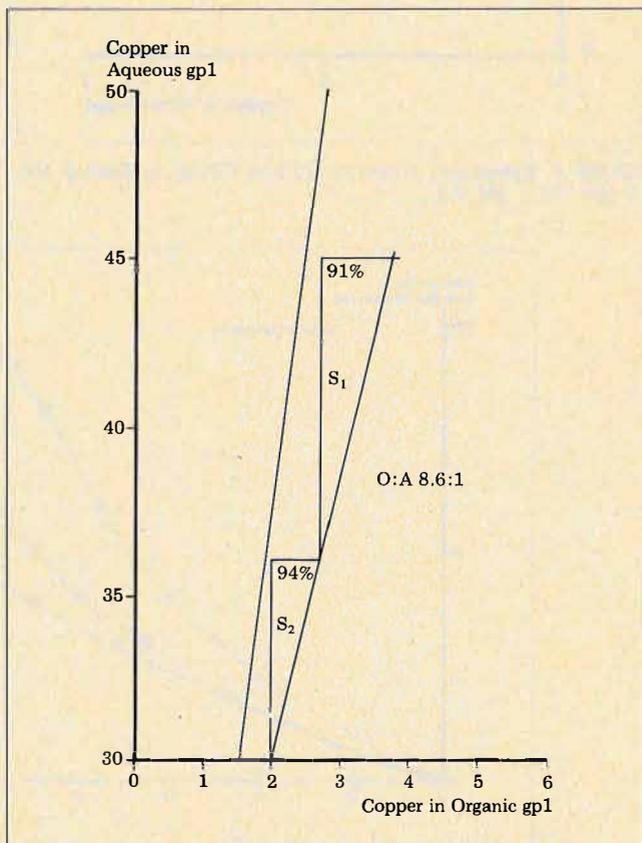


FIGURE 3. Strip isotherm 8 v/o P-5100 in Escaid 100. 30 gpl Cu^{2+} , 150 gpl H_2SO_4 .

fresh solutions containing only the metal ion under examination. A decrease in pH improves selectivity, relating this property to reagent strength which allows the Series to function effectively at lower pH values; the enhanced selectivity naturally accrues.

In most hydroxy oxime systems the distribution isotherm is much improved by operating at elevated temperatures.

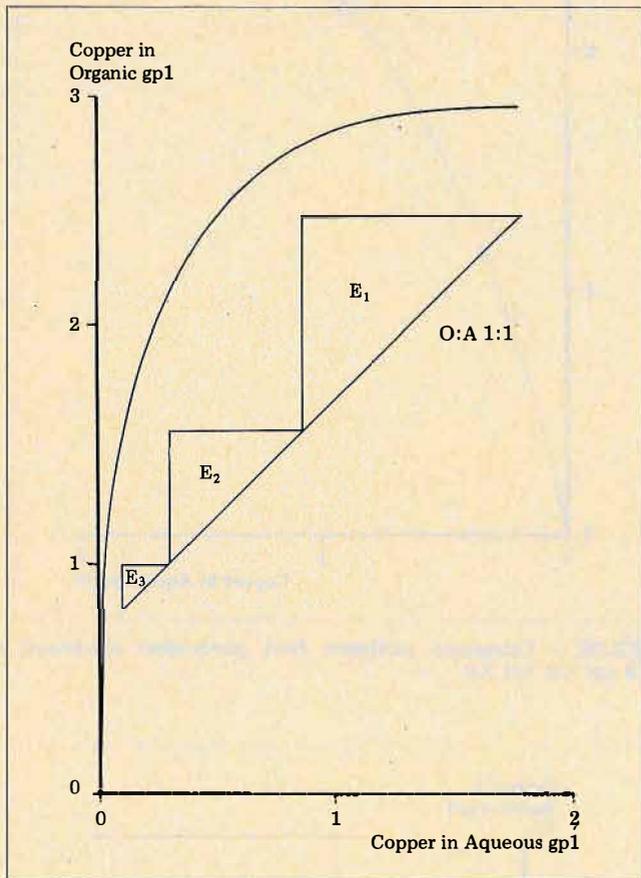


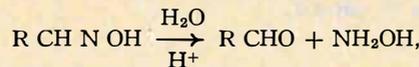
FIGURE 4. Extraction isotherm 12 v/o P-5300 in Escaid 100. 1.8 gpl Cu^{2+} , pH 2.0.

Some processes, having highly exothermic leach conditions and relatively high ambient temperatures, lend themselves naturally to this. There are, however, instances when the concept of external heating has been advanced to improve the effectiveness of a reagent. This costly and wasteful practice need not be applied to the P-5000 Series since temperature variation has little effect on the distribution isotherm⁽⁴⁾ (Figure 7). This situation provides added stability to an operating plant because it alleviates thermal fluctuations that inevitably occur in day to night running or during start-up periods.

The stability of a reagent is an important economic and technical property. All hydroxy oximes are hydrolysed and oxidized under severe conditions. In judging the significance of this limitation it is important, however, to evaluate this property within the constraints of the operation. Many and lengthy experiments have been conducted on this aspect under typical strip conditions (30 g/l Cu, 150 g/l H_2SO_4 , 25°C) and under more stringent conditions (200 g/l H_2SO_4 , 80°C, zero Cu). Data from this programme show the following trends:

- (i) The copper-extractant complex is completely stable to hydrolytic attack.
 - (ii) Increasing temperature and acid concentration increases the rate of hydrolysis.
 - (iii) Under continuously stirred strip conditions the hydrolysis rate decreased with time, approaching a limiting value after about 90 days continuous mixing.
- Data typical of such tests are shown in Table 1.

Because of the reagent purity it is possible to be precise as to the products of hydrolysis and the long-term effect of their presence on the systems considered. The standard text book reaction is followed:



the aldehyde being easily monitored by chromatographic techniques. Experiments have shown that excessive doses of aldehyde do not materially effect the reagent specification or circuit performance.

In the stripping circuit there exists the real possibility of oxidation of hydroxy-oximes by electrolytically generated nascent oxygen or species such as Mn(III). The

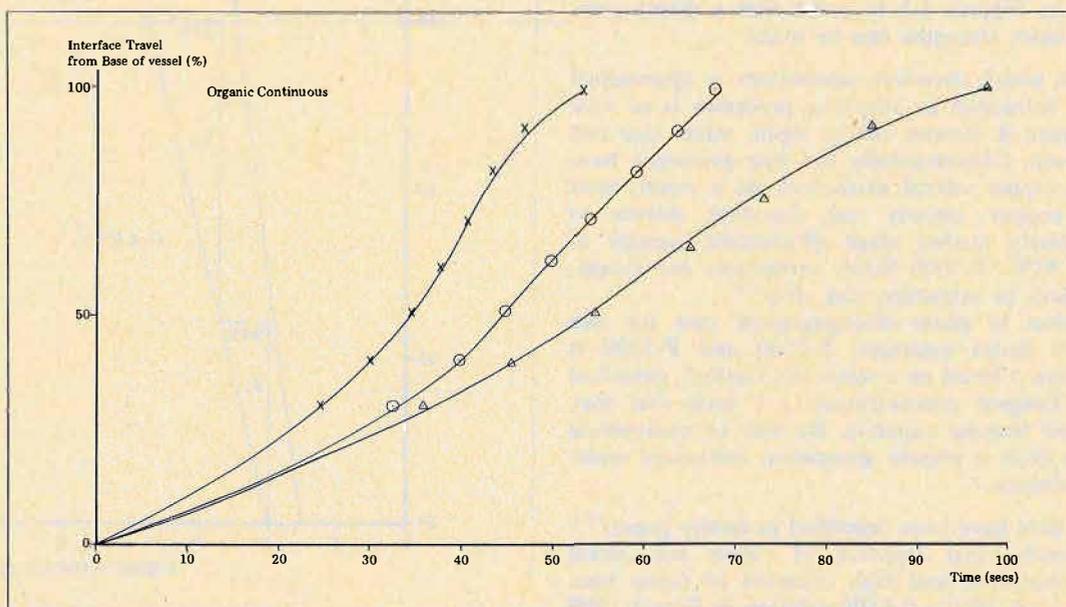


FIGURE 5. Relative phase disengagement curves using static test method. XP-5100 ○P-5300 ΔPresent generation extractant/Escaid 100. Comparative transfer capacities.

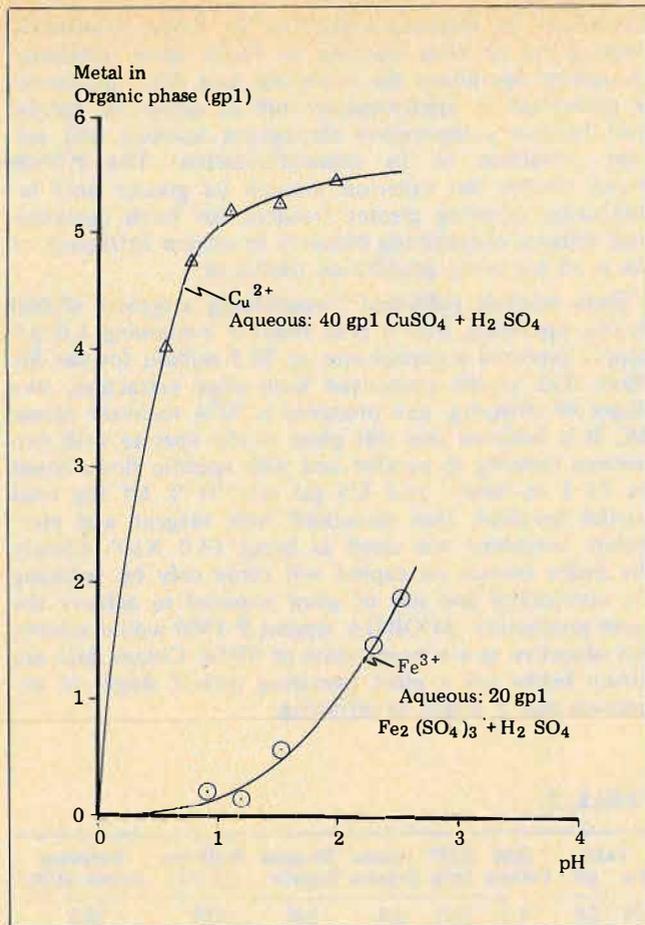


FIGURE 6. pH/loading curves for copper and ferric iron. 10 v/o P-5100.

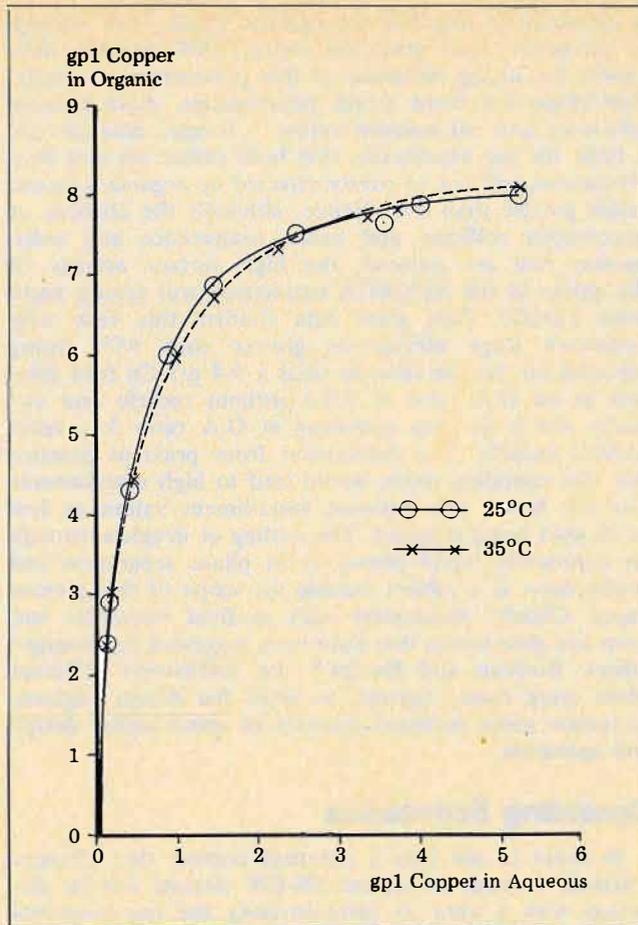


FIGURE 7. Extraction isotherms vs. temperature 30 v/o P-5300 in Escaid 100. 5.2 gp1 Cu^{2+} , pH 2.0.

transfer capacity modifier, p-nonyl phenol, present in the ACORGA P-5000 Series reagents, is a highly effective anti-oxidant. Thus, for these reagents loss of oxime by oxidation is obviated. Field trials using P-5100 reagent have confirmed laboratory data on product stability as is shown later.

Plant Design Implications

The plant capital element, in any consideration of cost, is always a major contributory factor in determining the overall economics of the process. To date, commercial installations have comprised a minimum of five mixer-settler unit operations. Usually the configuration of 3 stages of extraction and 2 stages of stripping has been adopted, but occasionally 4 plus 2, and in very early days even 4 plus 3 have been built. Clearly the emergence of a reagent, capable of performing effectively in no more than four mixer-settler units provides the industry with an immediate means of saving large amounts of capital, including that for the reagent inventory, as well as reducing overall operating costs.

As a further contribution to capital savings it is desirable that a reagent should allow the design of settlers to be as small as is compatible with producing good phase separation and hence low entrained losses. A very good assessment of this cost was provided recently in a paper by Rowden and Collins⁽⁶⁾. The size of a settler, or more precisely the specific flow attainable for a given dispersion band width, is a function of the reagent, its concentration, temperature, mixing parameters, mass transfer conditions, and diluent used. To date such considerations

TABLE 1. Hydrolysis Test Data

Reagent	Temp °C	Conditions		Hydrolysis Rate % hr ⁻¹		
		Cu g/l	H ₂ SO ₄ g/l	30 days	45 days	90 days
15v/o P-5100	22	30	150	0.111	0.009	0.006
30v/o P-5300	22	30	150	0.014	0.011	0.006
40v/o P-5300	50	30	150	0.058	0.042	0.028

have produced units with specific flows between 53-61 $1 \text{ m}^{-2}\text{min}^{-1}$ (1.3 to 1.5 US gal $\text{min}^{-1}\text{ft}^{-2}$) with occasionally a design figure of 81 $1 \text{ m}^{-2}\text{min}^{-1}$ (2.0 US gal $\text{min}^{-1}\text{ft}^{-2}$). It has been shown in a 40 gal min^{-1} pilot plant designed with a specific flow of 81 $1 \text{ m}^{-2}\text{min}^{-1}$ that 10V/o P5100 in Escaid 200® diluent (Exxon Corp.) produced no discernible dispersion band beyond a "picket" fence sited 10 in.-12 in. from the mixer over-flow when operating organic continuous. In other field trials using lower concentrations of reagent to treat dump leach and mine waste streams, even more optimistic settler area figures have been reported.

As expected, low temperatures adversely affect settling times. The consequence of lower temperatures still does not dictate, however, a settler area requirement as large as those currently employed. Figure 8 for 15V/o P-5100 in Escaid 100® diluent, (Exxon Corp.) shows a situation at an operating temperature of 15°C.

Commonly, mixer-settlers are designed to operate at an organic/aqueous flow ratio of 1.0. The drawback of this constraint, which allows little copper concentration,

is alleviated by recycling the aqueous phase, after settling, to the mixer. Data generated using LIX® reagents, have shown the strong influence of this parameter on specific flow/dispersion band depth relationships, mass transfer efficiency and entrainment values⁽⁷⁾. Kinetic data provide a basis for the expectation that both extraction and strip efficiencies will not be overly effected by organic/aqueous ratios greater than 1.0. Hence, although the chances of interdroplet collision and hence coalescence and redispersion rate are reduced, the high surface activity of the oxime in the ACORGA extractants will ensure rapid mass transfer. Pilot plant data confirm this view with extraction stage efficiencies greater than 95% being reported for an operation to treat a 3-4 g/l Cu feed solution at an O:A ratio of 1.2:1 without recycle and virtually 100% in strip operating at O:A ratio 3:1, again without recycle. The expectation from previous practice that this operating mode would lead to high entrainments was not borne out; aqueous entrainment values as low as 20 ppm being reported. The settling of droplets through an immiscible liquid phase, as in phase separation and coalescence, is a subject outside the scope of this present paper. Clearly, parameters such as fluid viscosities and drop size distribution that have been suggested by, amongst others, Rushton and Davies⁽⁸⁾ are sufficiently different when using these reagents, to allow the design engineer to review some accepted theories of mixer-settler design and operation.

Operating Economics

In order to put into a practical context the advances outlined, a range of typical SX-EW circuits will be discussed with a view to demonstrating the improvements in economics offered by the P-5000 Series.

Present-day Operations

All acid solutions treated today by solvent extraction contain copper between 1.0-6.0 g/l, the copper being

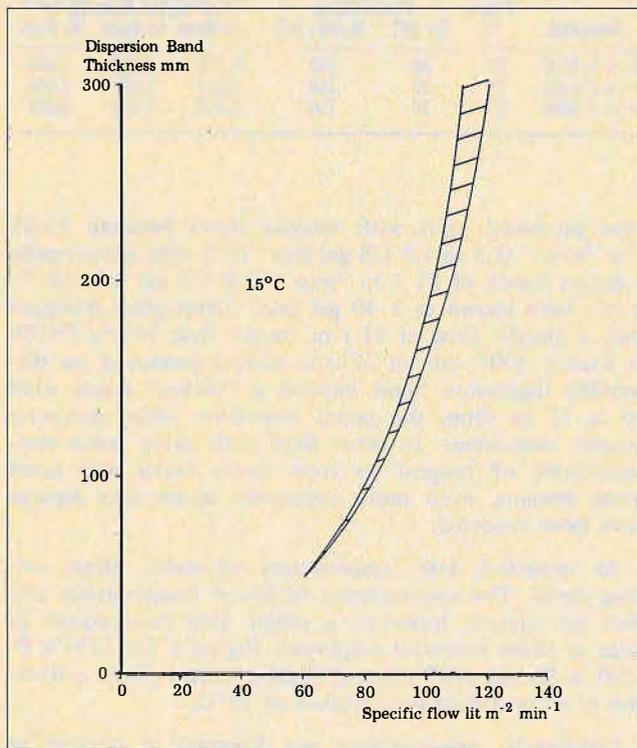


FIGURE 8. Dispersion band thickness versus specific flow for continuous system.

solubilized by leaching (agitation for higher concentrations, dump or heap leaching for lower tenor solutions). In current operations the important acid tenor parameter is controlled at approximately pH 2, either by careful acid balance compromises throughout leaching and solvent extraction or by preneutralization. The P-5000 Series relaxes this criterion through its greater acid insensitivity, allowing greater freedom for leach optimization without endangering recovery in solvent extraction or the need for costly presolution treatment.

Data recently published⁽⁹⁾ concerning a typical 40,000 lb/day operation with a feed solution containing 1.0 g/l copper reported a capital cost of \$2.5 million for the SX plant. The circuit comprised three-stage extraction, two stages of stripping, and produced a 90% recovery across SX. It is believed that this plant would operate with two streams running in parallel and with specific flows based on 74 l m⁻²min⁻¹ (1.8 US gal min⁻¹ft⁻²). Of the total capital involved, that associated with reagent and electrolyte inventory was cited as being \$3.0 X10⁵. Clearly the major impact on capital will come only by reducing the complexity and size of plant required to achieve the same production. ACORGA reagent P-5300 would achieve this objective at a concentration of 6V/o. Circuit data are shown below for a plant operating with 2 stages of extraction and 2 stages of stripping.

TABLE 2.

Feed Cu	pH	O/A Extract	O/A* Strip	Loaded Organic	Stripped Organic	Raffinate g/l Cu	Recovery Across SX(%)
1.08	2.2	1/1	21/1	1.4	0.40	0.08	92.6

*recycle to O/A 2/1.

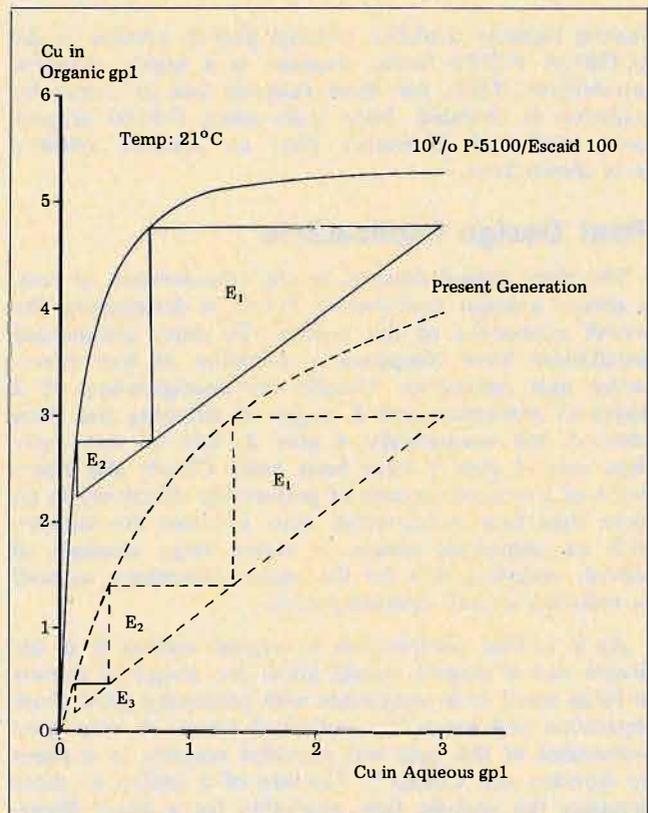


FIGURE 9. Comparison of Acorga P-5100 reagent vs present generation extractant — extraction isotherms. Aqueous: 3.0 gpl Cu²⁺, pH 1.9. Temp: 21°C.

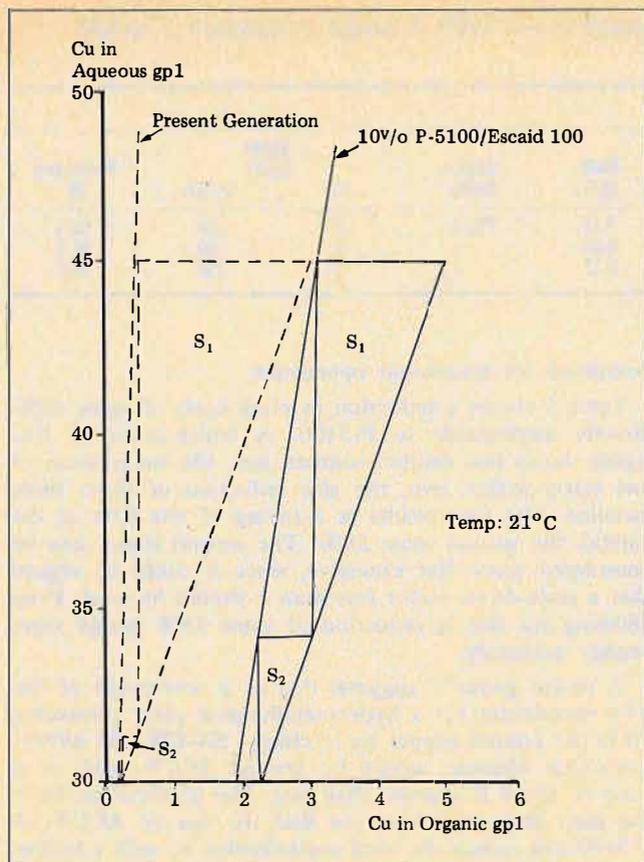


FIGURE 10. Comparison of Acorga P-5100 reagent vs. present generation extractant — strip isotherm. Aqueous: 30 gpl Cu^{2+} , 150 gpl H_2SO_4 . Temp: 21°C.

The use of P-5300 to deal with this type of feed offers an immediate saving in plant capital of 20%, in the case quoted, some \$0.5 million. The reduction in plant size will show other savings such as power costs (fewer mixers) and maintenance. The task of supervision is reduced as well as site costs.

Several of the larger present-day operations, producing between 25-70 kt per annum, treat a feed solution containing approximately 3 g/l copper at about pH 1.9. Typically, 3 stages of extraction and 2 stages of stripping are used although occasionally as many as 4 stages of extraction are used. The ACORGA reagent P-5100 would provide the optimum plant for the treatment of such feeds requiring only two stages of extraction and two stages of stripping. A comparison of McCabe-Thiele constructions on the extraction and strip isotherms for the present generation reagent and P-5100 demonstrates the difference in staging requirement (Figures 9 and 10).

pH insensitivity is an important economic parameter if an SX operation is to maintain recovery with a changing acid concentration in the incoming feed. Table 3 shows data from a pilot operation using actual leach solution in which this aspect of the reagent is well demonstrated.

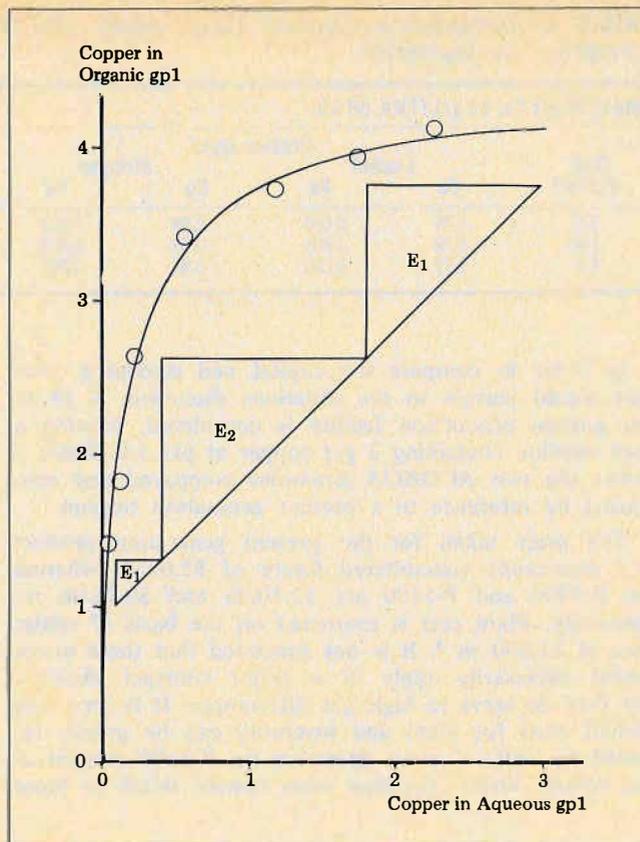


FIGURE 11. Extraction isotherm 16 v/o P-5300 in Escaid 100. 2.95 gpl Cu^{2+} , 8 gpl Fe^{3+} , pH 1.9.

It is notable that the recovery does not fall below 90% even in a situation where the copper in feed is increased by 7% and the free acid is increased from 2.6 g/l to 8.6 g/l.

The data relates to a situation in which P-5100 has been selected at the design stage of a project and therefore optimisation has been achieved using the strongest Series reagent. It is recognised that operators are reluctant, having once installed a process plant, to remove stages. In such cases if three stages of extraction were to be fully utilised then P-5300 reagent would be recommended at a concentration of 16V/o. Figure 11 shows the McCabe/Thiele construction and relevant isotherms, and Table 4 reports data obtained from continuous laboratory evaluation.

In order to ensure that overly optimistic recoveries were not obtained in the laboratory equipment, mixer efficiencies were set at about 90% in extraction, which is in line with ACORGA determinations of predicted stage efficiencies in flowing systems from batch data⁽¹⁰⁾ for this reagent. It proved impossible to reduce stage efficiencies in the strip (virtually 100%) and maintain hydrodynamic stability. Such data are also consistent with results obtained by the P-5000 Series reagents in practical operation.

TABLE 3. Variations in Acid in Feed Solutions using 10v/o P-5100 in Escaid 100® in 2 + 2 Plant

Feed Solution Cu	Feed Solution H_2SO_4	O/A Extract	Organic (g/l) Loaded	Organic (g/l) Stripped	Raffinate Cu	Spent Cu	Spent H_2SO_4	Recovery %
3.25	8.6	1.22/1	4.6	2.20	0.32	42.6	172	90.2
3.04	6.8	1.22/1	4.5	2.20	0.22	43.1	170	92.8
3.09	2.6	1.1/1	4.65	2.00	0.17	42.8	173	94.3
2.98	3.7	1.54/1	3.92	2.10	0.17	42.8	173	94.3

TABLE 4. Continuous Current Data using 16v/oP-5300/Escaid 100® 3 stage extraction 2 stage stripping configuration.

Feed: 2.95 g/l Cu, 3.0 g/l (T)Fe, pH 1.9

O/A Extract	Cu	Organic (g/l)		Stripped		Raff. (g/l)	Cu/Fe Ratio	Cu	Spent (g/l) H ₂ SO ₄	Recovery %
		Loaded Fe	Cu	Fe	Fe					
1.0	3.75	0.009	0.98	0.002	0.13	396/1	30	150	95.6	
1.0	3.78	0.008	0.99	0.002	0.08	—	30	150	97.3	
1.0	3.72	0.009	0.94	0.002	0.12	—	30	150	96.6	

In order to compare the capital and operating costs that would pertain to the situations discussed, a 30 kt per annum production facility is considered, treating a feed solution containing 3 g/l copper at pH 1.9. Table 5 shows the two ACORGA situations compared and contrasted by reference to a present generation reagent.

The price taken for the present generation product is a commonly encountered figure of \$2.65/lb whereas the P-5300 and P-5100 are \$2.10/lb and \$3.75/lb respectively. Plant cost is estimated on the basis of settler area at \$1,800 m⁻². It is not suggested that these prices would necessarily apply in a major contract situation but they do serve to highlight differences. It is seen that capital costs for plant and inventory can be greatly reduced by optimising an operation on P-5100 reagent at the outset, whilst operating costs remain much as those

computed for traditional operations.

Table 5 shows a reduction in plant costs of some 48% directly attributable to P-5100. A break-down of this figure shows two distinct sources; one, the suppression of one mixer-settler, two, the size reduction of those units installed. The first results in a saving of one fifth of the capital, the second some 28%. The second claim may be considered somewhat excessive, since it could be argued that a scale-down factor less than 1 should be used. Even allowing for this, a reduction of some 35% would seem readily achievable.

A recent paper⁽¹¹⁾ suggests that as a percentage of the total investment for a hydrometallurgical plant producing 30 kt per annum copper by leaching - SX-EW, the solvent extraction element would be around 15.4% split in a ratio of 56:44 Equipment:Site cost. The implications from the data presented here are that the use of ACORGA P-5100 can reduce the total capitalisation of such a hydro-metallurgical facility by up to 6%.

The operating cost calculations are based on an assumed organic in aqueous entrainment of 100 ppm lost via the raffinate. It is further assumed that the entrainment generated by different reagents is approximately the same, whereas field trials indicate that using ACORGA products it may be considerably lower. Earlier, the loss of active reagent through acid hydrolysis was discussed, and data presented under hydrolysis conditions. Table 5 shows the cost of hydrolysis losses in an operating circuit for ACORGA reagents. The basis of the estimation for the reagent P-5100 is shown in Table 6. Clearly hydrolysis

TABLE 5. SX Plant and Operating Costs Compared for Various Reagents

Feed: 3 g/l Cu pH 1.9 Nominal production: 30,000 mt p.a.

Reagent	Present Generation	P-5300	P-5100
Capital cost: — plant	7.30	as reference	3.82
\$ US × 10 ⁻⁶ — inventory	1.38	1.22	0.88
Operating Cost: (Organic losses)			
— entrainment	1.44	1.24	1.42
cents/lb Cu — hydrolysis	no data	0.04	0.05
Recovery (%)	93.3	96.6	94.0

TABLE 6. Estimate of Organic Loss Through Hydrolysis of the Oxime

10v/o P-5100 Single stream assumed (2 streams in parallel in practice)

Stage:	E ₁	E ₂	S ₂	S ₁	Storage, Piping, etc.
Vol. of reagent: — mixer %	8.0	8.0	8.0	8.0	20.4
— settler %	11.9	11.9	11.9	11.9	—
Reagent max. load (g/l)	5.25	5.25	5.25	5.25	5.25
++ Copper in organic (g/l)	4.75	3.00	2.25	3.00	4.50
++ Acid in Aqueous (g/l)	5.16	6.51	143.2	127.0	—
Mean value non-complexed reagent (%)	26.20	50.0	52.5	28.8	14.3
Non-complexed reagent distribution:					
— mixer %	2.11	4.02	4.22	2.31	2.87
— settler %	3.13	5.97	6.26	3.43	—
Hydrolysis rate:					
— mixer % hr ⁻¹	1 × 10 ⁻⁶	1 × 10 ⁻⁶	1 × 10 ⁻²	1 × 10 ⁻²	0
— settler % hr ⁻¹	—	—	—	—	—
Reagent loss:					
— mixer % hr ⁻¹	neg	neg	4.22 × 10 ⁻⁴	2.31 × 10 ⁻⁴	0
— settler % hr ⁻¹	neg	neg	neg	neg	—
Total reagent loss (% p.a.)	neg	neg	2.97	1.66	0
neg = negligible ++ exit conditions					

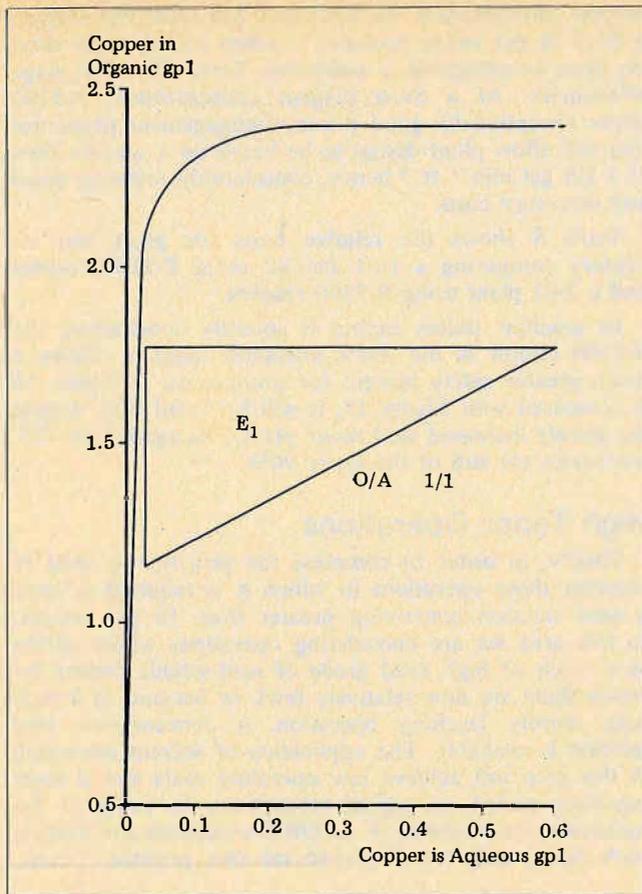


FIGURE 12. Extract isotherm 5 v/o P-5100 in Escaid 100. 0.6 gpl Cu²⁺, 1.5 gpl Fe (total) pH 2.5.

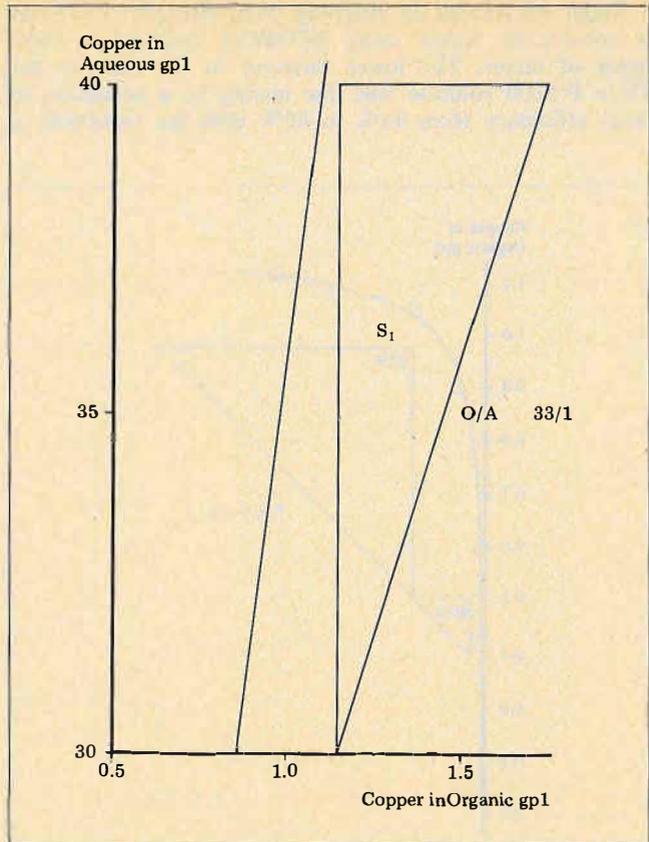


FIGURE 13. Strip isotherm 5 v/o P-5100 in Escaid 100. 30 gpl Cu²⁺, 170 gpl H₂SO₄.

losses in ACORGA circuits will have no impact on the overall economics of a project.

A similar table could be drawn up for the reagent P-5300 showing a final total reagent loss of 2.34% per annum. This compares with an annual loss through entrainment of 59.9%. The total hydrolysis loss for the P-5100 circuit is 4.63% per annum compared with a 100% annual turnover of reagent for this smaller plant.

Low Tenor Operations

There are a number of operators actively pursuing plans to treat acid solutions containing less than 1 g/l copper by solvent extraction-electro-winning. The solutions are in general naturally occurring mine waters or low copper tenor dump leach liquors. As such, they are high solution flow systems but relatively low in production capability — a situation well recognised as approaching

the limits of economic viability for SX-EW versus cementation. It is particularly appropriate when considering such a situation that new generation extractants are available, capable of producing very low raffinate in a minimal plant in order to keep capital costs low. Figures 12 and 13 show a McCabe/Thiele construction on an appropriate isotherm in which a feed of 0.6 g/l Cu²⁺ is treated by 5V/o P-5100 reagent in a one-stage extraction, one-stage stripping plant. Figures 14 and 15 show similar data for 4V/o P-5300 reagent in a 2+2 plant. The data generated from a continuous counter current laboratory run are shown in Table 7.

The data showed a Cu/Fe transfer ratio of about 60/1 for the above P-5100 circuit. This was not determined in the P-5300 case. Selectivity was determined according to the equation —

$$\frac{\text{Cu in loaded organic} - \text{Cu in stripped Organic}}{\text{Fe in loaded Organic} - \text{Fe in stripped Organic}}$$

TABLE 7. Continuous Counter Current Rig Data

Feed: 0.60 g/l Cu²⁺, 1.5 g/l Fe (total), pH 2.5 (synthetic)
Spent Electrolyte: 30 g/l Cu²⁺, 170 g/l H₂SO₄
Staging: 1 extract, 1 strip (P-5100) 2 extract, 1 strip (P-5300)

v/o Reagent	Mixer Ret'n Time (mins)	O/A Extract	Organic Cu (g/l) loaded	Organic Cu (g/l) stripped	Advance Electrolyte	Raff (g/l)	Recovery %
5v/o P-5100	3	1.04/1	1.52	0.98	35.2	0.040	93.3
5v/o P-5100	2	1.02/1	1.50	0.96	35.4	0.047	92.2
3v/o P-5100	3	0.99/1	1.02	0.50	36.4	0.087	85.5
4v/o P-5300	3	1/1	0.97	0.40	45.0	0.020	96.6

Stage efficiencies in stripping were virtually 100% as is consistently found using ACORGA reagents in most types of mixer. The lower recovery in the case of the 3V/o P-5100 solution was due mainly to a reduction in stage efficiency from 94% to 89% with the reduction in

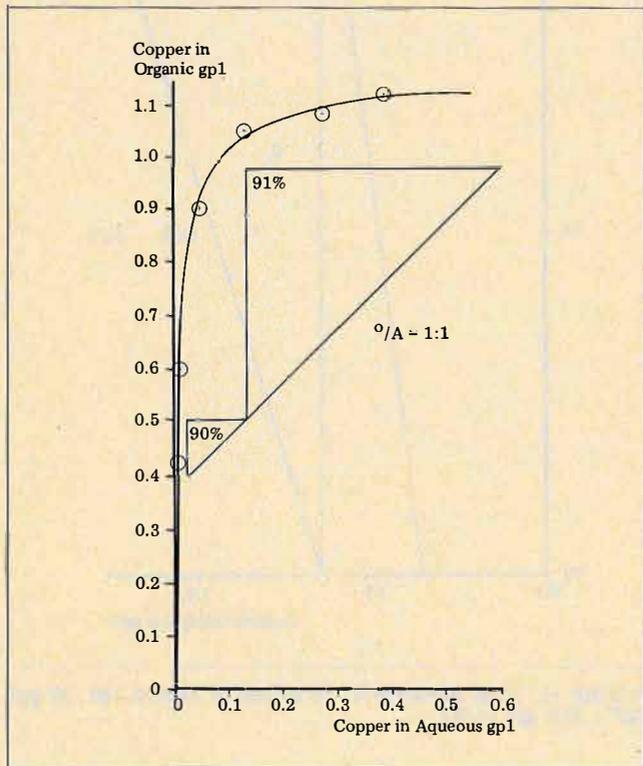


FIGURE 14. Extract isotherm 4 v/o P-5300 in Escaid 100. 0.59 gpl Cu^{2+} , pH 2.5.

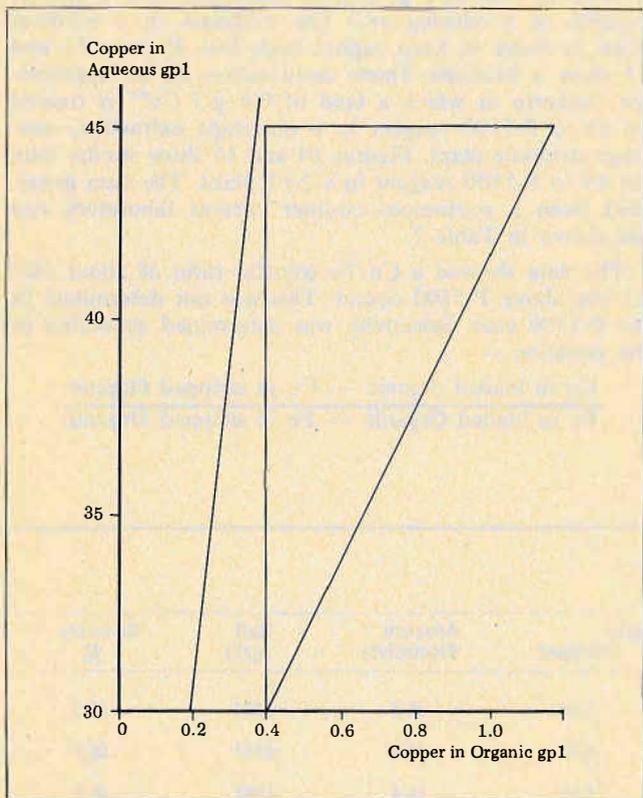


FIGURE 15. Strip isotherm 4 v/o P-5300 in Escaid 100. 30 gpl Cu^{2+} , 170 gpl H_2SO_4 .

reagent concentration. At these very low levels the surface activity of the oxime becomes lessened and thus the driving force to extraction is weakened, hence the lower stage efficiencies. At a 5v/o reagent concentration, P-5100 shows exceptionally good phase disengagement properties that will allow plant design to be based on a specific flow of 3 US gal $\text{min}^{-1} \text{ft}^{-2}$ hence, considerably reducing plant and inventory costs.

Table 8 shows the relative costs for plant and inventory comparing a 1+1 facility using P-5100 reagent and a 2+1 plant using P-5300 reagent.

In practice, unless capital is severely constrained, the P-5300 circuit is the more attractive since it allows a much greater safety margin for production. If Figure 16 is compared with Figure 15, it will be noted that, despite the greatly increased acid tenor pH 1.5 as against pH 2.5, recoveries are still of the order 90%.

High Tenor Operations

Finally, in order to complete the picture, we need to consider those operations in which it is required to treat a feed solution containing greater than 10 g/l copper. In this area we are considering operations where, either as a result of high head grade of acid-soluble copper (of which there are now relatively few), or because of a high pulp density leaching operation, a concentrated feed solution is available. The application of solvent extraction in this area will achieve low operating costs and a short pay-back period on capital investment. In order to demonstrate the potential of ACORGA reagents for treating such feeds, data are displayed for two possible circuits,

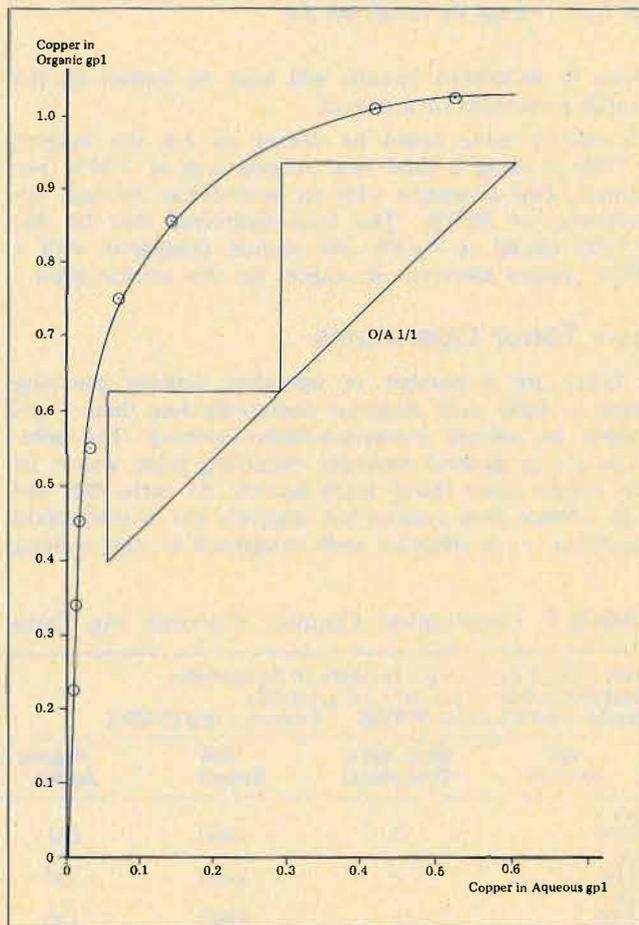


FIGURE 16. Extract isotherm 4 v/o P-5300 in Escaid 100. 0.6 gpl Cu^{2+} , pH 1.5.

TABLE 8. SX-EW Plant and Operating Costs Compared for 1 g/l Copper Feed

Feed: 0.6 g/l Cu, pH 2.5		Production: 40,000 lb/day	
		P-5300	P-5100
Capital cost \$ US × 10 ⁻⁶	SX	plant	2.87
		inventory	0.13
	EW	plant	3.00
Total capital, \$ US × 10 ⁻⁶		6.00	4.49
Operating Costs cents/lb Cu	Organic make-up	labour	1.40
		power	1.50
		*other	2.50
			3.10
Total operating \$ US/lb Cu		8.5	10.24

*Maintenance, supplies and service, taxes and insurance

one containing 11.8 g/l copper, 4 g/l acid (Table 9), and the other containing 20 g/l Cu, 7 g/l acid (Tables 10 and 11).

The chemical data shown in Table 9 are supported by physical data for the phase separation which show that at 25°C a design specific flow of 61 l m⁻² min⁻¹ (1.5 US gal ft⁻² min⁻¹) can be achieved when operating mixers organic-continuous.

As shown below in Table 11, such a circuit will produce excellent stage efficiencies without the need for recycle back to 1:1. The kinetic data quoted was generated in the laboratory by methods described by Birch⁽⁵⁾. Two+two circuit proposals serve to underline the flexibility that is offered by the P-5000 Series of reagents and it is anticipated that in the near future these reagents will find application in such circuits.

The cost of a solvent extraction plant is primarily governed by the volume of solution flow. As such, given the production of high tenor/low volume solutions and effective reagents to treat them, the profitability of designing flowsheets in this manner is apparent.

Conclusion

The ACORGA P-5000 SERIES of extractants offers the metallurgist the range of reagents required to treat virtually any chosen feedstock. In particular it allows him the freedom to optimize the total metallurgical circuit without recourse to artificial constraints imposed by solvent extraction as presently practised. Only acid media have been considered in this paper, but already commercial experience on a small scale is being gained in alkaline media and laboratory data for chloride systems confirms the Series' suitability without chemical carryover of chloride ion. The economic advantages of optimising the SX circuit at the design stage on ACORGA products has been demonstrated but also the advantage of use in existing operations has been shown.

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TABLE 9. Example 1 — High Tenor Copper Feed Treated with 25v/o P-5100/Escaid 100®

Feed: 11.8 g/l Cu, 4 g/l H ₂ SO ₄ (synthetic)		Spent electrolyte: 30 g/l Cu, 180 g/l H ₂ SO ₄				
Temp: 25°C		Staging: 2 extract, 2 strip				
Mixer Ret'n Time (mins)	O/A* Extract	Organic Cu (gpl) Loaded	O/A** Strip	Raff. gpl Cu	Recovery %	
3	1.44/1	12.0	4.5	2.7/1	1.0	91.5

*no recycle **recycle to O/A 1.5/1

TABLE 10. Example 2 — High Tenor Copper Feed Treated with 30v/o P-5100/Escaid 100®

Feed: 20 g/l Cu, 7 g/l H ₂ SO ₄ . Spent electrolyte: 30 g/l Cu, 150 g/l H ₂ SO ₄						
Temp: 22°C		Staging: 3 extract, 2 strip				
Mixer Ret'n Time (mins)	O/A* Extract	Organic Cu (g/l) Loaded	O/A* Strip	Raff. g/l Cu	Recovery %	
3	3/1	12.7	6.7	2.8/1	2.0	90.0

*recycle to O/A 2/1

TABLE 11. Kinetic Data for 30v/o P-5100/Escaid 100®

Time (secs)	% Approach To Equilibrium	
	Extract	Strip
10	55.7	68.3
20	82.7	89.1
30	100	95.1
45	100	100

Aqueous (extract) 20.2 g/l Cu, 7 g/l H₂SO₄
Aqueous (strip) 30 g/l Cu, 150 g/l H₂SO₄ O:A ratio 2:1

- (6) Rowden, G.A. and Collins, G., Paper presented at a Symposium on Solvent Extraction held at the University of Newcastle-Upon-Tyne, September 7-9, 1976.
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DISCUSSION

J. Agarwal: Have you tried P-5100 for ammoniacal system?

G. Seward: P-5100 is currently used commercially, in the U.K., in a small, ammoniacal-based secondary metal recovery operation. Its performance has been entirely satisfactory and is said to be particularly good during cold weather running when difficulties have been experienced with other reagents. We haven't carried out a full study of the situation that results from its use on an ammonia system. Selectivity is not an important factor with leaching solutions where only copper is present, but based on that situation, there is no reason why it would not work satisfactorily. Selectivity is something we have to study.

Sensitivity of LIX Plant Costs to Variations of Process Parameters

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SUMMARY

The interrelationship of the following process parameters was investigated for the extraction of copper from ammoniacal and acid solutions of cupric sulfate using liquid ion exchange in mixer-settlers: copper, sulfate ion, ammonia concentration and pH in feed, organic and raffinate; copper loading in rich and lean electrolytes; LIX concentration; organic to aqueous (O/A) phase ratio; number of stages; mixing time and settling rate in the extraction, scrubbing and stripping circuits; and feed flowrate. Typical ammonia systems include extraction, scrub and strip circuits. In acid systems, scrubbing is not used.

Based on the above variables, seven typical cases were defined and alternative plant designs were developed for each case. A range of investment and operating costs was then analyzed for sensitivity to plant capacity (12 to 240 tpd range), copper loading in feed (0.6 to 6 gpl), LIX concentration (2.4 to 40 vol. %) and other variables. It is demonstrated that costs are most sensitive to feed flowrate, plant capacity and copper loading in feed. These three parameters are interrelated. Other variables have a smaller effect and/or can not be significantly varied because they tie in with other fixed process parameters.

Parameters Considered

THIS STUDY ANALYSES THE SENSITIVITY of liquid ion exchange (LIX) plant costs to various process engineering parameters. The extraction of copper from acid and ammoniacal solutions of cupric sulfate using mixer-settler plants was investigated. A typical acid plant has an extraction and strip circuit (see Figure 1). Ammoniacal systems may have, in addition, one or two scrub circuits and different ammonia recovery or disposal equipment. One possible configuration is shown in Figure 2.

The following parameters were considered:

- (a) Capacity and efficiencies: copper production rate, overall copper recovery, scrub efficiency, organic losses, acid and ammonia losses.
- (b) Concentrations in major streams: copper concentration, LIX agent concentration in organic, pH.
- (c) Temperature.
- (d) Liquid volume related parameters pertaining to major streams: flowrates, external and internal organic to aqueous (O/A) ratios.
- (e) Mixer-settler size and configuration related parameters pertaining to individual circuits: number of trains, number of stages, mixer residence times, settling rates.
- (f) Equipment related parameters pertaining to individual units: type of equipment used, materials of construction, surge capacities, auxiliary equipment selection.

Most of these parameters are interrelated. Flowrate of the pregnant liquor feed, copper concentration in the

feed, and the overall copper recovery control the production rate. Feed flowrate, together with the external O/A in extraction, fixes the organic flowrate. Overall Cu recovery also depends on a number of mixer-settler size-related parameters. For example, copper recovery can be increased, within limits, by increasing either the number of stages, residence time or LIX agent concentration, other parameters being equal. A concentration increase results, of course, in higher reagent losses.

Equipment-related parameters (Item "f" above) are controlled by the detailed process design which will depend on the requirements for the particular application of LIX technology. These requirements will be affected by such factors as the actual feed composition, level of impurities tolerated in electrolyte, waste disposal restrictions, operating conditions of the selected LIX agent, expected life of equipment, cost and skills of available labor, etc.

The process design of the LIX plant will also depend on the type and parameters of the preceding and succeeding plants, such as leaching and electrowinning, respectively. For example, the copper concentration difference between rich and lean electrolyte required by electrowinning controls the flowrates of these two streams for a given copper production rate. A large temperature difference between the mixer-settlers and the electrolytic cells calls for heaters, coolers and heat exchangers. Finally, company policy may also influence the process design. For instance, management may prefer to spend less on investment at the expense of increased operating cost.

It is impractical to try to take into account all factors affecting a detailed process design. Rather, it was decided to define the following two limiting alternatives to bracket likely design options:

- (a) A conservative design which includes all equipment potentially needed and is generous in terms of size, materials of construction and quality.
- (b) A "bare-bones" alternative which limits equipment to the minimum required.

The two design alternatives will be defined in the next section.

Computer Model

The study had two parts. In the first part, a computer program was written to be used on a routine basis for future cost estimates. The following parameters were selected to constitute the input:

- A. Production rate (tpd Cu).
- B. LIX agent concentration in the organic (vol. %).
- C. Flowrates (gpm) of the following streams: pregnant liquor feed (to be referred to as "feed"), organic, primary scrub solution, secondary scrub solution, electrolyte.
- D. For extraction, primary and secondary scrub (if applicable) and strip circuits: number of mixer trains and stages, number of settler trains and stages, mixer residence times (sec), settling rates (gpm/sq ft).

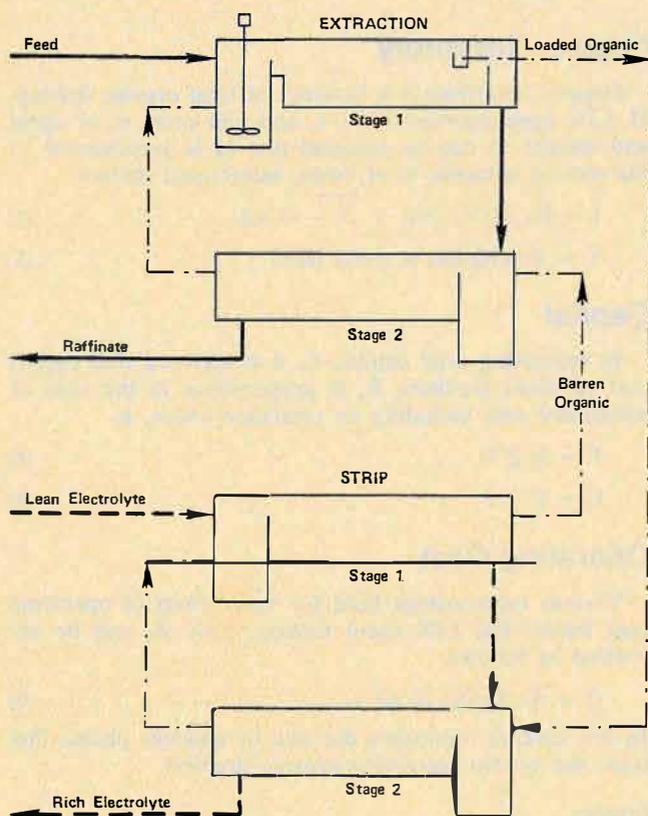


FIGURE 1. Acid plant. Internals are indicated for Stage 1 extraction only. Two stages have been selected for illustration.

E. Cost escalation factors for capital, various raw materials and utilities, and labor.

F. Chemical systems: acid, ammoniacal.

G. Design alternatives: conservative, bare bones.

It should be noted that some input data (e.g., flowrates) represent dependent variables to be first calculated by hand from basic parameters such as feed concentration, production rate, Cu recovery and O/A ratios. Also, the scrub-related input data do not apply to acid systems. Furthermore, the distinction between mixers and settlers in specifying the number of trains and stages makes the configuration flexible. For example, several mixers in series ("stages") or in parallel ("trains") may be connected to a single settler.

The following equipment units, included in the conservative design, are omitted in the bare-bones alternative:

- Feed filters,
- Lean electrolyte cooler and rich electrolyte heater,
- Electrolyte heat exchanger,
- Raffinate and primary scrub solution coalescers (the bare-bones version has only an electrolyte coalescer),
- An extra, second-stage crud removal centrifuge,
- Ammonia recovery column with accessories in the primary scrub circuit. (In the secondary scrub and in the bare-bones version, a bleed stream from the scrub circuit is assumed but no cost for the treatment of the bleed is included.)
- Tanks and pumps associated with the extra equipment.

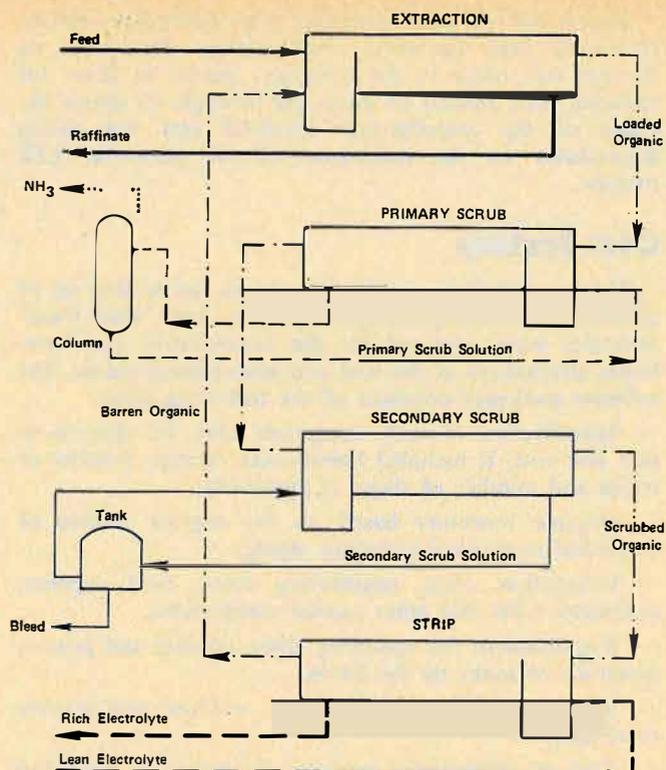


FIGURE 2. Ammoniacal plant. Separate stages are not shown.

In addition, the conservative alternative uses a more comfortable design in the following areas:

- Higher surge capacities for the major streams,
- Deeper settlers,
- A more advanced mixer type permitting scale up to larger sizes.
- More expensive materials of construction,
- More extensive instrumentation,
- In general, equipment of higher quality.

Conservative design in these areas is reflected in higher equipment purchase, installation and engineering costs.

Accordingly, the conservative alternative has higher utilities requirements (for the extra heaters, coolers and pumps) and higher investment cost. For that it buys the following advantages:

- (a) Lower process material losses (LIX agent, ammonia, etc.),
- (b) Lower labor requirements,
- (c) Possibly higher equipment reliability due to better materials of construction,
- (d) Possibly higher on-stream time because of less shut-downs for cleaning,
- (e) Possibly smaller volumes of waste and bleed streams to be disposed of or treated, such as crud, ammonium sulfate, etc.,
- (f) Possibly smaller throughput in some circuits; e.g., a scrub circuit with an ammonia recovery column (such as primary scrub in Figure 2) uses a smaller scrub solution flowrate than a circuit with ammonia buildup controlled by bleeding (such as secondary scrub in Figure 2). If ammonia is scrubbed with a small fraction of electrolyte which is then recycled to the extraction for copper recovery, the organic throughput has to be increased accordingly,
- (g) Lower risk in general.

Except for the latter item (g), these advantages can be translated into operating cost savings. However, no attempt was made in the computer model to allow for reduced costs related to items (c) through (f) above because of the uncertainties involved and the strong dependence on the conditions of the particular LIX process.

Cost Scaleup

This section discusses the algorithms for scaling up or down capital and operating cost. First, four "Base Case" estimates were prepared for the conservative and bare-bones alternatives of the acid and ammoniacal plants. The estimate packages consisted of the following items:

- Specification of each equipment unit. In addition to size and cost, it included horsepower ratings, number of trains and number of stages if applicable,
- Organic inventory based on the organic holdup of individual equipment including piping,
- Installation costs, engineering costs, field expense, contractor's fee and other capital components,
- Requirements for operating labor, utilities and process materials to make up for losses,
- Rates and unit cost of labor, utilities and process materials,
- Cost of supervision, services, maintenance, operating supplies, insurance, taxes, depreciation and other overhead.

Equipment

The cost of any equipment unit, E, can be scaled up or down using the following equation:

$$E = E_0 (Q/Q_0)^a nt (r/r_0)^a (s_0/s)^a \dots \dots \dots (1)$$

The controlling flowrate, Q, for mixers and settlers corresponds to the phase with the higher inlet volume because

the other phase is adjusted to it by an internal recycle to meet the required O/A ratio. The last four factors, representing the number of stages, n, number of trains, t, mixer residence time, r, and settling rates, s, are used only if applicable.

Organic Inventory

Organic inventory is a function of total organic holdup, H, LIX agent concentration, x, and unit costs, u, of agent and solvent. It can be assumed that H is proportional to the sum of volumes, v, of tanks, mixers and settlers:

$$I = H_0 (V/V_0) [xu_L + (1 - x) u_S] \dots \dots \dots (2)$$

$$V = \sum v_0 (Q/Q_0) nt (r/r_0) (s_0/s) \dots \dots \dots (3)$$

Capital

In estimating total capital, C, it is assumed that capital cost of plant facilities, F, is proportional to the sum of equipment cost including an escalation index, e:

$$F = fe \sum E \dots \dots \dots (4)$$

$$C = F + I \dots \dots \dots (5)$$

Operating Cost

Various relationships hold for the scaleup of operating cost items. The LIX agent makeup cost, A, can be expressed as follows:

$$A = A_0 (Q/Q_0) (x/x_0) u_A \dots \dots \dots (6)$$

In this case, Q represents the sum of aqueous phases that leave the system entraining organic droplets.

Power

Total electric power cost, P, is calculated based on horsepower ratings, h, of individual equipment units:

$$P = pu_p \sum h_0 (Q/Q_0)^b nt (r/r_0)^b \dots \dots \dots (7)$$

TABLE 1. Basic Process Parameters

Item	Case Denotation						
	Acid			Ammonical			
	1	2	3	4	5	6	7
Cu in feed, gpl	0.6	6	0.6	6	0.6	6	0.6
LIX in organic, Vol. %	2.4	24	24	24	24	40	40
Cu recovery, %	95	80	95	99	99	99	99
Flowrate example,* gpm							
Feed	35,100	4,170	35,100	3,370	33,700	3,370	33,700
Organic	35,100	4,170	3,510	3,150	3,970	1,890	2,380
Scrub Solution	—	—	—	3,150	3,970	1,890	2,380
Electrolyte	2,020	2,020	2,020	2,020	2,020	2,020	2,020
Number of stages							
Extraction	3	3	3	1	1	1	1
Scrub	—	—	—	2	2	2	2
Strip	2	2	2	2	2	2	2
Residence time, min							
Extraction	3	3	3	2	2	2	2
Scrub	—	—	—	2	2	2	2
Strip	3	3	3	3	3	3	3
Settling rate, gpm/ft ²							
Extraction	2.5	2	2	2	2	1.5	1.5
Scrub	—	—	—	2	2	1.5	1.5
Strip	2.5	2	2	2	2	1.5	1.5

*For 120 tpd Cu.

TABLE 2. Additional Process Parameters

Item	Acid Cases		Ammoniacal Cases	
Concentrations ^(a) , gpl or pH:				
Cu in loaded organic	0.6	— 5.8 ^(b)	5	— 11 ^(b)
Cu in barren organic	0.3	— 0.5 ^(c)	0.3	— 0.6 ^(e)
NH ₃ in feed	—	—	30	—
NH ₃ in loaded organic	—	—	0.3	— 1.2 ^(d)
NH ₃ in raffinate	—	—	30	—
SO ₄ in feed	—	—	30	—
Feed pH	1.5	— 2.2 ^(e)	9.3	—
Temperature, °C	40	—	40	—
Internal O/A ratio	1	—	1	—
On-Stream time, days/yr	333	—	333	—
Design alternative	bare bones	conservative	bare bones	conservative
Scrub efficiency per circuit, %	—	—	— ^(f)	90
Organic loss, ppm	100	50	100	50
Total number of operators				
Minimum — for 25 mixers or less	9 ^(g)	7 ^(h)	9 ^(g)	7 ^(h)
For any additional 25 mixers	5	4	5	4

- (a) Calculated.
- (b) 0.63, 5.8, 5.8, 6.7, 5.4, 11.2, 9.0 gpl Cu for Cases 1, 2, 3, 4, 5, 6, 7, respectively.
- (c) 0.5, 0.35, 0.35, 0.36, 0.36, 0.6, 0.6 gpl Cu for Cases 1, 2, 3, 4, 5, 6, 7, respectively.
- (d) 0.3, 0.72, 0.5, 1.2 gpl NH₃ for Cases 4, 5, 6, 7, respectively.
- (e) pH = 2.2, 1.5, 2.2 for Cases 1, 2, 3, respectively.
- (f) The bare bones scrub circuit has the same configuration as the conservative secondary scrub circuit.
- (g) 2 men/shift.
- (h) 1 man/shift, 1 day man, 2 part-time people.

For pumps and some agitator types, $b = 1$. The factor, p , reflects the difference between installed and consumed power. It also covers additional requirements, such as for lighting, and the conversion from HP to kW.

Process Materials and Utilities

The cost of the remaining process materials and utilities, R , depends on their individual requirements, i , and a controlling flowrate, Q , which may be copper production rate in some instances:

$$R = \sum i_0 (Q/Q_0) u_R \dots \dots \dots (8)$$

Labor

Operating labor cost, L , can be approximated as a linear function of the total number of mixers, m :

$$L = 2080 u_L [M + N J(m/25)] \dots \dots \dots (9)$$

where

$$2080 = (40 \text{ hours/week}) (50 \text{ weeks/year})$$

M is the minimum number of men to operate a plant with 25 or less mixers. N is the number of operators required for any additional group of 1 through 25 mixers. J is an integer function which truncates digits beyond the decimal point.

Total operating

Total operating cost, O , can be estimated as the sum of items computed by Equations (6) through (9) plus additional labor related costs (kL) and capital charges (depreciation, dC , and other, cF):

$$O = A + P + R + L + kL + dC + cF \dots \dots \dots (10)$$

Investigated Cases

Preliminary analysis indicated that costs are most sensitive to production rate and copper concentration in the pregnant liquor feed (called "feed" for short). These two parameters, together with the less important copper recovery, fix the feed flowrate which, in turn, controls the number of trains and size of most equipment. The next most important parameter is LIX agent concentration in

the organic. Accordingly, it was decided to develop plots of capital and operating costs versus feed flowrate with feed Cu concentration and LIX agent concentration as parameters. This combination of variables makes the Cu recovery irrelevant with respect to capital cost of the LIX plant.

Other variables have a smaller effect and/or can not be significantly varied because they tie in with other process parameters. For example, LIX concentration controls organic flowrate but has little effect on the size of extraction mixer-settlers, which primarily depends on feed flowrate as long as the external O/A ratio does not exceed 1.0 and the internal O/A ratio is kept constant, approximately around 1.0. Furthermore, it is not practical to exceed the 20 to 40, and 2 to 25 LIX % range for ammoniacal and acid systems, respectively.

Production rate has been investigated in the wide range of 12 to 240 tons per day. However, for simplicity, feed copper concentration and LIX agent concentration are limited to a high and low value for each chemical system in the present discussion. Feed Cu concentrations of 0.6 and 6 gpl have been selected for both systems. The nominal design LIX concentrations corresponding to these two Cu contents are 2.4 and 24 volume percent, respectively, for the acid system. For the ammoniacal plant 24 and 40% were chosen. While the former concentration represents a common point of comparison of the two systems, the 40% value is a recommended maximum for ammoniacal plants. More concentrated organic solutions are more viscous and may lead to precipitation of LIX-metal compounds. For acid systems, 40% LIX is too high because it would require interstage neutralization and is therefore generally not practical. The use of LIX agent concentration below 24% for a 6 gpl Cu acid feed is also impractical. It would lead to a relatively large organic flowrate, thereby increasing equipment size without any economic advantage.

Seven cases shown in Table 1 were defined, based on the selected feed copper and LIX agent concentrations, and the two chemical systems. Copper recovery, number of stages, residence times and settling rates, as well as additional parameters listed in Table 2, are normal design values recommended in published or company literature.

Some values in Tables 1 and 2 were calculated from literature data and correlations. For the ammoniacal system, a computer program was used for these calculations which is discussed in another Ledgemont paper

TABLE 3. Example of Number of Trains

Item	Basis: 120 tpd Cu						
	Case Denotation						
	1	Acid		Ammoniacal			7
Cu in feed, gpl	0.6	6	0.6	6	0.6	6	0.6
LIX in organic Vol. %	2.4	24	24	24	24	40	40
Bare-bones alternative*							
Extraction	30	4	30	2	20	2	20
Scrub	—	—	—	2	4	2	2
Strip	30	4	3	4	4	2	2
Total no. of mixers	150	20	96	14	36	10	28
Conservative alternative*							
Extraction	10	2	10	1	7	1	7
Scrub	—	—	—	1	1	1	1
Strip	10	2	1	1	1	1	1
Total no. of mixers	50	10	32	5	11	5	11

*Maximum liquid volume of mixer:
7,000 gals for bare-bones alternative
20,000 gals for conservative alternative

TABLE 4. Capital and Operating Costs for 120 tyd Cu

Item	(November, 1976 dollars)						
	Case Denotation						
	1	Acid		Ammonia			7
Cu in Feed, gpl	0.6	6	0.6	6	0.6	6	0.6
LIX in organic Vol. %	2.4	24	24	24	24	40	40
Bare bones alternative							
Capital, \$ million	32	6	20	8	19	7	21
Operating cost, ¢/lb	12	3	16	4	15	5	20
Conservative alternative							
Capital, \$ million	62	14	53	14	36	13	37
Operating cost, ¢/lb	17	5	18	5	15	6	18

presented at the 1977 International Solvent Extraction Symposium⁽¹⁾. Principal literature is listed in References (2) through (5).

Table 3 is an example of the number of trains selected at 120 tpd Cu for each case and design alternative based on maximum mixer volumes of 7 and 20 thousand gallons for the bare-bones and conservative alternatives, respectively.

A uniform number of trains is usually kept in the entire LIX plant. However, in view of the great difference between the minimum number of parallel extraction and strip (or scrub) mixers in the high flowrate cases, it was decided to use more trains in the extraction circuit than in the rest of the plant if necessary. In Case 4, more strip than extraction and scrub trains are required.

TABLE 5. Cost Factors

Factor	Symbol	Value
Capital cost		
Installation and engineering cost, field expense and contractor's fee	f	{ 180% (bare-bones) 250% (conservative)
Contingency	—	25%
Cost basis	—	November 1976
Unit costs of process materials		
LIX agent	u _A	\$20/gal
Solvent	u _S	40¢/gal
Sulfuric acid	—	\$35/ton
Ammonia	—	\$120/ton
Utility rates		
Power	u _E	\$30/MWh
Steam	—	\$2/1000 lb
Cooling water	—	5¢/1000 gal
Other operating cost items		
Labor rate incl. fringe benefits	u _L	\$11/man-hr
Supervision, services, and general and administrative cost	k	80% oper. labor cost
Maintenance, supplies, taxes, insurance, etc.	c	11% capital cost of plant facilities
Depreciation life	1/d	14 yr

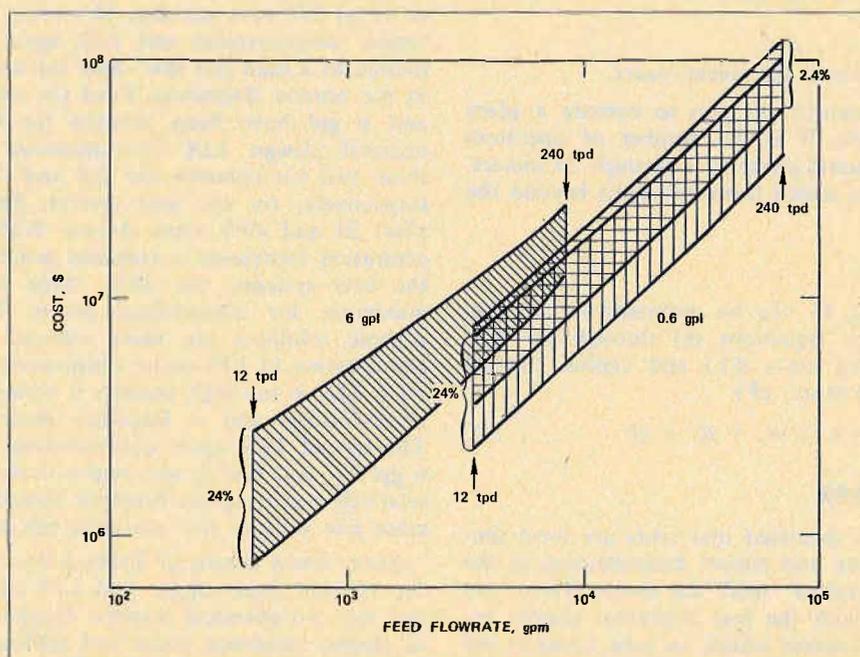


FIGURE 3. Capital cost of acid plants (November 1976 dollars).

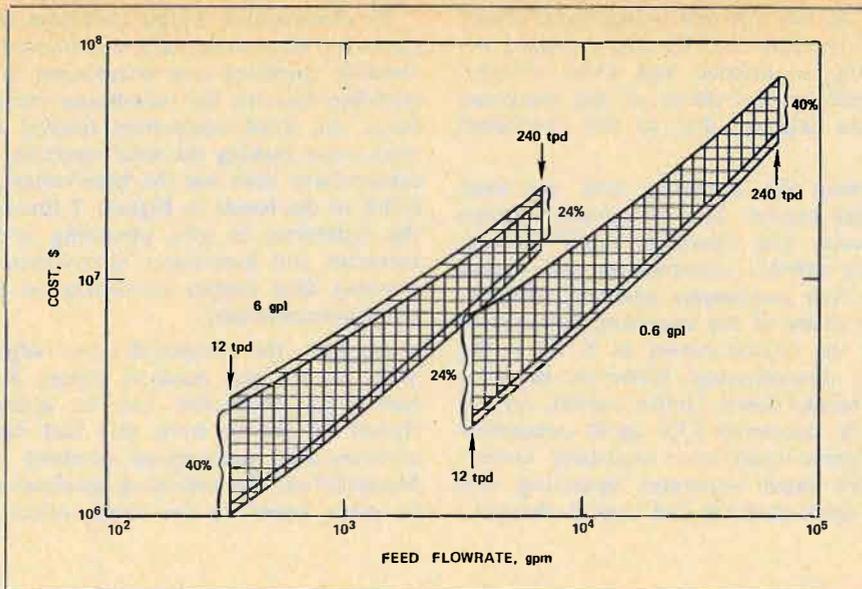


FIGURE 4. Capital cost of ammoniacal plants (November 1976 dollars).

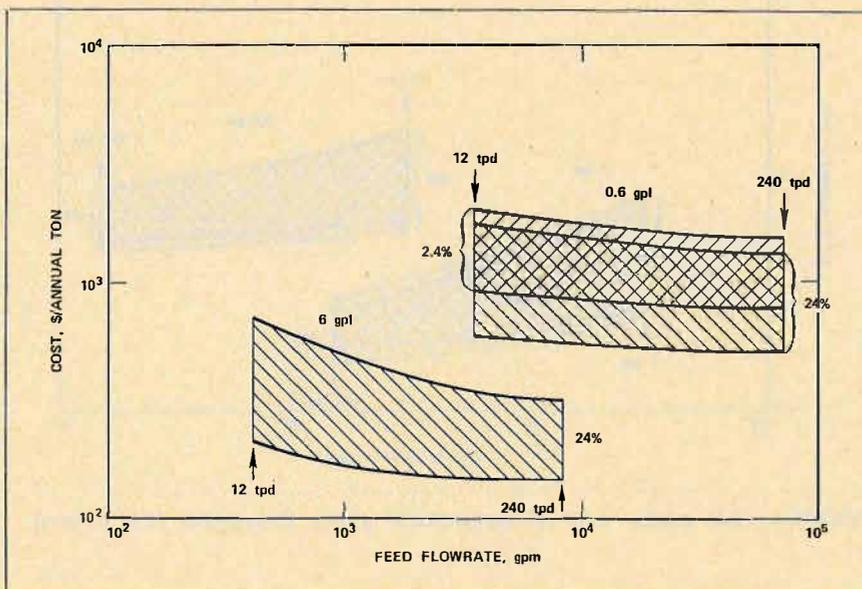


FIGURE 5. Unit capital cost of acid plants (November 1976 dollars).

Results

Costs are shown in Table 4 for the seven selected cases at a production rate of 120 tpd Cu, and plotted in Figures 3 through 10 as a function of feed flowrate, feed Cu concentration and LIX agent concentration. Assumptions underlying the cost estimates are listed in Table 5. As can be seen from the slopes of the bands in Figures 3 and 4, the capital for the conservative design is less sensitive to flowrate than that for the bare-bones alternative. The reason is the greater proportion of equipment not broken up into trains in the conservative design. Its cost varies with a power of flowrate while the cost of extraction mixer-settlers and accessories, arranged in trains, is proportional to feed flowrate.

For a given feed flowrate, capital costs of the conservative plants are 1.6 to 3.4 times higher than those of the bare-bones alternatives, depending on the other parameters. The difference is greater for the acid than for the

ammoniacal systems because of the smaller variations in the total number of mixer-settlers in the ammoniacal cases (see Table 3).

The increase in feed Cu concentration from 0.6 to 6 gpl increases capital cost by a factor of about 2 to 3 at constant flowrate and decreases capital cost approximately 2 to 4 times at constant production rate, other parameters being constant. These variations can not be explained solely on the basis of the total number of mixer-settlers because this equipment represents a far smaller cost fraction in the conservative than in the bare-bones alternatives.

The increase in LIX agent concentration reduces the organic flowrate, particularly in the acid system, and also the scrub solution flowrate in the ammoniacal cases. This causes a drop in capital in most cases. The effect is more significant for the bare-bones alternatives because of the relatively greater contribution of mixer-settlers to the

total cost. However, in the 0.6 gpl ammoniacal cases, capital increases with increase in LIX concentration because the modest drop in organic and scrub solution flowrates is outweighed by the effect of the increased size of the extraction settlers, due to the decreased settling rates.

The factors governing the operating cost are even more complex than for capital. The conservative design reduces process material and operating labor requirements while increasing utilities consumption and capital charges. As all these four parameters decrease with decreasing flowrate, the shape of the operating cost curves in \$/yr is similar to the capital curves in \$. So is the effect of feed copper concentration. However, in other respects, the analogy breaks down. Unlike capital, operating costs increase with increasing LIX agent concentration since it makes organic losses more expensive. Generally speaking, the two most important operating cost components are LIX agent makeup and capital charges.

As conservative design decreases process material and operating labor costs, and utilities are a minor factor, the variable operating cost component is lower for the conservative than for the bare-bones alternative. On the other hand, the fixed component (capital charges) prevails in most cases making the total operating cost higher for the conservative than for the bare-bones design. The relative width of the bands in Figures 7 through 10 indicates that the difference in total operating cost between the conservative and bare-bones alternatives decreases with decreasing feed copper concentration and increasing LIX agent concentration.

Actually, the computed upper edge of the 0.6 gpl — 40% ammoniacal band in Figure 8 corresponds to the bare-bones alternative but no quantitative conclusions should be drawn from this fact because of the inaccuracies and assumptions involved in the computation. Nevertheless, the following qualitative interpretation can be made based on the strong effect of LIX agent loss.

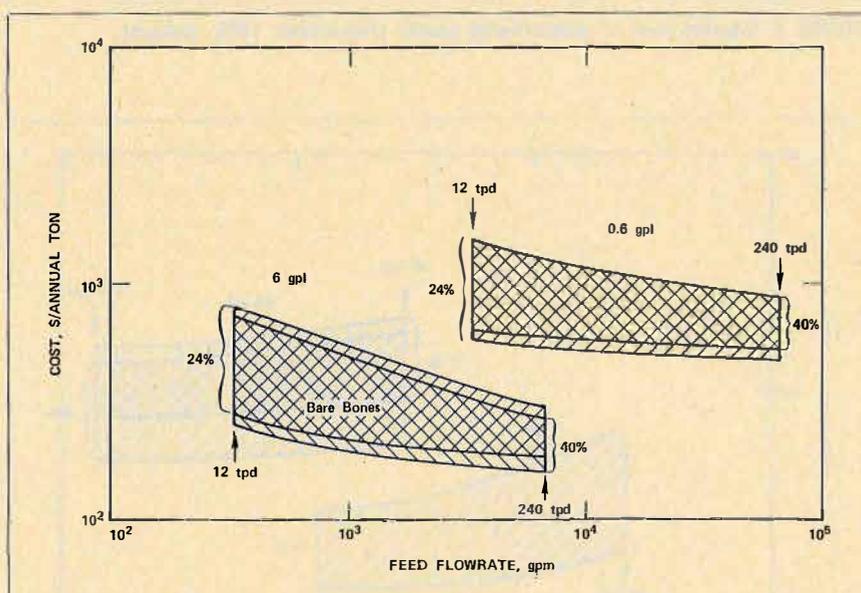


FIGURE 6. Unit capital cost of ammoniacal plants (November 1976 dollars).

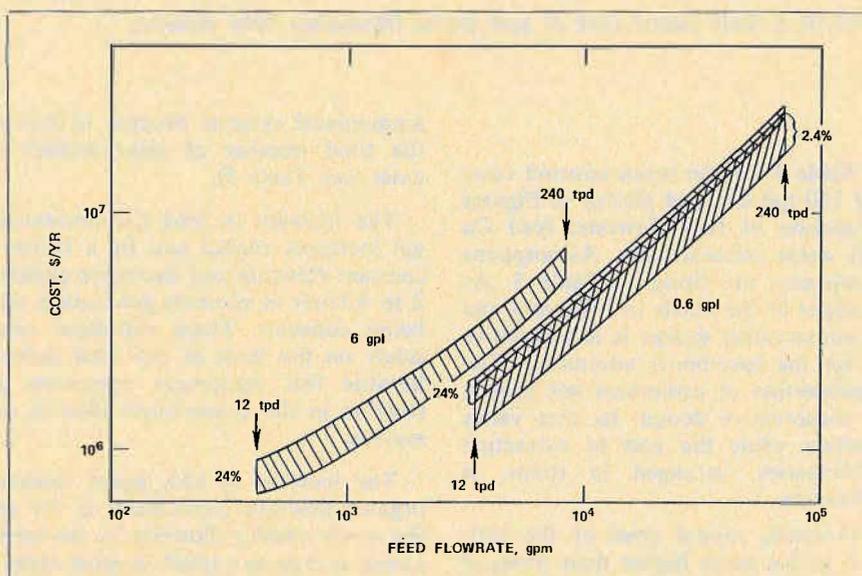


FIGURE 7. Operating cost of acid plants (November 1977 dollars).

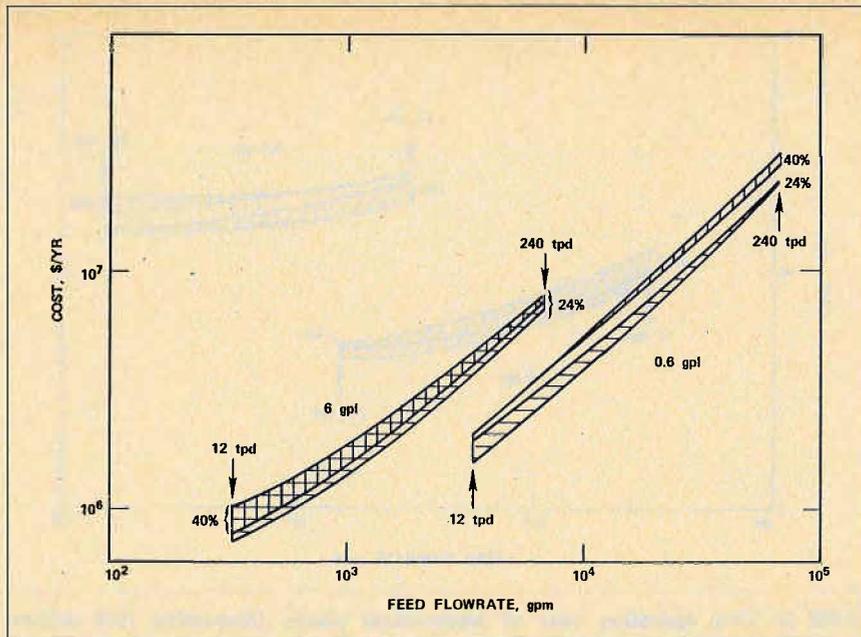


FIGURE 8. Operating cost of ammoniacal plants (November 1977 dollars).

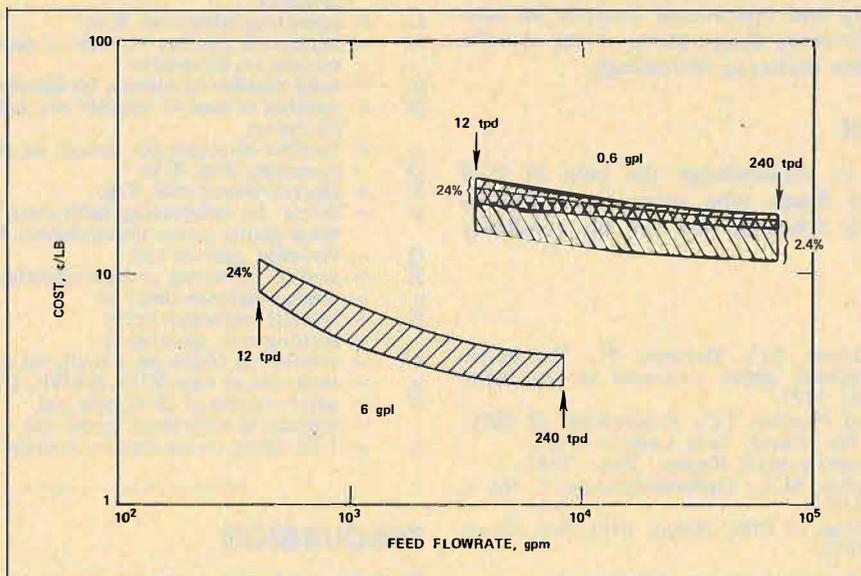


FIGURE 9. Unit operating cost of acid plants (November 1976 dollars).

Low Cu concentration calls for a high feed flowrate which, in turn, increases organic entrainment. The entrainment is reduced by conservative plant design. The reduction is more significant for concentrated organic because it costs more per unit volume.

Conclusions

Figures 8 through 10 express the generalized cost sensitivity of LIX plants to major process parameters. Depending on design philosophy and the conditions unique to a particular application, actual costs are likely to fall within the area ranges indicated on these charts. The charts can thus be used to develop preliminary estimates on the effects of the principal process parameters on costs.

The charts provide interesting insight into the different effects on capital and operating cost of a particular para-

meter. For instance, investment cost of a dilute feed (0.6 gpl Cu) acid plant is higher for a dilute (2.4% LIX) than for a concentrated (24%) organic, while the opposite is true for operating cost. Accordingly, a careful profitability analysis is required in such cases, particularly checking the actual copper recovery, and LIX agent price and losses.

The economics of this study appear to indicate that simple, inexpensive plants with minimum equipment are economically superior to more fully equipped conservative plants. This conclusion, however, is only valid for the particular assumptions used in the present analysis. As was pointed out above, the analysis did not quantify the cost impact of a number of potentially important engineering factors including equipment reliability as a function of materials of construction, on-stream time, crud treatment under high ppm solids load, and risk in general as a function of design. These factors are difficult to

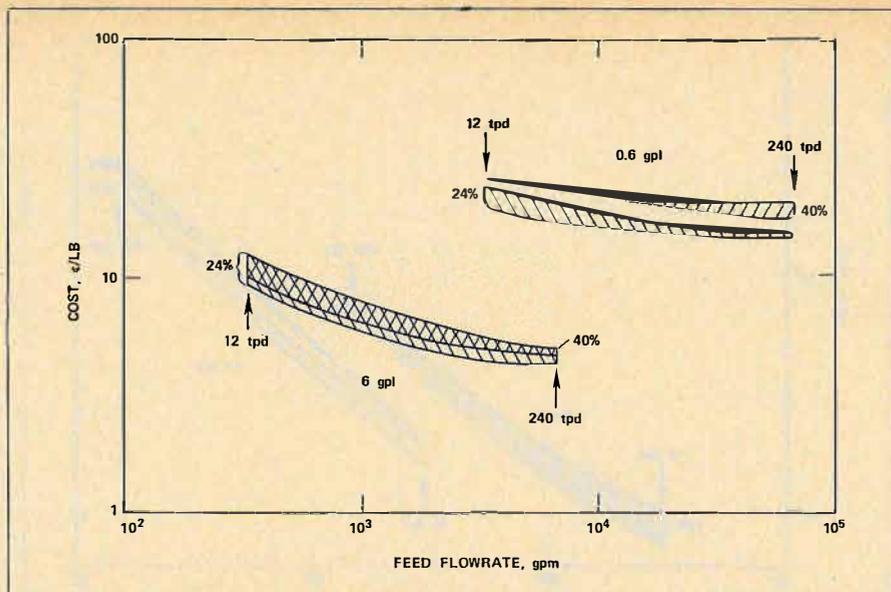


FIGURE 10. Unit operating cost of ammoniacal plants (November 1976 dollars).

generalize upon, but must be carefully evaluated in any specific application. Accordingly, it is recommended that a thorough engineering and operational analysis be conducted during the preliminary design phase of any specific application of liquid ion exchange technology.

Acknowledgment

The authors wish to acknowledge the help of Paul Beauchemin and Saul Rosen who wrote the computer program, and Timothy Schwalm who ran the sensitivity cases.

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SYMBOLS

- A = LIX agent cost, \$/yr
- a = equipment cost scale-up exponent, no dimension
- b = electric power scale-up exponent, no dimension
- C = total capital cost, \$
- c = factor for capital charges in operating cost (maintenance, supplies, taxes, insurance, etc.), no dimension
- d = depreciation factor (reciprocal of depreciation life for straight-line depreciation), no dimension
- E = individual equipment cost, \$
- e = escalation factor (ratio of cost indices), no dimension
- F = capital cost of plant facilities, \$
- f = factor for installation and engineering costs, field expense and contractor's fee, no dimension
- H = organic hold-up, gal
- h = individual equipment horsepower rating, hp
- I = organic inventory cost, \$
- i = individual requirements for process materials and utilities, lb/yr, gal/yr, etc.
- J = integer function

- k = factor for labor related items of operation cost (supervision, services, general, administrative, etc.) no dimension
- L = operating labor cost, \$/yr
- M = maximum number of men to operate the first 1 to 25 mixers, no dimension
- m = total number of mixers, no dimension
- N = number of men to operate any additional group of 1 to 25 mixers
- n = number of stages per circuit, no dimension
- O = operating cost, \$/yr
- P = electric power cost, \$/yr
- p = factor for integrating individual horsepower ratings to total plants power requirements, kW/hp
- Q = flowrate, gpm or tpd
- R = cost of remaining process materials and utilities, \$/yr
- r = mixer residence time, sec
- S = solvent (subscript only)
- s = settling rate, gpm/sq ft
- t = number of trains per circuit, no dimension
- u = unit cost or rate, \$/lb, \$/kWh, \$/gal, etc.
- V = total volume of all vessels, gal
- v = volume of individual vessel, gal
- x = LIX agent concentration in organic, volume fraction.

DISCUSSION

J. Dasher: Having only been associated with single-line plants and knowing no reason for multi-line plants, why did you assume the luxury of many small units for the bare bones case?

I. Klumpar: The paper is based on actual quotations and engineering reports. The design and scaleup of agitated tanks becomes a problem for the mixing of great volumes. Some contractors apparently find it less expensive to use multiple smaller standard mixers rather than bear the costs of developing a single bigger mixer and taking the risk of its malfunctioning. Please note that the less expensive "bare bones case" mixers and the more expensive "conservative case" mixers are limited to 7,000 and 20,000 gal, respectively. As feed flowrates range from 300 to 70,000 gpm and residence times from 2 to 3 min, (per phase), multiple-train plants become a necessity in some cases.

Operating Problems: Panel Discussion

Chairman: J. Dasher.

J.R. Orjans, Nchanga: Taking into account the sophistication of the solvent extraction operation as compared to a conventional concentrates leach — direct electro-winning process, I must say that we were astonished in Zambia that the start-up of our tailings leach plant went as smoothly as it did. Certainly we had mechanical problems but they were generally associated with the solids-handling circuit rather than the solvent extraction circuit probably because the solvent extraction circuit was studied in much more detail than the solids-handling circuit. However, we did have some mechanical problems particularly with bursting feed lines to the solvent extraction circuit. These lines were a composite PVC fibreglass resin product, and as a result of this, we have decided to install stainless steel piping in the new plant.

I would like to speak on some metallurgical problems we have had. The problems I would like to touch on are the filtration problem and the problem of gypsum-scaling in feed pipes and instrumentation, the excessive crud formation and large organic losses that result from that, and also the carryover of solid impurities into the tank house.

Starting first with the filtration, we have 100-200 ppm solids coming into the filtration circuit from the thickener where we separate the copper-bearing solution from the leach pulp. In the filters which are pressure sand filters, we have a problem with gypsum scaling, leading to agglomerates forming and the nozzles choking frequently. As a result of this we seldom reduce the solids below 100 ppm, and often the solvent extraction circuit is fed with solutions containing 150-200 ppm solids, probably a world record. This problem did not show up in the pilot plant work, possibly because of the better backwashing in a pilot plant filter compared with a commercial sand filter. The scaling of pipes results from the gypsum supersaturation (60-80%). The gypsum solubility is calculated at 0.5 gm/l CaSO_4 and generally the feed solutions are at the 0.7-0.8 level, so we have severe scaling both in the filter and in the pipes, causing downtime and restrictions in our feed flow rates.

The next problem I wish to touch on is crud formation. This partly results from gypsum precipitation and partly from silicates precipitating. We have up to 1 gm/l soluble silica in our pregnant liquor. We believe that the silicates are partially extracted with the organic phase and then the silicates polymerize when the organic is contacted with the strong acid at the slightly higher temperature of the strip circuit. The crud again causes down time. We have heavy organic losses in our crud, up to \$4,000,000 per year. Our twenty settlers are dug out twice a year, and we can find a couple of feet of crud in each settler. This is treated in the centrifuge which unfortunately is slightly undercapacity.

Also, as I said, we have a carryover of solids and solution impurities from the leach circuit into the electrolyte circuit. As most people do, we considered solvent extraction to be a means of concentrating the copper in solution and also a means of rejecting impurities. It has proved

however, that the impurities in our electrolyte are more or less the same as in our leach solution. In speaking to my American colleagues, I find that some of them have similar problems. This, of course, has quite an effect on the quality of the copper produced. There are two mechanisms whereby these impurities are coming into the electrolyte. One, because we operate our mixers in the aqueous continuous mode and because we have air entrained in our mixers, the dispersion bands and crud tend to expand and float up into the loaded organic phase and are carried over into the strip circuit. So we have large quantities of solids in our electrolytes. We also have large entrainments in the organic phase of the aqueous phase, up to 500 ppm. At 500 ppm aqueous phase in the organic phase, we turn over the whole electrolyte in a couple of months so high impurity levels are to be expected. This could be overcome by a wash stage which we have seen in a pilot plant in Zaire where the loaded organic is scrubbed to remove the solids and solution.

In summary, these problems which I have touched on here all depend more or less on the gypsum supersaturation of the leach solution. We have done considerable laboratory work on gypsum removal, and recently started a large pilot plant to study various means of gypsum removal and new filtration systems.

J. Dasher: I will ask Mr. Alan Kennedy to give us some additional information on his operating problems.

A. Kennedy: One of our minor problems, because of our big settlers and so on, has been the measurement of our organic losses. In the early stages of operation we went 5 months without adding any organic other than diluent to make up for evaporation losses, and we could not see any changes in our inventory according to our tankage. Since then we have been adding make-up organic on the assumption that our losses were 50 ppm and we have not observed any changes in inventory. This is somewhat worrisome since we do have crud in the settlers, and so on, which is measured as organic.

Recently our extraction dropped somewhat over a period of four months, about 6%. At the same time the acid concentration in our feed climbed significantly because of a change in our leaching practice. At first we attributed the drop in extraction to the higher acid concentration in our feed, but on checking all possible parameters, we found that the ratio of LIX 65 to LIX 63 in the LIX 64N had decreased significantly. General Mills is working on this problem now. I understand from them that the formulation of LIX 64N is such that if the make-up is 100 ppm, the correct ratio will be maintained. With us adding a make-up of 50 ppm the LIX 63 content has been decreasing, giving a small problem there.

Another problem we had is a result of the decision not to cover the settlers. With high wind velocities, the surface of the organic is stirred, penetrating down as far as the interface, stirring up some of the "gunk", with the result that the phases become hazy as they come over the weirs. This gives us a particular problem where the organic comes out of the final stripper stage and proceeds to the last stage of extraction. The entrained "gunk" also entrains electrolyte, and consequently causes a decrease

in efficiency in the third stage of extraction. This may increase the raffinate copper content, raising the level from 0.12 Cu up to 0.18. It usually takes about two days after a high wind for it to settle down again.

The only other thing I have is not a problem but one of our findings in checking the kinetics of our circuit. We were running our strippers at a 1.1-1.2 organic/ aqueous ratio because we understood that it was necessary to keep the organic continuous in order to keep down entrainment in the tank house. To see if we could get faster transfer, we reversed this and ran it aqueous continuous, and during our evaluation and for four or five days our tank house people asked us what we were doing because there was no longer any organic coming into the tank house. Formerly we transferred about 20 gallons a day back to the circuit. Since we made this change, the amount of organic going into our tank house is insignificant, a couple of gallons per week at the most. We have now been running aqueous continuous for eight months. I might just say that since that time our cathode impurities have climbed slightly. They were running 2 ppm Pb and are now 4 to 5 ppm Pb. At the same time we have noted a slight deterioration of our cathode "ears". We think that there is a relationship between these factors. For example, the organic which was getting into the tank house was coating the cathode ears and this was protecting them from deterioration. Certainly we noted that all of our demisting balls which were tanned-looking, cleared up within a week of the change.

J. Dasher: I would like to introduce Ron Longwell who is running the first solvent extraction plant for copper recovery, using LIX.

R. Longwell: I find that my colleagues have covered most of the problems that we also have, such as crud and entrainment problems. We do enjoy high extraction efficiency in our plant, about 93%. We have a differently designed plant in that we run with a top-fed mixer which mixes only, and has a bottom discharge through a pump to the settlers. Our total organic loss over the years consistently has been 180 ppm. We have high entrainment going to our tank house, about 100 ppm organic, and we have six cells of flotation on this stream which removes about 50% of the entrainment. Our electrolyte is quite a dirty electrolyte. Comparing it to the Nchanga operations, the soluble impurities of the electrolyte are quite high, not as high as our feed stream but still much higher than we would like to have. This is again due to aqueous and sludge entrainment in the pregnant organic coming over into the stripper circuit. This plant was designed 10 years ago and put on stream with a 3:1 organic to aqueous ratio hopefully for a higher copper feed tenor than currently enjoyed. The higher feed tenors were not realized and we are now operating on a 1.5:1 organic to aqueous in the plant, treating twice the volume throughput and running with a 50% greater copper output than we were at that time. While there were problems in that plant, it has operated very satisfactorily over the years.

J. Dasher: I would like to call on Mr. Richard Aros who has five plants at Benson, Arizona with Cypress Johnson.

R. Aros: The primary problem we have at Cypress Johnson is that we have an ambient circuit which means that the temperature varies from 74°F in the summer to 49°F in winter. Consequently, in winter-time our phase disengagement is poor. Our throughput has to be slowed sometimes by as much as 20% because of organic losses, gross entrainment that we get in the organic stream and the raffinate. Some of the things that have been done to conserve heat included changes in our

leach system, going from an evaporative application system like the Bagdad wiggler to a drip system. Over the past year our incoming temperature has on the daily average increased about 5°. Also our dumps have been getting greater and deeper, and the area has been increasing as well, and also our winter was not as cold. We feel, though, that the change in the leaching system had a great deal to do with this because in addition to the rise in temperature, the copper tenor went up, the acid consumption went up significantly and the pH has never dropped as low as it was prior to these changes in application.

Like the other plants up here, we also have problems in crud formation. As Mr. Dasher said, we have five parallel trains with three extractors and two strippers which are quite small. After six months of operation they were blocked to the point where they had to be shut down individually to remove the sludge material which had built up. This was stored until we had facilities to treat it. In the first year of operation our organic losses were 60 ppm. This year our losses are slightly higher because we are treating the sludge more often to avoid the difficulties experienced in the first year.

Hand in hand with the temperature problem there have been periods of gross entrainment of the leach liquor into the organic, and we stored loaded organic. This would give rise to excess electrolyte because we had no way of bleeding it off at a fast enough rate. We now have a way to bleed it off. In addition to that, the organic carryover into the tank house was significantly greater in cold weather. To help eliminate this, a couple of large tanks have been added to increase retention time and surface area to promote disengagement. The flow is drawn from the bottom of both tanks which have baffles to keep the feed from going directly out of the exit. There is air flotation in one of the tanks. One of the most significant things that was done was to place the tank after the starter cell so that even if there was entrainment, it was warmed in the starter cell, and underwent a certain amount of flotation by the starter cell gases. Then further disengagement took place in the tank before it got into the recirculating load.

Another problem we have is air-entrainment in our mixers. Vortexing takes place and the solutions drop perpendicularly into the bottom of the settlers which entraps considerable air. Standpipes have been installed to reduce the air surges but excess air still comes in. We had some trouble with the mixers due to their slightly conical design. Increasing the speed from 45 rpm to 55 rpm increased extraction efficiency 3 to 5%.

J. Dasher: We also have the representative of the Cypress Bagdad operation. I would like to ask Mr. Ray Jones to describe some of his problems.

R. Jones: Our plant was commissioned August 12, 1970. It was designed for 40,000 lb/day of copper cathode, which was reached by Sept. 10th. The plant has given 99.9% availability. We did have the sludge problem which is inherent to the rest of the industry. We have found two types of sludge. One is the fungus type which is predominant in the extractor part of the plant. It thrives in the aqueous phase but presents no problem in the plant operation, and contributes only slightly to the organic loss.

The major problem sludge is about 98% silica and is dispersed between the organic and aqueous band. Its characteristic is about 50% organic, 28% aqueous or electrolyte and 12% silica, to make up the total volume of material. It will collect to a point where it will overflow the settler discharge or go into the organic where it

causes what is called a sludge runaway. The raffinates become higher than the feed and the barren electrolyte becomes higher than the pregnant electrolyte. The iron assays are elevated tremendously due to the entrainment of the pregnant leach solutions into the number one strip so the irons go up dramatically in the tank house. About the only alternative available is to shut the plant down to settle down the circuit, and restart it. The sludge is dumped and has to be stored.

Chemical treatment of the sludge affected the organic. We finally developed, with De Laval, a centrifuge which would yield unaltered organic for return to the circuit. Prior to centrifuging of the organic, the organic losses were 60 ppm. After centrifuging of the sludge the organic losses for the past two years have run about 40 ppm or 0.04 gal per 1000 gal. The organic is worth about \$1.00 per gal.

J. Dasher: The audience can now direct questions to the panel.

K. Hester: If the panel had its choice, what would you do to design for removal of the sludge for treatment?

R. Aros: We have a very effective method for our relatively small system. We remove the sludge from the interface by suction with a pump through removable doors on the top of the settler. It is important to use a transparent plastic suction pipe so that the operator can see what he is drawing off.

J.R. Orjans: Our centrifuge is satisfactory although not of the right capacity. We have a semi-continuous horizontal bowl centrifuge. We remove our sludge as described above, and feed it into the centrifuge continuously as long as we get a clear overflow. When the overflow becomes cloudy, the feed is stopped and the bowl is automatically cleaned. Sewage treatment centrifuges should have good possibilities for sludge treatment.

A. Kennedy: I would like to make a comment on sludge removal. Getting sludge from an operating circuit by some limited manpower method is desirable, and I have a scheme in mind which I offer for comment. This would be a small trolley, mounted above the settler. It could go through a slot with possibly only four suction parts on it and a very low rate of pumping, extract the sludge to a holding tank for subsequent treatment. We have found that using a half-inch shrouded header pipe, it has to be continually moved, say every half hour. A small moveable unit which could be chain driven with a reversing switch, could move back and forth on a continuous basis and should work very well.

I. Itzkovitch: Our work shows that the solubility of LIX 65N is much greater than LIX 63. Would any member on the panel comment on whether they have had to add LIX 63 to their circuit, indicating that the LIX 63 is decomposing at a faster rate than the LIX 65N?

A. Kennedy: We did find that we had had to add LIX 63. Over the past two months we have added six or seven barrels. Our ratio had fallen to 60:1 whereas the recommended ratio is 30:1. We believe that we have it back to that now. My understanding is that

if your makeup is equivalent to 100 ppm based on the flowrate, it will approximately keep the ratio in that range.

J.R. Orjans: I would like to make a short comment on this also. Our effective LIX 63 content from kinetic tests and also laboratory tests seems to be about half that of the LIX 63 content in the makeup. This, in spite of the fact that we turn over our inventory in not much more than one year, indicates that there is a very fast degradation of LIX 63 in our circuit. I should point out that our circuit possibly runs at a slightly higher temperature, and definitely a slightly more acid tenor than the American circuits. We have bought LIX 63 recently and introduced it into the circuit. We do not have any figures yet on the overall economics.

C. Farrow: My question is particularly directed to Mr. Orjans but possibly other panel members could also possibly comment regarding the debate on covered or uncovered settlers. Does Nchanga have plans for the future settlers to eliminate the roof over them?

J.R. Orjans: I can definitely say, "No", regarding those for the tailings leach plant expansion. I am astonished to hear that City Service doesn't have large losses of organic. In fact, from the loading capacity test work and from the makeup we can see a preferential loss of the kerosene, in spite of the fact we have roofs, indicating that there is evaporation. Our roofs cover most of the settlers but the weir ends are open. As you may have seen from the photograph on display, the roofs next to the weirs were very dark, probably due to a spray or evaporation coming out of the weir. We are concerned about evaporation, and in fact we will have better roofs in the new plant, covering it entirely.

A. Kennedy: I would like to make a comment on our study as to whether we should have roofs or not. In the first place, I do not see that a roof helps to prevent evaporation, unless it is completely sealed. In Arizona particularly, a roof concentrates the heat, and it is much hotter in an enclosed space than outside, so it may actually increase the evaporation. Anyway, our losses have been very satisfactory despite our open units. The aspect that we worried about was phototropic reactions that we could not identify. We did an extensive literature search but found no references regarding them. The only thing that we have come up with is the wind action.

J. Dasher: I would like to make a comment on roofs from a historical viewpoint. At the time we were concerned with the Rancher's plant, there was knowledge from the Bagdad and Duval pilot work that there were bacteria which grew in solutions. They were promoted by air and it would be desirable to keep air away from the solutions so we put a cover over the settlers with the intent of excluding air. However, the solutions were high enough in copper to prevent any bacteria from growing.

If there are no further questions I would like to thank the members of the panel, and call on the chairman of the conference, Mr. Gordon Ritcey for his summary of the week.

The first part of the report deals with the general situation in the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The second part of the report deals with the financial situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The third part of the report deals with the military situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The fourth part of the report deals with the political situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The fifth part of the report deals with the social situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The sixth part of the report deals with the economic situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The seventh part of the report deals with the international situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The eighth part of the report deals with the cultural situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The ninth part of the report deals with the scientific situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The tenth part of the report deals with the artistic situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The eleventh part of the report deals with the religious situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The twelfth part of the report deals with the legal situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

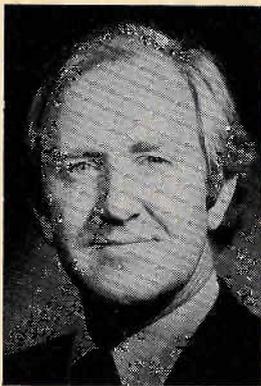
The thirteenth part of the report deals with the educational situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

The fourteenth part of the report deals with the health situation of the country and the progress of the war. It is a very interesting and well-written account of the events of the year.

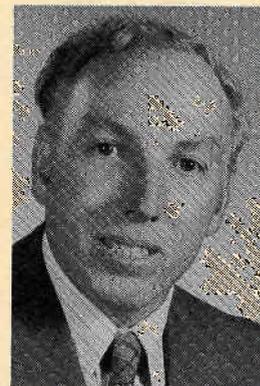
Chapter 12

Uranium Processing

Session 19



Dr. P.J.D. Lloyd



G.M. Ritcey

Session Co-Chairmen

Chapter 13

Thermodynamic Properties

Section 13.1

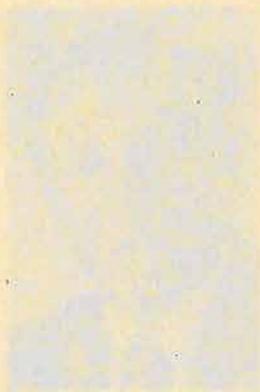


Figure 13.1

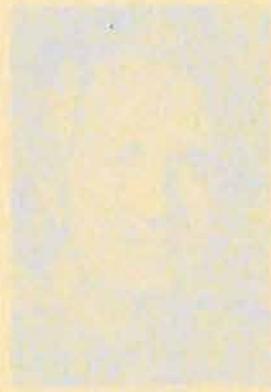


Figure 13.2

Section 13.2

A Review of Progress in the Application of Solvent Extraction for the Recovery of Uranium from Ores Treated by the South African Gold Mining Industry

S.A. Finney, Nuclear Fuels Corporation of South Africa (Proprietary) Limited

ABSTRACT

Gold, uranium and iron pyrites are present in the ores mined by the South African gold mining industry. While a high degree of efficiency can be achieved when recovering any one of these materials by itself, difficulties arise when all are recovered simultaneously because the operations of the three recovery circuits are interdependent. To a large extent the problems associated with recovery of uranium using resin ion-exchangers have been overcome by the use of solvent extraction. Of the twelve South African uranium plants, eight use solvent extraction solely, two use combined resin/solvent extraction and the two remaining plants retain the resin exchange process. A brief history of uranium recovery in South Africa and details of present solvent extraction operations appear in this paper.

CHAIRMAN'S INTRODUCTORY REMARKS

G.M. Ritcey: This afternoon one main paper on uranium (for ISEC an unfamiliar topic) is on plant operations. In the 16 years or so since the first ISEC at Gatlinburg I suppose that it is inevitable that solvent extraction, particularly in hydrometallurgy, should have gone from a toy to actual practice, and up to now we really haven't reviewed what it takes to run a plant. We have had a look at the basic chemistry over the years. We have had quite a good look at the design of plants. We have had a little bit of a look at the construction of plants, but when it comes to plant operation, we have done very little. In South Africa, there are quite a few solvent extraction plants running on the amine system for the recovery of uranium. They are all in close proximity, running on very similar chemistry, and we thought that the experience that has been gained from this would be of value to the people here this afternoon. Initially, we attempted to get separate papers out of all of the individual plants but in the end it was decided that it was best to put together a comparative paper and to call for any contributions to the final comparison from the individual groups which were responsible for the various plants. We have in fact two such contributions. The main paper comparing the various plants, contrasting their performance, is to be given by Mr. Stewart Finney.

Introduction

THE DEVELOPMENT OF SOLVENT EXTRACTION PROCESSES for the recovery of uranium from South African leach liquors has been described in several papers^(1,2,3,4,5,6,7). The intention of this paper is to summarize much of this information particularly insofar as it applies to the practical application of the processes and, by including more recent information, to present the current state of operations by uranium producers which are members of the Chamber of Mines of South Africa.

For those unfamiliar with the South African gold mining industry, there are 40 gold mines in operation. There are 12 uranium plants situated at ten of these mines and the material treated is drawn from 14 mines. The combined production rate is now over 4000 tonnes U_3O_8 per year. In the peak period of uranium production in 1959, nearly 6000 tonnes U_3O_8 were produced by 17 plants treating material from 27 mines. Many of those mines have now closed and the uranium plants have been dismantled.

In addition to uranium, many plants also produce a pyrite concentrate which is burned to produce sulphuric acid for use in the uranium plants. The pyrite calcine is usually treated to recover the gold it contains. There is thus a considerable interaction between the gold, uranium and pyrite sections of the various plants, which must be borne in mind both when operating and when making changes in any one of them.

Gold is extracted prior to uranium at five of the metallurgical complexes while at the others uranium is extracted first, both technical and economic considerations governing the choice of method used. Pyrite is recovered before gold and uranium extraction at several mines and in these cases uranium is extracted before gold in order to destroy the flotation reagents which otherwise interfere with cyanidation of gold.

Factors Influencing Recovery Methods

As an introduction to the present practice of solvent extraction in South Africa, it is necessary to refer to earlier investigations leading to the development of a suitable uranium recovery process.

While gold and uranium are found in combination in the ore it should be made quite clear at the outset that the South African industry is gold-orientated, uranium being considered by most mines as a by-product. This is understandable when it is realized that, although the mass of uranium in a tonne of typical ore treated is about 18

TABLE 1. Solvent Extraction: Information on Equipment and Operations.

		Buffelsfontein	Vaal Reefs (East)	Vaal Reefs (West)	West Driefontein	West Rand Consolidated	Western Deep Levels
<u>ORGANIC PHASE</u>	% v/v: Alamine 336	5	5	5	5	5	5
	Iso-Decanol	-	2	2	2	-	2
	Solvesso 150	35	-	-	-	35	-
	Kerosene	60	93	93	93	60	93
<u>EXTRACTION Mixers</u>	No. M/S units	2 x 4	4	2 x 4	4	4	4
	Type: Turbine		Lurgi pump	Lurgi pump	Pump mix	Turbine	Pump mix
Settlers	Ratio Organic: Aqueous	1 : 1	1,1 : 1	1 : 1	1,5 : 1	1,5 : 1	1,1 : 1
	Continuous phase	Organic	Organic	Organic	Organic	Organic	Organic
Settlers	Type	Circular	Lurgi	Lurgi	Rectangular	Rectangular	Circular
	Baffle	Pierced plate	-	-	-	Picket fence	-
	Solid contaminant	Fungus	Fungus	Fungus	Fungus: Tar	Nil	Fungus
<u>SCRUB Mixers</u>	No. M/S units	5	4	2 x 4	5	5	4
	Type: Turbine		Lurgi pump	Lurgi pump	Pump mix	Turbine	Pump mix
Settlers	Ratio Organic: Aqueous	1 : 1	1 : 1	1 : 1	1 : 1	6 : 1	2 : 1
	Continuous phase	Organic	Organic	Organic	Organic	Organic	Organic
Settlers	Reagent addition	SC 1	Bufflex eluate	Water	H ₂ SO ₄	Nil	Water
		SC 2	Bufflex eluate	Water	"	Nil	Water
		SC 3	Water	Water	NH ₄ OH	H ₂ SO ₄	Water
		SC 4	Water	Water	"	Nil	Water
		SC 5	Water	-	-	Water	-
Settlers	Type	Circular	Rectangular	Rectangular	Rectangular	Rectangular	Circular
	Solid contaminant	Crud	Crud	Ore fines	Crud	Nil	Nil
<u>STRIP Mixers</u>	No. M/S units	4	4	2 x 4	4	4	4
	Type: Turbine		Turbine	Turbine	Pump mix	Turbine	Pump Mix
Settlers	Ratio Organic: Aqueous	1 : 1	1 : 1	1 : 1	1 : 1	1 : 6	3 : 1
	Continuous phase	Aqueous	Organic	Organic	Organic	Aqueous	Organic
Settlers	Reagent additions	ST 1	NH ₄ OH : 3,9	NH ₄ OH : 2,5	NH ₄ OH : 4,0	NH ₄ OH : 3,4	Nil : 3,3
	and	ST 2	NH ₄ OH : 4,3	NH ₄ OH : 3,5	Nil	NH ₄ OH : 3,9	NH ₄ OH : 3,6
	pH	ST 3	NH ₄ OH : 4,7	NH ₄ OH : 4,0	NH ₄ OH : 4,5	NH ₄ OH : 4,2	NH ₄ OH : 4,0
		ST 4	NH ₄ OH + (NH ₄) ₂ SO ₄ : 5,0	(NH ₄) ₂ SO ₄ : 5,0	(NH ₄) ₂ SO ₄ : 5,0	NH ₄ OH + (NH ₄) ₂ SO ₄ : 4:8	NH ₄ OH + (NH ₄) ₂ SO ₄ : 4:8
Settlers	Type	Circular	Rectangular	Rectangular	Rectangular	Rectangular	Circular
	Solid contaminant	Crud	Crud	Crud	Nil	Crud	Crud
<u>REGENERATION Mixer</u>	No. M/S units	1	1	2 x 1	1	1	1
	Type: Turbine		Turbine	Turbine	Pump mix	Turbine	Pump mix
Settler	Ratio Organic: Aqueous	1 : 1	1 : 1	1 : 1	1 : 1	7 : 1	8 : 1
	Continuous	Organic	Organic	Organic	Organic	Organic	Organic
Settler	Regenerants	R 1	Na ₂ CO ₃ + NH ₃	NaOH	Na ₂ CO ₃ + NaOH	Na ₂ CO ₃ + NaOH	Na ₂ CO ₃ + NaOH
	pH		9,2	9,5 - 10,0	10 - 11	9,2	10
Settler	Type	Circular	Rectangular	Rectangular	Rectangular	Rectangular	Circular

times greater than the mass of gold present, (200 g uranium and 11 g gold) the money value of this gold (February 1977) is about four times that of the uranium.

As the gold price rises and working costs can be reasonably contained, lower grades of gold-bearing ore can be profitably mined but the uranium grade, already low by world standards, is less. Moreover, for a constant tonnage treated, a more intensive leach is required to recover the desired quantity of uranium and, in consequence, additional impurities are dissolved. This affects the recovery of the uranium and the purity of the final product.

In the early uranium plants a resin ion-exchange process was used, which gave problems when the milled pulp was treated for gold recovery prior to uranium extraction. Inevitably some of the cyanide reagent used in the gold process remained in the final filter cake. In the subsequent uranium leach, under the acidic, oxidizing conditions, an anionic cobaltcyanide complex was formed which adsorbed on the resin, seriously reducing its capacity and necessitating specialized and expensive regenerative treatment. The resin was often regarded as being "permanently poisoned". At one plant it was decided to replace the entire resin inventory of resin after no more than 17 months operation.

Other so-called "temporary poisons" such as silica, polythionate and thiocyanate were also progressively adsorbed on the resin but could be removed by simple, relatively inexpensive regenerative methods. In due course process changes were made ahead of the uranium leaching circuit, which in some instances eliminated the permanent poisoning of the resin and in others, reduced it significantly. Such developments in resin ion-exchange practice are outside the scope of this paper, but it is relevant to note that there were factors, both geological and chemical, specific to local conditions, which hampered the early uranium operations and charted the course for investigators attempting to overcome these problems.

History of Solvent Extraction in South Africa

Until 1955 much of the uranium investigations being carried out in the U.S.A. was classified and not available for publication. The raising of the security curtain in that year released a flood of information in which were reports on the work which had been carried out into solvent extraction processes. A study of these documents coupled with subsequent reports from an official of South Africa's General Mining and Finance Corporation temporarily attached to an overseas laboratory led the metallurgists of that mining Group to believe that application of the amine-based solvent extraction process might reduce the costs of uranium recovery and at the same time provide a high-purity product. Investigations were initiated at the University of Cape Town in 1959, sponsored by the Chamber of Mines of South Africa, and at the Group's two laboratories. The test work used the secondary amines LA 1 and LA 2 from Rohm & Haas. The Eluex method studied incorporated the use of a solid ion-exchanger to concentrate and partly purify the uranium from the pregnant solution, and this was followed by solvent extraction recovery of the uranium.

At West Rand Consolidated Mines Limited, the laboratory investigation, started in 1958, culminated in a small pilot plant using LA 1 in kerosene to treat concentrated eluate from the main plant. However, there were both design and operational problems: for example, the animal glue flocculant used in filtering the leached pulp caused severe fungal growth in the solvent extraction circuit. The project was abandoned.

At Stilfontein Gold Mining Company Limited the existing uranium plant was treating with resin ion-exchangers the combined material from five mines, some of it drawn from surface accumulations of many years standing. This blend of material presented about the worst possible case of potential poisons and impurities, and these played havoc with the resin. Thus, there was a large incentive to test solvent extraction and a laboratory investigation was initiated in 1960.

These investigations by the General Mining Group led to a "table-top" scale pilot unit being operated at its Stilfontein and Buffelsfontein gold mines. LA 1, LA 2 and later Alamine 336 from General Mills were used. These successful investigations have been reported in the paper by E.L. Goldblatt⁽¹⁾.

During this period the South African Atomic Energy Board (AEB) had been investigating the production of nuclear grade uranium metal and its compounds. As the preferred starting point for these products was a high purity ammonium diuranate (ADU) it was decided in 1963 that AEB and industry would collaborate in the commissioning and operation, at Buffelsfontein mine, of a large-scale solvent extraction pilot plant based on the AEB and General Mining investigations. The process, a variant of the Eluex process, became known locally as the Bufflex process: it incorporated both resin ion-exchange and solvent extraction, and scrubbing and regeneration steps in the solvent extraction process distinguished it from the Eluex process.

As a result of the operation of this pilot plant, described in detail in the paper by A. Faure and co-authors⁽²⁾, it was shown that solvent extraction could be applied successfully and without difficulty to the recovery of uranium from concentrated eluate, with a reduction in recovery costs and the added benefit of a higher purity ADU product. In consequence, a decision was made by Rand Mines Limited to convert the uranium plant at its Harmony gold mine to solvent extraction operation. The plant was commissioned in 1967.

Others producers contemplating the use of solvent extraction preferred to await the outcome of the next investigation in which the very low grade, clarified pregnant solution at Buffelsfontein was treated directly, without the prior concentration stage using resin ion-exchange. The pilot plant was modified and extended in 1966 for this purpose. After two years of further investigation the so-called Purlex process, a modified Amex process, was developed. This has been reported by A. Faure and T. H. Tunley⁽³⁾. By that time a second, similar pilot plant had been commissioned and operated at the Western Reefs mine.

The results of the investigations showed that for some mines there would be little to choose between the operation and costs of the Bufflex and Purlex systems. However the vulnerability of the resin ion-exchanger in the Bufflex process, particularly if a more intensive leach were to be called for, led those mines proposing to change from resin operation to adopt the Purlex method. The remaining mines retained their resin ion-exchangers as they experienced only temporary poisoning.

All new plants built since 1969 use the Purlex process. In 1970 the Harmony main uranium plant was extended considerably and the opportunity was taken to convert from Bufflex to Purlex, the Bufflex units being incorporated into the scrub and strip stages. Recently the plant at Blyvooruitzicht mine reverted from Purlex to Bufflex following a long-term investigation into the use of resin ion-exchangers for treating pregnant solution in a counter-current system. As uranium is extracted prior to gold, no cobaltcyanides are formed to affect the resin.

Purlex Plant Operations

There are at present ten solvent extraction plants operating at South African mines and no two are identical in design or operation. The following is a blanket description covering operations in a general sense only. For more specific information of six of the solvent extraction plants see Table 1 and the circuit diagram in Figure 1.

Pregnant Solution

The pregnant solutions treated are derived from the leaching of ores using sulphuric acid and an oxidant. The chemical composition of the pregnant solution is typically within the following range:

	Low	High
U ₃ O ₈ — g/l	0.11	0.32
Fe ²⁺ — g/l	0.54	2.68
Fe ³⁺ — g/l	0.69	2.15
H ₂ SO ₄ — g/l	2.05	3.90
SiO ₂ — ppm	0.07	1.43
S ₄ O ₆ — ppm	9.	15.
Anionic Co — ppm	0.3	2.
Cl — ppm	5.	189.
CNS — ppm	4.	27.
Solids — ppm	6.	107.

The volume of pregnant solution to be treated depends on the tonnage of ore treated, the solid-liquid ratio in leaching, and the degree of dilution during filtration. The flowrate to the different plants lies between 1 500 and 4 900 litres per minute.

Extraction Section

Extraction is carried out in countercurrent operation in four stages of mixing and settling, with a large fraction of the organic phase being recycled within each stage. The constituents of the organic phase differ among the plants. Alternatives with approximate concentrations (in % v/v) are:

	I	II
Alamine 336	5	5
Isodecanol	2	—
Solvesso 150	—	35
Kerosene	93	60

Alamine 336, produced by General Mills, is a long-chain tertiary alkylamine with 10 to 12 carbon atoms in each chain. Iso-decanol and Solvesso (a high-aromatic solvent produced by Esso Chemical) act to increase the solubility of amine salts in the kerosene and thus prevent a "third phase" from forming.

As reported later, fungus is a problem encountered by most solvent extraction plants in South Africa. Where the fungal growth is absent or not severe, iso-decanol is used. At other plants it was necessary to replace the iso-decanol with Solvesso 150, which is more expensive. There are however, other considerations — at one plant the raffinate solution is used in the pyrite flotation process and a change from iso-decanol to Solvesso had to be reversed because the small quantity of aromatic compound remaining in the raffinate adversely affected the flotation process.

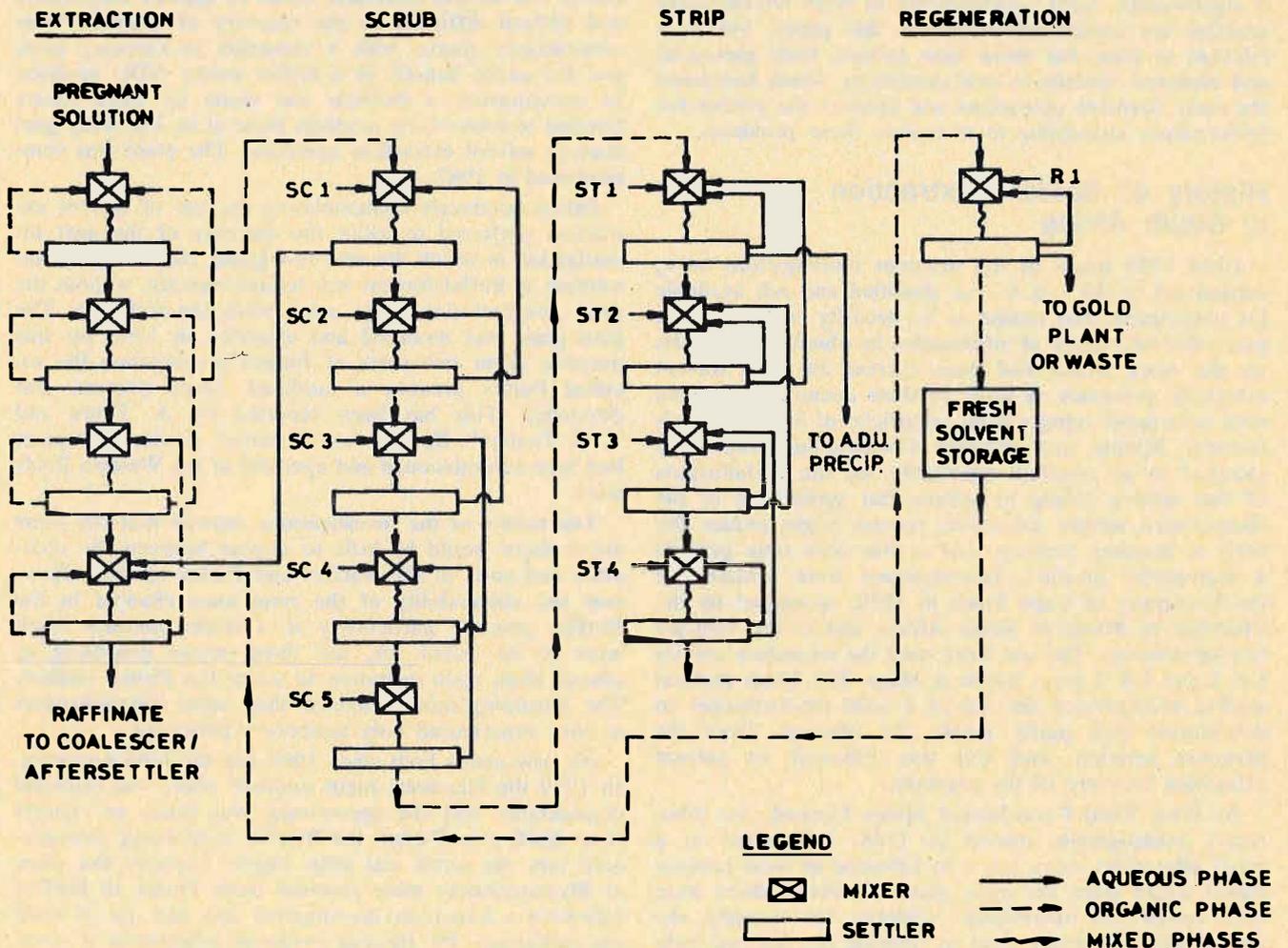


FIGURE 1. Solvent extraction operations in South Africa. For details of equipment and reagent additions SC 1-5, ST 1-4 and R1 see Table 1.

At another plant, Shellsol AB (a high-aromatic solvent produced by Shell Chemical) was used in place of iso-decanol. However, the relative density of Shellsol, 0.88, is significantly higher than Alamine and kerosene. This denser solvent used in the relatively large proportion of 35% by volume, resulted in a marked decrease in the depth of the organic phase in the extraction settlers. Thus, due to the fixed height of the organic overflow weirs, insufficient organic phase was available for recycle to the mixers and an aqueous-continuous emulsion was formed. Moreover it was found that the use of Shellsol resulted in a slower separation rate in the settlers. These two effects increased the solvent loss significantly, and the use of Shellsol was therefore discontinued.

Mixing of the Organic and Pregnant

The ratio of the volumes of the two phases entering each mixer is controlled at about 1:1. About 90% of the organic phase required to achieve this ratio is recycled from the associated settler in the bank while the remaining 10% is received from the following settler. 10% of regenerated solvent is added to the last mixer of the bank and 10% of loaded solvent is removed from the first settler for scrubbing and further treatment. Retention time in the mixer is: Lurgi, 2 seconds; others, about 30 seconds.

The mixers are operated to maintain an organic-continuous emulsion in order to reduce solvent losses. A conductivity probe is placed in the contents of each mixer to indicate any change from this state. Should the emulsion change to aqueous-continuous, the volume of the aqueous phase entering the bank is reduced until the condition is rectified.

Settling of the Emulsion

The emulsion is transferred from each mixer to its settler and is distributed in the organic layer. At some plants a baffle is fitted between the entry and the discharge section of the tank to impede the layers near the interface of the two phases to assist the final stages of separation. The separated aqueous phase is transferred from the settler to the downstream mixer.

Scrubbing of the Loaded Organic

Scrubbing is carried out in four or five stages of mixing and settling. Low aqueous flow rates are employed, so organic-continuous conditions are achieved without solvent being recycled. Retention time in the mixers is 4 to 10 minutes and reagent concentrations are 100 gpl. ammonium hydroxide and 50 - 100 gpl. sulphuric acid.

In the early period of solvent extraction operations, ammonium hydroxide was added to the last mixer with the object of stripping a small quantity of uranium from the solvent into the aqueous phase which provided a reflux of uranium through the section and assisted in scrubbing most of the impurities from the solvent. The addition of this ammonium hydroxide raised the pH of the last stage to about 2.5, resulting in the formation of a siliceous crud much of which eventually worked its way upstream to the extraction circuit, passing through it and being discharged with the raffinate. Dilute sulphuric acid was added to the second mixer, reducing the pH to 1.5 to assist in the transfer of iron to the aqueous phase.

Subsequently several plants modified their scrub procedure, replacing the ammonia and in some instances the sulphuric acid by water, with negligible increase in the impurity content of the final ADU product. Crud production was reduced by this step.

At one plant, after the ore is leached, the solution from the second stage of filtration is passed through columns containing redundant resin exchanger. This clarifies the solution and at the same time uranium adsorbs on the resin. This uranium is later removed using dilute sulphuric acid (7.5% mass/vol) and the resulting solution is then added to the first and second stage scrub mixers. The uranium present in this so-called "Bufflex eluate" provides a reflux of uranium similar to that referred to above.

Stripping of the Organic

The strip stage comprises four mixer/settler units. Where the type of pH unit used functions only in aqueous solutions, a portion of the aqueous phase is recycled to assist in maintaining an aqueous-continuous emulsion in the mixers. The strip mixers are fed continuously with ammonium hydroxide to effect a stage-wise change in the pH from about 3.0 in the first mixer to about 5.0 in the last mixer, and ammonium sulphate solution is added continuously to the last mixer. The loaded aqueous phase from the first strip settler is transferred to the uranium precipitation section. Retention time in the mixers is 4 to 7 minutes and reagents concentrations are 40 - 100 gpl. ammonium hydroxide and 100 - 150 gpl. ammonium sulphate.

Regeneration of the Organic

This section consists of a single mixer/settler unit and the aqueous phase only is recycled. The mixer is operated in the organic-continuous mode. Reagent concentrations are 20 - 100 gpl sodium carbonate and 20 - 200 gpl caustic soda. Mixing retention time is 3 to 9 minutes. Sodium carbonate solution is fed continuously to the mixer and the pH of the aqueous phase in the settler is maintained between 9 and 11 by the addition of caustic soda solution or gaseous ammonia to the mixer. On start-up of a new plant there is considerable emulsification in this section, but on continuing recycle it appears that the substances causing emulsification are washed out of the solvent.

The stripped organic solution passes through the unit and, upon regeneration, is pumped to a storage tank for reuse. The aqueous phase, which in some cases contains gold stripped from the organic phase, is largely recycled. The remainder, equivalent to the small volume of solution in the reagents being added, is transferred to the gold plant. The gold content also builds up in the recycling aqueous solution in the settler and the unit is drained periodically and fresh aqueous solution is added. The solution removed is treated as above.

Raffinate Treatment

After leaving the last extraction settler the raffinate is transferred to an "after-settler", a large tank having an overflow lip. Although in open circuit, the retention time in the tank is sufficient to allow a portion of the small quantity of entrained solvent to separate and rise to the surface, the level of which is kept below the overflow lip. When sufficient solvent has accumulated, the outlet valve is closed. The level in the tank rises and the solvent is recovered via the overflow lip after which the outlet valve is opened, lowering the solution level.

The solvent is returned to the crud circuit, described later, for regeneration. A portion of the raffinate may be recycled to the main uranium plant or to the pyrite flotation circuit while the rest is neutralised and discharged to waste.

At two of the plants the raffinate is first passed through coke-filled coalescers and thence to an after-settler.

Analyses

The U_3O_8 content in the raffinate generally varies between 0.0001 and 0.0007 g/l. The amine loss in the raffinate is between 3 and 14 ppm, while the inventory amine loss is between 7 and 23 ppm. Total solvent losses from all sources, including sampling, spillage, evaporation etc., range from 180 to 600 ppm. The loaded aqueous phase transferred to the ADU precipitation circuit varies between 5 and 8 g U_3O_8 /l.

Ammonium Diuranate Product

Gaseous ammonia is used to precipitate the uranium in the loaded solution from solvent extraction. At some plants, this is heated to between 30°C and 40°C. This ammonium diuranate differs physically from that produced by ion-exchange in that it settles and filters more rapidly. It is also chemically purer, as shown by the typical effect on six important constituents:

Constituent

U_3O_8	Increased by 6%
SO_4	Reduced by 30%
Fe	Reduced by 60%
SiO_2	Reduced by a factor of 34
Al	Reduced by a factor of 36
Ca	Reduced by a factor of 6

Fungus

Most plants are plagued at one time or another with fungus. The species has been identified as belonging to the family "Aspergillus" and differs from that sometimes encountered in the uranium leaching and filtration circuits. The fungus which is believed to be due to air-borne spores, multiplies rapidly in oxygen-bearing media between 25°C and 45°C. Growth of this fungus is supported by iso-decanol, but not by aromatic solutions. Organic phase is absorbed into the fungus which builds up on the bottoms, sides and on the lips of the overflow weirs of the settlers. Portions which break away in the aqueous phase pass through the circuit resulting in solvent loss in the raffinate.

Attempts were made to combat the fungus by isolating and emptying a settler, filling it with water and purging it with sulphur dioxide gas. While this killed the fungus present, it did not take long before new fungus developed during operations. In another case sulphur dioxide gas was passed through the fresh solvent inventory on a weekly basis. Fungus was killed for a few days but towards the end of the week reestablished itself. As a suitable fungicide became available about this time, the method was discontinued.

At present fungus is removed manually from the empty settler by scraping and brushing. It is then transferred to the crud treatment section where the solvent is recovered using the method referred to under "Crud".

The addition of a solvent-soluble fungicide, a derivative of benzo-thiazole, has alleviated the position considerably. The fungicide, Busan 71, produced by Buckman Laboratories, is added to the fresh solvent either continuously or batchwise at intervals of about one week. Several surfactant-base fungicides were tested in the laboratory but were found to form stable emulsions.

Crud

Crud is formed in the scrub and strip sections and spreads throughout the plant due to the diversity of flows. The re-cycling of some of the solutions helps to

break down the crud thus releasing some of the entrained solvent. Its major constituent has been identified as silica.

Crud is periodically bled from the circuit into a tank where dilute sulphuric acid or raffinate is added and the whole circulated by pumping which breaks down the crud. After a settlement period the crud separates from the organic solution and is discharged to waste. The organic solution is treated in the regeneration section.

Tar

Periodically a tarry substance is found in the extraction circuit at one plant and this forms soft lumps of coagulated stable emulsion which have to be removed manually. The source of the tar was eventually traced to oils which were used in mining operations underground, some of which found their way into the ore discharged to the metallurgical plant, eventually reporting in the pregnant solution treated in the solvent extraction section. This problem has largely been overcome since most of the used oil has been isolated underground and transferred to surface separately for refining.

Equipment Used

Mixers

The types of mixers used depend to an extent on the design of the complete plant. Where gravity flow is used for the transfer of particular solutions between units the plant has been designed as a cascade system with about 1.5 metres fall between stages. This is shown in the photograph, Figure 2. At other plants the mixers are designed to combine both mixing and pumping, as fully described in Reference (7), and mixers and settlers may be positioned at a common level.

Plant operating efficiencies are similar whichever method is used. Fewer pumps and ancillaries are necessary for cascade operation but additional foundations and supporting structures are required as will be noted in the photograph, Figure 2.

Turbine mixers

(a) See Reference (6), pp 57 and 58

Each mixer comprises a cylindrical tank having vertical baffles with a vertical shaft agitator positioned in the centre of the tank. As the extraction and scrub mixers must be operated in the organic-continuous phase, the following steps are taken to ensure that this state is maintained:

(i) The large volume of recycled organic phase enters the side of the tank and is directed at the agitator blades while the small volume of the transferred organic phase enters at the top of the tank. The aqueous phase enters near the top of the mixer, is divided and diverted around the periphery of the tank on a flat shelf or in a launder, and the liquid overflows and cascades as a thin continuous sheet onto the surface of the mixer's contents. This method of addition of the phases prevents the formation of discrete areas of aqueous-continuous and organic-continuous emulsions in the body of the mixer.

(ii) The blades of the agitator are positioned to be in the organic phase when the mixer is at rest. On restarting the agitator, the initial mixing occurs in the organic phase with the aqueous phase being drawn in.

After mixing the emulsion gravitates from the mixer to the settler.

(b) At most plants the mixer and its associated settler are separate units, as shown in Figure 3, but at the Lurgi plants, in the scrub and strip stages, the mixer and settler

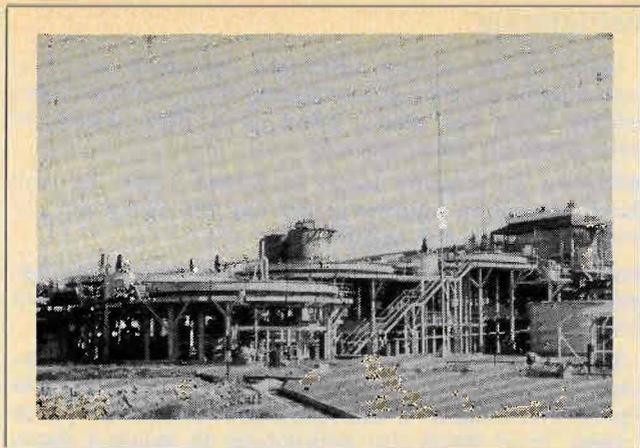


FIGURE 2. Design of plant: Cascade flow system.

are combined in one tank. One side of the mixer is open to its settler except that a screen separates the two sections. The small amount of turbulence transmitted from the turbine mixer to the settler has a negligible effect on the efficiency of phase separation. The power requirements for the agitators are about 4 kW per 5000 l of mixer volume and the tip speed is about 3.8 m/sec.

Pump-mixers⁽⁷⁾

(a) These mixers comprise a cylindrical tank having baffles with aqueous phase and organic recycle fed as above. However, to the shaft of the agitator are attached a paddle-type mixer uppermost, then below it a circular plate and, at the bottom, a low-lift pump impeller set in a helical casing. The two phases are mixed by the agitator and are drawn through the pump impeller and discharged through the side of the mixer to the settler. At one plant the low-lift pump was designed with too great a capacity and a restriction had to be introduced in the discharge pipe to reduce the flow. This in turn led to overemulsification in the mixer pump due to the longer retention time and additional shearing of the two mixing phases. The circular plate was raised slightly, thus reducing the pump's efficiency and a satisfactory emulsion was obtained. The restriction in the discharge pipe was retained.

(b) At another plant, the two phases are mixed in a well at the bottom of the mixer, above which is positioned a large double-shrouded turbine impeller having 8 blades. The partially mixed phases rise through the impeller, which finally mixes them, and the emulsion travels upwards through the body of the mixer and gravitates to the settler. The pump impeller has a variable speed drive adjustable between 34 and 49 rpm, equivalent to tip speeds of 3.3 and 4.7 m/sec. The pumping rate at 49 rpm is about 265 litres/ second.

Another design of mixer which has been investigated, incorporated an agitator in which the paddle blades were angled to produce a downward thrust towards an outlet at the bottom of the tank. It was found that, in large mixers, at the limiting agitator tip speed for satisfactory mixing, the hydrostatic head was insufficient to transfer the required volume of emulsion and the method was abandoned, although it worked well in mixers up to 0.7 m diameter.

Lurgi Pump/mixer

This type of unit is used in the extraction section of the Lurgi plants. Each unit comprises a pipe in which is

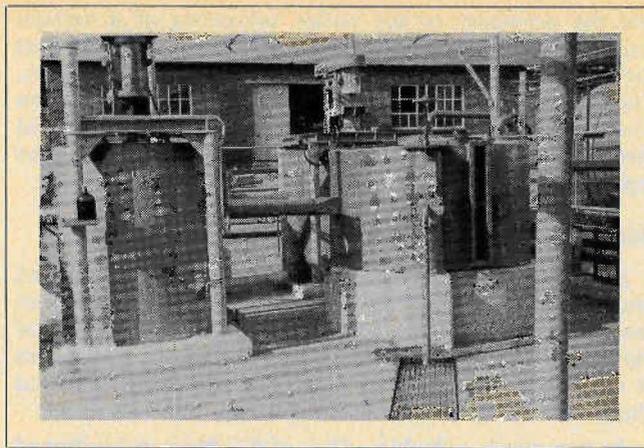


FIGURE 3. Pump/mix mixer/settler unit: mixer (left) and settler (right).

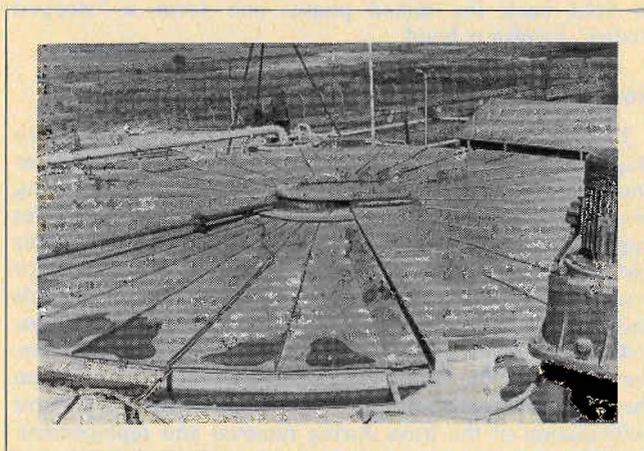


FIGURE 4. Emulsion feed to extraction settler: tangential entry.

fitted a truncated cone of heavy gauge stainless steel screening with the narrow end pointing down stream. The two phases join immediately ahead of the screen and pass through it, mixing almost completely. They then travel directly to a slowly rotating centrifugal pump having a variable pitch impeller where the final mixing takes place and the emulsion is pumped to the settler situated above it. The pitch of the impeller can be adjusted to cater for variations in flow rate. The pump must be removed from the pipe to carry out any adjustments to the pitch.

Extraction Settlers

Several geometrical designs of settler are used.

Circular

These are closed tanks from 316 L type stainless steel the largest of which are about 10.5 m in diameter and 1 m high, with the mixed phase entrance at the centre. Sightglasses are incorporated to view the interface between the settled phases.

At one plant the emulsion enters an annular feed well at a tangent, as seen in Figure 4, and spirals downwards to a horizontal plate on the central tube of the annular channel and positioned in the organic phase a little above the interface of the settled phases. This imparts a slight swirl to the contents of the tank to reduce the formation of dead areas. There is a radial baffle between the inlet

and the periphery of the settler, consisting of a vertical stainless steel plate pierced with holes except for a short section above and below the interface of the two phases. This blank area holds back the portion of the emulsion where separation is incomplete and provides additional retention time to allow more complete separation. The separated phases flow over peripheral launders.

Rectangular

At some plants rectangular settlers are used, the mixed phases entering the tank through a baffled, fish-tail shaped pipe to facilitate even delivery across the width of the tank, and the settled phases are drawn off at launders at the discharge end of the tank. Sightglasses are situated along the sides of the tanks to view the interface level.

At two plants a double, offset picket fence is positioned near the feed end to assist even distribution of the mixed phases, and in one plant vertical pierced plate baffles of successively lower heights are placed one quarter, one half and three quarters of the distance along the settler, to hold back the mixed phases and form a "stepped wedge" emulsion band.

Horizontal Cylinder

Each Lurgi extraction unit (see Figure 5) contains two stages of settling in a horizontal stainless steel cylinder enclosing tiers of trays to provide the required settling area. The trays in the organic phase have their open sides uppermost while those in the aqueous phase have their open sides facing down. Two such units are required for one bank of the extraction section. Over a period, solids and a small quantity of fungus accumulate in the trays, reducing their effective settling capacity; it is thus necessary to isolate the settler periodically to remove and clean the trays. Considerable care has to be taken to prevent deformation of the trays during removal and replacement.

Phase Removal and Interface Control

The settled phases pass over weirs. These weirs must be of sufficient length to permit overflow to a depth of between about 1 and 3 cm. At lower depths irregularities in the lip of the weir, either due to its not being consistently level or due to the presence of fungus or crud, may cause some surging in flow. A similar surging may occur at depths much greater than 3 cm. The height of the lip of the aqueous phase weir determines the level of the interface, and this weir in particular must be kept clean.

At some plants the organic phase weir is split to provide separate recycle and interstage streams, and care must be taken to keep this split reasonably exact and identical from one stage to the next.

The overflows are collected in launders which discharge into a pipe. This pipe is preferably close to horizontal, which reduces air entrainment and the consequent restriction of flow under low heads.

Pumps

The following types of pump are in use:

- (1) for transfer of organic or organic-containing aqueous solutions — (a) self priming Kestner APV vertical pumps with Keebush impellers and casings. (b) stainless steel centrifugal pumps. (c) polythene air lifts;
- (2) for transfer of organic-free aqueous and acidic solutions — (a) soft-rubber lined and stainless steel centrifugal pumps. (b) positive displacement pumps having neoprene rotors and stators.

Instruments

Many of the solvent extraction operations are controlled automatically and are directed from a control room isolated from the plant. There is a high degree of instrumentation which includes:

Indicators for solution levels in storage tanks, for fire alarm conditions, ammeters and On/Off lights for the motors of pumps and agitators.

Recorder/controllers for pH and for solution flows e.g. pregnant solution, fresh solvent to extraction and certain reagent additions.

The instruments and motor Stop/Start buttons are consolidated in a central control console as shown in Figure 6. A number of the functions above are linked to a mimic panel which also incorporates an indicator showing the conductivity state of the emulsions in the mixers. Many of the displays indicate a "satisfactory/unsatisfactory" condition in the unit concerned, some of the display circuits operating a siren when unsatisfactory conditions are registered.

Sampling and Analysis

The efficiency of solvent extraction operations is dependent on many factors, one of which requires the monitoring of the constituents in the solutions treated so that remedial action may be taken when an unsatisfactory condition becomes apparent. To this end, solutions are sampled either on a grab basis at fixed time intervals or are collected continuously, usually over longer intervals. The samples are analysed for the constituents as shown in Table 2.

TABLE 2. Analysis of Samples

Sample	Analysis
Pregnant solution	U ₃ O ₈ , Fe ³⁺ , Fe ²⁺ , H ₂ SO ₄ , SiO ₂ , S ₄ O ₆ , Cl, CNS anionic cobalt, suspended solids.
Solvent: to extraction	U ₃ O ₈
to scrub	U ₃ O ₈ , total Fe
to strip	U ₃ O ₈ , total Fe
to regeneration	U ₃ O ₈
ex regeneration	U ₃ O ₈
Ammonium sulphate to strip	U ₃ O ₈ total Fe
Aqueous ex scrub to extraction	U ₃ O ₈
Loaded aqueous to ADU precipitation	U ₃ O ₈ , SO ₄ , total Fe
Aqueous ex regeneration	U ₃ O ₈ , Au, where applicable
Raffinate	U ₃ O ₈ , amine
Bufflex eluate to scrub*	U ₃ O ₈ , H ₂ SO ₄

Materials of Construction

Supporting structure is fabricated from mild steel, and walkways and upper floors are mild steel egg-grating. The floors at ground level are concrete. All are protected by various paints. Some areas of concrete have been lined with acid proof brick.

Rubber

It was known that the natural rubber commonly used in the industry's metallurgical plants for lining mild steel tanks and pipes could not withstand the organic solutions used. Various types of synthetic rubber compounds were tested, and, while several were satisfactory, in a number of instances the adhesive used to bond the strips of rubber together failed at the overlap joint allowing solution to

penetrate behind the rubber, freeing it from the mild steel tank.

Stainless Steel

The low carbon stainless steel, type 316 L, was the preferred material for fabricating tanks and piping due to its corrosion resistant properties, particularly after welding. However, at certain solvent extraction plants a high chloride content in the acidic pregnant solution precluded the use of this material due to the corrosion which could be anticipated and fibreglass was used in its stead. At one of these plants the extraction mixer and settler tanks were fabricated from mild steel which was then lined with lead and has proved successful.

Fibreglass

Fibreglass has been used for the fabrication of tanks and pipes and for lining mild steel tanks. A number of redundant rubber-lined tanks used in the resin-exchanger circuit were successfully lined with fibreglass over the rubber. Several failures in fibreglass equipment were traced to incomplete sealing of the fibreglass by the clear gel coating used. Being transparent it was difficult to see which areas of fibreglass had not been coated. This resulted in exposure of the glass fibres to the solutions and capillary action drew the solution into the body of the fibreglass causing eventual failure. To overcome this a different colour dye was added to each coating of the gel thereby highlighting any areas not completely covered.

Protective Coatings

Three types of paint have been used for the protection of equipment:

Rubber-base paint has been used on the external sides and bottoms of tanks which contain acidic aqueous solutions.

Resin-base paint has been used on mild steel structures and concrete which are exposed to organic solutions. This type of paint, while relatively tough, does tend to chip with hard wear and is patched with the same paint or with an oil-base paint.

Oil-base paint has been used on mild steel in place of resin-base paint, but requires more frequent patching.

Safety Precautions

All solvent extraction plants are situated in the open as shown in the photographs in the figures and have been constructed on large concrete slabs with a corbel to contain any spillage. Electrical appliances and fittings are flame proof. All tanks are covered and fire fighting systems are reticulated throughout the plant. These deliver a water spray, carbon dioxide gas or a dousing foam onto or into tanks. Temperature sensor heads are fitted under the lids of all settlers and are connected to an alarm. In addition there are numerous high-pressure water points and hoses both inside and outside the plant as well as mobile fire fighting equipment. High pressure water showers are situated at the reagent make-up tanks where caustic soda and sulphuric acid are used. Denim overalls are worn by operators since the more usual synthetic, acid-proof material generates static electricity.

Unauthorised personnel are not allowed within the plant area and at certain plants the entire area is fenced. Notices are placed strategically about the plant warning against smoking and the use of naked flames. Smoking is allowed only in the isolated control room. As the plants

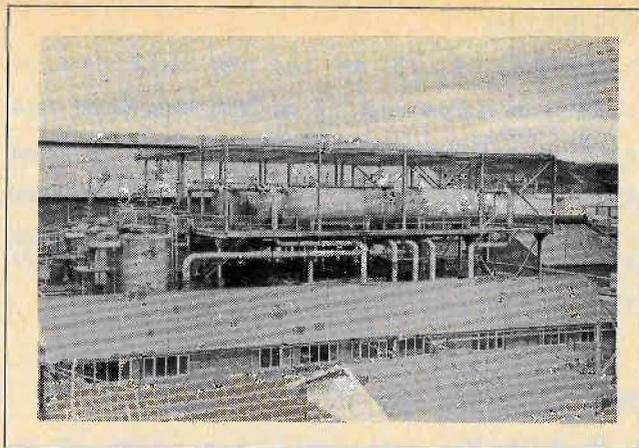


FIGURE 5. Lurgi extraction settlers.



FIGURE 6. Control console (mimic panel top, centre)

are situated in areas where electrical storms are prevalent, lightning conductors have been erected as will be seen in Figure 2.

Urine samples are taken monthly from operating staff and these are analysed for uranium content, the maximum permissible limit being $0.05 \mu\text{g U/ml}$. In addition, operators are medically examined annually. No examples of excessive ingestion have been recorded.

Environmental Control

Neutralised raffinate solutions contain traces of the extractants, which are believed to be hazardous to aquatic life. The solutions are discharged with plant tailings to slimes dams. Under South African weather conditions, evaporation exceeds precipitation and no contaminated solutions escape. Adsorption and oxidation are believed to remove the last traces of solvents.

Thanks

The author wishes to thank colleagues in the mining industry and the South African Atomic Energy Board for their assistance with the paper and the South African Institute of Mining and Metallurgy for permission to use extracts from Journals.

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DISCUSSION

T. Hardwick: You have mentioned a number of impurities that you have in your final product. I notice that you do not mention some of the problem elements that we have, such as molybdenum, vanadium and so on. Either you do not have them or else you have solved a very difficult problem. Could you comment please?

S. Finney: We are just lucky. With regard to the vanadium or molybdenum in the products from the solvent extraction plants, we are still well within conversion plant specifications. Earlier in resin ion exchange plants there was that problem but since conversion to solvent extraction plants, there has been no problem. All the ADU is sent to one final treatment plant. There are two producing plants operating resin ion exchange circuits and the remaining plants have pure solvent extraction or continuous-ion-exchange plus solvent extraction. The ADU material is blended in the one final treatment plant, and all the product is within conversion plant specifications. In the solvent extraction plants there is a decontamination of vanadium and molybdenum in the order of 20, in the scrub section.

K. Hester: You mentioned that you used stainless steel 316 L throughout the plant. Is this correct?

S. Finney: That is partly correct. Stainless steel 316 is used in several of the plants. In one plant stainless steel 316 is used in the extraction settlers and the remainder are fibre glass. We have had problems with this type of stainless steel at the welds due to the use of incorrect welding rod; a low carbon welding rod should have been used. Apart from this, there has been no trouble except when a slug of chloride enters the circuit. In particular, in the continuous-ion-exchange plant there has been trouble in the elution side where pitting and striations have occurred. This was observed

after several months of operation. In the Free State mines, where there is a lot of chloride, materials other than stainless steel have been used.

K. Hester: You also used fibre glass epoxy resin.

S. Finney: This is correct. Some difficulty was experienced in making sure that the contractors did a satisfactory job since the final "Jel" or "Due" coat was clear. This was resolved by using a red dye in the first two coats and a blue dye in the second two coats. At Buffelsfontein, rubber-lined tanks have been covered with fibre glass and spark tested. There has been no trouble since 1968.

K. Brown: What kind of refineries do you have in South Africa?

S. Finney: We produce mixed oxides only. The final diuranate product is filtered, dried and calcined. It is then put into drums and sent overseas. We did do some pilot plant tests on producing uranium tetrafluoride, using hydrogen fluoride. Ammonia was used to reduce the uranium to UF₄. We found snags in that the final material would either sinter or the pellets would not be completely reduced internally. On material from one plant we did produce a size of chip of required strength that allowed us to produce a very high-grade UF₄, but only on an experimental basis.

J.J. Robbertse and D.I. Watson* (contribution to discussion).

In the section of his paper, headed "Mixing", Mr. Finney mentions the use of conductivity probes to indicate the state of the mixed phase emulsion as being aqueous- or organic-continuous. In the 2 Lurgi plants at the West Uranium Plant of Vaal Reefs Exploration and Mining Co. Ltd., conductivity probes were initially installed in the mixed phase delivery line from the pump mixers. For reasons outlined below, these probes proved to be of no benefit and their use was discontinued.

It is considered that the unsuccessful application of the probes in this plant was because of partial phase separation taking place within the mixed phase delivery line in the vicinity of the probe. This unhomogeneous mixture prevented the probe* from giving reliable results.

As a substitute for the conductivity probes, ratio controllers have been installed on the organic recycle lines to the pump mixers thus ensuring an organic continuous emulsion in the face of varying flowrates of pregnant solution.

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Uranium Processing in South Africa

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Introduction

MR. FINNEY IS TO BE CONGRATULATED on his comprehensive paper, which has dealt most adequately with the status of uranium recovery by solvent extraction in South Africa. I have been asked to elaborate on some of the aspects dealt with by the author. My contribution is based on work undertaken by the Extraction Metallurgy Division of the Atomic Energy Board in close collaboration with the South African uranium industry over the past few years.

Instrumentation

Until a few years ago suitable and reliable instruments were not available for the measurements of many parameters on uranium-processing plants (e.g. pH in organic phases, and acid concentration in the leach). Certain instruments were available but these were not sufficiently robust to withstand the harsh environment normally encountered in these plants. Generally, the tendency had been for plant instrumentation to follow the instrumentation in previous plants, even though this was often unsatisfactory and only remained operative for short periods.

Improvements to Plant Instrumentation

(a) pH Measurement

pH is generally monitored in the aqueous phase as it flows through the mixer-settlers of the extraction and strip sections, although process requirements are optimized in respect of time lags and reagent control when pH is measured in the organic continuous phase. The measurement of pH in the discontinuous aqueous emulsion present in this phase involves difficulties because a high impedance is presented to both the glass and reference electrodes. Furthermore the solvent tends to block the pores at the tip of the reference electrode, causing discontinuity of the liquid junction. Standard pH systems cater only for single high-impedance input on the glass electrode because the reference junction normally has a relatively low impedance (Z_{rl}) to an aqueous solution, and common-mode interference, with respect to ground, is of little consequence.

However, in the discontinuous aqueous emulsion (Z_{rl}) is large, and common-mode effects are pronounced. A system using a separate-reference channel-source follower largely overcomes this effect, the input impedance of the reference channel Z_{ir} being much higher than $Z_{rP}^{(1)}$. The other difficulty, that of pore blockage, is overcome by the use of the "Lazaran" oil resist' electrode. Comparative results showed a constant difference of 0.3 pH unit between manual and on-line measurement. Several plants are now equipped with such equipment, and pH control has been considerably improved.

Side effects such as the formation of crud in the settlers and excessive use of reagents have been minimised by the introduction of the pH meters.

(b) Aqueous Ammonia Make-up by a Thermal Method

Ammonia is an important reagent in hydrometallurgy, especially as an aqueous solution for the control of pH values. In uranium hydrometallurgy an ammonia solution of 40 g/l is specified for the control of pH in the scrubbing and stripping sections of solvent-extraction plants. In that application, the direct use of gaseous ammonia is not acceptable. In most plants the ammonium hydroxide used for pH adjustment is prepared by the continuous metering of the water flowing into a make-up tank and by adjustment of the ratio of the ammonia gas flowing into this tank to the water flow. The measured values for the flow of ammonia gas are compensated for temperature and pressure. A new method for the preparation of ammonia hydroxide has been developed by the Instruments Division of the National Institute for Metallurgy. The method is based on the thermodynamic relationship between the heat evolved and the mass of the reactant in the process of solution. In the case of ammonia gas and water, the heat of solution is substantial.

The apparatus consists of a mixing chamber for ammonia gas and water, capable of measuring the temperature of the ingoing water and the outgoing solution. Mercury thermometers were used to determine the differential temperature of a particular solution in preparation. This solution was subsequently analysed by a gravimetric technique to determine the concentration of ammonia. A series of such determinations formed the basis for the graph in Figure 1 which demonstrates the linearity between differential temperature and concentration over the desired range.

The thermal method⁽²⁾ for the control of the production of aqueous ammonia is a cheaper, simpler, and more efficient system than that of ratio control. There is a reduction of instrument maintenance and calibration because the measurement of temperature is a direct quantity, whereas the measurement of flow is a pressure-related quantity. To date the new system is used continuously at several plants and is preferred to the ratio system.

A storage tank for the aqueous ammonia is not used, as the thermal make-up system makes storage unnecessary. Direct use of the ammonium-hydroxide is advocated. Figure 2 shows the mixer used to make up the solution.

(c) Uranium Loading

For reasons of economy, the solvent should be loaded with uranium at an optimum level which is 4.5 g of U_3O_8 per litre. A suitable analyser to determine the uranium in a solvent solution was developed. The technique used was based on X-ray absorption. The 60 keV radiation from an americium radioisotope is more heavily absorbed by uranium than by the kerosene of a Purlex solvent. In this instrument the sample-flow cell is placed between the radioisotope and the detector. The radioisotope is mounted in a lead enclosure that has a small hole through which radiation is collimated and emitted. The radiation passes through the sample and is partly absorbed and the remaining radiation is detected by a sodium iodide scintillator and photomultiplier, the pulses obtained being amplified and counted. A ratemeter con-

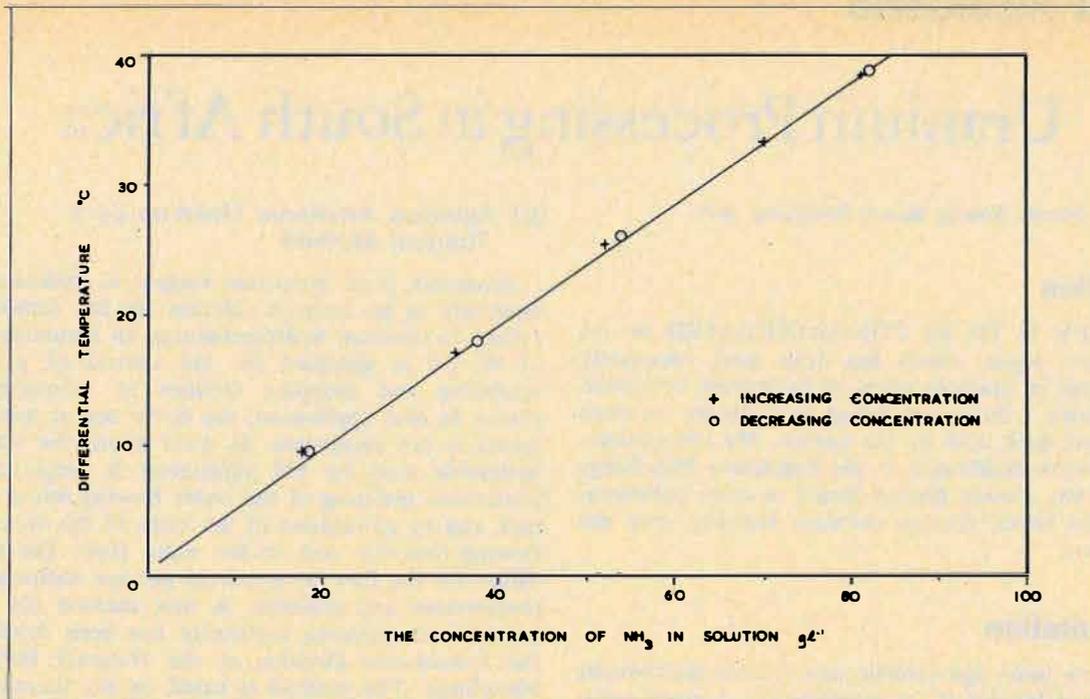


FIGURE 1. The concentration of ammonia solutions expressed as a function of the differential temperatures recorded in their preparation.

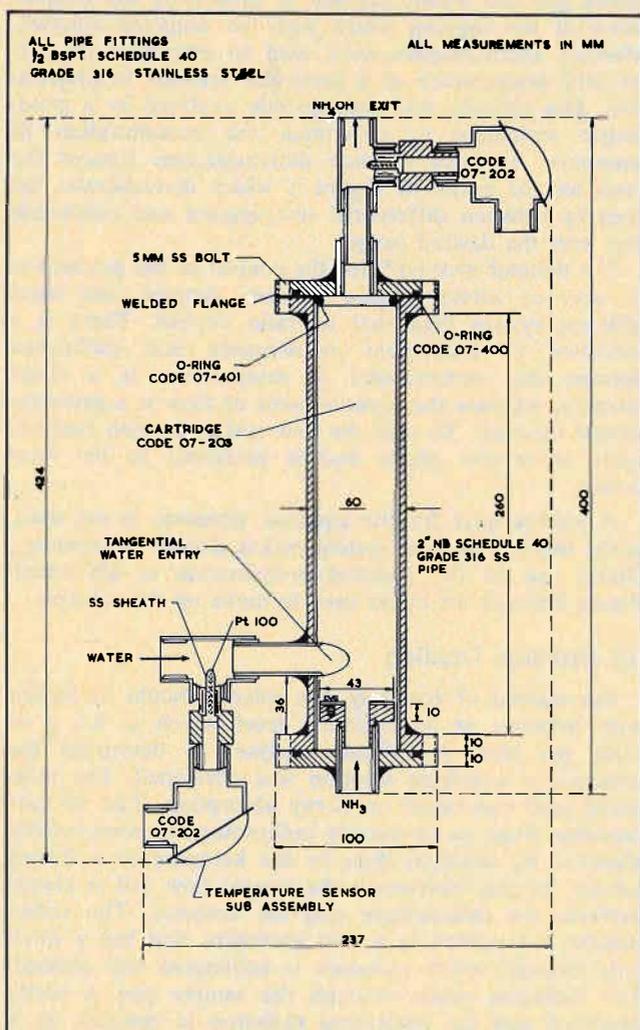


FIGURE 2. Ammonia mixer.

verts these pulses into a continuous analogue signal which is the predominant function of the uranium in the solvent. The radioisotope has a half-life of 458 years and, as the remaining equipment is based on the solid state technique, very little maintenance is required.

The accuracy of this method is sufficient for plant control. All three instruments are in use on several plants and have proved reliable and robust. A better control of ammonia make up, pH, and solvent load have resulted in

- (1) minimization of crud formation,
- (2) faster start-up and shutdown,
- (3) considerably easier operation of the plant,
- (4) substantial decrease in ammonia consumption,
- (5) lower solvent losses, and
- (6) lower uranium losses over the entire liquid/liquid plant.

Operating Problems Related to a Tar-like Substance

The operation of the Purlex plant at one of the South African mines is hampered by the presence of a black tar-like substance that accumulates in the stripping and regeneration sections. Its presence was noted soon after start-up and it was fairly soon established as coming into the plant with the leach liquor. Some evidence has been found that it is coming into the circuit via the underground sludge. Laboratory leaching tests provide strong evidence that old engine oil (from sumps of diesel locomotives) which is used for dust control underground, is a major source of tar. In view of analytical difficulties the results of laboratory tests cannot be regarded as completely conclusive. A tight control over the use of old motor oil for dust control underground reduced the tar content in the plant. No method for removing the tar before the solution reached the Purlex plant has been found.

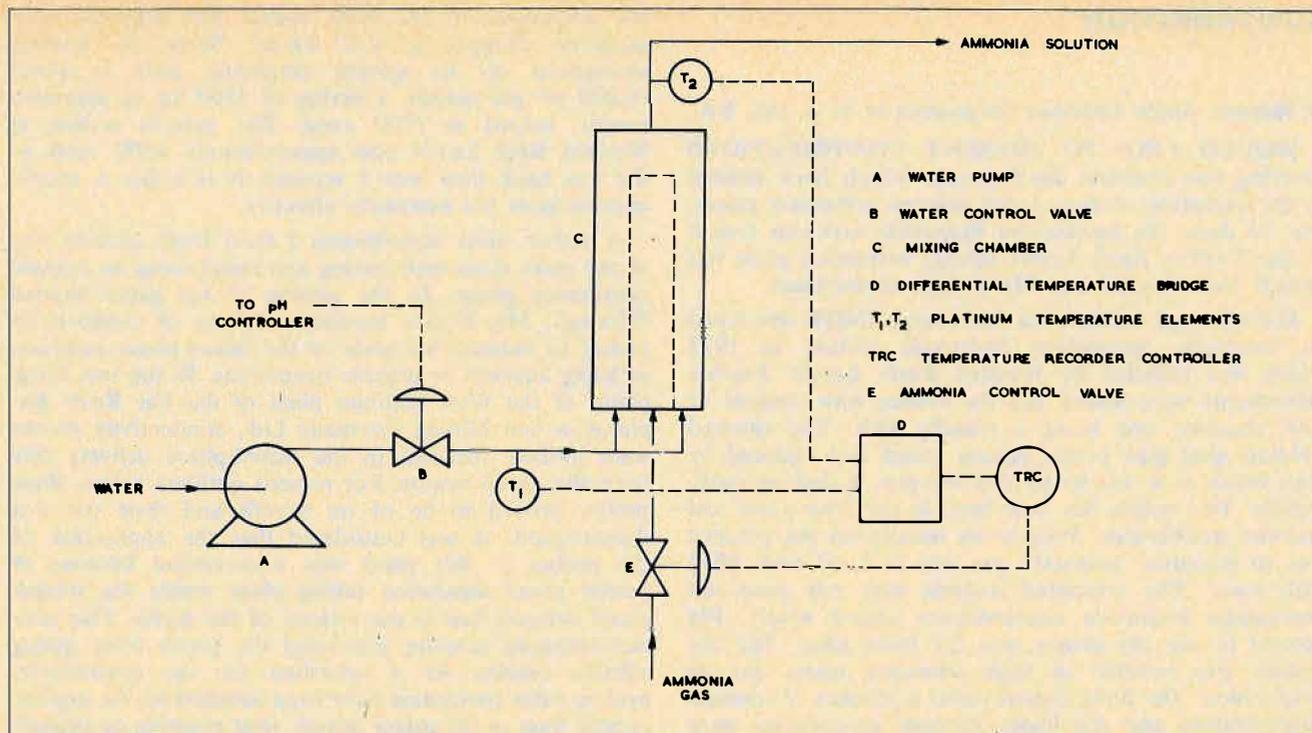


FIGURE 3. Control loop.

Extensive laboratory tests have confirmed that the major constituents of the tar are long-chain aliphatic carboxylic acids and evidence exists that isodecanoic acid, resulting from the oxidation in-situ of isodecanol in the extraction section, is present in the tar. It was established that the mixers in the extraction circuit, which function as pump-mixer combinations, were being operated under conditions conducive to oxidation reaction. The mixture of solvent and leach liquor in the mixer was of such a height that the stirrer paddle was not completely submerged in the solution, giving rise to a vortex that caused air to be sucked into the mixture, plus the fact that it was pumping against a restricted area. Because of the relative ease with which alcohols can be oxidized to carboxylic acid in the presence of oxidizing agents (the leach liquor being highly oxidative because of the presence of sulphuric acid and ferric iron) it is possible that the tar, or component of the tar, might be generated in situ by oxidation of the isodecanol. When the pump-mixer problem was corrected, the isodecanoic acid decreased yet the bulk of the tar problem remained.

The tar problem has also caused problems with stripping. An emulsion is formed before the pH required for complete stripping can be attained, resulting in loss of uranium via the regeneration aqueous phase.

Conversion of Purlex Plants to a Bufflex System Incorporating Continuous Ion-Exchange^(3,4,5)

A new continuous ion-exchange (CIX) system has been developed in South Africa and is being widely adopted for plant expansions and new uranium plants. The CIX system is of the upflow fluidized-bed type and comprises two columns and two resin-transfer vessels. It is operated according to the Cloete-Streat principle of reverse flow, in such a way as to give intermittent resin flow counter-current to the solution flow. The loading column is fed with unclarified leach liquor, the barren liquor being

TABLE 1.

Element	Results, ppm on basis of uranium		
	Bufflex	Purlex	UF ₆ specification
Silicon	25 ± 10	242	85
Iron	13 ± 5	349	150
Calcium	1	220	N/D
Aluminium	<10	122	50
N/D not determined			

recycled to the leaching circuit (no leach liquor to solvent extraction thus removes the main cause of the tar).

The process has been applied successfully to the conventional Bufflex or Eluex recovery cycle. This involves the loading of the uranium onto a strong-base resin and subsequent elution with dilute sulphuric acid, and the uranium is then recovered from the eluate by solvent extraction. The pump-mixer oxidation problem is easily rectified. An added advantage of this system as advocated above is that the ammonium diuranate precipitated from a Bufflex or Eluex system is purer than that of the Purlex system, as can be seen from Table 1. The uranium produced in the Bufflex system is pure enough to pass even the most stringent nuclear-grade specifications.

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CONTRIBUTION

W. Ruhmer, Anglo American Corporation of S. A. Ltd., S.A.

I WOULD LIKE TO PRESENT CONTRIBUTIONS covering two practical developments which have assisted in the operation of two of our solvent extraction plants. One of these, the ammonium hydroxide make-up system at the Western Reefs Levels solvent extraction plant has already been described in Mr. Craig's contribution.

The National Institute for Metallurgy (NIM) developed an automatic ammonium hydroxide system in 1973 which was installed by Western Reefs Levels. Further refinements were added and the system now consists of twin reactors, one being a standby unit. The sintered stainless steel pipe in the mixing vessel was replaced by glass beads as it was found that the pipe scaled up fairly rapidly. The system has now been in use four years and operates trouble-free. Prior to its installation the practice was to introduce ammonia gas into a 7 m³ tank filled with water. The associated controls were not good and ammonium hydroxide concentration varied widely. PH control in the old system was far from ideal. The old system also resulted in high ammonia losses due to evaporation. The NIM system yields a product of constant concentration and the losses through evaporation were minimal. The average consumption of ammonia prior to the installation of the NIM system was 0.15 kg/m³. After

the installation of the NIM system the ammonia consumption dropped to 0.10 kg/m³. Since the average throughput of the solvent extraction plant is about 70,000 m³ per month, a saving of 3500 kg of ammonia results, valued at 1000 rand. The present system at Western Reef Levels cost approximately 4500 rand so the pay back time was 5 months. It is rather a simple improvement but extremely effective.

A rather short contribution I have from another one of our plant deals with mixing and maintaining an organic continuous phase. In the section of his paper headed "Mixing", Mr. Finney mentions the use of conductivity probes to indicate the state of the mixed-phase emulsion as being aqueous or organic continuous. In the two Lurgi plants of the West uranium plant of the Far Reefs Exploration and Mining Company Ltd., conductivity probes were initially installed in the mixed-phase delivery line from the pump mixers. For reasons outlined below, these probes proved to be of no benefit and their use was discontinued. It was considered that the application of the probes in this plant was unsuccessful because of partial phase separation taking place within the mixed-phase delivery line in the vicinity of the probe. This non-homogeneous mixture prevented the probe from giving reliable results. As a substitute for the conductivity probes, ratio controllers have been installed on the organic recycle lines to the pump mixers, thus ensuring an organic continuous emulsion in the face of varying flow rates of pregnant solution.

URANIUM PROCESSING

Practical Processing of Uranium Panel Discussion

Introduction

G. Ritcey: In our panel discussion we would like to cover topics such as environmental considerations, hazards, materials of construction, contractors, a look at the future with respect to new low-grade complex feed material, equipment and possible use of continuous-ion-exchange.

Environmental

G. Ritcey: We will start off with environmental considerations and the aspects of amine losses and evaporation.

C. Lendrum: With regard to effluents, the problem in eastern Canada is that the rainfall is about 39" per year versus an evaporation rate of 18" per year so there is always an excess that has to be treated prior to discharge into the natural drainage systems. At the present time in Ontario we have three different environmental protection agencies, namely the Ministry of the Environment for Ontario (MOE), the Atomic Energy Control Board (AECB), and the Federal Environmental Protection Agency. There are various codes which we have to meet.

The radium 226 is probably the most important one at the moment. The Federal standard, based on a 3 micron

milipore filter, is 10 picocuries on an average, 20 on a two-week average and 30 on a grab sample. The MOE has an objective of 3 picocuries on a 1.3 milipore filter. There are rumors that a 10-20-30 total radium rather than dissolved radium is being considered.

The other problem that is important is nitrate because up to now the Elliot Lake producers are using nitrate elution and ammonia. Agnew Lake will be using Eluex with an ammonia recovery system to recover the ammonia from excess sulphate strip.

The current method of tackling the radium 226 problem is neutralization of barren solutions and tailings, and then treating the effluent from the tailings pond with barium chloride. The effluent is then passed through a secondary settling pond where the precipitated barium radium sulphate is retained. The nitrate problem is being looked at by all companies. The newest producer will use Eluex to avoid the nitrate problem. Some companies are looking at peat moss-humic acid pickup of the radium. Everybody is looking for what will be the final long-term solution to the radium problem.

One thing that has developed in eastern Canada is the thickened tailings discharge which gives a much more stable and denser dam with very little size segregation. All drainage is towards the pond at the discharge end. This technique has been described in a paper by E. J. Robinsky in the CIM Bulletin, Dec. 1975.

W. Ruhmer: I would like to add a little more about environmental problems in South Africa. First of all, the South African ore grades are only one fifth of Canadian grades, so therefore, there are not the same problems with radium 226. We normally neutralize the residues with lime, mix in the raffinate and deposit them in a dam.

We accidentally discovered that radium 226 concentrates in the red scale formed in the gas cooling and cleaning sections of the acid plant, which has necessitated a new code of practice for acid plant operation.

G. Ritcey: A meeting is to be held in Ottawa in October 1977 to further develop cooperative efforts toward finding a solution to the radium 226 problem.

Safety

Our next topic is hazards and safety aspects of the plant and its design — maintenance, fire and possible earthquake hazards. Perhaps someone could add to what has been said by the South Africans.

C. Lendrum: The new plant at Agnew Lake Mines Ltd. has a complete foam system telemetered back to the control room. The system was installed under direction of the underwriters.

S. Finney: All of our plants are situated in the open air. The plants are built on concrete pads with corbels around the edge to retain any spillage. Also, since lightning storms are prevalent, lightning conductors are installed. The tanks are all covered. No tanks may be worked on, say by welding, unless the plant has been cleared and cleaned. No synthetic clothing is permitted, to avoid static electricity sparking. Warning notices are posted but these are often overlooked by casual visitors. Fencing of plants is desirable to deter unauthorized visitors. Smoking is permitted only in the pressurized control rooms.

M. Ruhmer: I would like to comment further on the electrostatic problem. We had a look at solvent mixtures and found that these have a fair conductivity, lowering the hazard. On the solvent make-up side however, the kerosene and other diluents have low conductivity so it is necessary to make sure that the system is fully grounded.

The other aspect to which some attention has been given is the fire resistance of glass-reinforced polyester vessels. We had one bad experience with fibre glass-coated timber.

J. Dasher: I noticed in the illustration that there was a provision for adding foam in case of fire. If there was a fire, would there be any utility to any of the extinguished solvent that was left?

S. Finney: We have looked into this, and any remaining solvent should be written off.

I. Noble: We have been concerned about the accidental triggering of the protective foam stations, thereby ruining the whole solvent inventory. In one copper plant we have designed a water fogging spray system which has been acceptable to fire underwriters in at least two countries.

Construction Materials

G. Ritcey: We can now move on to materials of construction.

M. Grimes: Fibre glass coatings on concrete is an area of interest. However, in one case the coatings did not last. The matter is being investigated but it is not known whether the trouble lay with the adhesive

that was used, or possibly the concrete was not properly cured, or had an improperly prepared surface. Perhaps a free-standing polyester reinforced fibre glass lining with the concrete being just a support might have been a better choice in a case like that. Now, of course, fully fibre glass tanks of very large sizes are being used.

W. Ruhmer: We believe that stainless steel 316 L is a material to be avoided. In the Free State, a uranium plant was built in 1969 but was mothballed. After 5½ years, operations were undertaken, but after 6 months there were serious failures of the stainless steel. Due to the water shortages in the plant area, mine water with up to 2000 ppm chloride has to be used and this has played havoc with the stainless steel. Alternate river water containing 300 ppm chloride was then used which slowed the corrosion but it still occurred. There is a sort of copper sulphide depositing on the stainless steel, providing a starting point for corrosion. Severe pitting and perforation results.

C. Lendrum: At Agnew Lake we have generally gone to free-standing fibreglass. We have 5 tanks lined with Buna N rubber and, similar to South African experience, we have had more trouble with the bondings where rubber is bonded to rubber than where the rubber is bonded to steel although this is not certain. The rest is fibreglass or plastic. Our absorption columns are 316 stainless steel.

Complex Ores

G. Ritcey: We can now turn to factors relating to the future such as the lower-grade, more complex ores. We are thinking of difficult and more expensive leaching processes and therefore the recovery costs are going to be much higher. These ores include the shales, granites and phosphates.

T. Hardwick: Uranium is found in connection with phosphates in Florida, North Carolina and to a lesser extent in the western states. There is about 1 lb U_3O_8 per ton P_2O_5 .

With phosphates, the mining and extraction of uranium is taken care of in the production of phosphoric acid. The uranium however, is in a strongly acidic dirty solution. The uranium value is 5-10% of the value of the phosphoric acid so therefore the uranium process must fit into the current practice for phosphoric acid.

A phosphate plant takes the phosphate rock, running about 70% calcium phosphate and digests it with sulphuric acid, giving 28% phosphoric acid (6 mol) plus a gypsum precipitate. The gypsum is filtered off, yielding a solution at 150°F saturated with gypsum. This is the material from which the uranium must be extracted. There are rigorous conditions involved because in the phosphoric acid process the next step is evaporation to 40% volume to produce the final product. The evaporators are rubber-lined and therefore are very open to attack by kerosene or any other type of organic materials. To compound this, the solution has all the problems that arise in treating dirt with strong sulphuric acid. There are humatis, large amounts of aluminium, ferrous and ferric iron. The solution is about 1 mol fluoride. There is hydrofluosilicic acid present, and a few other difficult components, plus the fact that gypsum is always precipitating where it is not wanted. Conventional practice is to flush the lines out on a scheduled basis and this has to be pretty well followed.

There is one peculiarity in this system and that is in the 6 mol phosphoric acid. The ferrous ion oxidizes before the uranous ion so if the uranyl ion is to be extracted,

all the iron must be oxidized first. Normally after leaching, the natural material is U^4 in the presence of ferrous and ferric ion. There are two processes for the removal of uranium from phosphoric acid. One is the di-2-ethylhexyl phosphoric acid-tri-N-octyl phosphene oxide mixture. Because of the high association of U^4 or U^6 with phosphate, a high complexing agent is required, and the synergistic effect of these two compounds in kerosene is just sufficient to take the uranium into the solvent stage.

To strip the solvent, the uranium must be reduced to the U^4 form, either by addition of ferrous ion, or metallic iron, and then the uranium can be stripped back into the phosphoric acid. This gives a concentrate, and a second extraction can be done as a concentration step. One of the normal precipitating methods is to precipitate as ammonium uranyl tricarbonate, an easily filtered form.

The other method to recover the uranium from the phosphoric acid is the octyl phosphoric method, which is another mixture of commercially available compounds. This has the ability to extract U^4 from the rest of the system. It will also extract a fair amount of ferric ion so there is a subsequent separations problem. However, the extraction coefficients are rather more favorable in this case. The normal method of stripping is to oxidize the uranium to U^6 and strip with a strong phosphoric acid solution (10 mol). The oxidant can be either hydrogen peroxide or sodium chlorate. This produces a concentrate and the EHPA-TOPO system can be used to deal with the concentrate.

A number of companies are looking at this and, if fully adopted, the State of Florida could produce 5 to 6 thousand tons of uranium per year. The big problem is more of materials handling rather than chemistry.

Equipment

G. Ritcey: We would like to move now to solvent extraction equipment. Is there one type or design best suited for the uranium industry?

M. Grimes: What are the factors that decide the placing of organic or aqueous recycle lines inside or outside of the units?

S. Finney: From our experience, the problem is where the recycle lines can be taken from and still get flow through the settler. Our general design practice has been to take a fraction off the organic overflow weir, as the most satisfactory solution to the problem. It does mean that an external line is almost a necessity.

G. Ritcey: Would the South Africans like to comment on the Lurgi settlers — on their maintenance frequency, downtime and cost? Would they go for a different design in future?

W. Ruhmer: The first plants installed were the cylindrical settler type with two compartments. They had dished ends with a large number of bolts and it was a major operation to clear the trays, say of fungus, which was the main problem then. The subsequent plant was of different design and the access to the interior was much easier. The main feature of this design was its compactness. It is built like a chemical plant with the settlers on top and the scrubbers, strippers and turbo mixers below, which makes for a compact installation. We had considerable trouble in the original design when, for clearing, it was necessary to undo 164 bolts.

G. Ritcey: With this design of equipment and design of processes, and the environmental impact, coupled with economics we have reached a situation where it would appear that ion exchange should be used along with solvent extraction to produce a higher grade

product or for any of the other reasons. The Eluex process has been used for a number of years, and is being installed in other plants, and in recent years we have had continuous-ion-exchange. As discussed with Phillip Lloyd, an apt title could be "Is continuous-ion-exchange a threat or promise!"

C. Lendrum: This CIX route was chosen for Agnew Lake Mines Ltd. because it has a solution plant rather than a conventional mill. We have a stope-type leach and a surface leach. The unclarified solutions go through continuous ion exchange (Himsley column). We chose this route to avoid the use of classifiers, and yet with a ferric leach we had to have a pre-concentration stage before solvent extraction. Our choice of process was also governed by the small amount of liquor we would have to clarify for the solvent extraction plant. The purity of the product was a benefit rather than a criteria. While most processes will produce a product acceptable to the refineries, the Eluex system will produce a relatively pure product using two cheap reagents — ammonia and sulphuric acid. Environmental factors were also a consideration in that we have no nitrates going into the environment. We have only sulphuric acid to dispose of and while we do have calcium sulphate in the tailings, we believe that this can be handled in the local context. We have an ammonia recovery plant for the ammonium sulphate solution, and this should cut back to a large extent the ammonia which might go into the environment.

M. Grimes: I was associated for some years with one process that might have been a fifth cycle if it had been possible to develop it in the time and money that was available, and that was solvent extraction in a pulp, which of course achieved the main objective in going to continuous ion exchange, i.e. to avoid having to clarify the liquors. That is still a long piece in the future.

R. Hester: Rio Algom is presently mining 4500 tons/day and will be expanding to 18,000 tons/day over the next few years, increasing our uranium production from 5 million lb/year to 10 million lb/year, which indicates our ore grade will drop from 0.15% to 0.075% U_3O_8 . The system that has been in use for many years is based on the South African system which is an ion exchange system with nitrate elution, with two-stage precipitation (lime and ammonia). The ion exchange system has been very satisfactory with uranium recoveries of 99.9% and loadings of 4 lb/cu. ft. No resin has been replaced since start-up in 1960. There have been no poisoning of the resin and no regeneration problems.

There are other aspects though. Thorium is available for possible recovery and we do have water pollution problems, in that the nitrate and ammonia are going into the watershed since there is not total evaporation such as in South Africa.

We now have the constraints from the environmental protection agencies in that they want us to recycle and also to remove the nitrogen. We will be putting another plant on stream (Panel - 3300 tons/day). This plant will be using old equipment (from earlier operations) such as clarifier and ion exchange units. These are being renovated, and we are adding an Eluex plant, and sulphuric acid elution with an ammonia recovery system. This will comply with environmental agency regulations.

We have not yet decided what we will do at the existing operation at the Quirke mine which is being expanded from 4500 tons/day to 7000 tons/day. We have been looking at such things as chloride elution with magnesia precipitation to get away from the nitrogen problem, but this would not allow us to do very much with recycle.

Eluex might possibly be the answer at Quirke. In addition, we have been examining continuous-ion-exchange for Quirke, similar to the Agnew Lake plant. We have also done studies on straight solvent extraction. No decision has yet been made as to the preferred route.

As I mentioned, we have thorium. Is thorium a possible recoverable material? If so, solvent extraction might

be better than ion exchange. We do not have any fixed approach, but as an expanding producer we are working within governmental environmental constraints and, of course, the cost constraints.

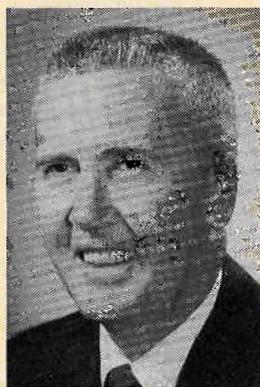
G. Ritcey: We have to close this Session 19 now. I would like to thank the members of the panel, and the participants in the audience.

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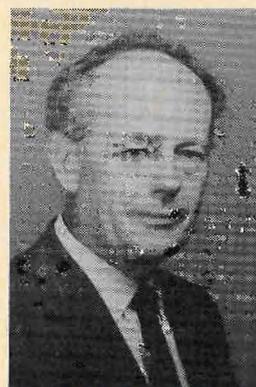
Chapter 13

Nuclear Processes

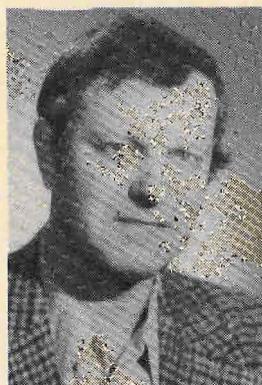
Sessions 18, 22 and 33



Dr. K. B. Brown



Dr. P. M. Mouret



Dr. P. Michel
Session Co-Chairmen

Chapter 13

Nuclear Processes

Sections 13.1 to 13.5



Dr. J. R. Dunning



Dr. J. R. Dunning



Dr. R. J. Dunning
General Chemistry

Solvent Extraction of Enriched Uranium Fuels at the Savannah River Plant*

M.C. Thompson, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, South Carolina.

ABSTRACT

A modified Purex process was developed in the Savannah River Laboratory and is now used routinely at the Savannah River Plant to recover enriched uranium (1 to > 90% ^{235}U) and either plutonium or neptunium from irradiated fuel. Performance is improved over the previous process except for zirconium decontamination. Laboratory tests at lower scrub acid concentrations show that the zirconium decontamination can be improved. Modifications which further improve uranium-neptunium partitioning have been tested in the laboratory, but not in the plant.

Introduction

THE SAVANNAH RIVER PLANT (SRP) recovers actinides from a wide variety of irradiated fuels containing ^{235}U enrichments of 1 to > 90 isotopic percent. The fuels come from a variety of sources, including the SRP reactors, government test reactors, the nuclear ship Savannah, and the Piqua power reactor. These fuels, clad with aluminum, stainless steel, or nichrome, could be chemically or electrolytically dissolved and processed in existing equipment; however, for the lower ^{235}U enrichments, the previously used solvent extraction flowsheet would not provide adequate throughput. A more flexible flowsheet has been developed that enables efficient and rapid processing of fuels of a wide range of ^{235}U enrichments. With this modified flowsheet, the uranium concentration in the process may be varied to provide maximum throughput consistent with ^{235}U concentration limits required for nuclear safety.

Solvent extraction separations at SRP are conducted in multistage mixer-settlers through which organic and aqueous streams flow countercurrently. The uranium and either neptunium or plutonium are processed through two successive solvent extraction cycles, and the recovered products are also separated from fission products and other impurities (decontaminated).

The flowsheet used previously (3.5 vol % TBP extractant) had limited capacity for uranium and required 1.2M $\text{Al}(\text{NO}_3)_3$ as a scrub stream to prevent high losses of uranium to the aqueous raffinate⁽¹⁾. The modified flowsheet utilizes 7.5 volume percent tri-n-butyl phosphate (7.5 vol % TBP) in the nitrate-nitric acid system. The flowsheet increases the flexibility of the separations equipment and lowers the amount of waste generated by about

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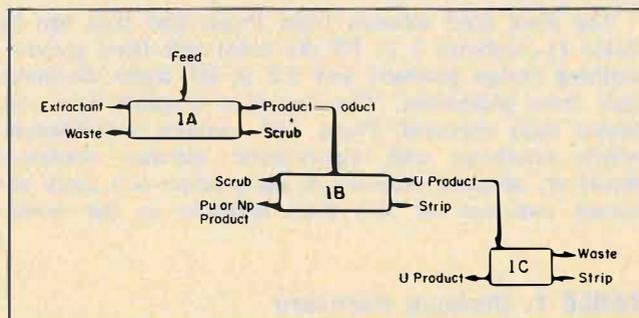


FIGURE 1. Present first cycle operation.

20%. The development and use of this improved solvent extraction process are discussed in this paper.

Process Description

In the first cycle (Figure 1), uranium and neptunium (or plutonium) are coextracted into the organic phase in the first mixer-settler (1A) and partitioned (separated) in the second mixer-settler (1B). Uranium is stripped in the third mixer-settler (1C). The organic extractant consists of 7.5 vol % TBP in n-paraffin hydrocarbon (C-12 to C-16).

Extractant flow is increased as the uranium concentration in the feed increases (100 grams per liter maximum) so that uranium does not reflux at any point to a concentration higher than that of the feed. The nominal nitric acid concentration of the feed and scrub streams in the first mixer-settler is 4.0M. Aluminum nitrate can be substituted for nitric acid in the feed, provided that sufficient acidity (0.5M) is maintained to prevent polymerization of plutonium.

When recovery of neptunium from the feed solution is desired, a reducing reagent (ferrous sulfamate) is added in the first cycle of solvent extraction to maintain plutonium in the nonextractable Pu(III) valence state and neptunium in the readily extractable Np(IV) state. Thus, the plutonium present will remain with the fission products in the waste streams, and neptunium will be extracted.

When recovery of plutonium is desired and the neptunium may be discarded, oxidizing conditions are maintained in the first cycle. Plutonium is extracted in the first mixer-settler as Pu(IV) and separated from uranium in the second mixer-settler by reducing Pu(IV) to Pu(III). Neptunium, if present in the feed, remains as Np(V) and is rejected to the aqueous waste stream.

In the second uranium cycle with two mixer-settlers, uranium is extracted into the organic phase and scrubbed with nitric acid in the first mixer-settler (1D). Uranium is stripped in the second mixer-settler (1E).

Uranium Recovery

Using miniature mixer-settlers, laboratory tests were made with solutions simulating dissolved stainless steel

clad fuels to determine the best solvent concentration for the uranium concentrations of interest. Boric acid, used in the plant to maintain nuclear safety in dissolving some fuels, was added to the test solutions. Test results for the first mixer-settler (Table 1) showed uranium losses to be high with 3.5 and 5.0 vol % TBP, although a very high extractant flow rate with 5.0 vol % TBP yields a marginally acceptable loss. Uranium losses with 7.5 vol % TBP were low at fairly low extractant flow rates. Thus, 7.5 vol % TBP allows greater flexibility for processing higher uranium concentrations.

The plant feed solution from Piqua fuel (last test in Table 1) combined 5×10^9 dis/(min) (ml) from gamma-emitting fission products and 4.2×10^7 alpha dis/(min) (ml) from plutonium. The apparent uranium loss was higher than expected. Piqua fuel contains molybdenum which interferes with colorimetric uranium analyses; therefore, uranium recovery in the product is a more accurate indicator of loss than uranium in the waste.

TABLE 1. Uranium Recovery

Extractant, % TBP	Flow Ratio		Uranium, %	
	Extractant To-Feed	Scrub- To-Extractant	In Product	In Waste
3.5	3.0	0.17	40.1	53.7
3.5	5.0	0.10	68.0	24.4
5.0	3.0	0.17	94.6	5.4
5.0	5.0	0.10	99.2	0.4
7.5	2.0	0.17	96.8	0.54
7.5	3.0	0.17	99.9	0.06
7.5 ^a	4.0	0.15	99.6	0.96

^a- Plant feed solution 40.2 g/l U.

TABLE 2. Plutonium Recovery

Feed Pu, dis/(min) (ml)	Flow Ratio		Plutonium, %	
	Extractant- To-Feed	Scrub- To-extractant	In Product	In Waste
1.96×10^7	2	0.25	100	0.14
2.30×10^7	2	0.17	100	0.04
4.2×10^7 ^a	4	0.15	92	0.03

^a- Plant feed solution 40.2 g/l U.

TABLE 3. Plutonium Partitioning

Temperature 30-35°C									
Extractant- To-Feed	Flow Ratio		Strip, M	Pu Product, %		U Product, %			
	Strip-to- Extractant	Scrub- To-Strip		U	Pu	U	Pu		
2.0	0.225	3.33	HNO ₃	FS	U	Pu	U	Pu	
2.0	0.225	3.33	0.90	0.02	0.10	99.9	100.0	0.14	
4.0 ^a	0.20	3.0	0.84	0.03	0.16	100.0	97.9	0.01	
4.0 ^a	0.20	3.0	1.99	0.075	< 0.02	82.8	99.6	0.27	
4.0 ^a	0.20	3.0	1.99	0.075	0.14	90.7	100.0	0.10	

^a- Plant feed solution 40.2 g/l U.

The losses observed during plant operation with this solution were much lower (0.01% uranium loss by isotope dilution analyses).

Plutonium Recovery and Partitioning

With the modified flowsheet, plutonium recovery was expected to be equivalent to uranium recovery because the distribution coefficients of plutonium and uranium are similar. Three tests were made to determine plutonium recovery (Table 2). Except for the test with the plant solution obtained from dissolution of Piqua power reactor fuel, plutonium mass balances were excellent. Plutonium losses were low in all tests. With plant feed, neptunium split approximately 85 to 15% between product and waste, respectively, in the first mixer settler, and 35% of the neptunium was in the uranium product after partitioning. Similar neptunium behavior has been observed in plant operation and is due to the high nitric acid concentrations in plant feeds (4.5 - 6.0M). The oxidation of extractable Np(IV) to inextractable Np(V) is inversely dependent on the fourth power of the hydrogen ion activity⁽²⁾. Thus, Np(IV) is stabilized and can be extracted along with uranium and plutonium.

The partitioning mixer-settler must be operated to separate uranium and either neptunium or plutonium with no reflux of uranium above the concentration in the feed to the first mixer-settler. Plutonium is partitioned by reducing extractable Pu(IV) to inextractable Pu(III) with ferrous sulfamate. The acid concentration can be high enough to prevent uranium reflux because Pu(III) is essentially inextractable.

Plutonium partitioning was tested in the miniature mixer-settlers (Table 3), and results were satisfactory as long as sufficient ferrous sulfamate was present. Nitric acid reacts slowly with ferrous sulfamate to destroy sulfamate and oxidize ferrous to ferric⁽³⁾. Thus, at the higher acid concentration used in the tests with plant solutions, more ferrous sulfamate was needed to ensure plutonium reduction. The higher acid was required to prevent uranium reflux which occurred in the first two tests with low acid.

During plant operation with the low enrichment uranium flow-sheet, uranium losses have averaged <0.05% to waste and 0.01% to plutonium product stream. Plutonium losses have averaged <0.05% to the waste and uranium streams. Operation at higher than predicted extractant flows have been necessary to obtain these low product losses. Consequently, the ultimate uranium capacity of the process is limited by the equipment in the plant.

Neptunium Recovery and Partitioning

With highly enriched uranium feed solutions, neptunium is recovered by extraction along with uranium, and plu-

TABLE 4. Neptunium Recovery

Scrub	4.0M HNO ₃ , 0.02-0.04M FS		
Extractant	7.5% TBP		
Feed	6 g/l U, 0.1 g/l Np, 1.1M Al(NO ₃) ₃ , 0.7M HNO ₃ , 0.02M FS		
Extractant-to-Feed Flow Ratio	Waste, %		
	U	Np	Pu
1.3	0.92	0.28	≈ 100
1.5	0.29	0.12	≈ 100
1.5	0.20	0.09	≈ 100
2.0	0.43	0.08	> 99
2.0	0.17	0.03	> 99
2.5	0.09	0.24	81

^a. Run made with plant feed 5.45 g/l U, 2.08 × 10⁸ dis/(min) (ml) Pu, 6 × 10³ dis/(min) (ml) Np, 1.47M Al, 1.93M HNO₃, and 8.36 × 10¹⁰ dis/(min) (ml) gross gamma activity.

onium is rejected to the waste. Neptunium and uranium are then partitioned in the second mixer-settler by adjusting the acid concentration of the strip stream and flows of the aqueous and organic streams. Tests were made to investigate recovery and partitioning. Neptunium losses were low (<0.3%) in all the tests (Table 4). The first five tests were made with simulated feeds, and ferrous sulfamate was added to the feed immediately before each test. The sixth test was made with plant feed in which ferrous sulfamate was added 3 to 4 days before the test. Bibler⁽⁴⁾ has shown that the ferrous ion is rapidly oxidized by radiolytically produced hydroxyl radicals. The ferric ion, thus produced, hindered reduction of neptunium in the mixer-settler and resulted in higher than expected neptunium losses⁽³⁾. The presence of ferric ion also results in incomplete reduction of plutonium⁽³⁾ as shown by the presence of only 81% of the plutonium in the waste. The apparent high uranium losses are probably due to inaccurate colorimetric analysis at these very low uranium concentrations. Uranium extracts better than neptunium; therefore, the actual uranium loss is believed to be less than the neptunium loss in all cases.

For neptunium partitioning, the flows of the various streams and the acid concentration of the strip must be carefully controlled to maintain the neptunium distribution coefficient as low as possible while maintaining the uranium distribution coefficient close to one. This condition necessarily requires operation with some uranium reflux to ensure low neptunium in the uranium product. The conditions necessary to partition neptunium and prevent reflux of uranium were calculated and confirmed by laboratory tests (Table 5). The first three tests demonstrate the effects of the flow ratios on partitioning. To effectively strip neptunium, a high strip-to-extractant flow ratio is necessary. However, a high scrub-to-strip flow ratio is necessary to re-extract uranium which is stripped along with neptunium. The fourth test illustrates the combined effects of high flow ratios. Uranium reflux did not occur in any of these tests.

In initial plant operation with the new flowsheet, valence adjustment of plutonium and neptunium with ferrous sulfamate was ineffective. Rejection of neptunium to the aqueous waste stream (1AW) ranged from 5% to 75%, while more than 90% of plutonium present was extracted, rather than rejected, in the first cycle.

Laboratory studies demonstrated that ferrous sulfamate, added to both the aqueous feed solution and the aqueous scrub stream in the first stage (1AS), was largely destroyed during the relatively long time between preparation and use of these solutions⁽³⁾. Radiolysis destroyed the ferrous ion in the feed in a few hours, and nitric acid

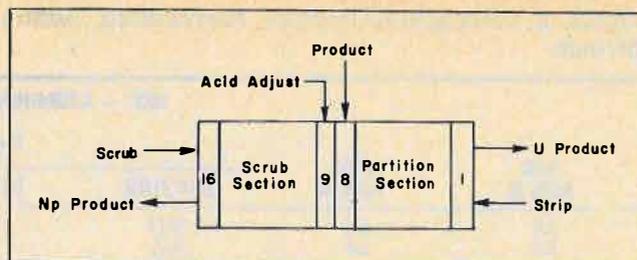


FIGURE 2. Proposed partitioning bank (1B) operation.

TABLE 5. Neptunium Partitioning.

Extractant and Scrub 7.5% TBP						
Strip-to-Extractant Flow Ratio	Strip ^a HNO ₃ , M	Scrub-to-Strip Flow Ratio	Neptunium Product, %		Uranium Product, %	
			Np	U	Np	U
0.20	1.59	3.0	22.4	0.25	77.5	79.5
0.38	1.59	2.4	93.1	6.1	1.9	95.0
0.46	1.59	2.0	98.0	13.8	0.09	133.6
0.45	1.50	3.0	103.4	0.6	0.6	106.8

^a. Strip also contained 0.02M ferrous sulfamate.

oxidized much of the ferrous ion in the scrub solution. To achieve the desired neptunium-plutonium separation in plant operation, the process flowsheet was modified as follows: ferrous sulfamate is added to the 1AS stream immediately before it enters the mixer-settler, and ferrous sulfamate is not added to the feed solution where it would be destroyed by radiolysis.

During subsequent routine plant operation, uranium losses have averaged <0.05% to waste and 0.01% to the neptunium product stream. These losses are within the range of expected losses based on laboratory tests and computer calculations. Neptunium losses have averaged <1% to waste. The losses to waste are considerably higher than those observed in laboratory tests, but better than the 2% obtained with the 3.5 vol % TBP flowsheet.

Neptunium losses to the uranium stream in the partitioning step have averaged 4%, but these losses are lower than those observed in the 3.5 vol % TBP process. Neptunium in the uranium stream is sent to the waste in the second uranium cycle (1DW) and is recovered in the second neptunium cycle. The large volumes and impurities in the recycled waste increase neptunium loss and decrease decontamination in the second neptunium cycle.

If partitioning could be improved so that only 1 to 2% of the neptunium remains with the uranium, neptunium would not have to be recovered from the second uranium cycle waste, and second neptunium cycle performance would be improved. Neptunium and uranium are partitioned by adjusting the acid concentration in the 1B mixer-settler so that the extraction factor of uranium is greater than one while the extraction factor of neptunium is less than one. Computer calculations were made to examine potential improvement in partitioning obtained by lowering the acid concentration in the strip solution (1BX). The calculations showed and tests confirmed that changes which decrease neptunium losses to the uranium stream increase uranium losses to the neptunium stream.

An alternative method of improving partitioning is to (1) lower the acidity of the strip solution (1BX) to ensure stripping neptunium, and (2) inject a high acid stream in the 1B scrub section to recover any uranium stripped with

TABLE 6. Neptunium-Uranium Partitioning with a Low Acid Strip Stream and a High Acid Side Stream

		1BX' — 8.2M HNO ₃ added at Stage 9				
1AS Acid, M	1BX Acid, M	Flow Ratios			Np ^a in U, %	U Reflux Ratio ^b
		1BX'/1BX	1BX/1AX	1BS/1BX+1BX'		
2.0	1.0	0.13	0.36	2.00	1.8	0.43
2.0	1.0	0.11	0.31	2.50	0.48	0.35

^a. Current nominal % Np in U is 4%.

^b. Ratio of maximum uranium concentration in any stage to uranium concentration in 1AF.

the neptunium. The feasibility of a low acid strip stream with a high acid side stream was tested (Figure 2). The tests (Table 6) showed that neptunium losses to the uranium stream can be reduced below the current nominal 4%. Computer calculations were made with a high acid stream in Stage 9 at a flow of 0.10 relative to the feed and a strip acid concentration of 1.0M. The results of the calculations showed that partitioning could be improved with side stream acidities of 4 to 8M. The plant will test this flowsheet change in the near future.

Decontamination

Decontamination of uranium, plutonium, and neptunium from fission products and inorganic ions is of prime importance to the separations process. Decontamination of the uranium product stream from inorganic ions (except for aluminum, molybdenum, and mercury) was better than decontamination of the neptunium or plutonium stream (Table 7). Decontamination is expected to be higher for the uranium stream because the partitioning mixer-settler acts as additional scrub stages for the uranium stream.

Molybdenum decontamination was studied extensively because Piqua fuel solutions contained 0.01M molyb-

denum. Molybdenum was moderately extractable, but did not easily strip into acid solutions. Decontamination was improved by addition of 0.05M phosphate ion and 0.5M aluminum ion which reduced molybdenum extractability by formation of heteropolymolybdates.

Fission product decontamination was measured with plant solutions with low and high ²³⁵U enrichments. The fission product activities of these solutions and the decontamination factors are shown in Table 8. At higher activities (high ²³⁵U enrichments) the fission product decontamination is better. Analyses of the product solutions for inorganic ions and fission products resulted in concentrations less than or equal to the detectability limit of the method used for analysis. Therefore, as fission product concentration in the feed increased, the decontamination increased because the product concentration remained unchanged.

In plant operation, the zirconium decontamination factor for the neptunium product during highly-enriched uranium processing with 3.5% TBP varied from 20 to 2600 and averaged ~600. Since 1974 when processing with 7.5 vol % TBP began, the zirconium decontamination factor for neptunium has varied from 10 to 450 and averaged 90. The zirconium distribution coefficient ($D_{o/a} = [Zr]_o/[Zr]_a$) increases as nitric acid concentration increases. Therefore, the zirconium decontamination should increase if the scrub acidity in the 1A mixer-settler is decreased from the present 4.0M HNO₃. Several laboratory tests were made to determine the minimum feasible scrub acid concentration (Table 9). If neptunium were not to be recovered, the scrub acid should be the same as in the second uranium cycle, i.e., a minimum of 0.8M HNO₃. Recovery of neptunium, however, prevents use of very low acid scrubs because the Np(IV) distribution coefficient is much lower than uranium. The tests (Table 9) show that neptunium loss is unaffected down to 2.0M acid in the scrub as long as the extractant flow rate is increased when the scrub acidity is below 2.5M. Uranium losses at 2.0M acid should not be so high (0.46%) since the uranium distribution coefficient is greater than 1.5 in the scrub section. In these tests, the

TABLE 7. Inorganic Ion Decontamination

Ion or Element	Concentration, M	Feed-to-Product Concentration Ratio	
		U Product	Np or Pu Product
Al	0.1	> 600	> 12,000
B	0.4	> 400	320
Fe	0.15	> 1,000	—
Ni	0.016	> 1,100	> 350
Cr	0.041	> 1,000	> 1,000
Mn	0.004	> 500	> 500
PO ₄ ³⁻	0.066	—	> 5,000
Hg	0.003	> 70	> 350
Mo	0.001	80 ^a	> 1,400

^a. Uranium product decontamination increased to >300 by addition of PO₄³⁻ and Al³⁺ to the feed.

TABLE 8. Fission Product Decontamination

Isotope	Feed Activity, dis/(min) (ml)		Feed-to-Product Activity Ratio			
	Low Enriched	High Enriched	U Product		Np or Pu Product	
			Low	High	Low	High
⁹⁵ Zr	—	2.81 × 10 ⁹	—	> 10 ⁴	—	10 ⁴
⁹⁵ Nb	—	1.72 × 10 ⁹	—	> 10 ⁵	—	> 10 ⁴
¹⁰³ Ru	—	5.98 × 10 ⁹	—	10 ⁵	—	10 ⁵
¹⁰⁶ Ru	5.74 × 10 ⁸	5.14 × 10 ⁹	3600	> 10 ⁵	10 ⁴	> 10 ⁵
¹³⁴ Cs	3.41 × 10 ⁸	2.34 × 10 ⁹	> 10 ⁴	> 10 ⁶	> 10 ⁴	> 10 ⁶
¹³⁷ Cs	2.03 × 10 ⁹	6.02 × 10 ⁹	> 10 ⁵	> 10 ⁵	> 3 × 10 ⁴	> 10 ⁶
¹⁴⁴ Ce	2.35 × 10 ⁹	5.51 × 10 ¹⁰	8600	> 10 ⁵	4900	10 ⁵

total uranium inventory increased, but no change was observed in the maximum uranium concentration in the 1A bank. The maximum uranium concentration in the bank will not change so long as the uranium distribution coefficient in the scrub section is greater than one.

Two tests were made using tracer zirconium to illustrate the improvement in decontamination obtained by lowering the scrub acid concentration. The zirconium decontamination factor increased from ~ 200 to > 1000 when the scrub acidity was decreased from 4.0 to 2.0M.

Second Uranium Cycle

Increasing the concentration of uranium in the feed to the second uranium cycle made it necessary to change the scrub acid concentration to prevent reflux of uranium above the feed concentration. For less than 5 g/l uranium concentrations in the feed, a minimum of 0.8M HNO₃ in the scrub was adequate. Several tests were made with high uranium concentrations in the feed, and the results were checked with computer calculations. The first four tests showed excessive reflux of uranium (Table 10). The last two tests were typical of normal operation except for low acid in the feed to one test which resulted in high uranium loss to the waste stream. Plutonium was added to the feed of the last test to determine the decontamination factor. The decontamination factor of 25 found in this test was not sufficient to ensure acceptable uranium product.

Uranium losses to waste have been less than 0.01% during plant operation. With ferrous sulfamate added in

TABLE 9. Effect of Scrub Acid Concentration on Uranium and Neptunium Recovery and Decontamination

HNO ₃ in Scrub, M	Extractant Flow Relative to Feed	Np Loss to 1AW, %	U Loss to 1AW, %	U Reflux Ratio ^a	Zr, DF ^b
4.0	1.6	>0.66	<0.10	0.68	200
2.5	1.6	0.15	<0.09	0.70	—
2.0	2.1	0.22	0.46	0.67	>1000

^a. Ratio of maximum uranium concentration in any stage to uranium concentration in feed.
^b. Decontamination factor = activity in 1AF/activity in 1AP.

the scrub section of the mixer-settler, plutonium contamination of the uranium product has been about 1000 alpha disintegrations per gram of uranium. Fission product decontamination has been sufficient to give an acceptable product.

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TABLE 10. Mini-Mixer Settler Tests of Second Uranium Cycle

Feed		Extractant 7.5% TBP Temperature 45°C			% U		U Reflux Ratio ^a
U, g/L	HNO ₃ , M	Extractant-to-Feed Flow Ratio	Scrub HNO ₃ , M	Scrub-to-Extractant Flow Ratio	Product	Waste	
15.25	4.18	2.00	0.89	0.145	100	<.08	1.56
19.9	4.08	1.85	1.73	0.17	100	<.04	1.37
29.7	4.19	2.50	1.04	0.10	98.1	.03	1.87
29.7	4.19	3.00	1.04	0.14	97.0	<.05	1.30
17.8	3.46	3.00	1.2	0.12	99.7	.29	0.73
21.34	3.87	3.00	1.2	0.14	100	<.08	0.43

^a. Ratio of maximum uranium concentration in any stage to uranium concentration in feed.

DISCUSSION

W.R. Burton: (a) What measurements of the profile were made with respect to, say, Zr and Np?
 (b) What computer code was used?
 (c) Was the Neptunium really at equilibrium in the column?

M.C. Thompson: (a) Np profiles were measured in many of our laboratory tests and were quite predictable. Zr profiles were measured only in the last test with 2M HNO₃ scrub. Zr refluxed slightly above the feed concentration with the highest concentration at the feed stage.

(b) Several computer codes were used during the work. Initially, the TRANSIENTS code by J.T. Lowe (*I & EC Proc. Design and Devel.* 1, 362 (1968)) was used with empirical equations derived from laboratory distribution measurements. Correlation was relatively good. More recently, better correlations have been obtained with SOLVEX code by W.C. Scotten (SERDA

Reports DP-1391, E.I. du Pont de Nemours & Co., Aiken, S.C. (1975)). This code used tables of distribution data with linear interpolation between points.

(c) I believe Np was at equilibrium. Our tests were continued until periodic samples indicated all components were at steady state. Mass balances for Np were 100% within our analytical reproducibility ($\pm 15-20\%$).

A. Naylor: In flowsheet development studies, one often has some difficulties simulating process conditions with non-active feed solutions. I am interested to know whether your experimental results on Np and Pu distribution, and in particular, losses to the raffinates, correlated well between your trials with active and non-active feed solutions? As you are aware, impurity and radiation degradation effects under active conditions mean that often there are wide discrepancies in raffinate levels between active and non-active (simulated feed) conditions.

M.C. Thompson: Some differences were observed be-

tween highly active and simulated feed results. Pu losses were slightly lower with active feeds. Presumably, generation of nitrite ensured the presence of only Pu^{4+} . Pu valence in simulated tests was adjusted by reduction with ferrous sulfamate and oxidation with NaNO_2 . Incomplete oxidation would yield higher losses. Np losses were higher for active tests due to the presence of radiolytically produced nitrite.

J.C. Mailen: The author noted that at higher $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratios the Pu^{4+} failed to reduce to Pu^{3+} . Can this failure be correlated to known electrode potentials of the $\text{Fe}^{3+}:\text{Fe}^{2+}$ and $\text{Pu}^{4+}:\text{Pu}^{3+}$ couples?

M.C. Thompson: Electrode potentials of the $\text{Fe}^{3+}:\text{Fe}^{2+}$ couple, calculated using the Nernst equation, correlate well with the reduction of Pu^{4+} to Pu^{3+} . We have measured the electrode potentials in the enriched uranium solutions in the laboratory. The potentials are a reliable method for predicting the behaviour of Pu during solvent extraction (see reference 3 in this paper).

V.C. Vaughen: Did you experience any improvement in decontamination factors attributed to the changes in TBP concentration? (As mentioned by the

British, the different dependencies of E_A° on TBP concentration result in improved DF's at lower TBP concentrations).

M.C. Thompson: Part of the decrease in decontamination factor for Zr in going from 3.5% TBP to 7.5% TBP, as observed in this paper, is probably due to changes in E_A° with the increase in TBP concentration. Part of the decrease is attributable to increased free TBP. We have observed increased retention of Zr by the solvent at high feed activities ($> 1.5 \times 10^{11}$ d/m/ml $\beta+\gamma$) during plant operation with 7.5% TBP but not with 3.5% TBP. This indicates increased formation of DBP which would also give lower decontamination factors.

G. Grossi: With reference to highly enriched uranium fuel reprocessing, could you give us a figure on the total amount of nonuranic alpha emitters in the final U product (dpm/gram of U)?

Is this figure lower than 75,000 dpm/g of U?

M.C. Thompson: The total non-uranic alpha emitters in the final U product from highly-enriched uranium fuel reprocessing has averaged 1000 dpm/g U (principally Pu).

NUCLEAR PROCESSES

Extraction and Selective Stripping of Uranium and Molybdenum in Sulfate Solution Using Amines

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COGEMA — Branche Uranium

ABSTRACT

The uranium solutions obtained by leaching of AKOUTA ores and containing large quantities of molybdenum are purified by solvent extraction. During the first test run, precipitation of complexes such as amine phosphomolybdate was observed. It was found that this precipitation could be prevented by oxidizing the molybdenum in the feed prior to solvent extraction. Information on the basic studies carried out to ensure the reliability of the process is presented.

Introduction

SINCE 1971 THE COGEMA HAS CARRIED OUT STUDIES, on laboratory and pilot scales, concerning the processing of uranium ores from AKOUTA (Republic of Niger). Coming from a sandstone area, these ores offer special characteristics, particularly the reduced form of the uranium species and a high molybdenum content

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After study of acid vat leaching of the ores, it was finally decided, in order to achieve a higher uranium yield, to use a strong acid leaching method followed by curing. This method was derived from the one applied by SOMAIR in Niger.

The process flowsheet is rather conventional and includes, after leaching, purification by means of solvent extraction and precipitation of a magnesium uranate from the uranium solution obtained by stripping. The solvent extraction step has presented some difficulties, which are reported in the present paper.

Process Flowsheet Principles

The Akouta ore, like all the ores of this area of Niger, needs strong leaching conditions and particularly the use of concentrated sulfuric acid. Moreover, the uranium is tetravalent and needs the addition of an oxidizing agent, i.e., sodium chlorate. The leaching is carried out at a relatively high temperature using very little water, and the uranium is then dissolved by adding some water with vigorous stirring. (Figure 1). The liquid/solid separation, effected on continuous belt filters, provides a rather concentrated solution (5 to 8 gpl in uranium), which means less than 1 m³ solution per ton of ore. This solution is then purified using an organic solvent (Alamine 336).

The presence of molybdenum and vanadium has been known for a long time. In fact, the uranium ores contain

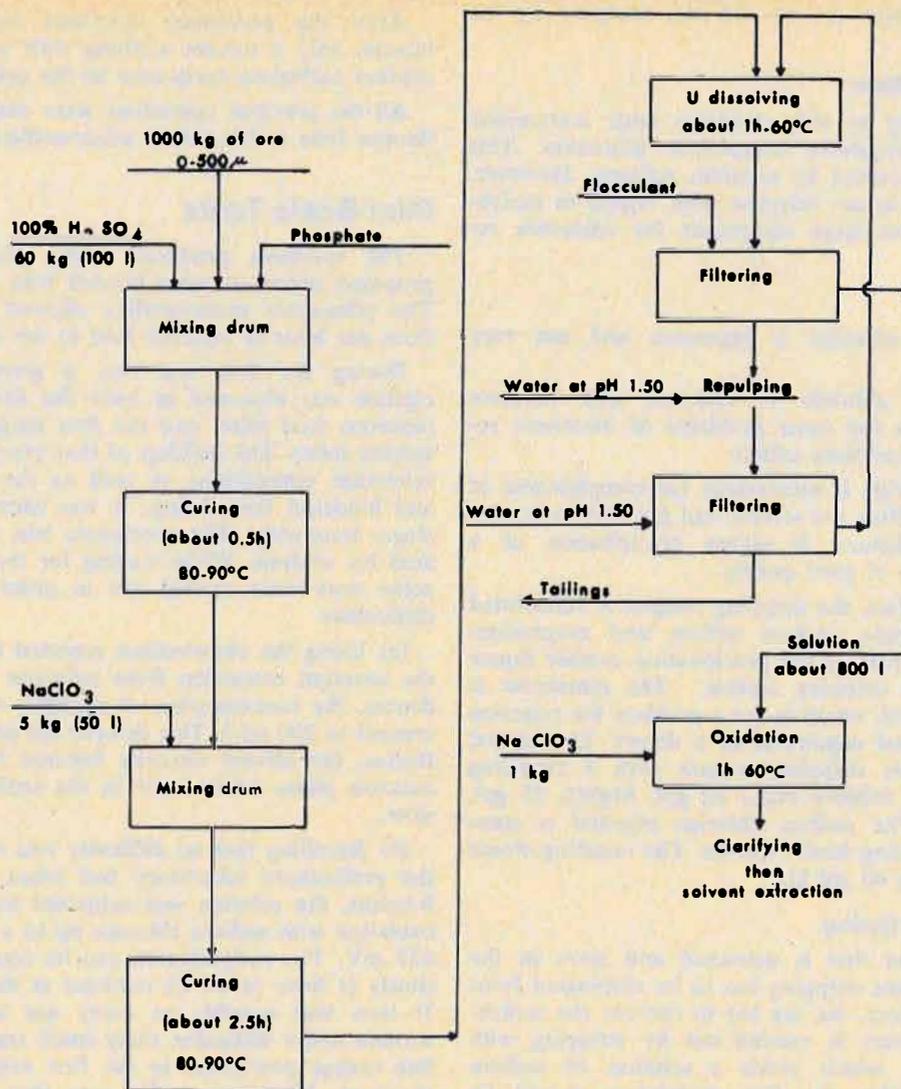


FIGURE 1. Simplified flowsheet of the Akouta ore processing.

molybdenum with a mean ratio Mo/U of 25%, varying within the 10 - 30% range. Vanadium content is lower, with a mean ratio V/U of 6%, varying within the 5 - 10% range. Therefore, it could be expected that most of the molybdenum, assuming it was at valence 6, would be extracted by the solvent. Thus, the preliminary studies have resulted in setting up a solvent extraction flowsheet (Figure 2) including the following steps: extraction, selective stripping of uranium, regeneration of all the solvent which is, in fact, the molybdenum stripping, and solvent washing with water. This flowsheet will be developed in the following sections.

The process ends with the conventional precipitation of magnesium uranate and the fabrication of a molybdenum compound to be defined according to its market potential.

Solvent Extraction Tests

Preliminary Tests

The preliminary tests have been carried out using partly synthetic solutions. This means that some 6-valent molybdenum has been added to achieve the desired molybdenum concentration. These tests were carried out without any difficulties and allowed definition of the main flowsheet parameters.

Solvent Composition

The solvent finally chosen has the following composition:

Alamine 336	0.2 M (i.e., about 79 gpl)
Tridecanol	50 ml
Kerosene	amount necessary for 1 liter

Average Composition of the Aqueous Feed:

Element or ion	Concentration in gpl
U	7
Mo	1.6 to 1.8
V	0.8
Cl	2
Fe	7.5
SiO ₂	0.1 to 0.3
SO ₄	90
H ₂ SO ₄	10 to 15
Eh	300 to 400 mV

Composition of the Stripping Solution (Eluant)

A priori the stripping solution could be selected from 3 types of eluant according to the desired uranium concentrate.

(a) Sodium carbonate:

Sodium carbonate allows an easy stripping using very

few stages, but it is not selective and precipitates a sodium uranate which is less and less accepted by the uranium refiners.

(b) Ammonium sulfate:

It is rather easy to strip uranium with ammonium sulfate which precipitates ammonium diuranate. This product is well accepted by uranium refiners. However, ammonium sulfate is not selective with regard to molybdenum and requires large equipment for ammonia recycling.

(c) Chlorides:

(1) Magnesium chloride is expensive and not very efficient.

(2) Ammonium chloride is efficient and selective (Figure 3) but has the same problems of ammonia recycling as does ammonium sulfate.

(3) Sodium chloride is satisfactory for completeness of uranium stripping from the solvent and for selectivity with regard to molybdenum. It allows precipitation of a magnesium uranate of good quality.

As a matter of fact, the stripping reagent is constituted with sodium chloride, sodium sulfate, and magnesium sulfate, because a part of the precipitation mother liquor is recycled to the stripping section. The remainder is eliminated as a bleed, which is not a problem for rejection in the environmental conditions of a desert. The typical composition of this stripping reagent with a recycling rate of 50% is as follows: NaCl 90 gpl, MgSO₄ 35 gpl, Na₂SO₄ 70 gpl. The sodium chloride rejected is compensated for by adding fresh chloride. The resulting eluate contains more than 40 gpl U.

Molybdenum Stripping

The molybdenum that is extracted and stays in the solvent after uranium stripping has to be eliminated from the solvent. Therefore, we are led to recover the molybdenum. This recovery is carried out by stripping with sodium carbonate, which yields a solution of sodium molybdate (see Table 2). This molybdate should be purified to eliminate mainly the phosphates and the vanadium.

Solvent Regeneration

After the previously described treatment with carbonate, only a solvent washing with water is needed, to prevent carbonate carry-over to the extraction section.

All the previous operations were verified through continuous tests in laboratory mixer-settlers.

Pilot Scale Tests

The solutions produced when piloting the various proposed processes were treated with solvent extraction. The pilot-scale mixer-settlers allowed processing of 10 litres per hour of aqueous feed in the extraction section.

During the first test run, a greenish gummy precipitate was observed in both the first extraction stage (aqueous feed inlet) and the first stripping stage (loaded solvent inlet). The buildup of that precipitate plugged the interstage connections as well as the stages themselves and hindered the stirring. It was necessary to clean the stages frequently. The precipitate was filtered and separated for analysis. While waiting for the analytical results, some tests were carried out in order to overcome the difficulties:

(a) Using the observations reported by Merritt⁽¹⁾ about the uranium extraction from solutions containing molybdenum, the concentration of modifier (tridecanol) was increased to 200 ml/l. This delayed the precipitation. Nevertheless, the solvent viscosity became very high, and the aqueous phase coalescence in the settlers was much too slow.

(b) Recalling that no difficulty was encountered during the preliminary laboratory test when molybdenum was 6-valent, the solution was subjected to a complementary oxidation with sodium chlorate up to a redox potential of 850 mV. The molybdenum can be completely but rather slowly (1 hour at 60°C) oxidized at that redox potential. It then was possible to carry out a second test run without major difficulty. Only small amounts of a crystalline orange precipitate in the first extraction stage were observed. However, to be sure that the problem was really solved in that way, it was necessary to achieve a good knowledge of the precipitation mechanism.

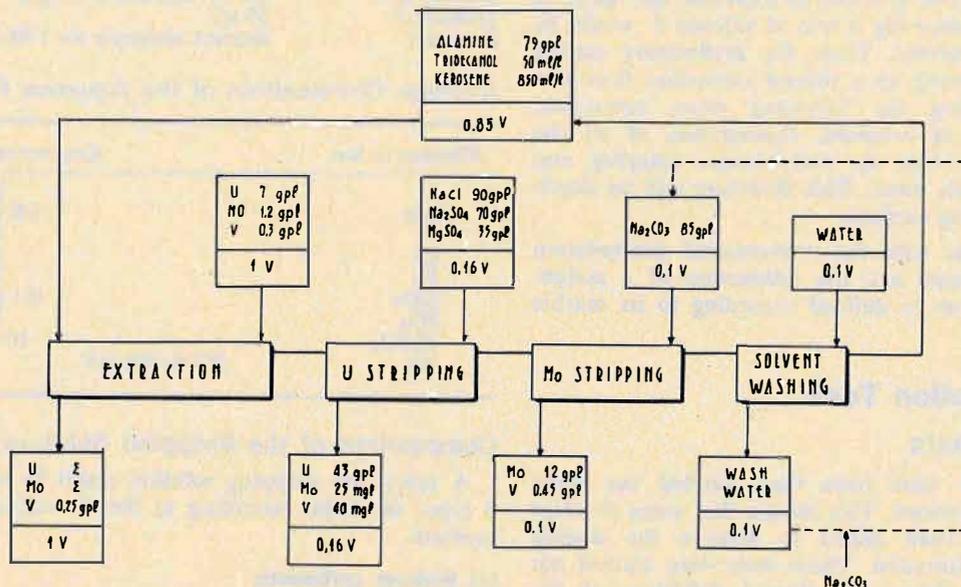


FIGURE 2. Basic flowsheet of the extraction process.

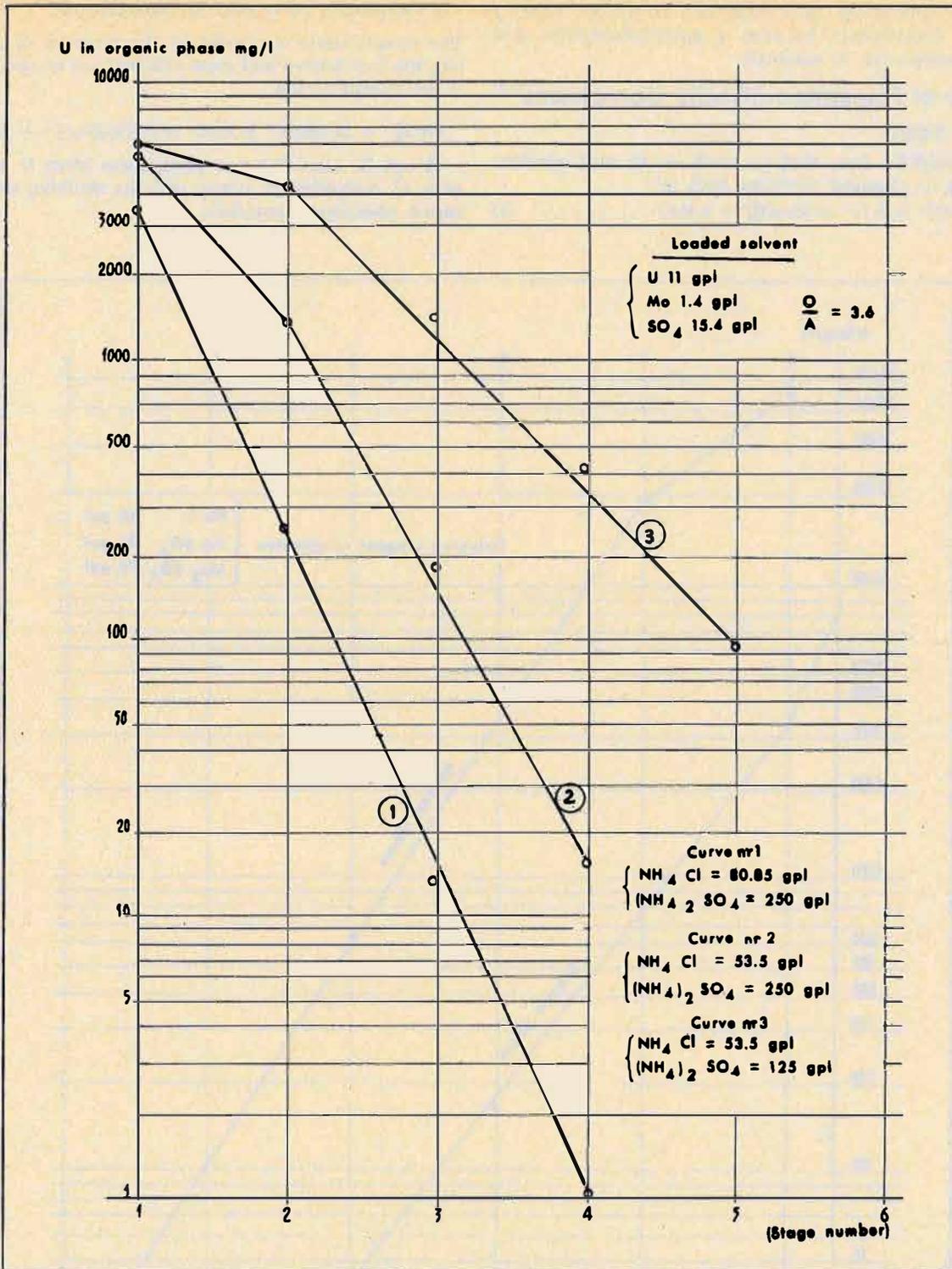


FIGURE 3. Influence of NH₄Cl and (NH₄)₂SO₄ concentration on U content in organic phase in the stripping section stages.

Study of the Molybdenum Compounds Generated During the Extraction and Stripping Steps

Elemental Analysis of the Greenish Gummy Precipitate

Table 1 shows the results of the analysis of two samples: There is an evident similarity between these figures. Moreover, it can be observed that the MoO₃/PO₄ ratio is the same in both samples. The ores actually contain, in most cases, enough phosphate to achieve this ratio. A

TABLE 1. Chemical Composition of Two Samples of the Gummy Precipitate

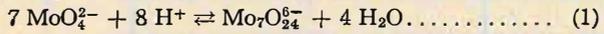
Element, ion or Group	Content in weight percent	
	Sample I	Sample II
MoO ₃	27	30
PO ₄	1.2	1.35
Amine	31	37
U	0.15	0.13
SO ₄	0.6	0.54
Kerosene + modifier	Difference to 100%	Difference to 100%

constant MoO/amine ratio may also be noted. Thus, a chemical combination between a phosphomolybdic acid and the amine can be assumed.

Review of Phosphomolybdic Complexes^(2,3)

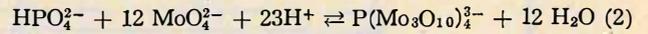
General Scope

The molybdc ions tend to condense in acid medium according to chemical reactions such as:



The $\text{Mo}_7\text{O}_{24}^{6-}$ ion is called paramolybdc ion.

The condensation is favored by the presence of a foreign ion; the best known and most efficient ion in acid medium is the phosphate ion.



It can be seen that one phosphorus atom is associated with 12 molybdenum atoms, and the resulting complex is called phospho-12-molybdc ion.

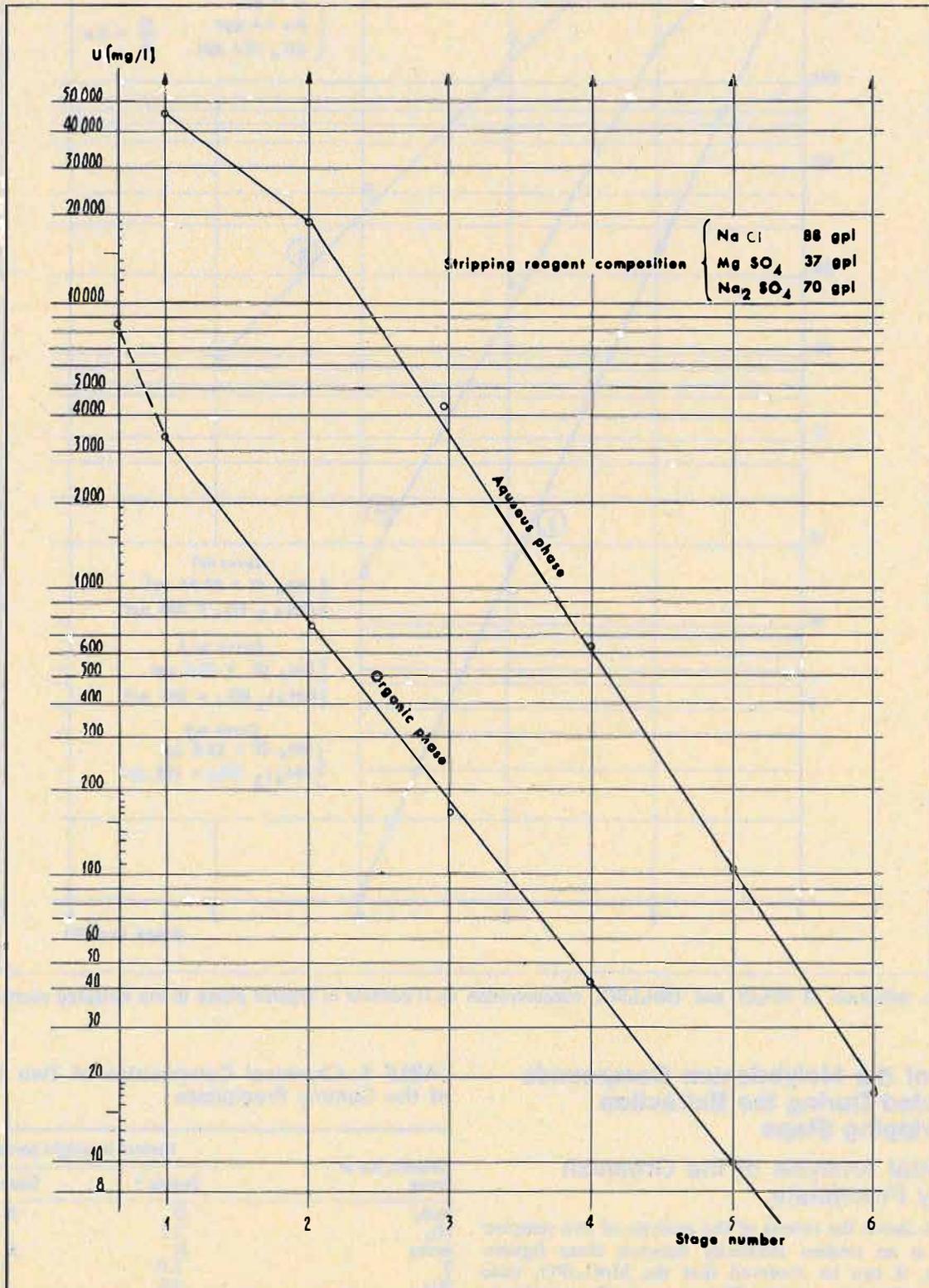


FIGURE 4. Uranium distribution when stripping with sodium chloride.

Bonds between the atoms of molybdenum are achieved with oxygen bridges, and in this complex the 12 molybdenum atoms are distributed in 4 Mo_3O_{10} groups, each group including an oxygen atom of the central tetrahedral group PO_4 . These complexes, which are stable in an acid medium, are destroyed when the pH increases. They give intermediate complexes in which the Mo/P ratio decreases, down to the regeneration of the initial ions.

Reduction

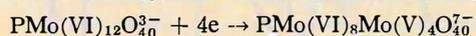
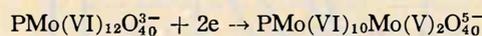
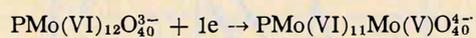
Inside the complex, the molybdenum can be partly reduced to valence 5 without changing the structure of the complex. Color is then modified and turns to a bright blue.

To simplify the next explanations, the following notations will be used:

Mo(VI) for 6-valent molybdenum

Mo(V) for 5-valent molybdenum

A series of complexes can be obtained containing Mo(VI) and Mo(V).



and so on.

The Heteropolyphospho-molybdates

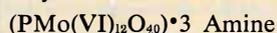
The phosphomolybdic ions, with and without Mo(V), are anions; consequently, they are able to combine with basic cations and hence with amines. In the case considered, the Alamine 336 plays this part under the ionic form R_3NH^+ . Since this cation is monovalent, three molecules of amine will be associated with each phosphorus atom and with each group of 12 molybdenum atoms.

Identification of the Precipitates

The study of the precipitating ions was carried out in the laboratory of Professor Jeannin (University Pierre and Marie Curie, in Paris) using polarography in hydro-organic medium and ultraviolet, infrared, and Raman spectroscopy.

The following results were obtained:

— The crystalline orange compound (called "A"), generated when molybdenum is completely oxidized to Mo(VI), has the following composition, as could have been reasonably assumed:



— The greenish gummy precipitate (called "B"), generated when molybdenum is incompletely oxidized, is a mixture of two amine heteropolyphosphomolybdates:

$(\text{PMo(VI)}_{12}\text{O}_{40}) \cdot 3$ Amine, in the proportion of 80% of the Mo,
and

$(\text{PMo(VI)}_{10}\text{Mo(V)}_2\text{O}_{40}) \cdot 5$ Amine, in the proportion of 20% of the Mo.

Figure 5 shows the similarity of polarographic behavior of a phospho 12 molybdate taken as a reference and of the A and B compounds.

To explain the difference of chemical behavior of the A and B compounds, it must be pointed out that the complex salt formed by the polyanion and the amine is much less soluble in the solvent when molybdenum is partly Mo(V).

TABLE 2. Typical Composition of Molybdenum Eluate

Element or ion	Content in gpl
Mo	12
V	0.5
PO_4	0.55
Na	33.5
Cl	42.5
SO_4	2.8
U	0.1
CO_3	0.9

Practical Consequences

During the pilot tests, difficulties were overcome by oxidizing the solution with chlorate. The studies presented above have shown that this was the right approach, since the heteropolyanions containing only Mo(VI) are much more soluble in the solvent.

It was thought, in order to simplify the process flow-sheet, of adding all the oxidizing reagent during leaching, where 5 kg NaClO_3 per metric ton (MT) of ore is already used. It is necessary to add a further 1.2 to 1.5 kg NaClO_3 /MT of ore to oxidize all the molybdenum. In fact, tests were made in that manner, but they did not give satisfactory results, and the final redox potential was still 300 to 400 mV. This can be explained by considering that the ore contains, besides uranium and molybdenum, large amounts of reducing materials, particularly ferrous iron. So, up to 10 kg NaClO_3 /MT of ore can be added without obtaining a redox potential higher than previously reached. It was then decided to carry out a redox potential adjustment after the solution clarifying step, but before the solvent extraction step.

Subsidiary Questions

Vanadium Behavior

Vanadium is present in the ore at a variable grade from 0.025 to 0.06%, i.e., one-half to one-fifth of the molybdenum grade. During the leaching step, vanadium is essentially completely dissolved at valence 4, and at this valence it is unextractable. When molybdenum is oxidized, vanadium is partly oxidized to 5, and so it becomes extractable. Vanadium does not form any complex with phosphates and is extracted by combining with amine as a vanadate. However, it is only partly extracted, as the solvent approaches saturation with the uranium and molybdenum. The vanadium is only slightly stripped by sodium chloride; however, it is completely stripped by the sodium carbonate along with molybdenum. The typical composition of the molybdenum eluate is shown in Table 2.

It can be observed that only relatively small amounts of vanadium are in the alkaline molybdenum eluate. A second remark can be made concerning the molybdenum itself: that $\text{Mo}/\text{PO}_4 \approx 22$ in the eluate. Since the true value in the phospho 12 molybdic complex is 12.8, this means that only a part of the molybdenum was extracted as a complex.

Zirconium Behavior

Zirconium is present in the ore at a very low concentration. It is dissolved under the strong leaching conditions. Usually zirconium, which is not affected by redox potential, is extracted by amine and stripped along with uranium. The uranium would then be contaminated by

some zirconium (0.3% with regard to uranium).

This contamination can be suppressed by sufficient amounts of phosphate ion in the solution (either present naturally or added). Zirconium forms very strong complexes with phosphate, even in competition with molyb-

denum. The solubility product of zirconium phosphate is not exceeded because of the low concentration of zirconium and probably because of the large excess of phosphate ions. It is then observed that zirconium remains in the raffinate, so that uranium pollution is prevented.

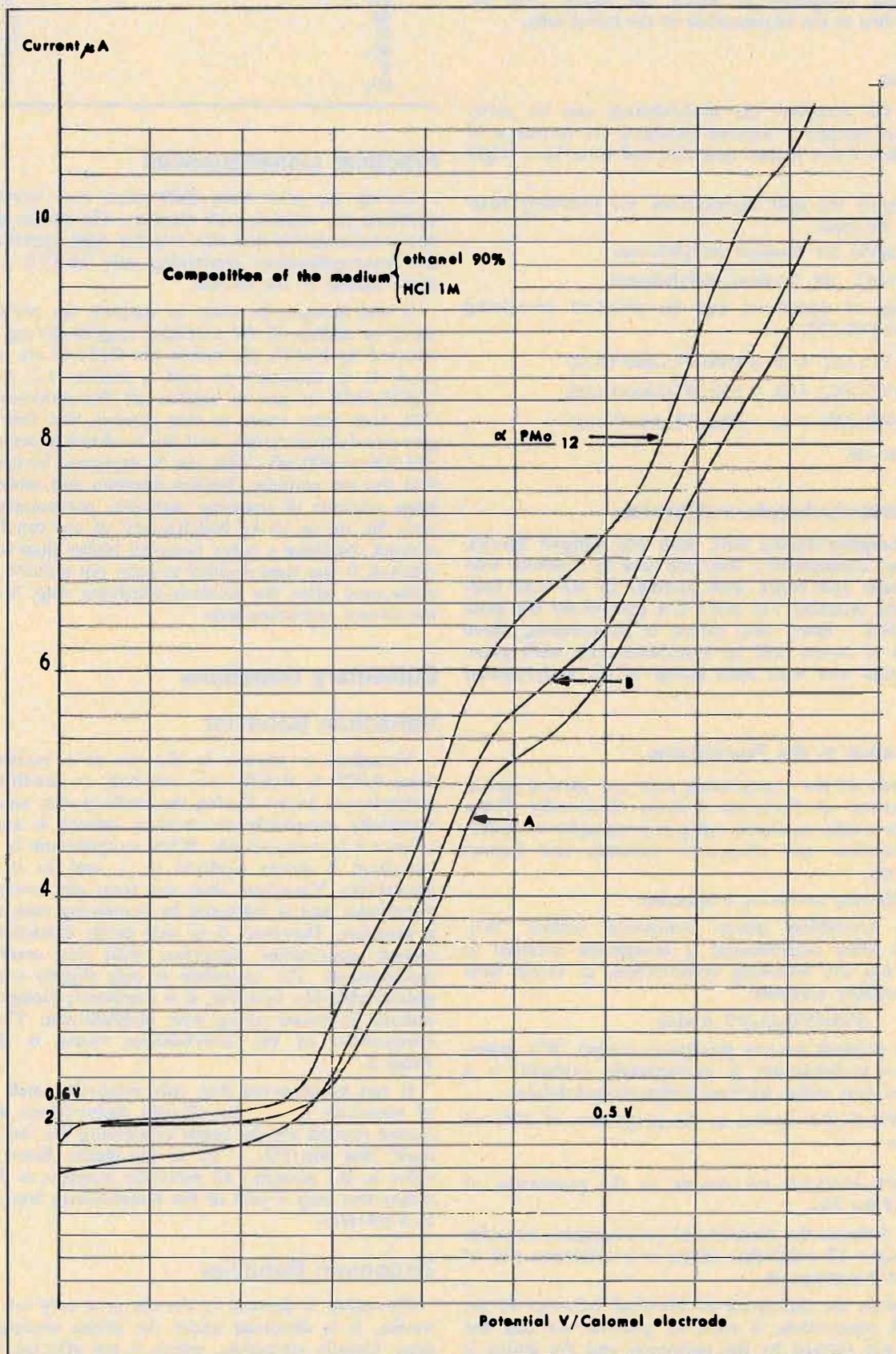


FIGURE 5. Polarographic behaviour of a phospho-12-molybdate taken as a reference and the compounds A and B obtained during the pilot tests.

Conclusions

The testing at pilot scale of the solvent extraction processing of uranium solutions rich in molybdenum has pointed out the risk of precipitation of amine phosphomolybdate complexes. The basic study has shown that precipitation was due to the 5-valence of molybdenum. This study confirmed assumptions on the basis of which an empirical solution was applied, consisting in oxidizing the aqueous feed up to a redox potential of 850 mV.

This study is a typical example of the applied studies calling upon basic studies to ensure the validity of empirical solutions.

Acknowledgment

We thank the scientists directed by Professor Jeannin and particularly M. Fournier for the important part they took in identification of the phosphomolybdic species and the explanation given about the oxidation and reduction of the molybdenum during the various operations of the process.

DISCUSSION

H. Ottertun: In the process described, the feed liquor was oxidized to a redox potential of 850 mV to give 6-valent molybdenum prior to extraction of uranium and molybdenum with an amine. Have you made any investigation of the reagent stability against oxidative degradation in this system?

P. Michel: During a pilot-plant run for a couple of weeks nothing was observed that indicated reagent degradation.

T.J. Hardwick: Why is phosphate added to the feed in the S-X of acid leach systems?

P. Michel: In fact, phosphate is naturally present in the ore and part of that phosphate is solubilized in the course of leaching, presumably due to the strong conditions of attack. Most of the dissolved phosphate is involved in the molybdenum complexes, but the phosphate is not in sufficient amount to complex all of the molybdenum. Therefore, molybdenum was present in the feed as at least two kinds of species, i.e., phospho-molybdic complexes and other chemical species such as molybdate. Both species were extracted and stripped in the molybdenum stripping section by sodium carbonate. The resulting solution contains all the molybdenum and all the phosphate and a typical ratio of Mo/PO₄ is 22, while the ratio in phosphomolybdic complex is about 3.

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NUCLEAR PROCESSES

A Solvent Extraction Flowsheet for a Large-scale LWR Fuel Reprocessing Plant*

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ABSTRACT

In 1974 a "Mark I" solvent extraction flowsheet for a German large-scale LWR fuel reprocessing plant was designed under the guidance of Gesellschaft für Kernforschung (GfK). Since then, several improved procedures have been developed, and have, step by step, been adopted into the original flowsheet. In preparing the GfK flowsheet, specific attention has been paid to safety and reliability of operation, to the minimization of liquid medium-level wastes, and to the minimization of environmental releases. This paper discusses several of the specific features of the present version of the GfK flowsheet.

*Work performed in the frame of the Project Wiederaufarbeitung und Abfallbehandlung (Reprocessing and Waste Treatment Project) of the Gesellschaft für Kernforschung, Karlsruhe.

General Block Diagram

Figure 1 PRESENTS A BLOCK DIAGRAM of the solvent extraction part of the flowsheet. Three extraction cycles are needed to obtain sufficient purification of the two product elements from fission products, which requires a decontamination factor (DF) of ca. 2×10^7 . The U/Pu separation has been placed in the first extraction cycle, as a consequence of the criticality control concept foreseen for the original "Mark I" flowsheet which was based on homogeneous poisoning, by gadolinium nitrate, of equipment containing U+Pu. Minimization of Gd consumption, and the required decontamination of products from the neutron poison (DF between 10^4 and 10^5), both required that the U/Pu separation be placed into the first extraction cycle^(1,2). Although the present GfK flowsheet no longer foresees homogeneous poisoning by dissolved Gd(NO₃)₃, but instead proposes heterogeneous poisoning of equipment containing U+Pu by use of the new construction material, hafnium⁽³⁾, the U/Pu separation has been maintained in the first extraction cycle, with the aim of minimizing the equipment fabricated from (expensive) hafnium, and of providing optimum purification efficiency of the process, in particular with regard to decontamination of U from Np⁽⁴⁾ and Pu.

First Extraction Cycle

Figure 2 presents a flow scheme of the first extraction cycle. It comprises six sieve-plate pulsed columns: extraction-scrub (HA), scrub (HS), tritium scrub (TS), plutonium backwash by electro-reduction (1BX), uranium scrub (1BS), and uranium backwash (1C). In addition, one mixer-settler for solvent clean-up (1CS) is included.

The HA-HS-TS Column System

The extraction-scrub system shows two unusual features. The first is the high solvent loading which amounts to 99 g U+Pu/l in the HAP stream, corresponding to > 75% of the maximum loading^(1,2). In addition, a relatively high acidity, slightly in excess of 3 moles HNO₃/l aqueous phase, is maintained over the whole length of the HA column. Most of the published flowsheets⁽⁵⁾ apply $\leq 65\%$ loading, exceptions being the Marcoule flowsheet (100 g U/l in HAP)⁽⁶⁾ and the USSR flowsheet (80 g U/l in HAP with 25 v/o TBP)⁽⁷⁾. We propose an increased loading on the basis of our experience^(1,8,9) that the formation of radiolytic cruds, which may lead to severe operational problems in the HA extractor (in particular with mixer-settlers)⁽¹⁰⁾, can be suppressed to non-critical limits by applying a high solvent loading in combination with a high acidity in the HA contactor. This effect has been demonstrated in the MILLI experimental facility at Karlsruhe both with LWR fuels (burn-up to 37000 MWd/t, cooling time down to 200 days) and with SBR fuel (burn-up 61000 MWd/t)^(8,9,11). Solvent loadings up to 110 g U+Pu/l have been used in the MILLI without operational problems. An explanation of the effect may be offered by the observation⁽¹²⁾ that the solubility of insoluble Zr-dibutylphosphate compounds, which form a major constituent of the cruds, both in the aqueous and in the organic phase increases with increasing acidity and uranium concentration, while at the same time the formation rate of these compounds drastically decreases.

The second specific feature is based on a proposal of the French C.E.A., and consists of the inclusion, after the HA and HS "double scrub" system, of an additional scrub column (TS) which serves for elimination of tritiated water from the organic solvent^(13,14). The TSS solution is made up from nontritiated water and acid (either fresh or recycled from later extraction cycles), and the tritiated water and acid dissolved or entrained in the organic solvent are exchanged against nontritiated species. Thus the tritium is prevented from "smearing" over the equipment beyond the TS contactor, and is concentrated in the aqueous streams of the dissolver, HAW evaporator, 1WW tank, and HA-HS-TS column systems. By making use of

extensive recycle of these tritiated streams, i.e. by using recovered tritiated water and acid for the dissolver acid, feed make-up, and HAS and HSS streams, the amount of tritiated waste water can be kept to a minimum, i.e. distinctly below 1 m³ T-water per ton of fuel⁽¹⁵⁾. Flow ratios aqueous : organic in the TS column (i.e. TSS : TSP) between 1 : 50 and 1 : 100 have been considered but a less extreme ratio of between 1 : 20 and 1 : 30 may be used without essential increase of the specific amount of tritiated waste water⁽¹⁴⁾. With such a ratio, about 4 theoretical extraction stages are needed to keep the amount of tritium escaping with the TSP solution below 1% of the input-tritium⁽¹⁴⁾.

The 1BX-1BS-1C Column System

For U/Pu partitioning in the 1BX-1BS columns, use of the electrolytic in-line reduction process developed by GfK^(16,17) is proposed. The 1BX column is very similar to a "normal" pulsed sieve-plate column. In our most recent design, the sieve-plates which are fabricated from titanium act as the cathodes, while the anode is formed by a central tube fabricated from platinized tantalum. The sieve-plates are fixed to the outer column tubing which is also fabricated from titanium, thus increasing the cathode area, while the electric insulation between the sieve-plates and the central anode tube is provided by ceramic annuli. Thus there is no separation between cathode and anode compartment as was provided in earlier designs⁽¹⁷⁾. The column is run with the aqueous as the continuous phase. The only chemical addition to the system is the hydrazine nitrate introduced with the 1BXX stream which serves as a nitrous acid scavenger. Extractable Pu(IV) and Pu(VI) is cathodically reduced to inextractable Pu(III) and a sufficient excess of U(IV) is cathodically formed to build a "barrier" against the break-through of non-reduced plutonium with the organic 1BXU stream. The particular advantage of the process, as compared against chemical reduction with ferrous sulfamate or with uranium(IV) nitrate / hydrazine nitrate, is that a fast and direct control is possible by regulation of the electric current supplied. Moreover, a high plutonium product concentration can be produced (GfK flowsheet: ca. 10 g/l Pu in 1BSP), the residual enrichment of the uranium remains unchanged, and the 1BSP solution contains no salt burden or corrosive reagents. The separation efficiency is similar to that of the U(IV) partitioning process, with DF(U/Pu) and DF(Pu/U) values routinely between 1000 and 3000. Hot tests of the process, using an electrolytic mixer-settler, have been performed with good success in the MILLI facility, with FBR fuel of 61000 MWd/t burn-up and 15% PuO₂ content⁽⁸⁾.

Backwash of U in the 1C column is performed in the usual way, with 0.01 molar HNO₃ at 60°C.

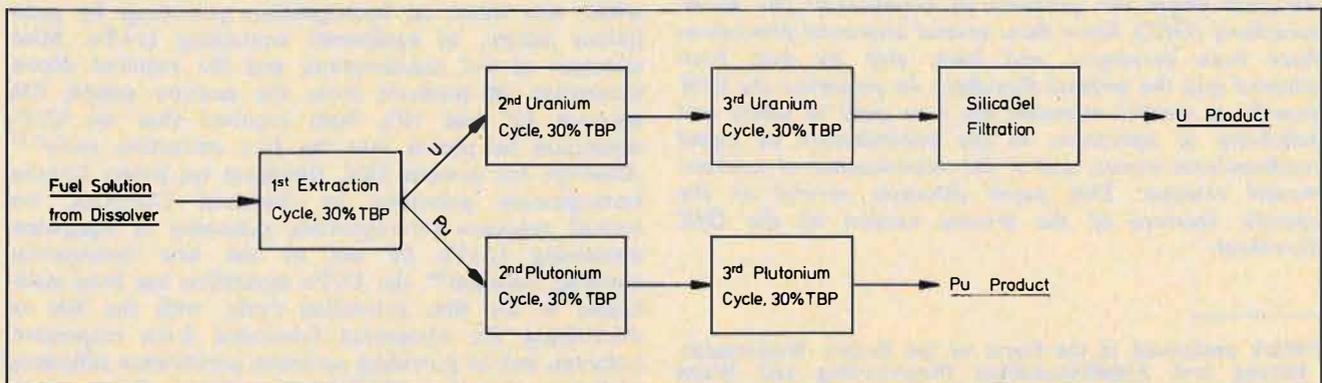


FIGURE 1. Block diagram of solvent extraction flowsheet.

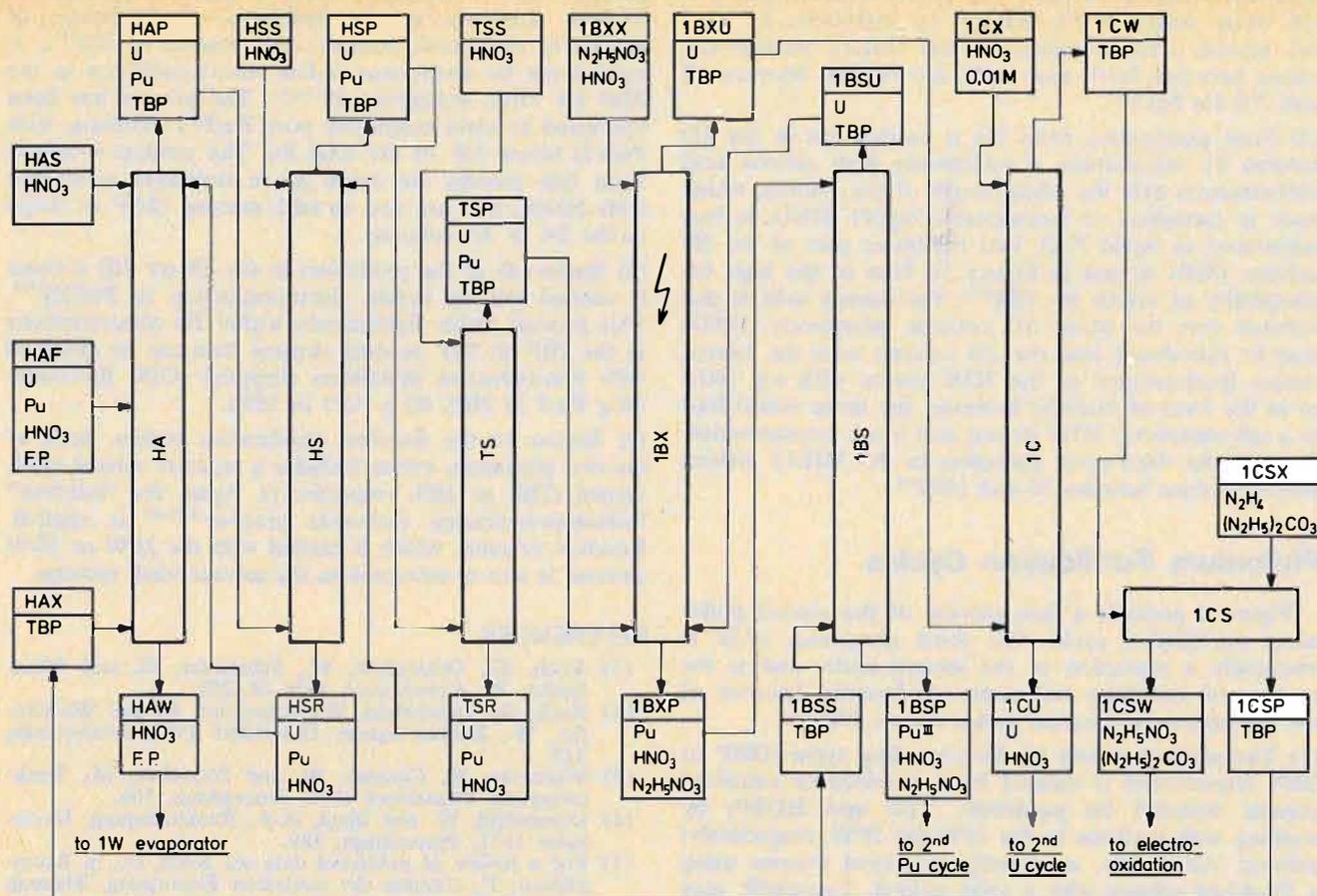


FIGURE 2. Flow scheme of the first extraction cycle. 1BX designates in-line electro-reduction. TBP designates 30 v/o TBP / n-alkane (mixture C₁₀ - C₁₃). Interim tanks are not shown.

The 1CS Contactor

For clean-up of the spent solvent, a "salt-free" process recently developed at GfK Karlsruhe^(15,18,19) is proposed. A hydrazine-hydrazine carbonate solution is applied for the removal of di- and monobutyl phosphoric acids and of fission products from the solvent. The washing efficiency is similar as with the "classic" Na₂CO₃/NaOH wash solution. A phase ratio aqueous : organic of about 1 : 20 is applied. Due to the slow kinetics of the washing process⁽¹⁶⁾, a mixer-settler with internal recycle (Holley-Mott type) is proposed as the 1CS contactor. The spent wash solution (1CSW) is mainly composed of hydrazine nitrate; the hydrazine can be decomposed into N₂ and H₂O by continuous electrooxidation^(15,19), and the resulting MAW which is essentially salt-free can be concentrated by evaporation to a very small volume, which can be added to the high-level waste without essential increase of the 1WW volume. By this way a major part of the medium-active liquid waste, together with its need for separate solidification and storage, can be eliminated.

The washed solvent still contains a variety of so-called "non-removable", high-molecular-weight radiolysis products which tend to form stable complexes with, e.g., Pu and Zr^(20,21). Although the formation rate of these products is low, they accumulate in the solvent and may finally limit the applicability of the solvent. Removal of these "non-removable" products is possible by oxidative breakdown with lead dioxide. For this reason, a partial stream of the washed solvent can be led through a fixed-bed PbO₂-SiO₂ column, before recycle of the solvent to the process.

Uranium Purification Cycles

Figure 3 presents a flow scheme of the two uranium purification cycles. Each cycle is equipped with two extraction columns (extraction - back extraction system) and one Holley-Mott type mixer-settler for solvent wash (hydrazine carbonate process). Specific features of this system are as follows:

(1) A "dilute" flowsheet, with no intercycle evaporation, is proposed for the 2nd and 3rd uranium cycles. The feeds to these cycles (2DF and 3DF) are directly made up from the uranium product solutions of the preceding cycles by addition of concentrated nitric acid, to yield concentrations of ca. 75 g U/l and 1 mole HNO₃/l. Organic uranium concentrations of ca. 80 g U/l in 2DU and 3DU are obtained with 3 to 4 theoretical stages. The main reason for proposing this flowsheet lies in the fact that two intercycle evaporators, together with their auxiliary equipment (kerosene wash of the evaporator feed, etc.), are saved⁽¹⁾. Regarding product purity, comparisons between a "dilute" and a "concentrated" flowsheet made in the MILLI yielded similar product purities in both cases; while the fission product DF values were the same, the DF(Pu) was slightly lower and the DF(Np) higher for the "dilute" flowsheet. Uranium product specifications are met with both types of flowsheet.

(2) For removal of residual plutonium, some U(IV) nitrate plus hydrazine nitrate is introduced with the 2DS stream in the upper stages of the 2D column. This measure serves at the same time for improved removal of Np since highly extractable Np(VI) is reduced to less extractable lower valency states, and since HNO₂ (cat-

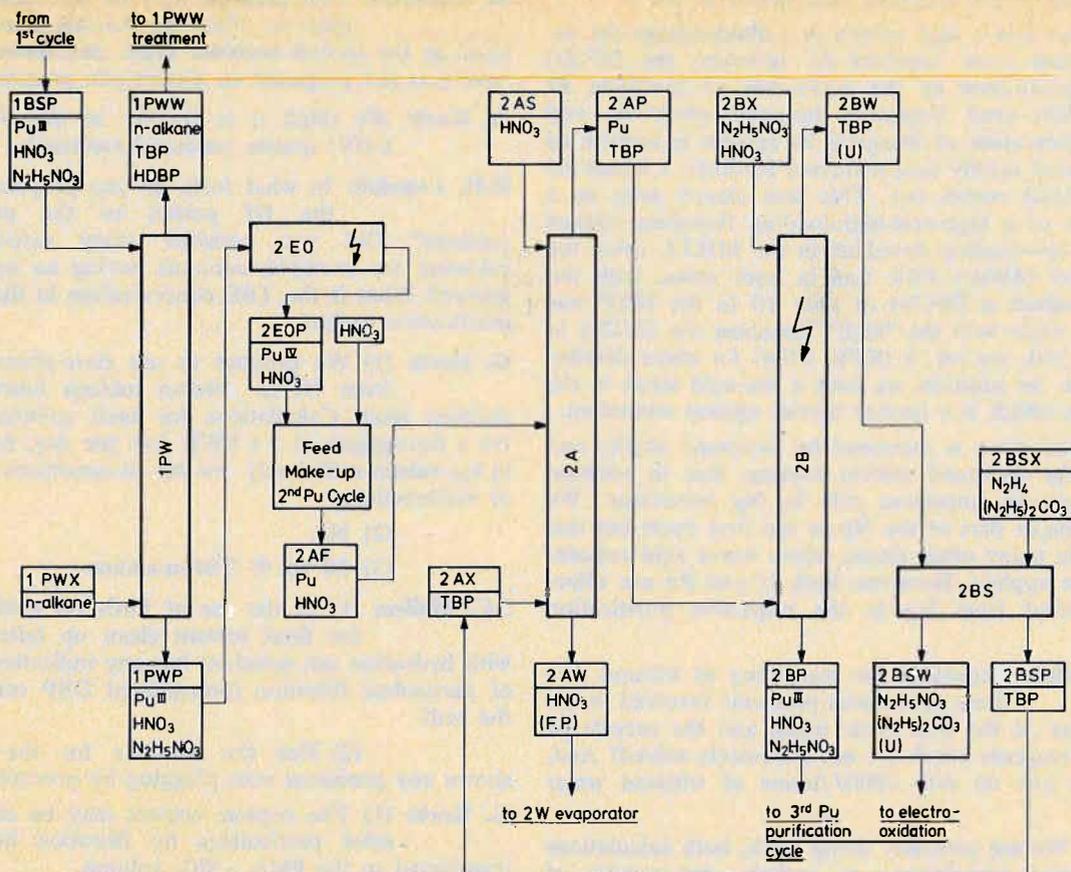


FIGURE 4. Flow scheme of the second plutonium purification cycle. Interim tanks not shown. 2B designates in-line electro-oxidation or in-line electro-reduction. TBP designates 30 v/o TBP / n-alkane (mixture C₁₀ - C₁₃). The third plutonium purification cycle is essentially a repetition of the 2nd cycle.

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DISCUSSION

A. Naylor: Your high acid-high solvent loading flowsheet for the HA column has been introduced to suppress crud formation. This flowsheet will be advantageous for processes susceptible to solids formation and more so where long residence contacting equipment is used.

For LWR reprocessing with pulsed columns of short residence time, this flowsheet will be advantageous to only a limited extent in relation to crud formation. Are there disadvantages in:

- (a) Pu build-up and criticality control,
- (b) Pu losses in the HAW raffinate,

- (c) Df values for Zr (high acid disadvantages, solvent loading advantages),
- (d) Np distribution and decontamination?

G. Koch: To overcome the crud problem in the HA contactor, we feel that both engineering and chemical improvements are needed when fuel of high burn-up is processed. From the engineering point, use of pulsed columns instead of mixer-settlers is the answer. From the chemistry point, "loading and acid" is the answer we give. We have tested the flowsheet intensely in the MILLI facility (see paper 18 e for more details), with the following answers to your questions:

- (a) With solvent loading of 100 g U/l no recycle of Pu was observed.

(b) Pu losses in the raffinate were below 0.1%.

(c) It is true that a high acidity is a disadvantage for decontamination from dissolved Zr, however, the DF(Zr) may be determined by the carry-over of insoluble Zr species when crud formation becomes excessive, and since the formation of insoluble Zr species is suppressed with increased acidity (and increased loading), a beneficial effect in total comes out. This was clearly seen in a comparison of a high-acid-high-loading flowsheet against a low-acid-low-loading flowsheet in the MILLI, using the same 61000 MWd/t FBR fuel in both cases; with the "low" flowsheet a DF(Zr) of only 10 in the HAP was measured, while with the "high" flowsheet the DF(Zr) in HAP was 330, see ref. 8 (KFK 2396) for more detailed information. In addition, we have a low-acid scrub in the HS column which is a further barrier against zirconium.

(d) Np distribution is increased by increased acidity and decreased by increased solvent loading, and in addition HNO_2 plays an important role in Np behaviour. We extract a major part of the Np in the first cycle but this is similar in many other plants where lower acid concentrations are applied. However, both U and Pu are effectively purified from Np in the respective purification cycles.

M.E. Whatley: Regarding the containing of tritium: Are there not serious problems involved in the management of the first cycle waste and the recycle of water and reagents which are not adequately solved? And, what does one do with 1000€/tonne of tritiated water waste?

G. Koch: We are presently doing work, both calculations and experiments, to optimize the recycle of tritium-water, and to minimize its output which, as I would like to stress, can be kept distinctly below lm^3 per ton of fuel. A decision on the further treatment and disposal of this T-water has not yet been made, but if no better solutions can be developed, tank storage would be a primitive but safe way. I would also like to point out that the procedure described, which was first proposed by C.E.A. workers, is in my opinion the only tritium retention process which at present can be operated on a technical scale.

A.D. Kelmers: (1) Since hydrazine, like ammonia, forms a carbamate rather than a carbonate, could you tell us how the "hydrazine carbonate" scrub solutions are prepared?

(2) Could you tell us the disposition of the nitrous acid formed from the addition of N_2O_4 to the 3D column?

(3) Have you measured the quantity of hydrazoic acid formed from the reaction of nitrous acid with hydrazine in the first cycle?

G. Koch: (1) The solutions are prepared by introducing gaseous CO_2 into $\text{N}_2\text{H}_4\text{-H}_2\text{O}$ solutions. The carbonate anion concentration is sufficient to keep the uranium as uranyl carbonate complex in solution, and no precipitation of U in the wash solution is observed.

(2) N_2O_4 disproportionates in the lower sections of the 3D column into HNO_2 and HNO_3 . The HNO_2 is extracted with the TBP, and to the 3E column, but since no reductant is applied in this column with which the HNO_2 could interfere, we do not specifically control HNO_2 in the 3E column.

(3) We have done a few scouting measurements of HN_3 , and a literature review on the formation of hydrazoic acid in reprocessing solutions. Our measurements, in accord with available literature data, indicate that HN_3 formation is not important.

M. Germain: You propose the use of tetravalent uranium to eliminate the last traces of plutonium in the second uranium cycle. My question is, why have you not proposed an electrolytic process?

G. Koch: We think it is simpler at this point to use U(IV) nitrate produced externally.

D.H. Logsdail: In what form do you propose to include the Hf poison in the pulsed plate columns? Did you consider using safe-by-geometry columns, for example, columns having an annular cross section? What is the TBP concentration in the U and Pu purification cycles?

G. Koch: (1) We propose to use sieve-plates fabricated from Hf in column tubings fabricated from stainless steel. Calculations for such columns, designed for a throughput of 5 t LWR fuel per day, have resulted in k_{eff} values sufficiently low for all conditions of function or malfunction.

(2) No.

(3) 30 vol.% TBP-n-alkane.

J.C. Mailen: (1) In the use of PbO_2 on a silica column for final solvent clean up (after treatment with hydrazine salt solution) has any indication been seen of particulate filtration (precipitated DBP complexes) by the bed?

(2) Has the prefilter for the PbO_2 bed shown any problems with plugging by precipitates?

G. Koch: (1) The organic solvent may be cleaned from solid particulates by filtration before being transferred to the PbO_2 - SiO_2 column.

(2) No. We are indeed now running a "hot" laboratory-scale solvent treatment test facility without a pre-filter to the oxidation column. Up to now, no indication of column plugging or other difficulties was observed.

J. Kendall: (1) Have you prototyped any of your electro-cell columns; in particular the 2B and 3B columns? (2) Would you explain the purpose of removing the solvent from the IBSP stream and the method of disposal for the diluent or the material removing the solvent from the aqueous IBSP stream?

G. Koch: (1) We are operating both an electro-column ("ELKE") and an electro-mixer-settler ("EM-MA"), and in addition an electro-reoxidation cell, of pilot-plant size, i.e. with throughputs equivalent to ca. 150 to 200 kg U per day. These tests are presently made on a "cold" basis, i.e. with uranium only. In addition we have operated a laboratory-size electro-mixer-settler and re-oxidation cell, with a throughput of 1 kg/d, in connection with the MILLI facility (see paper 18 e); with this equipment FBR fuel of 61000 MWd/t has been successfully processed.

(2) TBP and other organic material are removed from 1 BSP to prevent the intercycle build-up of HDBP and other degradation products which would interfere with Pu decontamination and Pu recovery in the Pu purification cycle. A diluent wash of the 1 BSP is commonly used in several reprocessing plants. The loaded diluent is separately treated and disposed of. As an alternative, we have developed and are testing a process for 1 BSP treatment using a fixed-bed sorbent, Lewapol®, a product of Bayer AG, Leverkusen, which has a high specificity for sorption of TBP. The loaded sorbent can be washed free from sorbed TBP by, e.g., methanol, and can be re-used for sorption. The methanol can be recovered by distillation and recycled, and the distillation residue (mainly TBP and degradation products) can be disposed of.

Experience with the Reprocessing of LWR, Pu Recycle, and FBR Fuel in the MILLI Facility*

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ABSTRACT

This paper summarizes the results of recent reprocessing studies made in the experimental facility MILLI at Karlsruhe. MILLI is a highly shielded, critically eversafe laboratory-scale solvent extraction facility with a nominal throughput of 1 kg U+Pu per day. Processing of three types of fuel is reported: (1) LWR fuels burned up to 37000 MWd/t and cooled between 240 days and 2 years, (2) LWR plutonium recycle fuels burned up to 21000 MWd/t and cooled between 1 and 2 years, and (3) FBR-UO₂/PuO₂ fuel burned to 61000 MWd/t and cooled for 8 years. Particular attention is given to fuel dissolution, first-cycle solvent extraction, and neptunium behaviour, during solvent extraction.

*Work performed in the frame of the Project Wiederaufarbeitung und Abfallbehandlung (Reprocessing and Waste Treatment Project) of the Gesellschaft für Kernforschung, Karlsruhe.

1. Introduction

EXPERIMENTS ON THE EXTRACTION of high-burned fast breeder fuels are reported from Dounreay⁽¹⁾, Windscale⁽²⁾, Fontenay aux Roses, La Hague⁽⁴⁾ and Karlsruhe⁽³⁾. In Oak Ridge the dissolution of irradiated ceramic fuels has been studied for a number of years⁽⁵⁾.

Recently, studies on dissolution and solvent extraction of high-burnup LWR fuels have been reported from Karlsruhe⁽⁶⁾ and Oak Ridge⁽⁷⁾. The present paper describes the results of several reprocessing campaigns on LWR, Pu-recycle, and FBR fuels of high burn-up which have been performed in the MILLI facility at Karlsruhe. Characteristic data of the fuels are presented in Table 1. One of the goals of these campaigns was to demonstrate the applicability of the PUREX process to the processing of power reactor fuels with high burn-up levels and short cooling times. Another goal was to demonstrate and test the chemical flowsheet proposed for large-scale reprocessing of LWR fuels, as discussed in the preceding paper⁽⁸⁾.

2. The MILLI Facility

The miniature pilot plant, MILLI, is a partly shielded, critically eversafe, laboratory-scale facility designed for dissolution and extraction of highly irradiated fast breeder

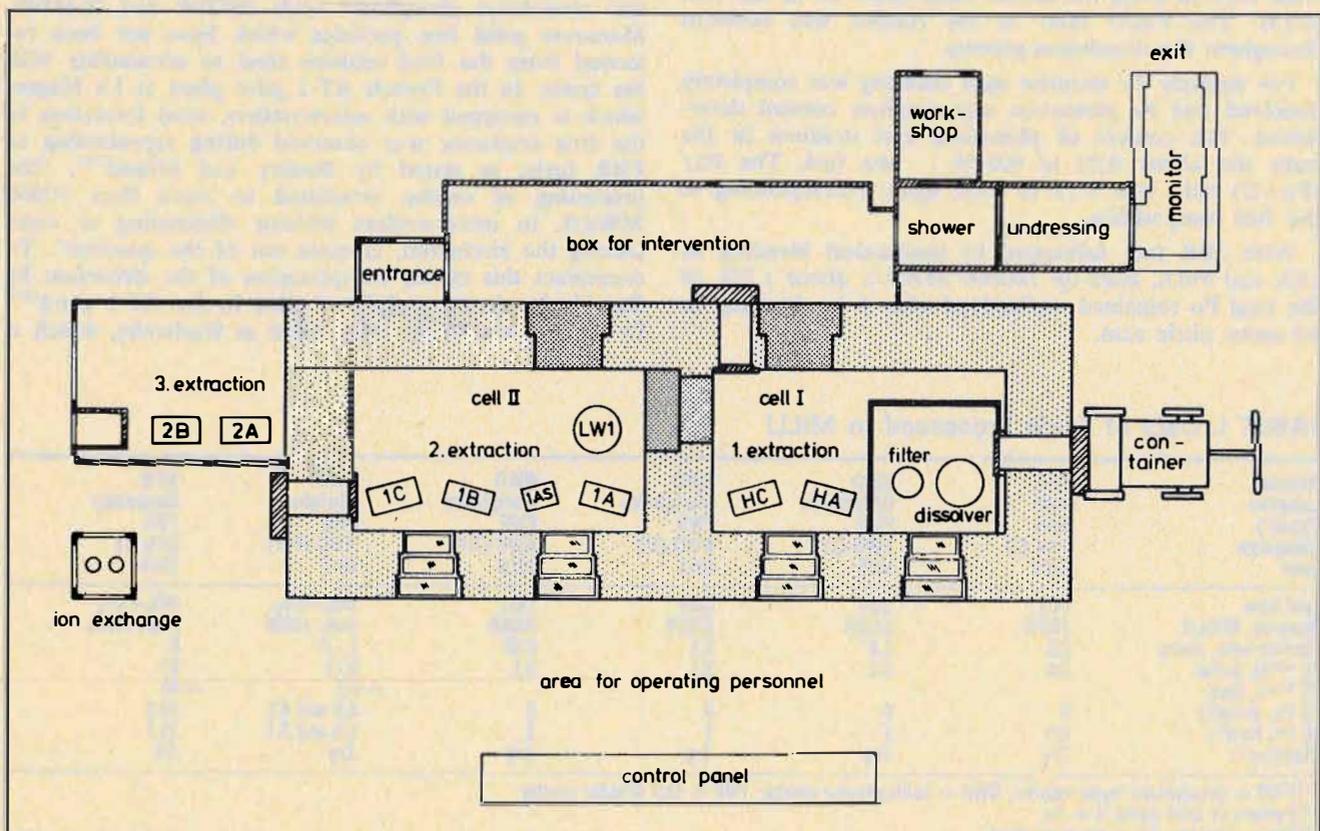


FIGURE 1. Outline of the MILLI facility.

fuels.⁽⁹⁾ The capacity is 1 kg fuel per day and per cycle, or 1 milliton, from where the name MILLI is derived. The facility has been in hot operation since 1971. One dissolver and filter, the first "co-decontamination" cycle and the second participating cycle are located in two hot cells (Figure 1). The HC and the 1A mixer-settlers can be circumvented so that flowsheets with first-cycle separation can also be performed (Figure 2). The third extraction cycle is contained in a slightly shielded gas-tight glove-box. The extractors used are slab-type mixer-settlers, critically safe by geometry. The installed slab tanks and other equipment are also critically safe by geometry. Over a period of six years different experiments with highly active materials have been achieved in MILLI.

3. Fuel Dissolution

The fuel pins were cut into pieces of about 5 cm length, and were leached with boiling nitric acid. The dissolver solution was filtered over sintered metal filters of < 14 μm or < 1 μm pore size, and the residues collected, weighed, and analyzed for fissile materials content.

Uranium oxide LWR fuels from the Obrigheim (KWO) and Kahl (VAK) power stations were dissolved in 6 molar HNO_3 within 2 to 4 hours. Undissolved residues amounted to 0.2 to 0.3 wt-% of the fuel.

The $\text{UO}_2\text{-PuO}_2$ fuel irradiated in the Dounreay Fast Reactor (DFR) was of the "coprecipitated" type, i.e. the fuel had been manufactured by coprecipitation of U and Pu with subsequent calcination⁽¹⁰⁾. The fuel was essentially completely dissolved with 8 to 10 molar nitric acid within 2 to 3 hours⁽⁹⁾. Undissolved residues amounted to 0.3 to 0.7% of the fuel, and were mainly composed of fission products and of products from the stainless steel cladding, in the following sequence of decreasing quantities: Mo, Ru, Fe, Ni, Rh, Tc, Pd, Sn, Zr. The heavy metal content of the insolubles was very low, i.e. 0.04% of total U and 0.04% of total Pu. The Pu/(Pu+U) ratios in the residues were 0.13 to 0.18, i.e. in the same order as in the fuel (0.15). The Pu/U ratio in the residue was constant throughout the dissolution process.

For analysis the stainless steel cladding was completely dissolved and its plutonium and uranium content determined. The content of plutonium and uranium in the hulls was about 0.02 to 0.04% of the fuel. The Pu/(Pu+U) ratio was 0.13 to 0.16, again corresponding to the fuel composition.

With FBR fuel fabricated by mechanical blending of UO_2 and PuO_2 , burn-up 100000 MWd/t, about 1.5% of the total Pu remained undissolved after 6 hr. leaching in 10 molar nitric acid.

Dissolution experiments were done with unirradiated and irradiated $\text{UO}_2\text{-PuO}_2$ plutonium recycle fuel. The fuels were of the "mixed-oxide" type, i.e. they have been manufactured by blending of UO_2 and PuO_2 , powders. Material with different grain size was investigated. Some samples were fabricated from relatively coarse grain, the others from fine-grain oxide powder. The fuel contained about 2% and 3% plutonium respectively. Irradiation was performed in the Obrigheim power station.

Dissolution was achieved in boiling nitric acid of different concentrations. When dissolved in boiling 10 molar nitric acid, unirradiated material fabricated from coarse-grain powder resulted in a significant amount of undissolved plutonium. With fuel of at least 25000 MWd/t burn-up, the amount of insoluble Pu was reduced to ca. 2% of the total Pu. Even in this case the undissolved amount of Pu is not satisfactory. The insoluble residues could be completely dissolved with 10 M HNO_3 -0.1 M HF. However, due to the well-known problems inherent with HF, we do not recommend the use of HNO_3 -HF as a dissolution reagent in a large-scale re-processing plant.

Dissolution experiments with other unirradiated samples of a $\text{UO}_2\text{-PuO}_2$ fuel which were fabricated from a fine-grain oxide powder mixture showed a much better dissolution behaviour.

4. First Extraction Cycle

Particular attention was given to the examination of the highly-active first extraction cycle since difficulties with this cycle have been reported when high-burnup fuels were processed. A major cause for the reported difficulties is the formation of interfacial "cruds", i.e. insoluble, slimy materials which may lead to irregular extraction behaviour or even to plugging of extraction equipment. The cruds are composed primarily of fission product zirconium and TBP radiolysis products, dibutyl and monobutyl phosphoric acids (HDBP and H_2MBP). Moreover solid fine particles which have not been removed from the feed solution tend to accumulate with the cruds. In the French AT-1 pilot plant at La Hague, which is equipped with mixer-settlers, crud formation in the first contactor was observed during reprocessing of FBR fuels; as stated by Boudry and Miquel⁽¹¹⁾, "the processing of oxides, irradiated to more than 50000 MWd/t, in mixer-settlers without eliminating or complexing the zirconium, is quite out of the question". To counteract this effect, complexation of the zirconium by fluoride ion is successfully applied in the AT-1 plant⁽¹¹⁾. In the German WAK pilot plant at Karlsruhe, which is

TABLE 1. Data of Fuels Processed in MILLI

Reactor Location Type ⁽¹⁾ Campaign Year	VAK Kahl BWR VAK (I) 1974	KWO Obrigheim PWR KWO (I) 1975	KWO Obrigheim PWR KWO (II) 1975	KWO Obrigheim PWR KWO (III) 1976	KWO Obrigheim PWR KWO (PuI) 1977	DFR Dounreay FBR DFR (I) 1974
Fuel type	UO_2	UO_2	UO_2	UO_2	$\text{UO}_2\text{-PuO}_2$	$\text{UO}_2\text{-PuO}_2$
Burn-up, MWd/t	18000	31000	37000	33000	max. 21000	max. 61000
Cooling time, years	2.5	1.8	2.1	0.68	1 - 2	8
% ^{235}U , initial	2.5	3.1	3.1	3.1	0.72	60
% ^{235}U , final					~0.5	~40
% Pu, initial ⁽²⁾	0	0	0	0	2.5 and 4.1	15.0
% Pu, final ⁽²⁾	0.5	1	1	1	1.9 and 3.1	15.1
Cladding ⁽³⁾	Zry	Zry	Zry	Zry	Zry	SS

⁽¹⁾PWR = pressurized water reactor, BWR = boiling water reactor, FBR = fast breeder reactor

⁽²⁾Percent of total metal U + Pu

⁽³⁾Zry = Zircaloy, SS = stainless steel

The formation rate of the precipitate in a two-phase system is low. Figure 3 presents a picture of the amount and rate of precipitation for different HNO_3 concentrations. The Zr:HDBP ratio used in these experiments was 40% in excess of the "stoichiometric" 1:2 ratio. Both the amount and the rate of formation of the precipitate decrease with increasing nitric acid concentration.

Figure 4 shows the influence of uranium on the amount and rate of precipitate formation from a 3 M HNO_3 - 30% TBP/n-alkane two-phase system. In the presence of 220 g U/l, both the amount and rate of precipitate formation is low while in the absence of uranium, a much greater part of the zirconium is precipitated. Since HDBP is consumed by the precipitation, the distribution

TABLE 4. Solubility of Zirconium Dibutylphosphate in Aqueous Solutions at 20°C

M HNO_3	Zr (OH) (NO_3) (DBP) ₂ mg/l	M HNO_3	U g/l	Zr (OH) (NO_3) (DBP) ₂ mg/l
0	1.8	0	11	10.6
0.1	4.4	0	110	94
1	12.3	0	220	160
3	25.6	3	11	37
4	31.6	3	110	142
6	57.2	3	220	344

TABLE 5. Solubility of Zirconium Dibutylphosphate in 30% TBP/alkane

M HNO_3	U g/l TBP	Zr (OH) (NO_3) (DBP) ₂ mg/l
0	3	5340
0	93	8180
0.025	0	7150
0.02	114	6780
0.59	0	2100
0.60	0.6	2610

coefficient of the dissolved zirconium is decreased during precipitate formation.

"Cold" counter-current experiments with synthetic solutions in laboratory-scale mixer-settlers were performed with feed solutions containing 240 g U/l and 0.7 g Zr/l at different acidities, and with 30% TBP/n-alkane extractant containing 200 mg HDBP and H_2MBP /l. Cruds were formed with low acidities and with low uranium loadings of the organic phase, but could be suppressed when the aqueous acidity was kept at 3 to 4 moles HNO_3 /l and the organic uranium loading was high. A high acidity is also favourable with regard to low plutonium losses. The upper limit of solvent loading is set by possible plutonium losses. It was found that a loading of 100 g uranium per liter organic phase (ca. 80% saturation of the TBP) is still tolerable. With higher loadings, internal buildup of plutonium in the extractor starts to become significant, which, if the loading is further increased, finally leads to plutonium losses in the aqueous raffinate.

For the LWR fuel flowsheet discussed in the preceding paper⁽⁶⁾, we have therefore fixed the solvent loading at < 100 g U+Pu/l at the HA product outlet (HAP solution). The first test of this flowsheet with a true high-burnup fuel was performed in 1974 with FBR fuel of 60000 MWd/t burn-up and ca. 8 years cooling time (see "DFR(I)" campaign in Table 1⁽³⁾). In this campaign a first-cycle co-decontamination flowsheet was applied (HA-HC contactors). In order to demonstrate the benefits of the new flowsheet, two different conditions were tested for the first cycle:

(a) "low load" flowsheet: 52 g/l U+Pu in HAP (42.6 g/l U, 9.3 g/l Pu), aqueous acidity over the HA contactor 2 to 3 moles HNO_3 /l;

(b) "high-load" flowsheet: 110 g/l U+Pu in HAP (91.4 g/l U, 18.8 g/l Pu), aqueous acidity over the HA contactor 3 to 4 moles HNO_3 /l.

With flowsheet (a), severe crud formation was observed in the extraction (HA) and in particular in the back-extraction (HC) mixer-settlers which caused hydraulic

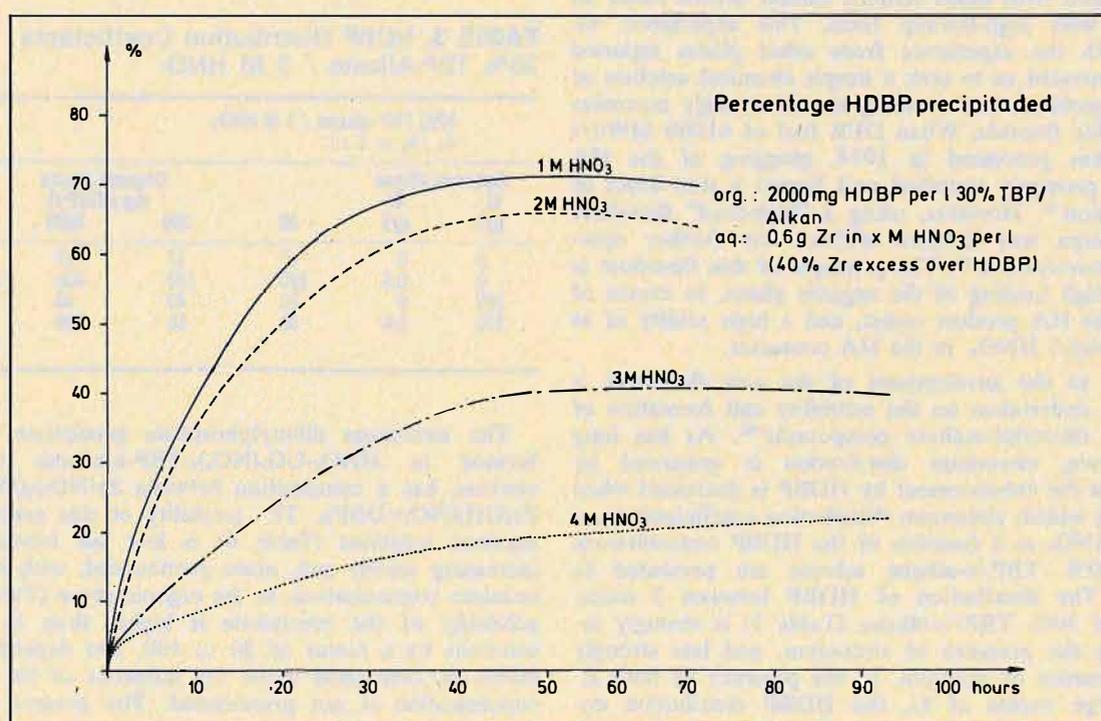


FIGURE 3. Zirconium dibutylphosphate precipitation, influence of acidity.

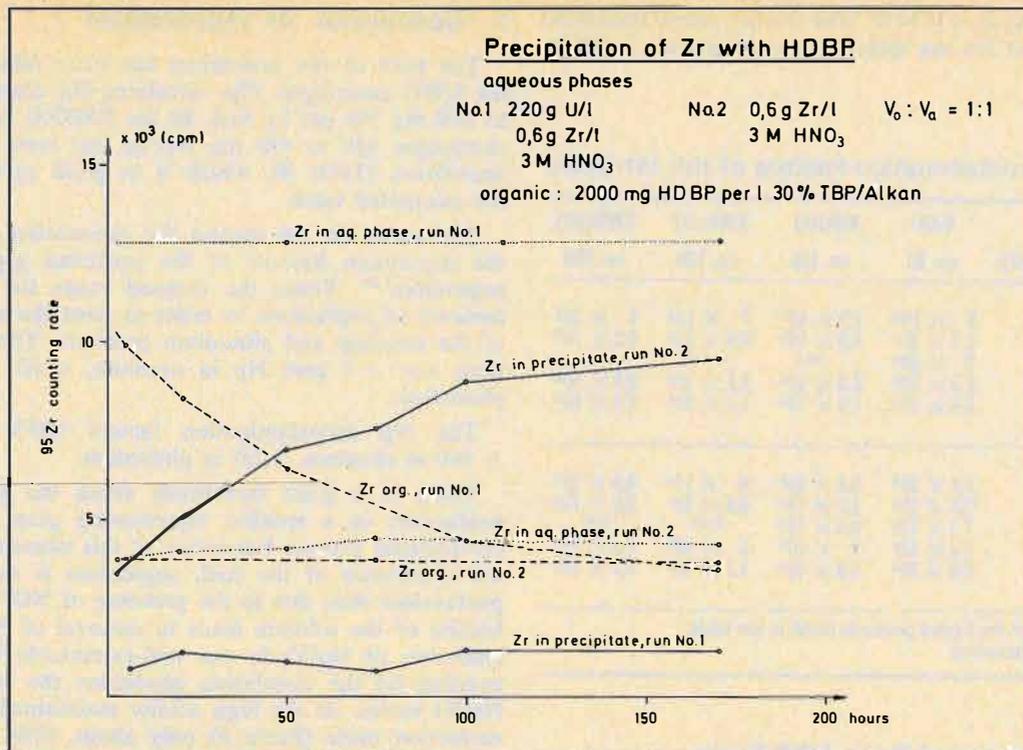


FIGURE 4. Zirconium dibutylphosphate precipitation, influence of uranium.

TABLE 6. Decontamination Factors Obtained in the HA Mixer-Settler with Low and High Organic Loading, DFR(I) Campaign.

	Saturation of the 30% TBP low	high
U g/l	42.6	91.4
Pu g/l	9.26	18.8
Decontamination factors		
Cs ¹³⁷	3630	11400
Ce ¹⁴⁴	100	> 33000
Ru ¹⁰⁶	3.5	500
Zr ⁹⁵	10	310
γ gross	700	$5.8 \cdot 10^3$

disturbances and finally a plugging of the equipment; after 30 hours the plant had to be shut down. As expected the decontamination achieved was poor (see Table 6).

The operation was resumed, after thorough cleaning of the plugged equipment, with the "high-load" flowsheet (b). No further interferences by crud or other problems were observed over the whole campaign. The concentration profile (Figure 5) shows an increase of the U and Pu concentrations near to the feed stage, demonstrating a build-up at this high loading. Nevertheless, the plutonium loss of ca. 0.04% in the aqueous raffinate appears to be not a consequence of the high loading, rather the low distribution coefficients of < 1 in the last three extraction stages point to the presence of some inextractable Pu species as the cause for these losses.

Subsequent demonstration tests of the flowsheet have been made with LWR fuels (see Table 1). In these cases, the first cycle was run with U/Pu partitioning (HA-1AS-1B-1C mixer settlers). The campaigns were run with fuel charges of 10 to 15 kg, with operation times of the first cycle up to 10 days. In all cases, crud accumulation in the mixer-settlers remained low, and did not interfere

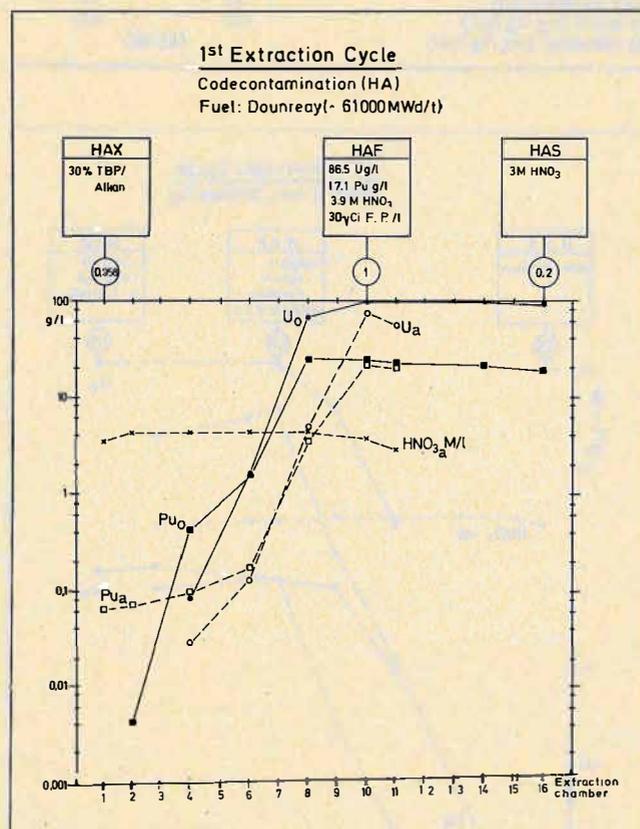


FIGURE 5. U, Pu, and HNO_3 concentration profiles in the HA extractor, LWR fuel campaign.

with the operation. As an example, a concentration profile is shown for the "KWO(II)" campaign in Figure 6. With 105 g/l U+Pu in the HAP, no evidence for Pu accumulation in the extraction part of the HA mixer-settler is found. The plutonium loss with the aqueous

raffinate (HAW) is < 0.04%. The overall decontamination factors obtained for the different campaigns are listed in Table 7.

TABLE 7. Decontamination Factors of the 1st Cycle

Fuel (campaign)	VAK	KWO(I)	KWO(II)	KWO(III)
Feed activ. (Ci/l)	ca. 50	ca. 150	ca. 120	ca. 230
U product				
Zr-95	8×10^3	$3,5 \times 10^3$	7×10^3	4×10^3
Ru-106	$1,3 \times 10^3$	$2,0 \times 10^3$	$0,8 \times 10^3$	$0,6 \times 10^3$
Ce-144	3×10^5	(xx)	(xx)	(xx)
Cs-134/7	$1,5 \times 10^5$	$2,5 \times 10^5$	$1,5 \times 10^5$	$0,4 \times 10^5$
Total γ	$1,6 \times 10^4$	$1,5 \times 10^4$	$1,0 \times 10^4$	$0,3 \times 10^4$
Pu Product				
Zr-95	$0,9 \times 10^3$	$0,4 \times 10^3$	9×10^3	$0,3 \times 10^3$
Ru-106	$0,6 \times 10^3$	$1,5 \times 10^3$	$0,9 \times 10^3$	$0,8 \times 10^3$
Ce-144	$1,0 \times 10^5$	$0,6 \times 10^5$	(xx)	(xx)
Cs-134/7	$0,3 \times 10^5$	5×10^5	3×10^5	$1,3 \times 10^5$
Total γ	$0,6 \times 10^4$	$1,0 \times 10^4$	$1,1 \times 10^4$	$0,1 \times 10^4$

(x) Feed inventory of the fission products listed in the table
 (xx) Below limit of detection

TABLE 8. Analysis of Np in LWR Fuels

Experiment	KWO(II)	KWO(III)
Burn-up (MWd/kg)	37	33
Np found (mg/kg fuel)	410	430
Np calculated (mg/kg fuel)		440-460

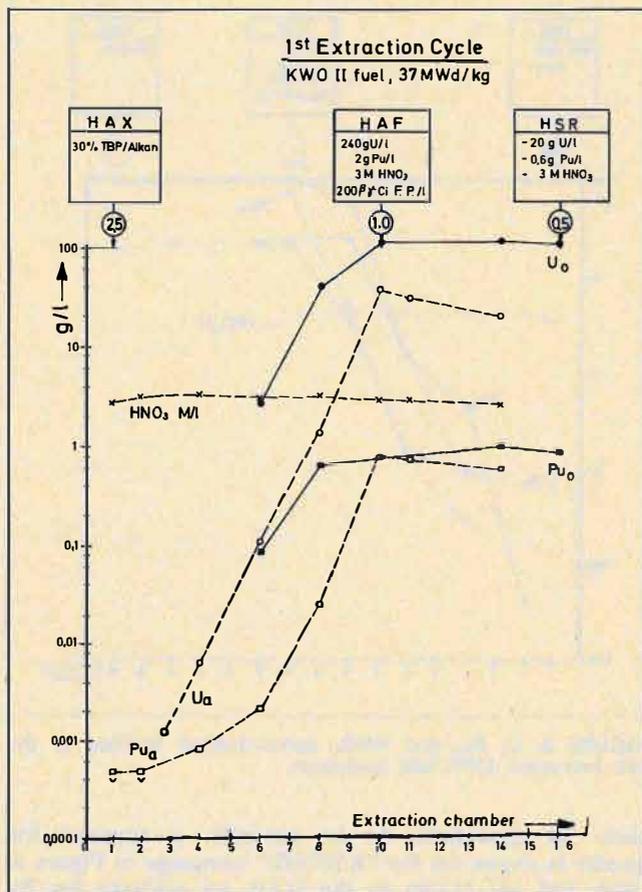


FIGURE 6. U, Pu, and HNO₃ concentration profiles in the HA extractor, FBR fuel campaign.

5. Behaviour of Neptunium

The path of the neptunium has been followed during the KWO campaigns. The calculated Np content was 440 to 460 mg Np per kg fuel. In the KWO(I) and KWO(II) campaigns 410 to 430 mg Np/kg fuel were found after dissolution (Table 8), which is in good agreement with the calculated value.

Ten years ago we studied the quantitative recovery of the neptunium because of the predicted application for neptunium⁽¹⁸⁾. Today the demand exists for quantitative removal of neptunium, in order to meet the specifications of the uranium and plutonium products. These specifications are: < 1 ppm Np in uranium, < 10³ ppm Np in plutonium.

The Np decontamination factors (DF) needed are > 500 in uranium, > 50 in plutonium.

There is a great uncertainty about the behaviour of neptunium in a specific reprocessing plant due to the complicated process behaviour of this element⁽¹⁹⁾. During the dissolution of the fuel, neptunium is mainly in the pentavalent state due to the presence of NO₂⁻. Prolonged boiling of the solution leads to removal of NO₂⁻ and to oxidation of Np(V) to the well-extractable Np(VI). Depending on the dissolution conditions the ratio Np(VI):Np(V) varies. At the high acidity maintained in our first extraction cycle (Table 9) only about 10% of the neptunium is removed with the aqueous raffinate (HAW) while ca. 90% is extracted with the products. In the organic extractant the concentration of nitrous acid was 0.003 M. With little or no nitrous acid present the formation of extractable Np(VI)⁽²⁰⁾ is promoted.

The distribution behaviour of neptunium in the U/Pu partitioning step, which in the MILLI normally is performed with U(IV)nitrate, is not uniform. It is known that the reduction of Np(VI) to Np(V) with U(IV) is fast, while the Np(V) → Np(IV) step is slow. In "cold" counter-current laboratory tests with synthetic solutions, about 70% of the neptunium was in the uranium and 30% in the plutonium stream after partitioning with U(IV). In the tests with highly irradiated KWO fuel, between 50 and 85% of the extracted neptunium was found in the uranium stream (Table 9). The neptunium values given in this and the following tables are overall values of one campaign on the basis of analysis from tank inventories.

The second uranium cycle serves primarily for the removal of plutonium from uranium⁽⁸⁾. Plutonium is reduced with hydrazine-stabilized U(IV) nitrate; up to 99.9% of the plutonium present in the 2D feed solution is removed with the aqueous raffinate. Simultaneously Np(VI) is reduced to lower valencies. Depending on the organic to aqueous flow rates, varying proportions of the neptunium are removed (Table 10) with the aqueous waste. In the second cycle, overall DF values for neptunium were between 100 and 200 with the "dilute" flowsheet and about 10 with the "concentrated" flowsheet⁽²¹⁾.

Figure 7 presents the concentration profiles of neptunium, plutonium, uranium, and nitric acid in the second uranium purification cycle of the KWO(II) campaign.

TABLE 9. Np Distribution (%) in the 1st Partitioning Cycle

Experiment	KWO (I)	KWO (II)	KWO (III)
Raffinate (HAW)	0.4%	14%	9%
U product (ICP)	76 %	51%	35%
Pu Product (I BP)	14 %	28%	38%

TABLE 10. 2nd Uranium Cycle Np Removal by U(IV)

Experiment	KWO (II) dil.	KWO (III) dil.	conc.
Feed, U g/l	50	47	293
Extraction, V_o/V_{aq}	0.6	0.6	2
Scrub, V_o/V_{aq}	4.5-5.2	6	6
Scrub, U(IV) g/l	1.3-5	0.2-0.4	0.5-1
DF(Np), overall	125	200	10

TABLE 11. Np Removal by Nitrous Acid, 3rd Uranium Cycle

Experiment	KWO (I)	KWO (II)
U in org. phase, g/l	75	69
HNO ₂ phase, mmol/l	0.1-0.4	40-100
DF (Np), overall	70	10 ³

TABLE 12. Np Removal by Nitrous Acid, 2nd Plutonium Cycle

Experiment	KWO (I)	KWO (II)	KWO (III) ^(*)
HNO ₂ in org., mmol/l	15-50	40-70	20-80
HNO ₃ in aq., mol/l	3	1.9	2
DF(Np), overall	7-14	330	30

^(*)disturbance by HDBF

The neptunium DF was 130 in this case, while the DF for plutonium was 150. An amelioration of these results was achieved by changing the acid concentrations in the extractor.

Removal of residual neptunium must be performed in the third uranium cycle. This can be achieved by the introduction of sufficient nitrous acid to produce inextractable Np(V). With concentrations of HNO₂ in the TBP between 0.04 and 0.1 moles/l decontamination factors up to 10³ for neptunium were achieved (see Table 11). Addition of nitrous acid to the plutonium purification cycles yields adequate DF values for neptunium already in one cycle (see Table 12, KWO(II) campaign).

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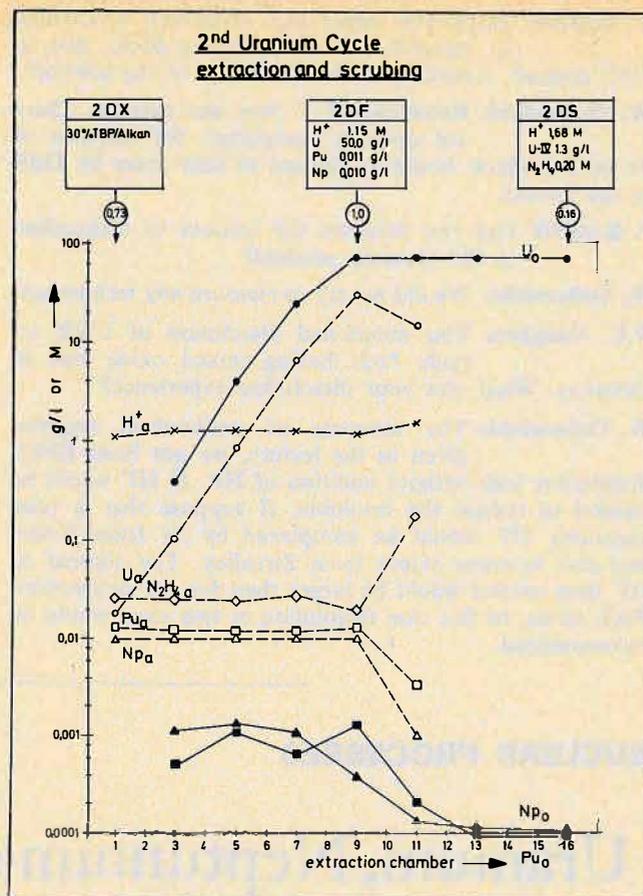


FIGURE 7. U, Pu, Np, N₂H₄, and HNO₃ concentration profiles in the 2D-extractor.

DISCUSSION

A. Naylor: In your work you have processed different fuels of varying irradiation and cooling time. Have you attempted to correlate DFZr in the HA column and Pu loads in the HAW raffinate with feed activities, formation of HDBP in the Ha column, crud amounts, etc?

W. Ochsenfeld: As can be seen from Table 7 of the full paper (not given) in the lecture, DF's are getting worse with increasing feed activity.

C. Bernard: Have you noted any difference concerning U retention in the stripping bank, due to DBP content, according to the saturation of the solvent?

W. Ochsenfeld: Retention of U was not noticed. There are stronger complexes, for instance of Zr or Pu, which would be formed in first order by DBP in the solvent.

J. Kendall: Did you measure the amount of technetium in the uranium product?

W. Ochsenfeld: We did not try to measure any technetium.

V.C. Vaughan: You mentioned dissolution of LWR recycle fuels having mixed oxide clad in Zircalloy. What was your dissolution experience?

W. Ochsenfeld: The amounts of undissolved material given in the lecture, we got from HNO_3 dissolution tests without addition of HF. If HF would be needed to reduce the insoluble, (I suppose that is your question), HF would be complexed by Zr from fission and also to some extent from Zircalloy. The amount of HF then needed would be larger than for the undissolved PuO_2 alone. In this case dissolution in two steps would be recommended.

L. Maya: How was the DBP-Zr complex prepared and characterized? How representative is a synthetic product DBP-Zr of the complexes formed in the actual system?

W. Ochsenfeld: The complex was prepared by mixing both $\text{Zr}(\text{NO}_3)_4$ and DBP in 3M HNO_3 and analyzed for Zr, NO_3^- , and DBP content. The precipitate was washed free of acid and dried at 60°C . Molecular weights were not determined.

The synthetic product we take as a model only. We tried to separate and analyze "cruds" from active runs. But isolating and washing of these cruds turned out to be very difficult because cruds are emulsions of water and diluent (dodecane) mainly, with very low content of solids.

G. Grossi: Some experiments carried out in our laboratory with simulated solutions have shown that molybdenum may form precipitates with DBP in particular conditions. Have you found any molybdenum-DBP compounds in the cruds formed during the hot operation in the Milli facility?

W. Ochsenfeld: We have not noticed Mo-DBP compounds.

NUCLEAR PROCESSES

Uranium, Neptunium and Plutonium Kinetics of Extraction by Tributylphosphate and Trilaurylamine in a Centrifugal Contactor

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ABSTRACT

The extraction kinetics of uranium, plutonium and neptunium were investigated, involving extraction by tributylphosphate and trilaurylammonium nitrate from aqueous nitric acid solutions in a centrifugal contactor, leading to the following conclusions:

Extraction and stripping are faster with tributylphosphate than with trilaurylammonium nitrate and suggest a significant contribution by a diffusion process. With trilaurylammonium nitrate, the transfer mechanism seems more complex, suggesting a strong contribution by chemical reactions at the interface.

Introduction

CENTRIFUGAL CONTACTORS HAVE BEEN USED for fuel reprocessing in the United States since 1965⁽¹⁾. They have been applied in France more recently and their application is foreseen in many other countries.

Residence time is very short in these contactors and the kinetics of transfer of the chemical elements appear to be one of the limiting factors in their utilisation. Knowledge of the transfer kinetics of metallic compounds becomes an important factor in optimizing the

operating conditions of these contactors. The first results of transfer kinetics studies of some transuranium elements are described in this paper. These elements were extracted from a nitric acid aqueous solution by tributylphosphate and trilaurylammonium nitrate solutions in the aliphatic diluent TPH (produced by Progil).

Experimental

The Centrifugal Contactor

Drawings of the experimental device and apparatus itself, are shown in Figures 1, 2, 3, 4.

The purpose of constructing this centrifugal contactor was twofold:

- (1) to obtain mixing times lower than transfer rates (mixing times as low as 0.4 s were reached),
- (2) to design a new mixing chamber using friction phenomena.

This is a single-stage contactor. All metallic parts were made of stainless steel (frame, drive components, cylinders). The settling chambers are located in a plexiglas rotor so as to permit visual observation of the interface by transparency.

Mixing of the aqueous and organic phases is performed by friction in the 0.5 mm annular space between the two cylinders (Figure 2). The inner cylinder is stationary while the outer cylinder rotates. Rotation speed is the same for the mixing and settling sections.

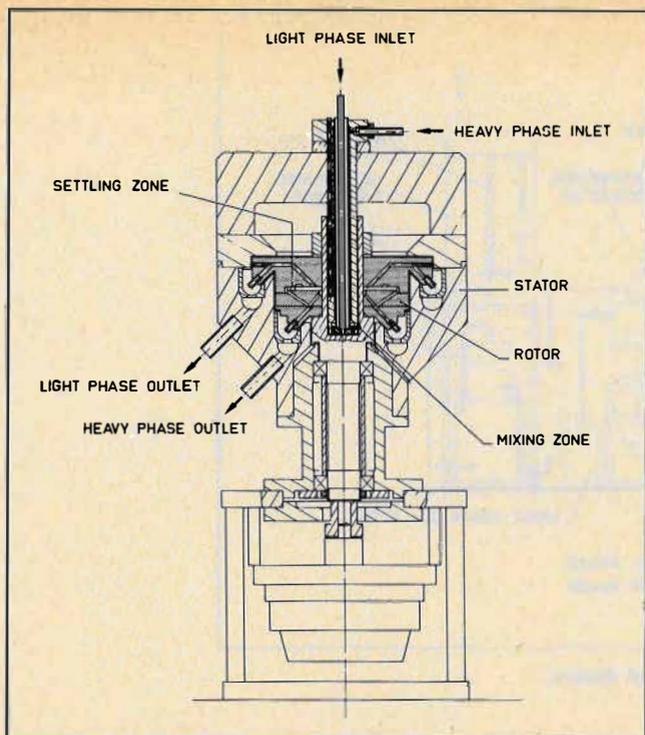


FIGURE 1. Centrifugal extractor (ECP type) — General view.

The emulsion is evacuated into two diametrically opposed settling chambers and passes through the organic phase. Each phase is then collected in a groove located in the stator, and removed from the contactor. The interfacial area is not yet known, nevertheless a current study shows that, in the present operating conditions, the continuous phase is the aqueous one⁽²⁾.

The main characteristics of the contactor are: maximum total flow: 18 l/h (a maximum of 1 percent of one phase carried over into the other was allowed), mixing volume: 1.95 cm³, and maximum speed of rotation: 3600 rpm (centrifuge field: 500 g), the interface position can be calculated from the overflowing level of the heavy and light phases and the density ratio of the solutions, which is about 1.3. (Figure 3).

The extractor is continuously fed at constant flow rates by means of a feed system shown in Figure 4. The solutions are stored in two containers and pumped at flowrates ranging from 1 to 10 l/h, with a pulse frequency of 75 per minute. The pulsed flow is regulated by passage through a damping-out system, and monitored by means of a flowmeter. The flowrate variations are of about 1%.

The mixing temperature is obtained by preheating the feed solutions in the storage containers and by complementary heating of the emulsion in the extractor (Figure 2). The temperature is continuously controlled in the damping-out system and in the extractor by a platinum thermistor and maintained within $\pm 0.5^\circ\text{C}$.

The procedure is as follows: (1) aqueous phase pump turned on, (2) start centrifugal rotation, (3) organic phase pump turned on, (4) extractor heater on. Sampling is performed after 10 minutes, this interval being generally required for flowrate and temperature stabilization. Only one sample is usually taken, except when reproductibility measurements are made, requiring two samples.

Compounds and Analysis

— $\text{U}(\text{NO}_3)_4$ solutions are prepared by catalytic reduction

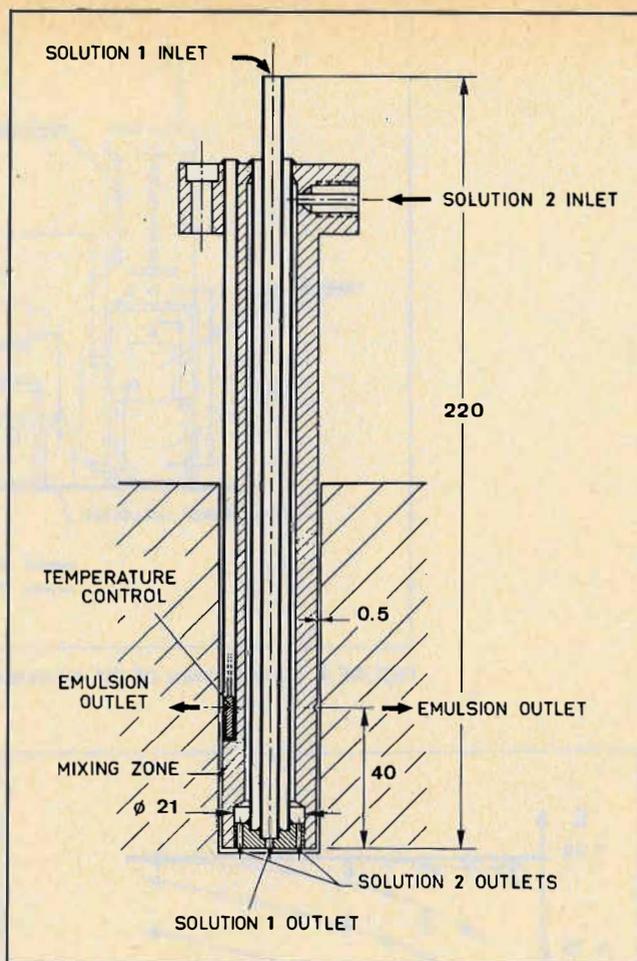


FIGURE 2. Centrifugal extractor (ECP type) — View of the mixing zone and solutions introduction device.

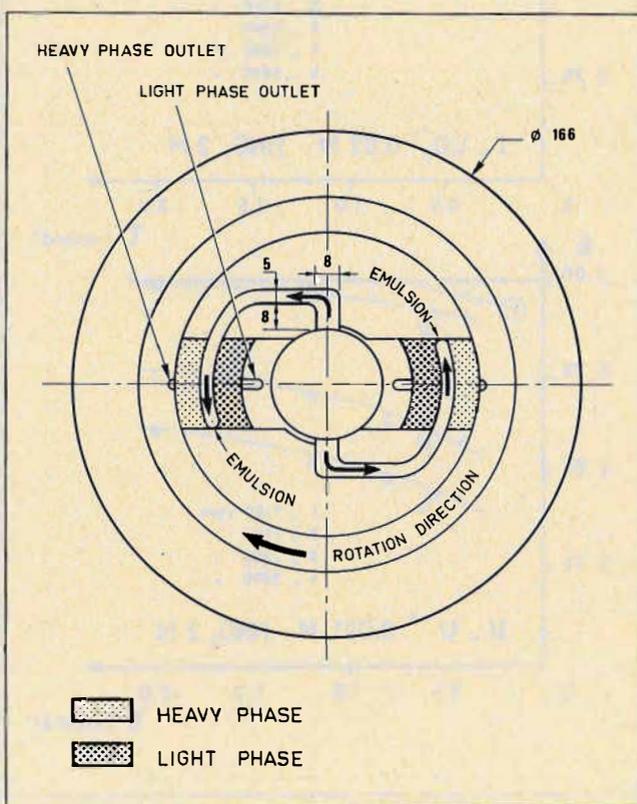


FIGURE 3. Centrifugal extractor (ECP type) — View of the rotor — emulsion outlet and settling zones.

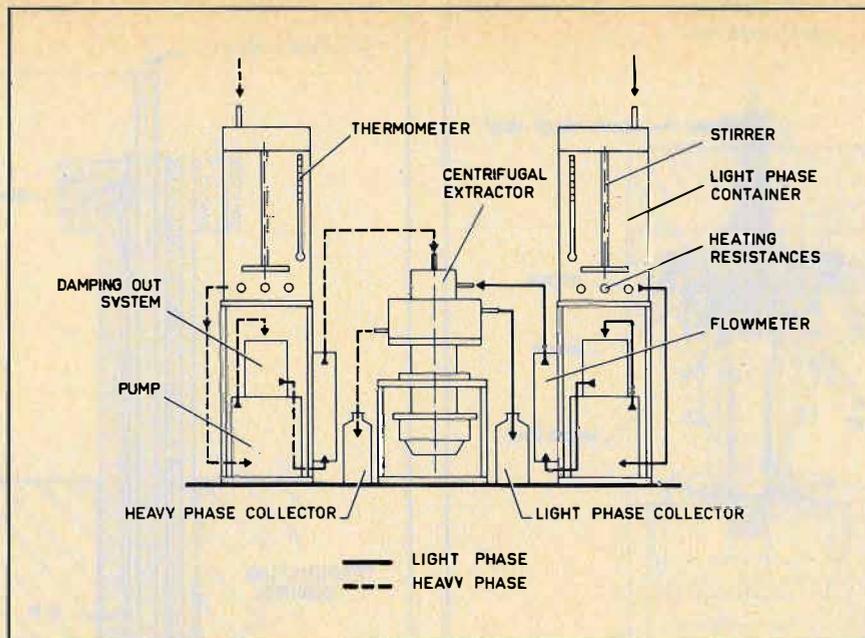


FIGURE 4. General view of the experimental device.

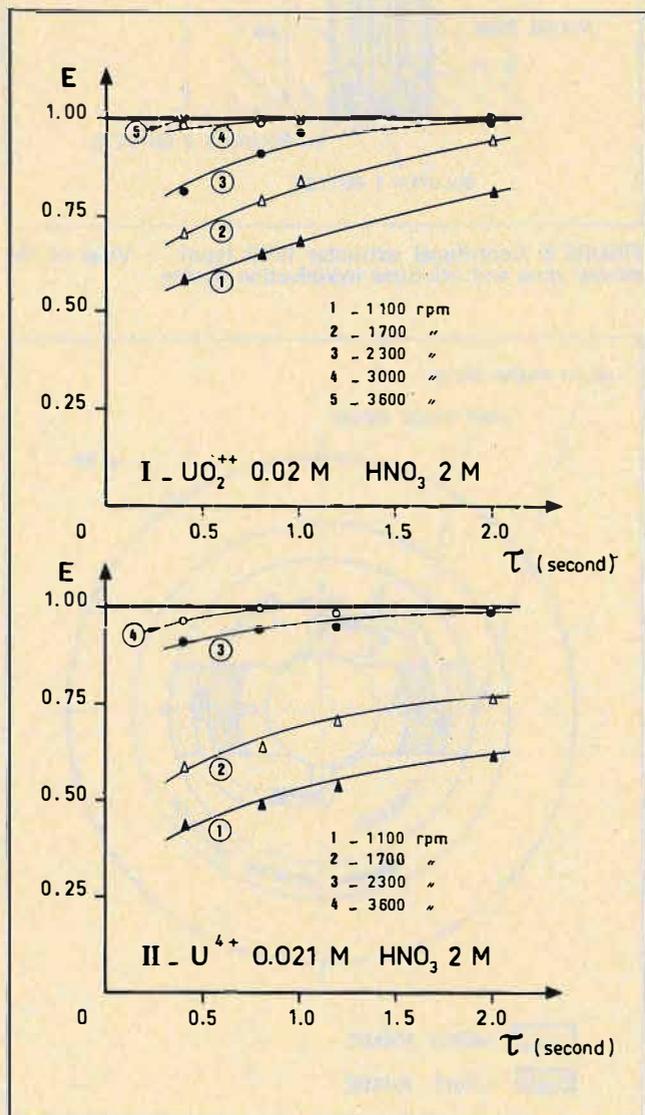


FIGURE 5. Dependence of the extraction efficiency with phases contact time — 30% TBP (Progil), $\theta = 28^\circ C$.

of U(VI) by hydrogen, and supplied by the fuel reprocessing plant of La Hague. The tetravalent uranium content is about 95 percent.

— Uranyl nitrate solutions are made with $UO_2(NO_3)_2 \cdot 6H_2O$ (Prolabo).

— HNO_3 is a commercial product (Prolabo or Merck).

— $Pu(NO_3)_4$ solutions are obtained by dissolution of PuO_2 in a mixture of HNO_3 and HF, precipitation with 10 M NaOH, washing with distilled water and final dissolution in HNO_3 . The total impurity content is less than 0.5 percent of plutonium.

— $Np(NO_3)_4$ solutions are purified by solvent extraction.

— TBP is a commercial product (Melle Bezons).

— the diluent TPH is a hydrogenated tetrapropylene supplied by Progil S.A., France. It is a branched paraffin with 12 carbon atoms; its main characteristics are: (1) viscosity at $20^\circ C$: 1.3 cp, (2) specific gravity at $20^\circ C$: 0.760.

The TBP-TPH mixture is purified as follows: (1) washing with sodium carbonate, (2) washing with caustic soda, (3) washing with distilled water (three times). TLA is a pure product supplied by Rhône Poulenc. The TLA-TPH mixture is purified in the same manner as the TBP. The amine is acidified by two contacts with 2M HNO_3 solution just before use.

Nitric acid is determined by volumetric analysis. U(IV) and U(VI) are determined by volumetric analysis by means of Ce(IV). Pu(IV) and Np(IV) are analysed by a radiometric method.

Results and Discussion

Typical extraction curves are given in Figure 5. They show that at high rotation rates the efficiency is nearly 100 percent when the mixing time reaches 2 seconds. Mathematical data processing can be achieved if:

(1) we assume that the transfer rate follows a first order law with regard to the concentrations of the solute in both phases.

(2) the mixer can be treated as a chemical reactor whose resolution is known. Two models can be considered:

(a) a perfectly stirred continuous reactor, (b) a tubular reactor. We shall successively develop the calculations

regarding these models in order to check if our experimental results match one of them.

$$\text{Hypothesis (1) implies that: } v = k_1 C_A - k_2 C_S \dots \dots \dots \text{ (I)}$$

At equilibrium $v = 0$, $k_1 C_A^{eq} = k_2 C_S^{eq}$.

If the phase volumes are equal: $C_A^0 = C_A + C_S$.

Then $v = k_1 C_A - k_2 (C_A^0 - C_A)$, $C_A^0 = C_A^{eq} + C_S^{eq}$, and $v = (k_1 + k_2) (C_A - C_A^{eq})$.

$$\text{If } k = k_1 + k_2, v = k(C_A - C_A^{eq}) \dots \dots \dots \text{ (II)}$$

This equation is valid irrespective of the chemical reactor chosen to simulate the mixer.

(a) Perfectly Stirred Continuous Reactor.

The characteristic equation of this reactor is:

$$A \cdot v = F_A \cdot (C_A^0 - C_A) \dots \dots \dots \text{ (III)}$$

with $v = k(C_A - C_A^{eq})$ (II), and $A = a \cdot V$

$$k \cdot a = \frac{F_A}{V} \cdot \frac{C_A^0 - C_A}{C_A - C_A^{eq}}$$

$$\text{Hence, if } \beta = \frac{F_A}{F} = 0.5, k \cdot a = \frac{\beta}{\tau} \cdot \frac{E}{1 - E} \dots \dots \dots \text{ (IV)}$$

(b) Tubular Reactor

If S is the mixer cross-sectional area and L its length, the characteristic equation becomes:

$$F_A \cdot C_A(x) - F_A \cdot C_A(x + dx) = S \cdot a \cdot dx \cdot v$$

$$\text{Hence: } -F_A \cdot \frac{dC_A}{dx} = S \cdot a \cdot v \dots \dots \dots \text{ (V)}$$

$$-\frac{dC_A}{dx} = (k \cdot a) \cdot \frac{S}{F_A} \cdot (C_A - C_A^{eq})$$

$$-\frac{dC_A}{C_A - C_A^{eq}} = (k \cdot a) \cdot \frac{S \cdot dx}{F_A}$$

Thus $\text{Log} \frac{C_A^0 - C_A^{eq}}{C_A^L - C_A^{eq}} = (k \cdot a) \cdot \frac{S \cdot L}{F_A}$, where C_A^L = outlet concentration, $S \cdot L = V$.

$$\text{Hence } (k \cdot a) = \frac{\beta}{-\tau} \text{Log}(1 - E) \dots \dots \dots \text{ (VI)}$$

These two models give quite different mathematical solutions. If we assume that the mixer is a perfectly stirred continuous reactor,

$$\frac{E}{1 - E} = K \cdot \tau, \text{ with } K = \frac{k \cdot a}{\beta};$$

whereas if it is a tubular reactor, as may be suggested by the mixer shape in our centrifugal contactor, we have:

$$\text{Log}(1 - E) = -K \cdot \tau, K = \frac{k \cdot a}{\beta}$$

We plotted the variations of $\text{Log}(1-E)$ and $E/1-E$ from our experimental results. as a function of mixing time, in Figures 6-7 respectively. It may be concluded that our results show fairly good agreement with (IV). The same conclusion was drawn by Pushlenkov et al^(13,14,15,16), also using a laboratory centrifugal contactor, while Olander⁴ and Fomin^(5,6), using a stirred transfer cell obtained results matching (VI).

As stated above, the specific interfacial area in our contactor is not yet known. The overall results will thus be interpreted in terms of apparent overall transfer coefficient (k.a.). Activation energies were estimated from the slope of the curve,

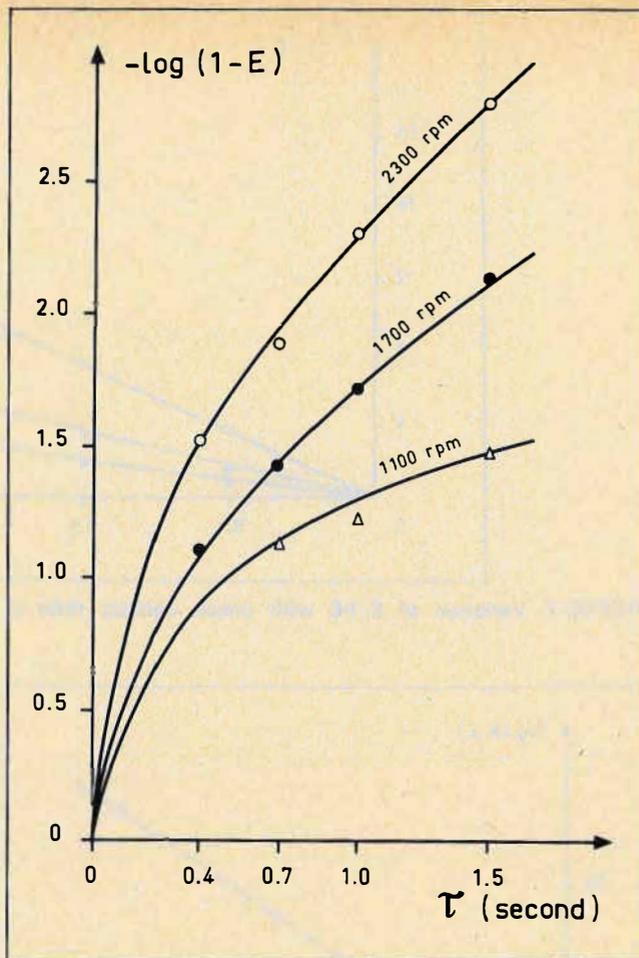


FIGURE 6. Variation of $-\text{Log}(1-E)$ with phase contact time at various rotation rates. The system is as follows: $\text{UO}_2(\text{NO}_3)_2$ 0.21 M - HNO_3 2.0 M - 30% TBP in TPH (Progil), $\theta = 28^\circ\text{C}$.

$$\left(\text{Log}(k \cdot a), \frac{1}{T} \right)$$

The influence of speed of rotation, temperature, initial nitric acid and metal concentrations on (k.a) were investigated for both extraction and stripping.

The results were interpreted according to the principles established by Fomin⁽⁷⁾, Lawson⁽⁸⁾ and Glastone et al⁽⁹⁾. With our extraction conditions, chemical reactions occur only in the very near interfacial zone. With these conditions, Fomin classifies the kinetics into three systems:

- (1) the kinetic system: extraction rate is limited by a chemical step,
- (2) the diffusion system: extraction rate is diffusion controlled,
- (3) the composite system: extraction rate depends on both processes.

According to Glastone et al⁽⁹⁾, the extraction is diffusion controlled if $E_{exp} < 5-7$ kcal/mole, and limited by the chemical reactions at the interface if $E_{exp} > 10$ kcal/mole.

Lawson⁽⁸⁾ demonstrated that the drops coalescence rate is raised by temperature and mass transfer out of the drops, and inhibited by mass transfer into the drops.

From these considerations, the various extraction conditions can be classified according to Fomin's principle if the variations in (k.a) with rotation speed and E_{exp} are known. Figures 8 and 9 show typical variations in (k.a) with rotation speed and temperature respectively.

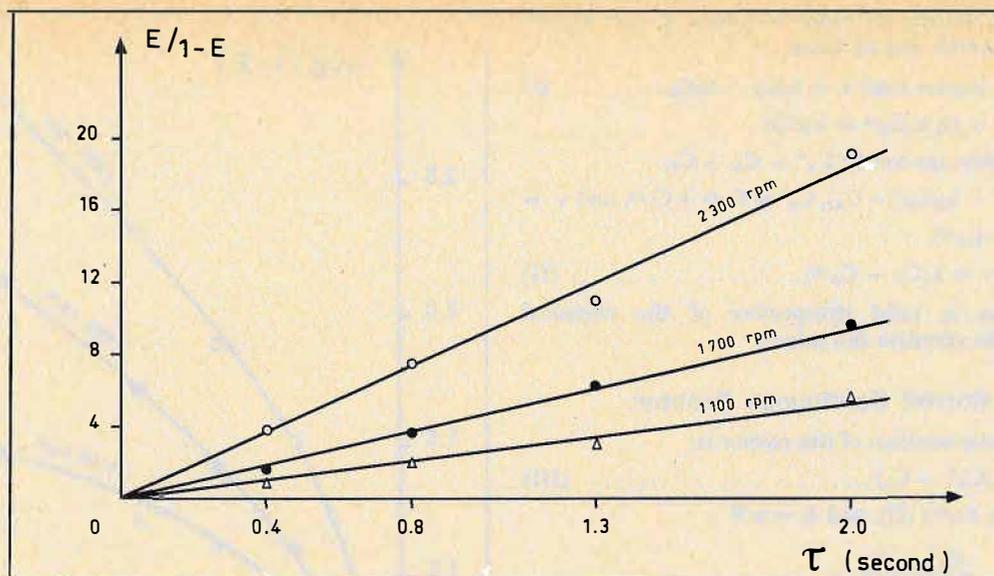


FIGURE 7. Variation of $E/1-E$ with phase contact time at various rates. System as in Figure 6.

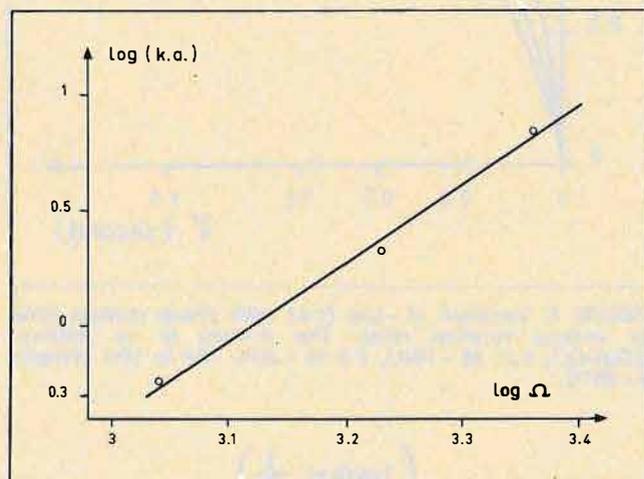


FIGURE 8. Dependence of the Logarithm of $(k.a.)$ as function of the logarithm of the rotation rates. The system is as follows: $\text{Pu}(\text{NO}_3)_4$ 0.04 M - HNO_3 2.0 M - 30% TPB in TPH (Progil), $\theta = 28^\circ\text{C}$.

Extraction with Tributylphosphate

Nitric Acid Transfer

Pushlenkov^(3,10) and Olander⁽⁴⁾ found that the extraction rate of nitric acid is limited by the diffusion process in the organic phase. In addition, Pushlenkov found that in a centrifugal contactor the transfer time required to reach equilibrium was about 2 seconds at high rotation speeds⁽³⁾. The experimental activation energy, measured in a transfer cell, was about 1 Kcal/mole⁽¹⁰⁾.

Our experimental data on nitric acid extraction with 30% TBP in TPH are given in Table 1. These results show a strong effect of the speed of rotation on the extraction rate, with $(k.a.) \sim \Omega^{(2.5-2.7)}$, and a mean activation energy value of 7.7 kcal/mole, which would indicate a slight contribution of the chemical step.

The extraction rate does not seem to depend upon the initial nitric acid concentration but the accuracy of these results is not sufficient to assert this. One interesting result is that the nitric acid extraction rate is increased by the addition of metallic compounds in the aqueous phase, i.e. U(VI) - U(IV). This may be related to the

TABLE 1. Extraction of Nitric Acid with 30% TBP in TPH

(a) Effect of Rotation Speed

$\theta^\circ\text{C}$	$(\text{H}^+)_{\text{in}}$	s
28	2M	2.7
35	2M	2.5

(b) Effect of Temperature

Ω_{rpm}	$\theta^\circ\text{C}$	$(\text{H}^+)_{\text{in}}$	$k.a(1/s)$	E_{exp} Kcal/M
1700	28	2M	2.8	8.8
1700	35	2M	3.9	
2300	28	2M	6.2	6.6
2300	35	2M	7.9	

(c) Effect of Initial Nitric Acid and Metal Concentrations

Ω_{rpm}	$\theta^\circ\text{C}$	$(\text{H}^+)_{\text{in}}$	$(\text{U VI})_{\text{in}}$	$(\text{U IV})_{\text{in}}$	$ka(1/s)$
1100	28	0.5 M	—	—	1.9
1100	28	2.05 M	—	—	1.5
1100	28	4.1 M	—	—	2.2
1700	28	2 M	0	—	2.8
1700	28	2 M	0.021 M	—	3.6
1700	28	2 M	0.21 M	—	∞
1700	28	2 M	—	0	2.8
1700	28	2 M	—	0.021 M	4.1
1700	28	2 M	—	0.084 M	4.1

variation in the HNO_3 activity coefficient.

In conclusion, it seems that, in our centrifugal contactor the mechanism of nitric acid extraction is a composite one, with contributions by both processes, diffusion and chemical reaction.

Tetravalent and Hexavalent Uranium Transfer

The extraction of hexavalent uranium has already been investigated, but we failed to find any publication related to uranium(IV) extraction kinetics. In studying U(VI) transfer, Pushlenkov et al.^(3,11,12) found that the limiting

TABLE 2. Comparative Results of Extraction of U (IV) and U (VI) by TBP

Ω_{rpm}	$\theta_{\circ C}$	$(H^+)_{in}$	$(metal)_{in}$	k_a U VI (1/s)	k_a U IV (1/s)	E_{exp} U VI Kcal/mole	E_{exp} U IV Kcal/mole
1100	28	2M	0.021 M	1.2	0.7		
1700	28	2M	0.021 M	2.6	1.2	5.4	7.4
2300	28	2M	0.021 M	6.7	5.7		

step depends upon both type of contactor and nature of the diluent. With carbon tetrachloride as diluent they found a controlling chemical step when using a transfer cell⁽¹¹⁾, and a diffusion-controlled step with a centrifugal contactor⁽⁸⁾. With an aliphatic diluent, they found, whatever the contactor, a diffusion-controlled system^(3,12).

Farbu and McKay found a controlling chemical step in using the single-drop method⁽¹³⁾.

Our experimental data on $UO_2(NO_3)_2$ and $U(NO_3)_4$ extraction with 30% TBP in TPH are given in Table 2. They reveal a strong effect of the speed of rotation on the U(VI) extraction rate ($k_a \sim \Omega^{1.5-2.3}$) and an experimental activation energy of 5.4 kcal/mole. We observed no effect of the initial nitric acid concentration, and a slow decrease in (k_a) with increasing U(VI) concentration. This last result has a physical explanation (Lawson's assumption is confirmed). The activation energy value enables us to assume that we have a diffusion-controlled system.

For U(IV), we found $(k_a) \sim \Omega^{2.5-3}$, and an activation energy of 7.4 kcal/mole. The concentration range used is not broad enough to enable meaningful interpretation of the effect of U(IV) concentration. On the other hand, nitric acid has no significant effect. These results show that the process is not a pure diffusion system.

A comparison of U(VI) and U(IV) extraction rates leads to the following observations:

- the rotation speed effect is roughly the same in both systems.
- the U(IV) extraction rate is lower than that of U(VI). This is probably due to the great difference in the hydration energies of U^{4+} and UO_2^{2+} cations.

Tetravalent, Uranium, Neptunium and Plutonium Transfer

No systematic study has been made of the extraction kinetics of tetravalent transuranium elements with TBP. Pushlenkov et al.⁽³⁾ published some results concerning the extraction kinetics of Pu(IV) in a centrifugal contactor. They found that the extraction is diffusion controlled. Fomin and Leman⁽⁶⁾ reached the same conclusion for extraction of trace amounts of Pu(IV), and assumed a resistance to diffusion in the organic phase.

The experimental results that we obtained concerning the extraction of tetravalent transuranium elements are given in Table 3. They show, whatever the element, a strong rotation speed effect ($k_a \sim \Omega^{2.5-3.6}$). The experimental activation energies of about 7.4 - 8.4 kcal/mole, indicate that the process is a composite system, where both diffusion and chemical processes are involved in the extraction. The initial nitric acid concentration has no effect on the extraction rate. The rotation speed and temperature effects are roughly the same for the different elements. Nevertheless the extraction rate for U(IV) is half that of Pu(IV) and Np(IV). This fact corroborates the assumption of a chemical-step contribution.

We also investigated Pu(IV) and U(IV) stripping from 30% TBP in TPH by a nitric acid solution. Our results show a strong rotation speed effect ($k_a \sim \Omega^{1.3-1.5}$) for

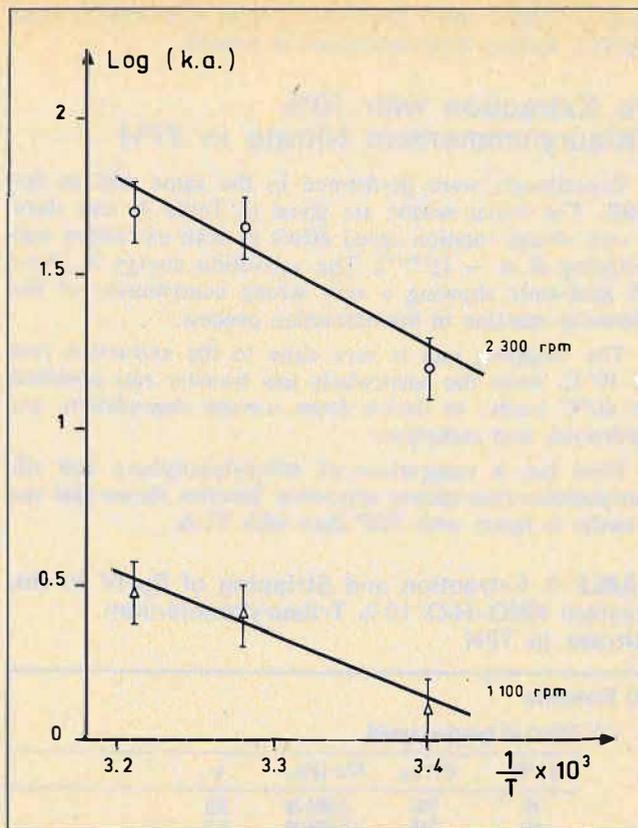


FIGURE 9. Variation of Log (k.a.) with temperature. System as in Figure 6. Rotation rates: 1100 and 2300 rpm.

TABLE 3. Comparative Results of Extraction and Stripping of Tetravalent Transuranium Elements

(a) Extraction and Stripping

element	factor					
	Ω_{rpm}	$\theta_{\circ C}$	$(H^+)_{in}$	$(metal)_{in}$	k_a (extr.) (1/s)	k_a (re-extr.) (1/s)
U IV	1700	28	2M	0.021 M	1.2	2.1
Pu IV	1700	28	2M	0.021 M	2.4	2.0
	2300	28	2M	0.021 M	5.3	2.9

(b) Transuranium elements extraction

Ω_{rpm}	$\theta_{\circ C}$	$(H^+)_{in}$	$(metal)_{in}$	k_a U IV (1/s)	k_a Np IV (1/s)	k_a Pu IV (1/s)
1700	28	2M	0.021 M	1.1	2.5	2.4
2300	28	2M	0.021 M	—	5.5	5.3
1700	35	2M	0.021 M	1.5	3.5	3.4
2300	35	2M	0.021 M	—	7.1	7.0

(c)

Ω_{rpm}	$(H^+)_{in}$	$(metal)_{in}$	E_{exp} U IV Kcal/mole	E_{exp} Np IV Kcal/mole	E_{exp} Pu IV Kcal/mole
1700	2M	0.021 M	7.4	8.3	8.4

both Pu(IV) and U(IV), no significant temperature effect ($E_{exp} = 3$ kcal/mole for Pu(IV), and $E_{exp} \neq 0$ for U(IV)). The latter result implies that the diffusion process limits the transfer. This conclusion is corroborated by the fact that similar results were found for Pu(IV) and U(IV).

A comparison between extraction and stripping is difficult to make, owing to the fact that the laws of variation are different. For U(IV), it is clear that strip-

ping is faster than extraction, while for Pu(IV) and Np(IV), further experimentation is needed.

Pu Extraction with 10% Trilaurylammonium Nitrate in TPH

Experiments were performed in the same way as for TBP. The initial results are given in Table 4, and show a very strong rotation speed effect in both extraction and stripping ($k_a \sim \Omega^{3.2-3.7}$). The activation energy is about 15 kcal-mole showing a very strong contribution of the chemical reaction in the extraction process.

The stripping rate is very close to the extraction rate at 30°C, while the particularly low transfer rate obtained at 40°C seems to derive from solvent degradation, i.e. hydrolysis and radiolysis.

Thus far, a comparison of tributylphosphate and trilaurylammonium nitrate extraction kinetics shows that the transfer is faster with TBP than with TLA.

TABLE 4. Extraction and Stripping of Pu IV in the System HNO₃-H₂O/10% Trilaurylammonium Nitrate in TPH

(a) Extraction

(1) Effect of rotation speed

Ω °C	(H ⁺) _{in}	(Pu IV) _{in}	s
30	2M	0.004 M	3.2
40	2M	0.004 M	3.7

(2) Effect of temperature

Ω	θ	(H ⁺) _{in}	(PU IV) _{in}	k_a (1/s)	E _{exp} Kcal/mole
1700	30	2M	0.004 M	1.3	13
1700	40	2M	0.004 M	2.6	
2300	30	2M	0.004 M	3.3	16
2300	40	2M	0.004 M	7.8	

(a) Stripping

(1) Effect of rotation speed

θ	(H ⁺) _{in}	(Pu IV) _{in}	s
30	2M	0.004M	3.6

(2) Effect of temperature

Ω_{rpm}	θ °C	(H ⁺) _{in}	(Pu IV) _{in}	k_a (1/s)
1700	30	2M	0.004 M	1.2
1700	40	2M	0.004 M	0.6
2300	30	2M	0.004 M	3.4
2300	40	2M	0.004 M	1.2

Conclusions

The extraction of nitric acid, uranyl nitrate and tetravalent transuranium elements by tributylphosphate and trilaurylamine in our centrifugal contactor yielded the following results:

— All elements, except U(VI), seem to be extracted by 30% TBP in TPH in a composite system, in which the chemical process, and, to a greater extent, the diffusion process are involved.

— For U(VI) extraction by TBP, and tetravalent compounds stripping from TBP, the transfer is severely limited by the diffusion process.

— The extraction by TLA and stripping from TLA of

Pu(IV) is slower than with TBP, and involves chemical reactions at the interface.

SYMBOLS

A	=	interfacial area
a	=	specific interfacial area
V	=	mixing volume (l)
C _A	=	aqueous concentration of solute (mole/l)
C _S	=	organic concentration of solute (mole/l)
C _A ^o	=	initial aqueous concentrations of solute (mole/l)
C _S ^o	=	initial organic concentration of solute (mole/l)
C _A ^{eq}	}	= experimental equilibrium concentration of solute
C _S ^{eq}		
v	=	extraction rate (mole/time/area)
k ₁	=	individual mass transfer coefficient (1/s)
k ₂	=	individual mass transfer coefficient (1/s)
k	=	overall mass transfer coefficient (1/s)
F _A	=	aqueous flow (l/s)
F _S	=	organic flow (l/s)
F	=	F _A + F _S : total flow
τ	=	$\frac{V}{F}$ = mixing time (s)
E	=	$\frac{C_A^o - C_A}{C_A^o - C_A^{eq}}$: Murphee's efficiency
E _{exp}	=	experimental activation energy (kcal/mole)
Ω	=	speed of rotation of the centrifugal contactor (rpm)
θ, T	=	extraction temperature (°C, °K)
β	=	$\frac{F_A}{F}$: flow ratio
s	=	slope of the curve (Log Ω , Log k_a)
TBP	=	tributylphosphate
TLA	=	trilaurylamine
TPH	=	hydrogenated tetrapropylene

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DISCUSSION

B.F. Warner: The results presented give a valuable insight into Pu and U mass transfer, and support the growing body of evidence that rapid mechanisms are involved.

It would be of considerable value to continue the work with ferrous products present as one might expect the slower kinetics of some species could lead to improved decontamination. Do you propose to work on this line?

M. Germain: I quite agree with you that improved decontamination preparation might be obtained

with these contactors. However, we intend to have a better knowledge of our contactor under α activity before studying it under gross gamma activity.

A. Siczek: Have you used any reducing agents in the contactor to help plutonium stripping?

The differences in the kinetics of extraction of ruthenium and zirconium as compared to uranium and plutonium were studied before (and are presently, at Argonne National Lab). They are known to allow for better decontamination of U and Pu from these fission products. However, stripping and partitioning of U and Pu were not studied extensively enough before, and thus, the work of the French group can be considered to be a step forward in applying the short-time residence contactors into all cycles of the Purex process (at the Savannah River group the partitioning cycle was carried out in the traditional mixer-settlers - D. Orth, ISEC 1971).

M. Germain: Yes, we have studied the stripping of tetravalent plutonium with hydroxylamine nitrate in this contactor; half reaction times have been found of some seconds. Stripping with tetravalent uranium is just under study.

A. Naylor: In your studies, you have worked in an aqueous continuous system.

To examine your hypotheses on mass transfer rates, have you looked at solvent continuous systems? Secondly, have you studied the mass transfer rates of Pu(IV) in the presence of U(VI) and have you found any differences?

M. Germain: No, we have worked with an O/A flowrate of 1/1 and in our extractor the continuous phase is the aqueous one. We're studying the continuous phase as a function of the O/A flowrate. We shall study the solvent-continuous system when this last study is finished.

In another type of centrifugal contactor we have not observed significant differences in uranium and plutonium extraction rates.

V.S. Schmidt: Have you observed any changes in temperature of solutions as a result of fast reaction of extractions? In what part of the experimental equipment was the temperature measured?

M. Germain: To answer your second question first, I can say that the temperature is measured at the equilibrium of the solutions in the extraction and at the final outlet. The temperature change is 0° to 2°C increase, depending upon the temperature, the total flow rate, and the rotation rate.

M.E. Whatley: Clarification on inference chemical kinetics vs. diffusion.

M. Germain: Concerning tetravalent transuranium elements, we believe that the slight contribution of chemical reaction in the extraction that we observed, from the variation of apparent overall mass transfer coefficient with temperature, is due to the fact that extraction and stripping are achieved in an aqueous continuous phase.

NUCLEAR PROCESSES

Bidentate Organophosphorus Extractants: Purification, Properties and Applications to Removal of Actinides from Acidic Waste Solutions

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ABSTRACT

At both Hanford and Idaho, DHDECMP (dihexyl-N,N-diethylcarbonylmethylene phosphonate) continuous counter-current solvent extraction processes are being developed for removal of americium, plutonium, and, in some cases, other actinides from acidic wastes generated at these locations. Bench and, eventually, pilot and plant-scale testing and application of these processes has been substantially enhanced by the discovery of suitable chemical and physical methods of removing deleterious impurities from technical-grade DHDECMP. Flowsheet details as well as various properties of purified DHDECMP extractants are enumerated.

Introduction

BIDENTATE ORGANOPHOSPHORUS EXTRACTANTS such as carbonylmethylene phosphonates extract trivalent actinides (e.g. Am³⁺, Cm³⁺) and lanthanides very well from moderately concentrated (2-5 M) HNO₃ solutions. Common monodentate extractants such as tri-n-butyl phosphate and di-n-butylbutyl phosphonate do not.

The favorable extraction properties of certain bidentate organophosphorus compounds, first disclosed by Siddall⁽¹⁻³⁾, are being exploited at the U.S. Energy and Development Administration Idaho Falls and Hanford sites to develop solvent extraction processes for removal of ²⁴¹Am and other actinides from acidic wastes generated at these locations. We have made considerable progress in developing and demonstrating suitable extraction processes and also in characterizing and purifying commercially available bidentate reagents. One of us (Lyle D. McIsaac) has also started detailed studies of the use of dihexyl-N,N-diethylcarbonylmethylene phosphonate to extract +4 and +6 as well as +3 actinides from Purex process high-level liquid wastes.

This paper summarizes our latest findings and updates results presented earlier at New Orleans⁽⁴⁾ and Baden Baden⁽⁵⁾ or published elsewhere⁽⁶⁾.

Bidentate Extractant Characterization and Purification

Types

There are obviously many organic functional groups which could possibly be combined with a phosphoryl (PO) group to yield a neutral bidentate organophosphorus reagent potentially suitable for use in solvent extraction applications. All the workers in the field have, however, confined their attention to bidentate compounds where the phosphoryl group is combined with a carbonyl (CO) group or another phosphoryl grouping. Thus, Siddall^(1,2) and later McIsaac and Schulz⁽⁴⁻⁶⁾ have studied the extraction properties of various methylene diphos-

phonates $[(RO)_2P(=O)-CH_2-P(=O)(-OR)_2]$, carbamylphosphonates

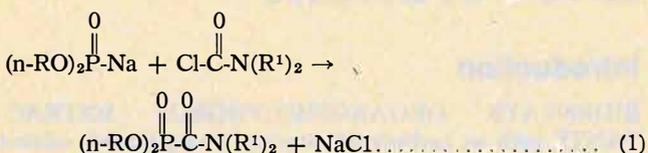
$[(RO)_2P(=O)-C(=O)-N(-R)_2]$, and carbamylmethylene phospho-

nates $[(RO)_2P(=O)-CH_2-C(=O)-N(-R)_2]$. O'Laughlin⁽⁷⁾ has reviewed the synthesis and extraction properties of various neutral bidentate organophosphorus compounds.

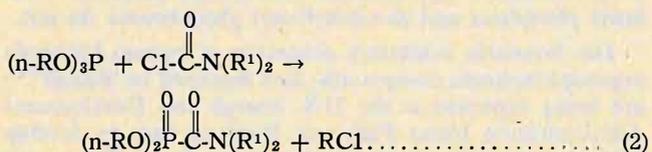
Screening tests at both Idaho Falls and Hanford have shown that carbamylmethylene phosphonates are far superior to either carbamyl phosphonates or methylene diphosphonates for extracting Am(III) from the nitric acid solutions of interest. In particular, because of its commercial availability, suitably low aqueous phase solubility, and other favorable properties, the preferred bidentate extraction reagent at both Idaho Falls and Hanford is dihexyl-N,N-diethylcarbamylmethylene phosphonate, DHDECMP. Much work at Idaho Falls has also been done with the dibutyl analogue, DBDECMP.

Synthesis

Carbamylmethylene phosphonates as well as methylene-diphosphonates and carbamyl phosphonates can be prepared (in 40-60% yield) most conveniently via the Michaelis reaction as illustrated in Equation 1.



The Arbuzov rearrangement (Equation 2) can also be used to prepare these classes of bidentate extractants.



Siddall⁽²⁾ notes that, especially with larger alkoxy substituents, the Arbuzov rearrangement takes place with dialkylcarbamyl chloride and N,N-dialkylhaloacetamides $[(R)_2N-CH_2X]$ only at temperatures around 200°C. Visible degradation of product occurs at such temperatures.

Reagent Source and Cost

Wateree Chemical Company, Lugoff, South Carolina, has been and is currently, as far as we know, the major

U.S. supplier of neutral bidentate organophosphorus compounds. On a custom synthesis basis, Wateree Chemical Company has made a wide assortment of diphosphonates, carbamyl phosphonates and carbamylmethylene phosphonates including all the DHDECMP used in the studies reported here. Multiliter amounts of technical-grade DHDECMP are currently (spring 1977) available from Wateree Chemical at a cost of \$75-100 per liter.

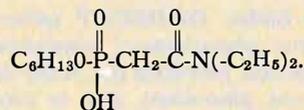
Very recently, one of us (Lyle D. McIsaac) has been in contact with the Eastman Chemical Company, Rochester, New York, regarding their interest and ability to supply large amounts of technical-grade DHDECMP. Although no commitments have been made, Eastman Chemical Company has indicated their interest in producing and marketing this chemical and, hence, may someday be a second U.S. source of multilitered amounts of DHDECMP.

Gram quantities of purified (99%) dibutyl-N,N-diethylcarbamyl phosphonate (DBDECMP) are available as an off-the-shelf item from Richmond Organics, Richmond, Virginia. In 1975, this company estimated 100 kilograms (~1000 liters) amounts of DBDECMP would cost about \$50-\$60 per kilogram. Experimental quantities of diisopropyl-N,N-diethylcarbamylphosphonate have also been made by Richmond Organics.

Purity

Not unexpectedly, technical-grade DHDECMP and other commercially available carbamyl- and carbamylmethylene phosphonates made by either the Michaelis reaction or Arbuzov rearrangement contain unreacted starting materials and a whole host of impurities. Research to identify at least some of these impurities has been performed over the last two years by three different groups of scientists in the U.S.: (1) by P. Fagerness and T. Elwood at the University of Utah under the sponsorship of the Allied Chemical Corporation; (2) by E. Martin of Battelle's Pacific Northwest Laboratories in Richland, Washington under the sponsorship of the Atlantic Richfield Hanford Company; and (3) by R. R. Shoun, W. J. McDowell, and C. H. Bahner at the Oak Ridge National Laboratory*. Using modern physicochemical techniques, including coupled gas chromatography and mass spectrometric methods as well as NMR analyses, these scientists successfully identified many of the impurities in as-prepared DHDECMP. Table 1 lists some of the compounds identified by the Utah group⁽⁹⁾. P. Fagerness and T. Elwood note that many of the impurities remain unidentified because of the complexities associated with interpreting mass spectral data; assignments that have been made (Table 2) are derived from molecular weights, mass fractionation patterns found in the literature, and experienced intuition. Weight percentages cited in Table 1 were determined by current integration in the mass spectrometer, assuming equal response functions for all compounds, and must be considered only as estimates.

Unquestionably, the most important and offensive impurity in technical-grade DHDECMP is:



The presence and identity of this contaminant has recently been established by Shoun, McDowell, and Bahner⁽⁸⁾ at Oak Ridge and also by Martin of the Pacific Northwest Laboratory. This particular acidic impurity has a very

*A detailed account of the researches of Shoun, Bahner, and McDowell was in press⁽⁸⁾ when this paper was written.

TABLE 1. Compounds Identified in Typical Technical-Grade Dihexyl-N, N-Diethylcarbonylmethylene Phosphonate

Compound	Wt %	Compound	Wt %
DHDECMP	49	$C_6H_{13}P(C_6H_{13}O)_2$	9.2
$C_1CH_2CN(C_2H_5)_2$	0.9	$(C_6H_{13}O)_3P$	10.2
$C_{12}CHCN(C_2H_5)_2$	0.4	$(C_6H_{13}O)_2PCH_2COC_6H_{13}$	12.1
$(C_2H_5)_2NCH_2C(C_2H_5)_2$	0.7	$(C_6H_{13}O) \left\{ \begin{array}{l} O \\ O \end{array} \right. PCH_2CN(C_2H_5)_2$	3.7
HOP(OC ₆ H ₁₃) ₂	3.4	$(C_8H_{17}O)$	
$(C_6H_{13}O)_2PCH_3$	4.1		

*Results of P. Fagerness and T. Elwood⁹

high affinity for Am³⁺, Pu⁴⁺ (and other actinides) at low HNO₃ concentrations (Figure 1); its removal is essential to permit use of dilute HNO₃ solutions for partitioning of trivalent actinides from coextracted tetravalent and/or hexavalent actinides.

Much effort, described in the succeeding text, at both Hanford and Idaho Falls has been devoted to establishing techniques for obtaining satisfactorily pure DHDECMP solutions for use in proposed actinide removal processes. (Most of this work was done before the identity of the deleterious acidic impurity was established). Solvent purification studies at Idaho Falls have emphasized vacuum distillation and, more recently, liquid chromatography methods to separate DHDECMP from the acidic contaminant and also from most of the neutral impurities. Conversely, special solvent washing and/or ion exchange procedures have been developed at Hanford to remove the acidic impurity from DHDECMP and the other neutral components present in technical-grade material. Simple washing of DHDECMP or its solutions in a carrier solvent with Na₂CO₃ or NaOH solutions does not remove the acidic impurity.

Purification

Vacuum Distillation

From technical-grade DHDECMP, the DHDECMP fraction distills at 0.001 torr and ~110°C. At the Idaho site, an all glass pot still of a design used by Hickman and Sanford⁽¹⁰⁾ has been used to prepare liter quantities of ~86% pure DHDECMP. Such vacuum distilled DHDECMP can be used without further treatment for actinide extraction and stripping studies. Martin, at the Pacific Northwest Laboratories, has prepared less pure, but still equally acceptable pure DHDECMP by distilling at 0.2 torr and 140°C.

Liquid Chromatography

Very recent research at the Idaho site has demonstrated that > 98% pure DHDECMP can be obtained by high

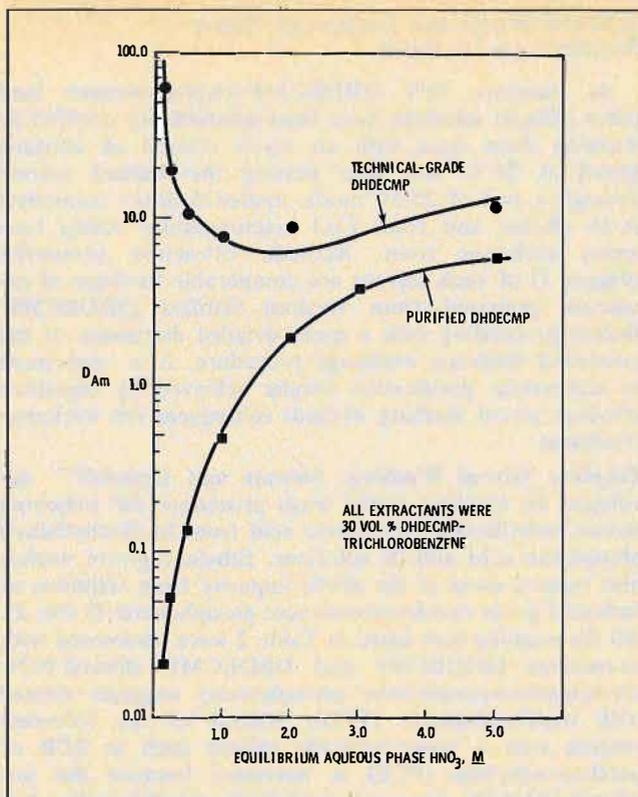


FIGURE 1. Extraction of americium by purified and technical-grade DHDECMP.

TABLE 2. Ethylene Glycol Washing of Bidentate Organophosphorus Solvents

Conditions: 30 volume % DHDECMP (or DBDECMP) — TCB solvents washed as shown with ethylene glycol; americium extraction of washed extractants determined by contacting them at 25°C three times with equal portions of 0.1M HNO₃ containing ~ 10⁵ μCi/liter ²⁴¹Am.

Wash Conditions ^(a)					
Solvent ^(b) Number	Number of Washes	Wash Temperature, °C	Volume Ratio Ethylene Glycol: Solvent	D _{Am} at ^(c) 0.1M HNO ₃	
1	NOT WASHED				11.4
	1	25	1:1	0.937	
	2	25	1:1	0.232	
	3	25	1:1	0.109	
	3	60	1:1	0.0621	
	3	25	1:4	0.596	
	3	25	1:10	0.607	
	3	25	2:1	0.0657	
2	NOT WASHED				4.14
	3	25	1:1	0.0971	
3	NOT WASHED				70.8
	3	25	1:1	0.620	

(a) All washes were for 10 minutes.

(b) For identification purposes only; Batches 1 and 3 — DHDECMP; Batch 2 — DBDECMP.

(c) D_{Am} = Concentration Am in organic phase/concentration Am in aqueous phase.

pressure liquid chromatography with silica gel as the stationary phase. Preparative liquid chromatography working in tandem with a centrifugal molecular still (e.g., CVC Products, Inc. Lab 5 Still) is being considered for preparing kiloliters of purified DHDECMP for engineering-scale flowsheet tests.

Solvent Wash/Ion Exchange Resin Purification Methods

At Hanford, 30% DHDECMP-trichlorobenzene (and other diluent) solutions have been satisfactorily purified by washing them once with an equal volume of ethylene glycol at 25°C and then passing the washed solvent through a bed of 25-50 mesh, hydroxide-form Amberlyst A-26 (Rohm and Haas Co.) macroreticular strong base anion exchange resin. Actinide extraction properties (Figure 2) of such solvent are comparable to those of extractant prepared from vacuum distilled DHDECMP. Before proceeding with a more detailed discussion of the combined wash-ion exchange procedure, it is convenient to summarize purification results achieved by repetitive ethylene glycol washing without subsequent ion exchange treatment.

Ethylene Glycol Washing. Stewart and Crandall⁽¹¹⁾ developed an ethylene glycol wash procedure for removing mono(2-ethylhexyl) phosphoric acid from bis(2-ethylhexyl) phosphoric acid and its solutions. Ethylene glycol washes also remove most of the acidic impurity from solutions of technical-grade carbamylmethylene phosphonates (Table 2). All the washing tests listed in Table 2 were performed with as-received DHDECMP and DBDECMP (dibutyl-N,N-diethylcarbamylmethylene phosphonate) reagents diluted with trichlorobenzene (TCB); dilution of the bidentate reagent with a water-insoluble solvent such as TCB or perchloroethylene (PCE) is necessary because the undiluted bidentate reagent is completely miscible with ethylene glycol.

Data in Table 2 clearly show that ethylene glycol washing effectively removes the offensive acidic impurity from solutions of bidentate extractants. Thus, $*D_{Am}$ at 0.1 M HNO₃ for 30 volume percent DHDECMP and DBDECMP solvents washed three times with fresh equal-volume portions of ethylene glycol is 100- to 200-fold lower than for unwashed solvents. The efficiency of ethylene glycol

$*D_{Am} = \text{Conc. Am in Org.}/\text{Conc. Am in Aq.}$

washes in removing the acidic impurity is a function of the number of washes, the volume ratio of ethylene glycol to bidentate extractant, and wash temperature. Washing at 60°C is definitely more effective than washing at 25°C. For batch-type washing, three equal volume washes at 60°C, preferably, or at 25°C are recommended. (A smaller volume ratio of ethylene glycol to bidentate extractant may be suitable in counter-current extraction equipment). Other results, not shown in Table 2, indicate that transfer of the acidic impurity to the ethylene glycol phase proceeds rapidly — wash times as little as five minutes are suitable.

The ethylene glycol wash procedure meets most of the desiderata for a method for removing the offending acidic contaminant from technical-grade bidentate extractants. It is a simple, inexpensive procedure which can be routinely performed in stainless steel equipment and which yields suitably purified (D_{Am} at 0.1 M HNO₃ ≤ 0.1) extractant in most cases. Unfortunately, the ethylene glycol washing procedure will not completely and satisfactorily purify bidentate reagents containing large amounts of the acidic impurity (e.g., Solvent 3, Table 1). In addition to this very serious disadvantage, the second and succeeding ethylene glycol washes disengage only very slowly, even at 60°C, from the bidentate phase. Centrifuging is required to obtain satisfactory phase separation.

Combined Ethylene Glycol Washing — Resin Purification. Previously, Schulz^(11,12) showed that Amberlyst A-26 resin could be used to remove dibutylphosphoric acid from tri-n-butyl phosphate solutions. Schulz and Honaker⁽¹³⁾ have also recently made use of the Amberlyst A-26 resin in an ion exchange method for preparing highly-purified bis(2-ethylhexyl) phosphoric acid. Work at the Hanford and Idaho sites as well as by Navratil⁽¹⁴⁾ at the U.S. Energy Research and Development Administration Rocky Flats site has shown that the A-26 resin will also remove acid impurities from solutions of DHDECMP.

Because most technical-grade DHDECMP contains such a high concentration of acid impurities, a single pass of a

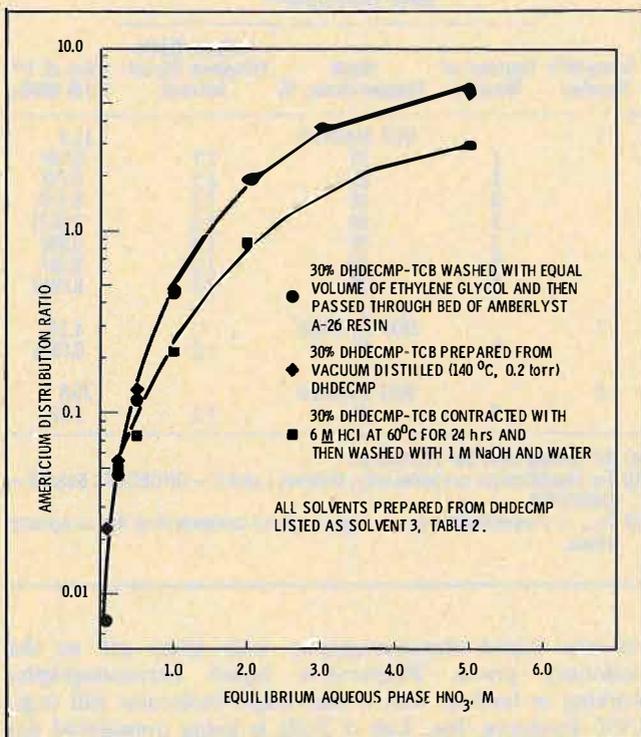


FIGURE 2. Americium extraction behaviour of various purified DHDECMP solvents.

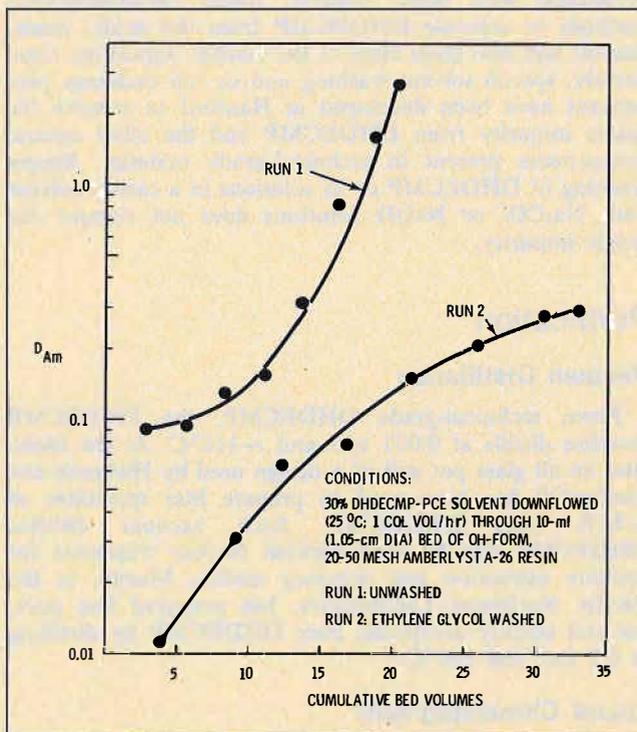


FIGURE 3. Amberlyst A-26 resin purification of DHDECMP extractant.

DHDECMP solvent through a bed of A-26 resin will not yield extractant for which D_{Am} at 0.1 M HNO_3 is the required 0.1 or less (Figure 3). Satisfactorily pure extractant can be prepared, as Navratil⁽¹⁴⁾ has demonstrated, by passing the resin treated solvent through one or two more beds of fresh or regenerated A-26 resin. Alternatively, the DHDECMP-diluent solution can be washed once with an equal volume of ethylene glycol and the washed solvent then flowed through a bed of A-26 resin. Removal of the bulk of the acid impurities by a preliminary ethylene glycol wash substantially extends the capacity of the A-26 resin to yield acceptably pure extractant (Figure 3).

Very successful pilot-plant scale tests of the combined ethylene glycol wash — A-26 resin system were recently performed at Hanford. In these runs, three separate 40-liter batches of ethylene glycol washed 30% DHDECMP diluted with either TCB, PCE, or a mixture of TCB and PCE were downflowed at $\sim 25^\circ C$ through a 25-liter bed of A-26 resin. The resin bed between each load cycle was regenerated by successive water, 3M HNO_3 and 2 M NaOH washes. Americium extraction properties of the DHDECMP solvent batches before and after resin treatment are tabulated in Table 3. All the final products easily met the specified $D_{Am} \leq 0.1$.

Hydrochloric Acid Hydrolysis

Siddall⁽¹⁾, in his pioneering researches, observed that the acidic impurity in bidentate organophosphorus reagents could be removed by contacting an 0.5 M benzene solution of the bidentate compound with 6 M HCl for four hours at $60^\circ C$ and then washing the resulting solvent with NaOH and water. Such treatment presumably converts the monobasic impurity to a dibasic entity soluble in NaOH solutions. Subsequently, the acid hydrolysis procedure was studied extensively at Hanford and used to satisfactorily purify several different batches of DHDECMP⁽⁴⁾. The key element in this purification scheme, which is difficult to judge, is how long to contact the bidentate-diluent solution with 6 M HCl at $60^\circ C$. Short hydrolysis times (1-4 hours) are adequate to purify technical-grade bidentate impurity. But, long (24 hour — even 48 hour) hydrolysis times are needed with highly-impure bidentate solutions such as Solvent 3, Table 2.

The acid hydrolysis procedure suffers from a number of disadvantages which preclude its being recommended for laboratory-scale, let alone plant-scale applications. Foremost of these is that the bidentate compound as well as the acidic impurity is attacked by HCl with a concomitant decrease in the power of the purified extractant to extract actinides from moderately concentrated (e.g., 2-5 M) HNO_3 solutions. This effect is illustrated in Figure 2 for 30% DHDECMP-TCB solvent contacted 24 hours at $60^\circ C$ with 6 M HCl. For plant-scale usage specialized, corrosion-resistant equipment would be needed to perform the HCl hydrolysis step.

Extractant Properties

Solubility in Aqueous Solutions

Data for the solubility of DHDECMP and DBDECMP in various aqueous solutions were reported earlier^(5,6). Dibutyl-N,N-diethylcarbamylmethylene phosphonate is highly soluble (60 g/liter) in 0.1 M HNO_3 at $23^\circ C$ and still appreciably soluble (9 g/liter) when diluted to 15 volume percent with xylene. The solubility of DHDECMP in 0.1 M HNO_3 at $23^\circ C$, however, is low (0.5 g/liter) and comparable to that of tri-n-butyl phosphate (TBP) in water (0.4-0.5 g/liter). The relatively large aqueous

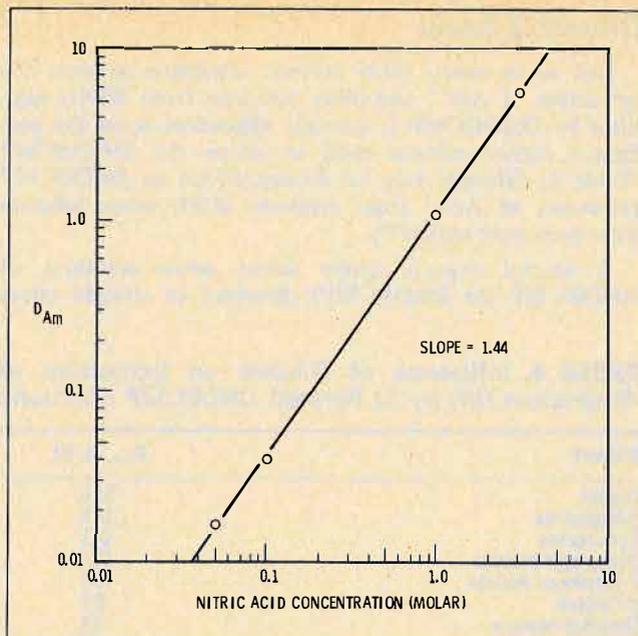


FIGURE 4. Acid dependency of Am(III) extraction by DHDECMP.

TABLE 3. Pilot-Plant Scale Purification of 30% DHDECMP Solvents

Run ^(b) Number	Diluent	D_{Am} at 0.1M HNO_3 ^(a)	
		After Ethylene ^(c) Glycol Washing	After A-26 Resin Treatment
1	PCE	2.02	0.0347
2	TCB	2.53	0.0604
3	30% PCE - 70% TCB	2.08	0.0470

(a) D_{Am} before ethylene glycol washing was 60.5.

(b) 150 liters of solvent purified in each run.

(c) 22 hours washing at $\sim 25^\circ C$.

phase solubility of DBDECMP is obviously a serious drawback to its plant-scale use.

Extraction Mechanisms

Logarithmic plots of Americium distribution ratios versus DHDECMP concentration from either 1M HNO_3 or synthetic ICPP zirconium-aluminum first-cycle raffinate are straight lines of slope 2.9. Assuming that the slope of such plots indicates the dependency of the extraction reaction on bidentate reagent concentration, extraction of Am(III) by DHDECMP can be represented as:



Siddall⁽²⁾ also observed a third power extractant dependency in extraction of Ce(III) by dihexyl-N,N-dibutylcarbamylmethylene phosphonate (DHDBCMP).

Siddall's studies with DHDBCMP also indicated that at least two molecules of HNO_3 were associated with each Ce-DHDBCMP moiety. Our acid dependency results (Figure 4) with 30% DHDECMP-DIPB (diisopropyl benzene) solvent indicate an acid dependency significantly less than two. The discrepancy between our data and that of Siddall has not yet been resolved. Additional studies of reagent and acid dependencies of DHDECMP and other carbamylmethylene phosphonates are presently being made by Shoun and McDowell at ORNL.

Diluent Effects

Just as in many other solvent extraction systems the extraction of Am^{3+} and other actinides from HNO_3 solutions by DHDECMP is strongly dependent upon the particular carrier solvent used to dilute the DHDECMP (Table 4). (Similar data for diluent effects on DBDECMP extraction of Am^{3+} from synthetic ICPP waste solution were presented earlier⁽⁶⁾).

A second organic phase forms when solutions of DHDECMP (or DBDECMP) dissolved in straight chain

TABLE 4. Influence of Diluent on Extraction of Americium (III) by 33 Percent DHDECMP Solutions

Diluent	D_{Am} (a, b)
Decalin	21.0
3-Heptanone	14.6
Cyclohexane	14.1
Diisopropyl benzene	13.6
2-Ethylhexyl Acetate	10.3
p-Cymene	9.7
Dimethyl benzene	9.4
Mesitylene	7.8
Toluene	7.5
Xylene	7.2
Carbon Tetrachloride	4.0
Heptane	(c)
Trimethylpentane	(c)
Kerosene	(c)

(a) DHDECMP solvent contacted 5 minutes at 23°C with equal volume of ^{241}Am -spiked synthetic Idaho Chemical Processing Plant (ICPP) zirconium-aluminum first cycle raffinate of composition listed in reference 5.

(b) All values have an estimated uncertainty of $\pm 10\%$.

(c) Second organic phase formed.

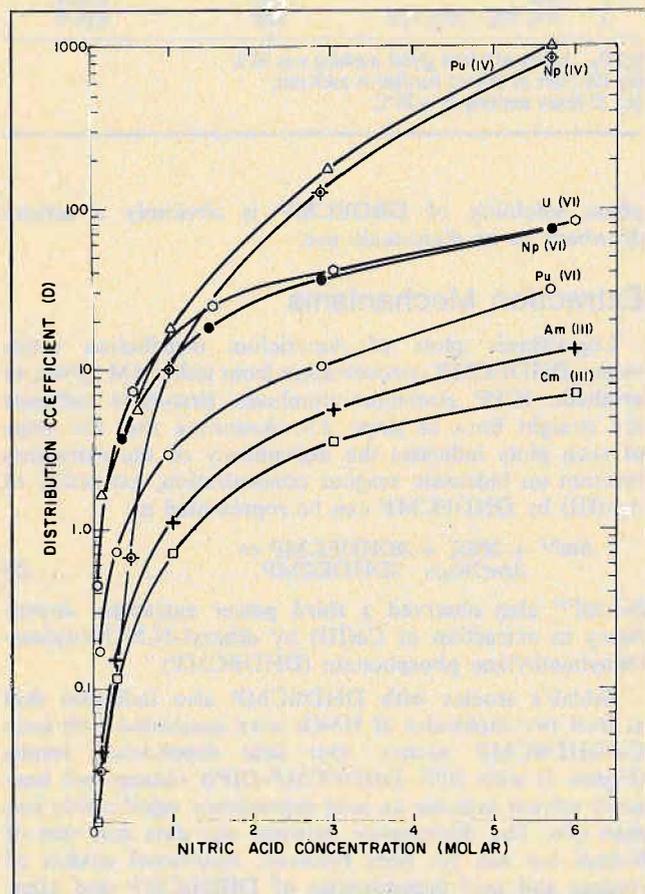


FIGURE 5. Extraction of +3, +4, and +6 actinides from HNO_3 solutions by 30% DHDECMP-DIPB solvent.

aliphatic hydrocarbons are contacted with aqueous HNO_3 solutions. Formation of a second phase in such systems can be avoided by diluting the DHDECMP with aromatic or chlorinated (e.g., CCl_4 , PCE, TCB, etc.) diluents. Decalin, decahydronaphthalene, is somewhat of an intermediate diluent in that a second organic phase forms only when DHDECMP-decalin extractants are contacted with $\geq 3\text{M}$ HNO_3 solutions. Addition of a small amount of an aromatic solvent like xylene or toluene to a DHDECMP-decalin extractant prevents formation of a second organic phase even at aqueous acidities as high as 6 M HNO_3 .

Because of current existing equipment design limitations, bidentate solvent extraction applications at Hanford are restricted to use of a heavier-than-water diluent such as CCl_4 , PCE, or TCB. At Idaho, much of the laboratory work has been done with xylene solutions of DHDECMP; for plant-scale applications, consideration is being given to use of diisopropyl benzene as a diluent.

Typical Actinide Distribution Data

Plotted in Figure 5 are typical data for the equilibrium distribution at 22°C of selected +3, +4, and +6 actinides between aqueous HNO_3 solutions and 30% DHDECMP in diisopropyl benzene. Some distribution data for other elements in relevant acidic waste solutions at the Idaho site are reported elsewhere in this paper; additional distribution data for non-actinide elements are cited in references 4 and 9.

The 30% DHDECMP-DIPB used to obtain the results shown in Figure 5 was prepared from vacuum distilled (86% purity) DHDECMP and was sequentially washed with 0.5 M Na_2CO_3 and water prior to use. Equal volume portions of aqueous and organic phases were shaken for five minutes. Adjustments of Pu(IV) and Pu(VI) oxidation states were made with 0.025 M NaNO_2 and 0.025 M NaBrO_3 — 0.001 $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, respectively. Neptunium(IV) and neptunium(VI) states were adjusted with 0.025 M $\text{Fe}(\text{NH}_4\text{SO}_3)_2$ and 0.025 M NaBrO_3 — 0.001 M $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, respectively. Erratic results, not shown here, were obtained for the distribution of Pu(III) between HNO_3 - $\text{Fe}(\text{NH}_4\text{SO}_3)_2$ solutions and 30% DHDECMP-DIPB extractant.

Reaction Kinetics

Empirical batch contact studies at both Hanford and Idaho show that Am(III) and Pu(IV) both transfer rapidly at 23-25°C between DHDECMP-diluent solutions and aqueous HNO_3 media. In such tests, the equilibrium distribution ratio in both extraction and stripping modes was attained in approximately 30 seconds of mixing. Such rapid mass transfer rates indicate DHDECMP extraction systems can be operated satisfactorily in short residence time contactors, e.g., centrifugal contactors.

Radiolytic Effects

Alpha radiolysis of DHDECMP-TCB solvents has been investigated at Hanford⁽⁴⁾; while at Idaho, the effects of exposing DBDECMP-xylene solutions to gamma (^{60}Co) radiation have been determined⁽¹⁵⁾. The principal effect of radiolysis of either DHDECMP or DBDECMP solvents is to increase the amount of americium and plutonium not readily strippable by dilute HNO_3 or HNO_3 -HF solutions. Deleterious liquid radiolysis products of DHDECMP and DBDECMP can be effectively removed by washing irradiated solutions with dilute aqueous carbonate solutions. Because of the low dose expected per extraction cycle (0.01 to 0.05 watt-hr/liter) in the proposed Hanford ap-

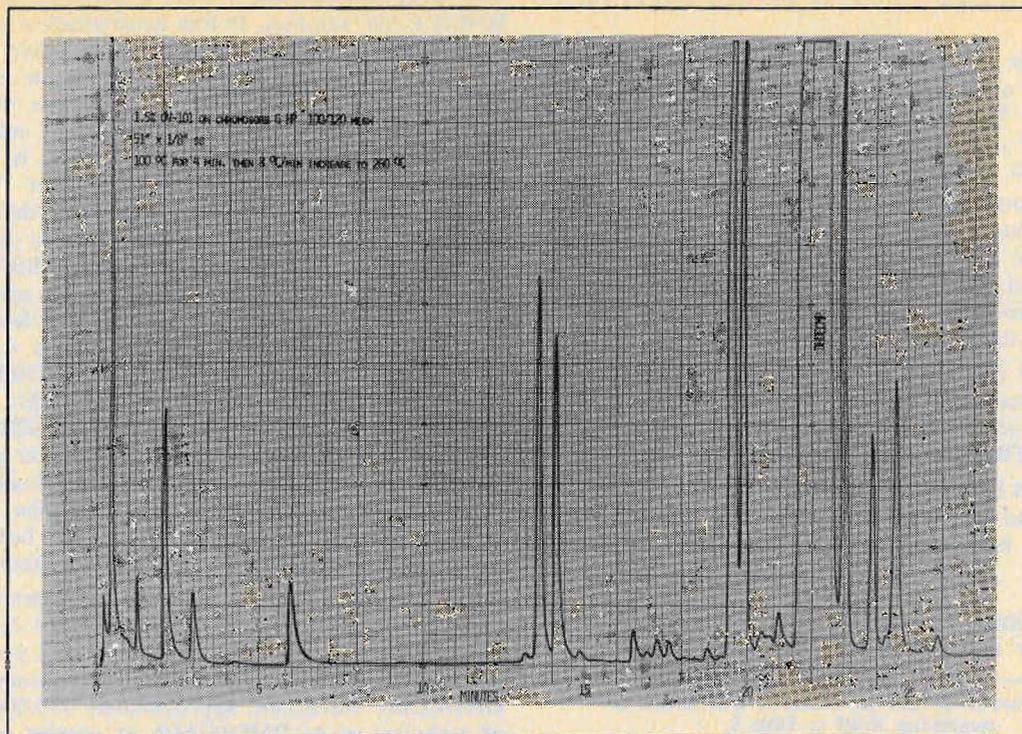


FIGURE 6. Typical gas chromatograph of crude DHDECMP.

plication and considering the expected solvent inventory turnover time⁽⁵⁾, performance of a DHDECMP-diluent extractant is expected to be satisfactory even without intercycle carbonate washing. However, even when performed in centrifugal contactors, anticipated bidentate extractant radiation dose rates in projected Idaho site process applications are such that intercycle carbonate solvent washing will be necessary.

Gas Chromatography

Gas chromatographic methods have been developed at both Idaho and Hanford to monitor the effectiveness of various methods for purifying crude DHDECMP and to measure the concentration of DHDECMP in various solutions. The Idaho work has been done with a Varian Aerograph (Varian Associates, Palo Alto, California) Model 2740 dual column machine equipped with a flame ionization detector and automatic linear temperature programmer. Stainless steel and glass columns packed with 1.5% OV-101 on Chromosorb G-HP have both been used successfully. A typical gas chromatographic spectrum of technical-grade DHDECMP obtained with the Idaho instrument is shown in Figure 6; the temperature was programmed from 100 to 260°C at 8°C per minute. Only the peak corresponding to the DHDECMP component is labeled in Figure 6. Spectra of increasingly pure DHDECMP, up to 98% purity, indicate thermal degradation during gas chromatographic analysis is negligible.

Process Applications

Americium-Plutonium Extraction from Hanford Plutonium Reclamation Facility Waste

Research at Hanford on the properties of bidentate organophosphorus compounds relates to the potential use of such reagents to recover Am(III) and Pu(IV) from the acid waste (CAW stream) resulting from operation of Hanford's Plutonium Reclamation Facility. (Typically, the

TABLE 5. Typical Composition of Hanford and ICPP Actinide Wastes

Hanford CAW Solution		ICPP First-Cycle Waste ^(a, b)	
Component	Concentration	Component	Concentration
NO ₃	5.0M	F	3.12M
H	2.2M	NO ₃	2.36M
Al	0.8M	H	1.51M
Na	0.5M	Al	0.68M
F	0.3M	Zr	0.44M
Fe	0.009M	B	0.22M
Si	0.002M	Fe	0.005M
Ca	0.001M	²³⁹ Pu	1.4 × 10 ⁻³ g/liter
Ce	0.007M	²³⁸ Pu	5.0 × 10 ⁻⁴ g/liter
Mg	0.006M	²⁴⁰ Pu	3.4 × 10 ⁻⁴ g/liter
Ni	0.003M	²⁴¹ Pu	1.5 × 10 ⁻⁴ g/liter
Pu	0.002-0.01 g/liter	²⁴² Pu	4.8 × 10 ⁻⁵ g/liter
²⁴¹ Am	0.002-0.01 g/liter	²⁴¹ Am	4.4 × 10 ⁻⁶ g/liter
		²³⁷ Np	1.2 × 10 ⁻⁵ g/liter
		²⁴³ Am	1.2 × 10 ⁻⁶ g/liter
		²⁴⁴ Cm	7.3 × 10 ⁻⁷ g/liter

(a) From co-processing of Zr-clad and Al-clad fuels.

(b) Partial analysis of actual waste from tank WM-185; estimates of concentrations of other components of ICPP first-cycle waste given in Reference 6.

CAW stream contains 0.002 to 0.01 g/liter each of americium and plutonium [Table 5]). The Plutonium Reclamation Facility is operated to recover and purify plutonium from a wide variety of metallurgical scrap including metal, oxide, and alloys. Chemical flowsheets for the reflux-type TBP solvent extraction process employed to recover plutonium from HNO₃ and HNO₃-HF solutions of such scrap have been described elsewhere^(16,17).

The latest bidentate extraction flowsheet for direct operation with CAW solution is presented in Figure 7; this flowsheet supersedes and updates earlier^(4,5) versions. Americium and plutonium losses cited in Figure 7 are based on laboratory-scale mixer-settler tests in which four mixer-settler stages were used in extraction column runs and three mixer-settler stages in Am-partition and Pu-strip

column runs. Principal features of the flowsheet in Figure 7 include:

— Coextraction of 95 to 98% of the americium and > 99% of the soluble plutonium from acidic CAW solution with 30% DHDECMP-PCE (or TCB) solvent; equal flows of CAW and organic solvent are used in the extraction column.

— Use of a small volume of 0.1 M HNO₃ to strip 75 to 85% of the extracted americium and 5 to 10% of the plutonium. The recovered americium and plutonium can be concentrated either by simple evaporation or, alternatively, by cation exchange prior to final separation and purification of the ²⁴¹Am.

— Stripping of residual americium and about 80 to 90% of the plutonium still left in the organic phase into a small volume of dilute HNO₃-HF solution for return to the mainline TBP plutonium recovery process.

The Hanford DHDECMP extraction scheme of Figure 7 is designed and intended to replace the present DBBP process which has been operated since 1970 to recover

americium and plutonium from neutralized (0.1 to 0.25 M HNO₃) CAW solution. In-line neutralization (with NaOH) of unbuffered CAW solution is a sensitive, difficult-to-control, head-end step. Failure to adjust the acidity of the CAW solution to the proper range for use with a DBBP solvent coupled with marginal extraction equipment and restricted aqueous-to-organic flow ratios is reflected in poor (~60%) plant-scale recovery of ²⁴¹Am. The DHDECMP process largely overcomes these disadvantages. Mixer-settler data in Table 6 evidence the advantages of the DHDECMP process over the DBBP scheme in providing easier and better recovery of americium and plutonium. Even under the presently-used feed: extractant flow ratio of 4.2, the DHDECMP solvent recovers more americium (and plutonium) than does the DBBP extractant from a feed adjusted to near optimum acidity. (The superiority of the DHDECMP process over the DBBP extraction method is even more striking when the latter process operates with a more acidic [pH 0.33] feed). Finally, at a more favorable feed: extractant ratio of 1, the DHDECMP flowsheet readily recovers over 95% of both the americium and plutonium from acid CAW solution.

The present DBBP Am-Pu recovery process operates with a nominal inventory of about 1000 liters of 30% DBBP-CCl₄ which is replaced about twice a year. Assuming a similar inventory and replacement frequency for a 30% DHDECMP extractant, approximately \$30,000 to \$45,000 of technical-grade DHDECMP, at present prices, would be required per year. Considering the improved recovery of valuable ²⁴¹Am which the DHDECMP flowsheet provides, this cost does not appear prohibitively high and, hopefully, might be reduced by improved solvent inventory management practices.

TABLE 6. Hanford Bidentate Flowsheet: Typical Mixer-Settler Extraction Column Tests

Aqueous feed for all runs was actual PRF CAW solution of composition listed in Table 5.						
Extractant ^(a)	Stages		Relative Flows		Percent In Raffinate	
	Extraction	Scrub	Feed	Extractant	Am	Pu
30% DHDECMP	4	0	1	1	4.4	0.55
30% DHDECMP	4	0	2	1	15.6	2.9
30% DHDECMP	3	1	4.2	1	22.7	2.6
30% DBBP	3	1	4.2 ^(c)	1	33.8	8.0
30% DBBP	3	1	4.2 ^(e)	1	51.8	7.7

(a) Diluent in all cases was TCB

(b) Scrub was 0.01M HNO₃

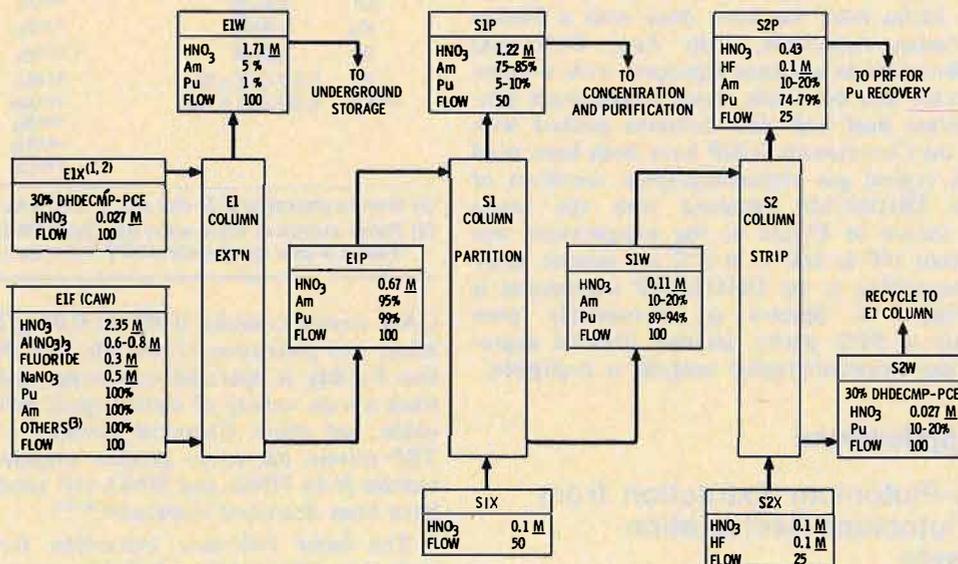
(c) Feed was adjusted to 0.26M HNO₃, pH = 0.66

(d) Scrub was 0.1M HNO₃ — 4M NaNO₃

(e) Feed was adjusted to 0.51M HNO₃, pH = 0.33

Actinide Extraction from Idaho High-Level Waste

The Idaho Chemical Processing Plant, located at the Idaho National Engineering Laboratory near Idaho Falls, is a multipurpose reprocessing facility for irradiated reactor fuels containing highly enriched uranium. Fuels routinely processed at ICPP include stainless-steel-clad fast-reactor



NOTES:

(1) TCB MAY BE SUBSTITUTED FOR PCE

(2) DOES NOT INCLUDE RECYCLED Pu

(3) INCLUDES SMALL CONCENTRATIONS OF Ca, Mg, Fe, Cr, Ni, etc.

FIGURE 7. DHDECMP flowsheet for Am-Pu recovery from Hanford CAW solution.

fuels, aluminum-clad test-reactor fuels, and zirconium-clad fuels for which the enrichment before burnup varies from 50 to 93%⁽¹⁸⁾. The stainless-steel-clad fuel is electrolytically dissolved in HNO₃, the aluminum-clad fuels are dissolved in HNO₃-Hg(NO₃)₂, and zirconium-clad fuels are dissolved in HF. These multi-head-end dissolver solutions provide the feed for a single-solvent extraction system that is composed of a first cycle of TBP extraction followed by two cycles of methyl-isobutyl ketone extraction. The uranyl nitrate product from the extraction system is denitrated in a fluidized-bed denitrator to UO₃ for shipment.

The aqueous fission product wastes resulting from the ICPP solvent extraction operations contain small amounts of uranium and transuranium elements, primarily neptunium, plutonium, and americium, with traces of curium and transcurium isotopes. The safe and effective management of these nuclear wastes has been a primary goal of the ICPP operation for the past 25 years. The major technique has been to store the liquid waste safely for a period not to exceed five years and then solidify it into a granular oxide for storage in stainless steel bins inside a concrete vault. A program has been under way for the past three years now to assess the feasibility of removing alpha-emitting elements from ICPP liquid wastes prior to calcination. Because the estimated life of the calcine storage vaults is 1000 years, the goal of the program is to develop and demonstrate a process that will reduce the alpha activity in the calcined waste to less than 10 nCi/gram after 1000 years of decay.

The bulk of the waste generated at the ICPP to date has resulted from co-processing of Al- and Zr-clad fuel. A chemical analysis of a typical tank containing first-cycle raffinate from such co-processing is listed in Table 5. The only actinides of significance in such raffinate after 1000 years of decay are americium and plutonium. A decontamination factor for these actinides of approximately 200 is needed to reach the 10 nCi/gram criteria 1000 years after calcination.

Early studies indicated DBDECMP was an effective extractant for removing actinides from ICPP first-cycle raffinate. However, as noted earlier, the high aqueous phase solubility of DBDECMP is a major deterrent. For this reason, current bidentate flowsheet development studies at Idaho are concentrated on the use of DHDECMP as the extractant.

Comprehensive data for the distribution of actinide, fission product, and inert constituents of ICPP high-level waste into 30% DHDECMP-xylene solvent are presented in Table 7. Also listed are partial data for the distribution of these elements between the DHDECMP extractant and potential scrub (6 M HNO₃) and strip (0.05 M HNO₃ — 0.05 M oxalic acid) solutions. The extraction data were obtained by contacting synthetic Zr-Al raffinate, containing appropriate radiotracers, for five minutes at 23°C with 30% DHDECMP-xylene solvent prepared from vacuum-distilled (80% pure) DHDECMP. (Neutron activation techniques were used to obtain data for extraction of aluminum and fluorine). Distribution data for neptunium cited in Table 7 were obtained with synthetic raffinate to which Cr(VI) had been added to oxidize Np(V) to Np(VI). The oxidation state of neptunium in actual ICPP first-cycle raffinate is not known; a mixture of Np(V) and Np(VI) is suspected. These data illustrate the efficiency of the DHDECMP solvent in extracting actinides and lanthanides [and Hg(II)] from ICPP first-cycle waste. Palladium, technetium, and ruthenium also extract fairly well into the DHDECMP solvent but, unlike Hg(II), can be removed by scrubbing the organic extract.

The data in Table 7 were used to draw up a conceptual flowsheet (Figure 8), a slightly modified version of which

TABLE 7. Distribution Data for Idaho 30% DHDECMP-Xylene Extraction Systems

Feed Component	Distribution Coefficient				
	Extraction ^(a, b) Contact	Scrub ^(a, c) Contact	Strip Contacts ^(a, d)		
			1	2	3
U(VI)	91.	27.	9.2	0.076	0.014
Np(VI) ^(e)	44.	29.	4.8	< 0.10	
Pu(IV)	7.6	43.	0.04	< 0.01	
Am(III)	5.0	3.7	0.34	0.006	
Ce(III)	3.6	3.8	0.52	0.015	
La(III)	3.5	4.2	0.48	0.016	
Nd(III)	3.1	3.4	0.34	< 0.1	
Hg(II)	2.6	8.5	~ 30.	~ 20.	
Eu(III)	2.1	2.7	0.22	0.002	
Pd(II)	1.65	0.23	0.45	~ 3.	
Tc(VII)	1.10	0.25	1.8	2.3	
Ru(III, IV)	0.58	0.34	6.7	5.7	5.4
H ⁺	0.34				
Y(III)	0.30	0.66	0.039	< 0.02	
Mo(VI)	0.27	0.14			
Nb(V)	0.13	0.074	0.032		
Rh(III)	0.12	0.056			
F ⁻	0.043				
Ag(I)	0.032				
Zr(IV)	0.015	0.066	0.044		
Sr(II)	0.0094	< 0.006			
Cr(III)	0.0087				
Ba(II)	0.0075	0.053			
Al(III)	0.0025				
In(III)	< 0.004				
Cu(II)	< 0.002	< 0.02			
Fe(III)	< 0.002	< 0.005			
Co(III)	< 0.001				
Cs(I)	0.00026	< 0.004			
Rb(I)	0.00018				

- (a) All values, except where noted, have an estimated uncertainty of $\pm 10\%$.
 (b) Measured with synthetic ICPP first-cycle high-level waste: 1.7M HNO₃ — 3.0M F — 2.11M NO₃ — 0.6M Al — 0.5M Zr containing 2.2 g/liter B, 0.24 g/liter Fe, 0.24 g/liter Na, 0.32 g/liter Sn, and 0.10 g/liter La.
 (c) Organic phase from extraction contact contacted with one-fifth volume of 6M HNO₃.
 (d) Organic phase from scrub contact stripped three times with fresh equal volume portions of 0.05M HNO₃ — 0.05M H₂C₂O₄.
 (e) Synthetic extraction feed adjusted to 0.01M Cr(VI).

was subsequently successfully tested in miniature mixer-settler equipment with actual ICPP-produced waste⁽¹⁹⁾. The aqueous raffinate from the extraction column test (8 stages) contained, without any decay, only 6.6 nCi/gram of total actinides corresponding to decontamination factors from americium and plutonium of 1000 and 2700, respectively. (These decontamination factors are larger than the required 200, thus providing a safety margin to take care of possible variations in feed actinide concentration). The organic raffinate from the strip column (8 stages) contained no detectable americium or curium, ¹⁰⁶Ru as the only gamma emitting fission product radionuclide, and only 0.2% of the plutonium in the extraction column product. Unstripped plutonium in this experiment represents, it is thought, material tightly bound by radiolysis products of DHDECMP generated during the 80 minutes the extractant was in contact with the high-level waste. Such bound plutonium can be effectively removed by contacting the DHDECMP phase with dilute oxalic acid solution. Radioruthenium can be removed from the bidentate solvent by washing with 0.5 M Na₂CO₃ solution.

A flowsheet step still requiring resolution is how to remove mercury from the DHDECMP extractant before recycle to the extraction column. Electrolytic methods for removal of mercury have been demonstrated but need to be scaled up. Efficiency of intercycle Na₂CO₃ washing for adequately removing solvent radiolysis products also remains to be demonstrated in continuous countercurrent

tests with actual feed. No decision has been made on final disposition of separated actinides.

Removal of Actinides From Purex Process High-Level Waste

A study to determine the technical feasibility of partitioning actinides from Purex process high-level waste solutions is currently under way in the United States under the direction of the Oak Ridge National Laboratory. As part of this program, work is in progress at Idaho to explore possible applications of DHDECMP (and perhaps other bidentate extractants) for removing actinides from Purex process first-extraction cycle aqueous raffinate (HAW solution). The principal thrust of the Idaho investigations so far has centered on extraction-scrub-strip contacts (Table 8) to measure distribution of various ions between a 30% DHDECMP-DIPB extractant and synthetic HAW solution containing 2.9 M HNO₃, and 0.1 M NaNO₂, and the various other constituents listed in Reference 19. Experimental and analytical techniques used in these distribution ratio measurements were identical to those used with synthetic ICPP waste (cf. above).

As expected, 30% DHDECMP-DIPB extractant has a very high affinity for Pu(IV) and U(VI) in Purex process HAW solution. Distribution coefficients for Am³⁺ (and likely for Cm³⁺) are similar to those for the lanthanides; hence, trivalent actinides and lanthanides will report to the DHDECMP phase along with Pu(IV) and U(VI). Under the conditions used, (0.1 M NaNO₂ in the HAW) neptunium extraction was marginal; presumably, the HAW solution contained both Np(V) and Np(VI). Extraction behavior of Np(IV) from HAW solution containing a reducing agent such as N₂H₄ or NH₂OH·HNO₃ has not yet been established. Of the non-actinide and lanthanide constituents of HAW solution, only Tc, Zr, Y, Pd, Nb, Mo, and Ru are extracted to any large extent by the DHDECMP solvent. Zirconium, niobium, and molybdenum are easily scrubbed from the DHDECMP phase by a 3 M HNO₃ — 0.05 M oxalic acid solution.

Dilute HNO₃ solutions containing a reducing agent such as NH₂OH·HNO₃ readily strip trivalent lanthanides and actinides including Pu(III) from the DHDECMP-DIPB phase. Rare earth oxalate precipitates form when the DHDECMP solutions resulting from extraction of syn-

thetic HAW feed are contacted with dilute oxalic acid strip solution. Uranium is tightly held in the DHDECMP phase and is not removed by HNO₃·NH₂OH; it can, however, be stripped with 0.05 M HNO₃ — 0.05 M H₂C₂O₄ solution. Uranium is also efficiently removed from DHDECMP solvents by washing them with 0.5 M Na₂CO₃ solution. Alkaline solvent washes also remove ruthenium from the organic extractant. Behavior of technetium and palladium during scrubbing, stripping, and solvent washing steps has not yet been determined.

The very preliminary work completed thus far certainly indicates a satisfactory DHDECMP flowsheet can be devised for adequate removal of actinides from acidic Purex process waste streams. Much more batch data with both synthetic and actual wastes are required, however, before a conceptual flowsheet suitable for testing in laboratory and pilot plant scale continuous countercurrent extraction equipment can be prepared.

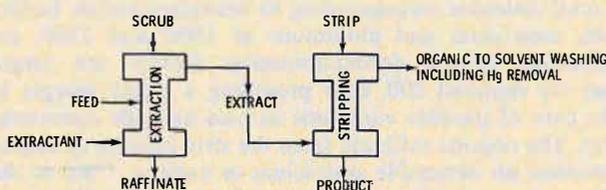
Summary — Future Work

Research at both Idaho and Hanford has established efficient, practicable physical and chemical methods for preparing satisfactorily pure DHDECMP extractants from commercially-available technical-grade reagent. Mixer-settler tests at both sites have also demonstrated the capability and utility of DHDECMP-based solvent extraction processes for adequate removal of +3, +4, and +6 actinides from acid aqueous waste solutions. These

TABLE 8. DHDECMP Extraction-Scrub-Strip Studies with Synthetic PUREX Process First-Cycle Waste (HAW) Solution

Feed Component	Extraction ^(a, b) Contact	Distribution Coefficients				
		Scrubs Contacts ^(a, c)		Strip Contacts ^(a, d)		
		1	2	1	2	3
Pu(IV)	304.	122.	25.	0.70	0.068	0.16
U(VI)	51.	62.	52.	13.9	2.74	2.40
La(III)	6.5	6.1	7.8	1.01	0.16	0.085
Ce(III)	5.8	5.2	7.1	1.02	0.18	<0.1
Pr(III)	5.3					
Nd(III)	4.3					
Am(III)	4.3	4.1	5.7	0.70	0.13	0.18
Pm(III)	4.2					
Sm(III)	3.4					
Eu(III)	2.9	3.2	3.3	0.46	0.086	0.048
Tc(VII)	2.3					
Np(V,VI)	2.2	2.0	3.6			
Gd(III)	2.1	2.4	2.6	0.33	0.861	
Zr(IV)	1.8	0.022	0.0028			
Y(III)	0.60	0.66	0.70	0.076	< 0.1	
Pd(II)	0.53	0.47	0.41	1.10	1.20	2.8
Nb(V)	0.51	0.017	0.75			
Mo(VI)	0.39	0.10	0.041			
Ru(III, IV)	0.27	0.96		15.	15.	
H ⁺	0.23					
Ag(I)	0.028	0.026				
Rh(III)	0.018					
Sr(II)	0.017	0.019				
Ba(II)	0.013	0.012				
Cd(II)	0.0067					
Cr(III)	0.0033					
Fe(III)	0.0015					
Rb(I)	0.00064					
Cs(I)	0.00050					

- (a) All values, except where noted, have an estimated uncertainty of ± 10%.
 (b) Synthetic HAW solution of composition given in Reference 19 made 0.1M NaNO₂, spiked with appropriate radio-tracers, and contacted five minutes at 23°C with an equal volume of 30% DHDECMP-DIPB.
 (c) Organic extract contacted twice with fresh one-fifth volume portions of 3M HNO₃ — 0.05M H₂C₂O₄ solution.
 (d) Organic phase from final scrub contact stripped three times with fresh equal portions of 0.05M HNO₃ — 0.05M NH₂OH·HNO₃.



	FEED	EXT'NT	SCRUB	RAFF	EXTRACT	STRIP	PROD	ORG
FLOW RATE l/hr	20	10	2	22	10	10	10	10
DHDECMP		30%			30%			30%
XYLENE		70%			70%			70%
F (M)	3.2			2.91				
NO ₃ (M)	2.4		6.0	2.48	0.66	0.05	0.652	0.008
H (M)	1.6		6.0	1.70	0.66	0.05	0.652	0.008
Al (M)	0.6			0.55				
Zr (M)	0.5			0.45				
H ₂ C ₂ O ₄ (M)						0.05	0.05	
Hg (M)	0.002				0.004			0.004
Pu (μg/l)	2200			1.0	4398		4398	
Am (μg/l)	40			0.036	79.92		79.92	
U (μg/l)	1000				2000		2000	

FIGURE 8. Conceptual flowsheet for DHDECMP extraction of actinides from ICPP high-level waste.

actinide removal processes are now judged ready for engineering-scale tests with both synthetic and actual waste solutions.

Future bench-scale studies, in addition to developing new and/or improved DHDECMP extraction flowsheets, should emphasize determination of the properties of pure DHDECMP including identification of its gaseous and liquid radiolysis products. Studies to elucidate the nature and type of interactions between DHDECMP and carrier solvents and the consequences of such interactions upon actinide and lanthanide extraction are also needed. New, simplified, and hopefully, cheaper methods of synthesizing DHDECMP and other bidentate reagents may prove fruitful.

Acknowledgments

We are grateful to Paul Hammitt and Judy Watts (Hanford) and John Baker and Dave Meikrantz (Idaho) for their unflagging assistance with the experimental work. Secretarial and editorial skills were expertly provided by Trudy Jones at Hanford.

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DISCUSSION

M. Whatley: Regarding the Am reclamation flowsheet for Hanford: it is noted that the efficiency of the process is not good by usual standards, yet only 4 stages are specified in the first contactor. Why has the process been so constrained, and has an optimization been performed to assess the number of stages that should be used?

W.W. Schulz: The DHDECMP flowsheet for recovery of Am from plutonium reclamation facility aqueous waste is deliberately intended to operate with existing equipment; this choice is strictly an economic one to avoid the expense of building new columns. Unfortunately, as Dr. Whatley observes, the inadequate design of the present first contactor limits Am recovery by both the DHDECMP and DBBP flowsheet. Much of this constraint can be removed, however, by increasing the extractant flow relative to that of the feed. We have not attempted to optimize the DHDECMP process to ascertain the ideal number of extraction stages.

A. Naylor: I am interested in the application of DHDECMP to Pu, Am and Cm recovery from Purex waste solutions other than the HAW stream. For reprocessing systems, ideally one would like to separate Pu by DHDECMP and then recycle back to the TBP process, while the Am and Cm also will be separated but dispatched for ultimate disposal.

For this type of process I will then be interested to know whether the extracted Pu from the DHDECMP system has been examined for efficiencies under TBP extraction inlet ions, i.e. does the Pu solution recovered from the DHDECMP system contain any impurities or ions which affect TBP conditions?

The other question relates to disposal of DHDECMP. What retention levels of Pu, Am & Cm remain after solvent purification and recycle?

W.W. Schulz: In response to the first question, we are not aware that the Pu product solution contains

any ions or impurities that would interfere with succeeding TBP extraction except, of course, for entrained and soluble DHDECMP itself. Because DHDECMP is such a powerful extractant for Pu, this concentration in the recycled Pu stream must be carefully regulated. In the Hanford PRF operation we have established that the 20% TBP-CCl₄ solvent can contain up to about 2 vol % DHDECMP without compromising stripping of Pu by HNO₃·HF solution.

We do not have anywhere near enough laboratory let alone plant experience to state exactly what the actinide content of recycled DHDECMP solvent would be. Obviously this value will depend upon the life of the extractant and upon feed activity levels. In the Hanford application we do not anticipate routine intercycle solvent cleanup and, in this case, the recycled solvent will contain up to 20% of the plutonium in the feed. In the Idaho flowsheet, the DHDECMP solvent will be routinely washed with Na₂CO₃ solution; we anticipate the washed solution will contain 0.1% or less of the actinides in the feed.

A.D. Kelmers: Reagent losses are always of concern in solvent extraction systems and particularly so with expensive reagents. Do you have any data on the solvent losses to be expected either due to solubility and entrainment or due to chemical and radiolytic degradation?

W.W. Schulz: The solubility (0.5 g/l) of DHDECMP in 0.1 M HNO₂ at 25°C is comparable to that of TBP. Obviously, we do not yet have any solvent loss data from actual plant-scale operation of a DHDECMP extraction process. However, for purposes of calculating required solvent inventories and replacement costs, we estimate DHDECMP losses would be comparable to TBP losses in plant-scale Purex process operation or to DBBP losses in operation of the Hanford Plutonium reclamation facility.

Z. Kolarik: What is the position of Am in the extractability sequence of lanthanides? Would it be pos-

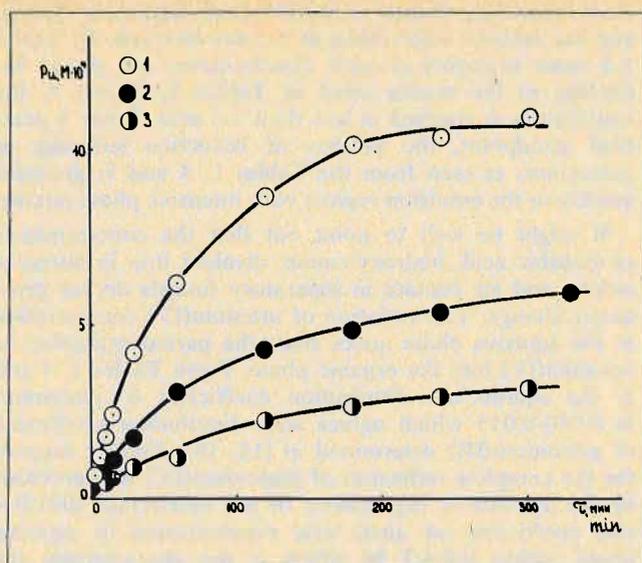


FIGURE 3. Variation of plutonium concentration in aqueous phase during stripping with hydrazine.
Initial solution:
(1) — 0,05 M hydrazine nitrate — 1,03 M nitric acid;
(2) — 0,05 M hydrazine nitrate — 2 M nitric acid;
(3) — 0,052 M hydrazine nitrate — 3,0 M nitric acid.
Temperature: 1 — 19,5°C; 2 — 20°C; 3 — 19°C.

TBP and CCl_4 and checked by density. Before the experiment, 1.1 M TBP solution in CCl_4 was shaken 3-4 times for 5 minutes with alkaline solution of potassium permanganate and washed out with water. The concentration of reductants in stripping solutions was 0.05-0.08 M. The U(IV) — solution was prepared by reduction of uranyl nitrate on mercury cathode in the presence of hydrazine. Uranyl nitrate was first purified by means of double extraction with diethyl ether followed by recrystallization from the aqueous solution. The solution of divalent iron was obtained by dissolving iron metal in nitric acid with cooling. To stabilize ascorbic acid, iron(II) and uranium(IV) in nitric acid solution, hydrazine nitrate was added. The reagents of "chemical pure" and "analytical pure" grades were used. The solutions were prepared by using distilled water.

Plutonium concentration was determined radiometrically. The content of iron(II) and uranium(IV) was determined by titration with ammonium vanadate solution using sodium diphenyl-amino-sulphonate or phenylanthranilic acid as an indicator⁽¹²⁾. Hydrazine and hydroxylamine were titrated with iodine solution⁽¹³⁾, ascorbic acid — with ferric chloride solution in hydrochloric acid medium at 60°C in the presence of ammonium thiocyanate⁽¹⁴⁾. Nitric acid concentration was also determined

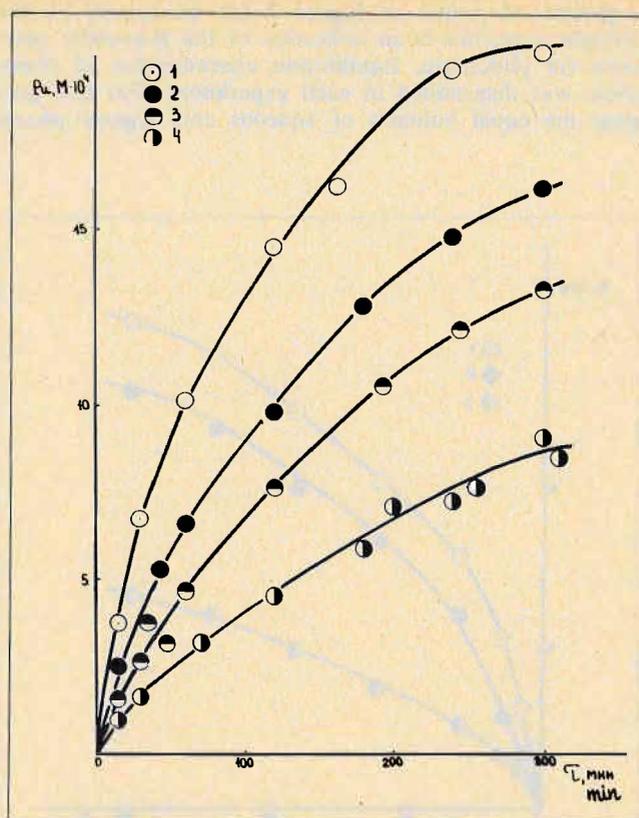


FIGURE 4. Variation of plutonium concentration in aqueous phase during stripping with hydroxylamine.
Initial solution:
(1) — 0,048 M hydroxylamine nitrate — 0,31 M nitric acid;
(2) — 0,052 M hydroxylamine nitrate — 0,5 M nitric acid;
(3) — 0,05 M hydroxylamine nitrate — 1,04 M nitric acid;
(4) — 0,048 M hydroxylamine nitrate — 1,52 M nitric acid;
Temperature: 1 — 21°C; 2 — 20,6°C; 3 — 21°C; 4 — 21,1°C.

by a volumetric method, i.e. by titration with 0.1 M KOH using methyl orange as indicator.

Results and Discussion

The increase of plutonium concentration in the aqueous phase after stripping with various reducing agents is shown in Figures 2-6. As can be seen, the rate of reduction stripping of plutonium depends on the reductant nature and nitric acid concentration. In Figure 7 the kinetic curves in semi-logarithmic scale are presented. The $\phi \lg(1-E)$ function includes E-value — the efficiency of stripping process (the degree of approach to equilibrium state) expressed as x/x_{eq} , where x — plutonium concentration in strip (reextract). φ — share of aqueous phase in the total volume of organic and aqueous solutions. The

TABLE 1. Determination of Equilibrium Distribution of Plutonium Stripping with Ascorbic Acid from 1,1 M TBP Solution in Carbon Tetrachloride.

Time, min.	Plutonium conc. $M \cdot 10^5$		Balance of plutonium		Nitric acid conc. M		Ascorbic acid conc. in aq. phase, M	Hydrazine conc. in aq. phase, M
	org. phase	aq. phase	$M \cdot 10^4$	%	org. phase	aq. phase		
0	15,2	0	1,52	100	0,32	1,07	0,053	0,1
3	—	15,27	—	—	—	—	—	—
6	—	15,1	—	—	—	—	—	—
10	—	16,6	—	—	—	—	—	—
15	—	15,9	—	—	—	—	—	—
30	0,17	15,27	1,54	101,3	0,2	1,2	0,051	0,1

experimental points on Figure 7 fall adequately on the straight lines; this is an indication of the first-order reactions for plutonium. Equilibrium concentration of plutonium was determined in each experiment. For this purpose the equal volumes of aqueous and organic phases

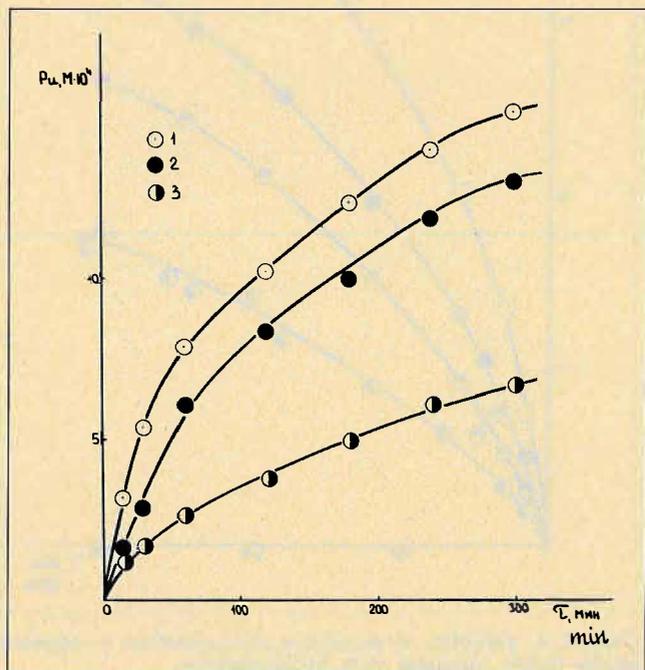


FIGURE 5. Variation of plutonium concentration in aqueous phase during stripping with tetravalent uranium.

Initial solution:

(1) — 0,052 M uranium(IV) nitrate — 0,025 M uranyl nitrate — 1,35 M nitric acid — 0,1 M hydrazine nitrate;

(2) — 0,049 M uranium(IV) nitrate — 0,007 M uranyl nitrate — 2 M nitric acid — 0,13 M hydrazine nitrate;

(3) — 0,051 M uranium(IV) nitrate — 0,002 M uranyl nitrate — 4,2 M nitric acid — 0,12 M hydrazine nitrate.

Temperature: 1 — 21,6°C; 2 — 20,3°C; 3 — 21,6°C.

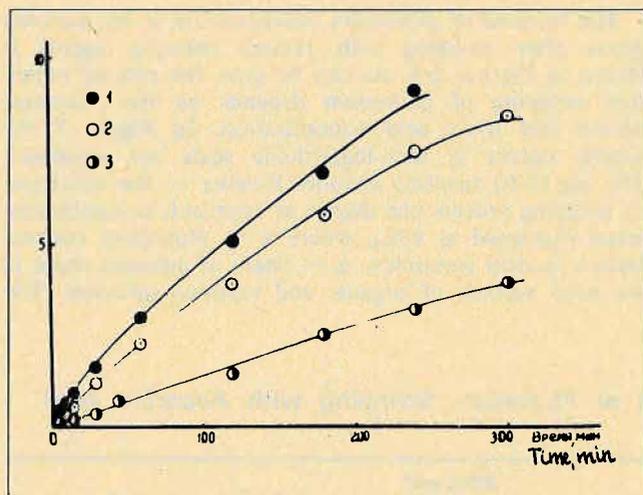


FIGURE 6. Variation of plutonium concentration in aqueous phase during stripping with divalent iron.

Initial solution:

(1) — 0,08 M iron(II) nitrate — 0,9 M nitric acid — 0,1 M hydrazine nitrate;

(2) — 0,075 M iron(II) nitrate — 1,95 M nitric acid — 0,1 M hydrazine nitrate;

(3) — 0,88 M iron(II) nitrate — 5 M nitric acid — 0,06 M hydrazine nitrate;

Temperature: 1 — 18,4°C; 2 — 20,2°C; 3 — 20°C.

were intensively shaken in thermostated separatory funnels and the samples were taken at regular intervals. In Tables 1-5 some examples of such determination are given. According to the results cited in Tables 1, 4 and 5, the equilibrium is reached in less than 1-3 min. From a practical standpoint, the process of reduction stripping of plutonium, as seen from the Tables 1, 4 and 5, proceeds quickly in the emulsion regime with intensive phase mixing.

It might be well to point out that the concentrations of ascorbic acid, hydroxylamine, divalent iron in intensive mixing and air contact in separatory funnels do not practically change. The variation of uranium(IV) concentration in the aqueous phase arises from the partial extraction of uranium(IV) into the organic phase. From Tables 1, 4 and 5, the equilibrium distribution coefficient of plutonium is 0.010-0.015 which agrees with distribution coefficient of plutonium(III) determined in (15, 16). Further support for the complete reduction of plutonium(IV) was provided by the absence of dependence of the determined distribution coefficient on nitric acid concentration in aqueous phase within 0.8-4.2 M which is not characteristic for plutonium(IV)⁽¹⁷⁾. Using hydroxylamine (Table 3), the values of equilibrium distribution coefficients were some-

TABLE 2. Determination of Equilibrium Distribution of Plutonium in Stripping with Hydrazine from 1,1 M TBP Solution in Carbon Tetrachloride

Time, min.	Plutonium concentration, M · 10 ⁵		Balance of plutonium		Nitric acid conc. M		Hydrazine conc. M aq. phase
	org. phase	aq. phase	M · 10 ⁴	%	org. phase	aq. phase	
0	20,3	0	2,03	100	0,33	1,00	0,05
1	—	5,02	—	—	—	—	—
3	—	5,61	—	—	—	—	—
6	—	5,52	—	—	—	—	—
10	—	5,31	—	—	—	—	—
15	—	5,31	—	—	—	—	—
30	15,9	5,10	2,10	103,5	0,18	1,2	0,054

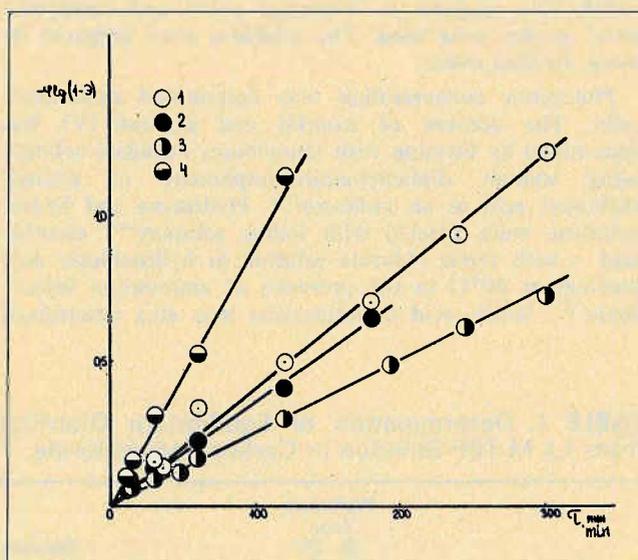


FIGURE 7. Semi-logarithmic anamorphoses of the curves of plutonium stripping process.

(1) — 0,052 M uranium(IV) nitrate — 0,025 M uranyl nitrate — 1,35 M nitric acid — 0,1 M hydrazine nitrate;

(2) — 0,05 M ascorbic acid — 1 M nitric acid — 0,1 M hydrazine nitrate;

(3) — 0,05 M hydroxylamine — 1,04 M nitric acid;

(4) — 0,051 M hydrazine nitrate — 1,03 M nitric acid.

TABLE 3. Determination of Equilibrium Distribution of Plutonium in Stripping with Hydroxylamine from 1,1 M TBP Solution in Carbon Tetrachloride

Time, min.	Plutonium conc. $M \cdot 10^5$		Balance of plutonium		Nitric acid conc. M		Hydroxylamine concentration in aqueous phase, M
	org. phase	aq. phase	$M \cdot 10^4$	%	org. phase	aq. phase	
0	17,11	0	17,11	100	0,4	1,03	0,046
30	1,63	14,69	16,32	95,4	0,21	1,18	0,046

what higher than those found under the corresponding conditions by using ascorbic acid, divalent iron and tetravalent uranium. It is evident that a portion of plutonium is distributed between phases in the form of plutonium(IV). During stripping with hydrazine solution at 20°C, the distribution coefficient corresponds to the distribution coefficient of plutonium(IV).

The apparent rate constants of plutonium stripping were determined according to the slope of semi-logarithmic anamorphoses (see Figure 7). In Figure 8 the dependence of apparent rate constants of plutonium stripping on phase-mixing intensity using divalent iron as a reductant is shown. At a rotation rate of stirrer below 250 rpm, a sharp break of the process rate is observed. Over the range of mixing intensity 300-500 rpm, the values of constants vary only by 10%. Such a character of the change in rate constants with increasing rotation rate seems to depend on the limitation on the process first by molecular diffusion, then by increase of convective-diffusion contribution and finally by increasing contribution of chemical constituents in the total process. The region of 500 rpm

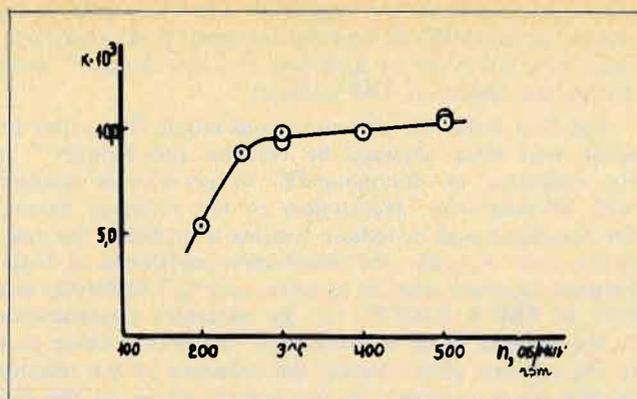


FIGURE 8. Dependence of apparent rate constants of stripping (K , cm. min⁻¹) on rotation rate of stirrers (n , rpm). 0,075 M iron(II) nitrate — 1 M nitric acid — 0,1 M hydrazine nitrate. Temperature: 20°C.

was chosen for the work. However, it should be noted that at 600 rpm the motion amplitude of the interface surface increases, so that separate drops tear off the surface⁽¹⁸⁾.

It should be also mentioned that the substitution of reductants at the low concentrations of the components used does not effect the physical properties of the phases, i.e. the mixing conditions in the case of divalent iron can be extended to a certain approximation for the systems using the other reductants.

In Figure 9 the dependence of rate constants on nitric acid concentration in aqueous phase is presented. Process order for nitric acid proved to be equal in the case of ascorbic acid to minus 0,8, hydrazine — minus 1,2, hydroxylamine — minus 0,5, uranium(IV) — minus 1,8, iron(II), as it was reported earlier⁽¹⁹⁾, minus 1. The ob-

TABLE 4. The Determination of Equilibrium Distribution of Plutonium in Stripping with Tetravalent Uranium Solution from 1,1 M TBP Solution in Carbon Tetrachloride

Time, min.	Plutonium conc. $M \cdot 10^5$		Balance of plutonium		Nitric acid conc. M		Uranium (IV) conc. M		Uranium (VI) conc. M		Hydrazine conc. in aqueous phase, M
	org. phase	aq. phase	$M \cdot 10^4$	%	org. phase	aq. phase	org. phase	aq. phase	org. phase	aq. phase	
0	19,7	0	19,7	100	0,34	0,95	0	0,05	0	0,008	0,12
1	—	19,7	—	—	—	—	—	—	—	—	—
3	—	19,5	—	—	—	—	—	—	—	—	—
6	—	19,8	—	—	—	—	—	—	—	—	—
10	0,26	18,9	19,16	97,3	—	—	0,011	0,035	—	—	—
15	—	20,6	—	—	—	—	0,011	0,035	—	—	—
30	0,23	18,6	18,83	95,6	0,20	1,06	0,011	0,035	0,012	0	0,12

TABLE 5. Determination of Equilibrium Distribution of Plutonium in Reduction Stripping with Divalent Iron from 1,1 M TBP Solution in Carbon Tetrachloride

Time, min.	Plutonium conc. $M \cdot 10^5$		Balance of plutonium		Nitric acid conc. M		Iron (II) conc. in aqueous phase, M	Hydrazine conc. in aqueous phase, M
	org. phase	aq. phase	$M \cdot 10^4$	%	org. phase	aq. phase		
0	23,7	0	2,37	100	0,29	0,92	0,0785	0,1
1	0,36	22,66	2,30	97	—	—	—	—
3	0,24	22,64	2,29	96,5	—	—	—	—
6	0,26	23,06	2,33	98,5	—	—	—	—
10	0,23	22,66	2,29	96,5	—	—	—	—
15	0,23	22,77	2,30	97	—	—	—	—
30	0,24	22,99	2,32	98	0,19	1,07	0,0765	0,1

tained process order for plutonium and nitric acid in the case of uranium(IV) as the reducing agent is in good agreement with the works by Koltunov and Marchenko⁽¹⁰⁾ using a different diluent of TBP (sintine).

The first order for plutonium and minus first order for nitric acid were obtained by Newton and Kowan⁽²⁰⁾ at the reduction of plutonium(IV) in perchlorate solution with divalent iron. Mechanism of the reducing process for one-phase and two-phase systems is probably the same in this case. Actually, the distribution coefficient of Fe(II) between aqueous solution of nitric acid (4.7 M HNO₃) and 0.55 M TBP is 0.005⁽²¹⁾, i.e. the reductant concentration in the organic phase is more than two orders lower than in the aqueous phase; hence, the influence of the reaction of plutonium reduction in the organic phase on the rate of the total process can be neglected.

As in the process of reduction stripping of plutonium used for the separation of plutonium and uranium, the latter is always present in aqueous and organic solutions, and it is advisable to define the influence of uranium(VI) on stripping rate. In Figures 10 and 11 the dependencies of apparent rate constants of plutonium stripping with uranium(IV) on concentration of uranyl nitrate in organic

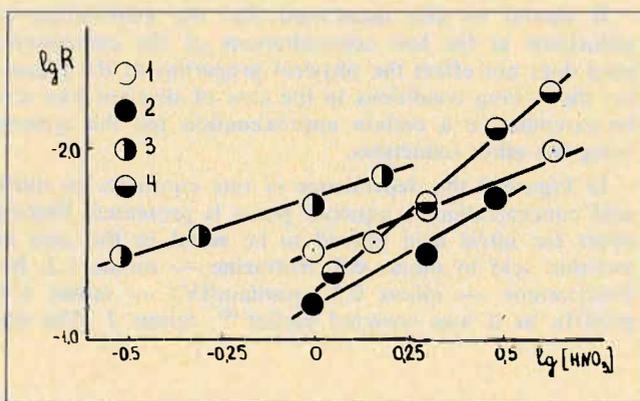


FIGURE 9. Dependence of apparent rate constants of plutonium stripping (K , cm. min^{-1}) with solutions of ascorbic acid, hydrazine, hydroxylamine, tetravalent uranium on nitric acid concentration in logarithmic coordinates.

(1) — 0,05 M ascorbic acid — 1-4,3 M nitric acid — 0,1 M hydrazine nitrate;

(2) — 0,05 M hydrazine nitrate — 1-3 M nitric acid;

(3) 0,05 M hydroxylamine nitrate — 0,3 — 1,5 M nitric acid;

(4) — 0,05 M uranium(IV) nitrate — 0,002 — 0,007 M uranyl nitrate — 1 — 4,2 M nitric acid — 0,1 M hydrazine nitrate.

Temperature: 20°C.

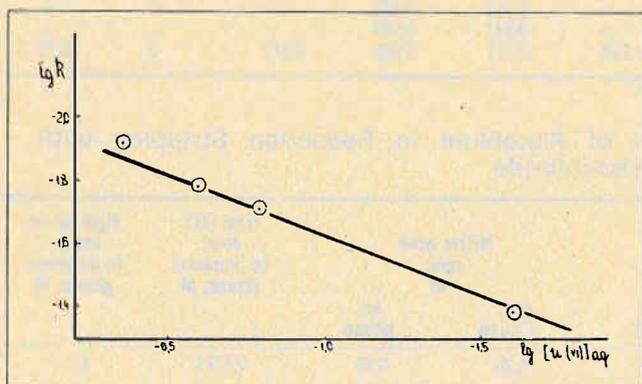


FIGURE 10. Dependence of apparent rate constant of reduction stripping of plutonium on uranyl nitrate concentration in aqueous phase in logarithmic coordinates.

0,05 M uranium(IV) nitrate — 1,2 M nitric acid — 0,1 M hydrazine nitrate — 0,02 — 0,45 M uranyl nitrate.

and aqueous phases are presented. The order of the process for uranyl nitrate turned out to be equal — 0.4 irrespective of whether uranium(VI) is initially in aqueous or organic phase which points to the similarity of mechanism of plutonium reduction process in one-phase (aqueous) and two-phase systems. To ascertain the role of chemical interaction of components, it is important to determine the temperature dependence of the process rate, since the diffusion step is known to be characterized as a rule by a much lower experimental activation energy. The tests were carried out on the study of the rate of plutonium reduction stripping at different temperatures.

Some values of the rates of apparent constants depending on inverse temperature are presented in logarithmic coordinates in Figure 12. The values of experimental activation energy calculated from these data for the solutions of ascorbic acid and tetravalent uranium in 1 M nitric acid were about 7 and 3 kcal/M and 9 and 5.5 kcal/M respectively for solutions of these reducing agents in 4 M nitric acid. At the same time, the values of experimental activation energy for the process using divalent iron are equal to nearly 4 and 13 kcal/M at the concentration of nitric acid 1 and 5 M, as it was reported in⁽¹⁹⁾. So, on the basis of the data on activation energy, it can be said that the contribution of chemical constituents to the reduction stripping process of plutonium increases with increase of nitric acid concentration in the cases of using ascorbic acid, divalent iron or tetravalent uranium as reductants under the investigated conditions. In Table 6 the mean rates of plutonium stripping $\Delta C/\Delta \tau$ performed under comparable conditions are presented for various reductants. The highest rate of stripping was attained with the use of tetravalent uranium as the reductant.

Conclusion

1. With the help of an extractor having a fixed surface of phase contact, the reduction stripping of plutonium was studied using solutions of ascorbic acid, hydrazine, hydroxylamine, divalent iron and tetravalent uranium in the system TBP — carbon tetrachloride — water — nitric acid.

2. The order of the reduction stripping process was

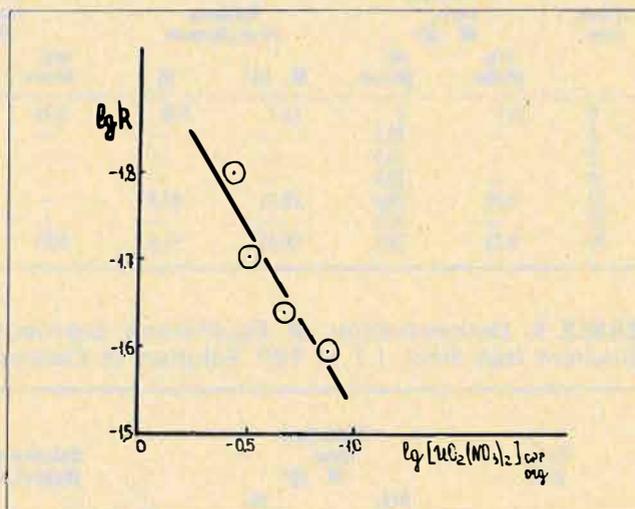


FIGURE 11. Dependence of apparent rate constant of reduction plutonium stripping on uranyl nitrate concentration in organic phase in logarithmic coordinates.

0,05 M uranium(IV) nitrate — 1,2 M nitric acid — 0,1 M hydrazine nitrate.

Initial organic solution:

$2 \cdot 10^{-4}$ M plutonium(IV) nitrate — 1,1 M TBP — carbon tetrachloride — 0,1 — 0,37 M uranyl nitrate.

TABLE 6. Mean Rate of Reduction Stripping of Plutonium for 120 Minutes from the Beginning of Experiment

Reducing agent	Nitric acid conc. M	Temp. °C	$\frac{\Delta c}{\Delta \tau} \cdot 10^7$ M · min. ⁻¹	Note
Ascorbic acid	1,0	23,5	6,2	
	2,0	20,9	4,9	
Hydrazine nitrate	1,0	19,9	3,9	
	2,0	20,3	1,75	
Hydroxylamine nitrate	1,05	21,1	6,3	
	2,0	21,5	3,1	
Iron(II) nitrate	0,9	18,4	4,25	
	2,0	20,2	3,2	
Uranium(IV) nitrate	1,35	21,6	8,45	U(VI) conc. in aq. soln. — 0,025 M.
	2,0	20,3	6,9	U(VI) conc. in aq. soln. — 0,007 M.

determined for plutonium and nitric acid.

3. The decrease in the process rate of reduction stripping of plutonium by tetravalent uranium was shown to take place with the increase of uranyl nitrate concentration in aqueous and organic phases.

4. The increase of experimental activation energy of the process with increase of nitric acid concentration in the system seems to be connected with the increase in the contribution of chemical stage to the total convective-diffusion redox process.

5. The investigation carried out allows the possibility to compare the various reductants and to give some recommendations for the reduction stripping of plutonium in the system TBP — carbon tetrachloride — water — nitric acid. In particular, hydrazine and hydroxylamine are too slow-acting reductants under the common conditions, although they do not practically form salts during the further reprocessing of aqueous solutions. Ascorbic acid reduces plutonium rather fast, but it is unstable in acid solutions and requires a further investigation of the influence of its degradation products on the separate operations in spent fuel reprocessing. Divalent iron is a fast reducing agent, but it adds foreign ions to aqueous solution. Tetravalent uranium is a most fast reductant which adds no impurities to the system. Its advantages are of greater importance when taken into account that uranium(IV) can be obtained with electrochemical reduction directly in the extraction apparatus where the plutonium stripping is performed.

As for the optimization of process conditions of reduction stripping, it is advisable to decrease the acidity of aqueous solution up to 1 M, and to provide intensive mixing resulting in a decrease of diffusion contribution.

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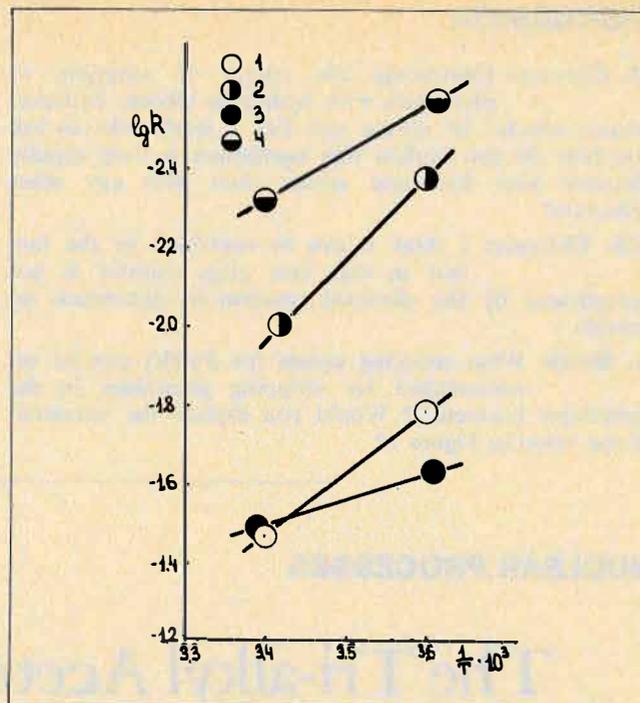


FIGURE 12. On calculation of experimental activation energy of plutonium stripping process from 1.1 M TBP solution in carbon tetrachloride with nitric acid solutions of uranium(IV) and ascorbic acid.

- 0,05 M ascorbic acid — 1 M nitric acid — 0,1 M hydrazine nitrate.
- 0,052 M ascorbic acid — 4,3 M nitric acid — 0,1 M hydrazine nitrate.
- 0,051 M uranium(IV) nitrate — 0,022 M uranyl nitrate — 1,2 M nitric acid — 0,1 M hydrazine nitrate.
- 0,048 M uranium(IV) nitrate — 0,006 M uranyl nitrate — 4,2 M nitric acid — 0,1 M hydrazine nitrate.

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DISCUSSION

M. Germain: Comparing the curves of stripping of plutonium with hydrazine nitrate, hydroxylamine nitrate, U^4 nitrate and Fe^2 , I would like to ask you—how do you explain that equilibrium is most rapidly obtained with hydrazine nitrate than with any other reductant?

N.S. Tikhanov: I think it can be explained by the fact that in this case mass transfer is not complicated by the chemical reaction of plutonium reduction.

A. Siczek: What reducing agents for Pu(IV) can be recommended for stripping plutonium in the centrifugal contactors? Would you explain the operation of the vessel in Figure 1?

V.S. Tikhanov: I think Pu(IV) is obtained with electrochemical reduction directly in the extraction apparatus.

The vessel in Figure 1 is carefully filled with the organic solution of Pu through the hole 6 and the ring gap 4 with help of a thin tube (the lower compartment); the upper compartment is filled with the reducing solution through hole 6 by means of another thin tube. Stirrers are put into operation and samples of organic and aqueous phases are periodically taken.

W. Nitsch: You have measured the transfer rate in a stirring cell with a horizontal baffle. What is the reason for the observed plateau-rate?

V.S. Tikhanov: I think the rate is determined mainly by the contribution of the chemical stage of the process in question in this interval.

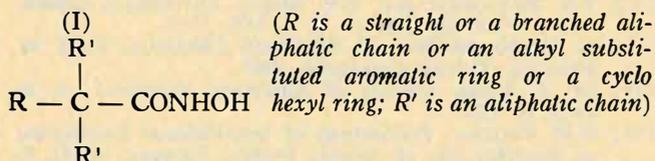
NUCLEAR PROCESSES

The Tri-alkyl Aceto Hydroxamic Acids as Selective Extractants in the Reprocessing of Irradiated Nuclear Fuels

Giulio M. Gasparini: Comitato Nazionale per l'Energia Nucleare, C.S.N. della Casaccia — Laboratorio Ricerche sul Rittrattamento, Roma, Italy.

ABSTRACT

Hydroxamic acids show a good extracting capacity with regard to some metal ions of nuclear interest, such as neptunium, plutonium and some fission products (Zr, Nb, Mo). A series of new tri-alkyl aceto hydroxamic acids with the general structure (I) has been prepared with the purpose to improve their performances as extractants in liquid-liquid separations.



Their solubilities in non-polar diluents and their radiolytical and chemical stability with regard to nitric acid and other mineral acids have been comparatively examined as a function of the molecular structure.

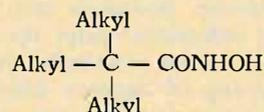
Their extracting capacity for several metal ions of nuclear interest as a function of the contact time, the concentration of the extractant, the acidity of the medium and the nature of the diluent have been verified.

Introduction

HYDROXAMIC ACIDS FORM STABLE COMPLEXES with a great number of metal ions such as Fe^{3+} , V^{5+} , Zr^{4+} , Nb^{5+} , Mo^{6+} , Hf^{4+} and generally with actinides and lanthanides^(1,2,3). Unfortunately the poor stability with respect to acidic and oxidant solutions and the hydrophilic properties of the hydroxamic function do not permit a wide

application of these compounds in separation procedures.

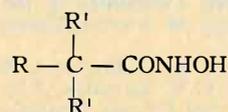
In our laboratory it has been shown that neo tridecano hydroxamic acids:



can be conveniently employed as an extracting agent in analytical as well as in liquid-liquid procedures for the separation and the purification of metals⁽⁴⁾. The increase and the branching of the aliphatic chain in the "neo" structure transmit to the hydroxamic acids different physical and chemical properties with respect to the corresponding straight-chain isomers; they have a higher solubility in organic solvents and a lower solubility in water.

The steric hindrance of the branched aliphatic chain increases the chemical stability with regard to oxidative or acid attack as well as the radiolytical stability. This fact has suggested the application of these kinds of hydroxamic acids for the final purification of fissile materials in aqueous reprocessing of irradiated nuclear fuels as well as for the recovery of some expensive metals, and induced us to start a study on the influence of a branched alkyl structure to improve the extractant properties of these compounds.

In the present paper the results are reported of the preparation and a comparative evaluation of the chemical and physical properties, the stability and the extracting capacity of a series of trialkylated aceto hydroxamic acids with this general structure:



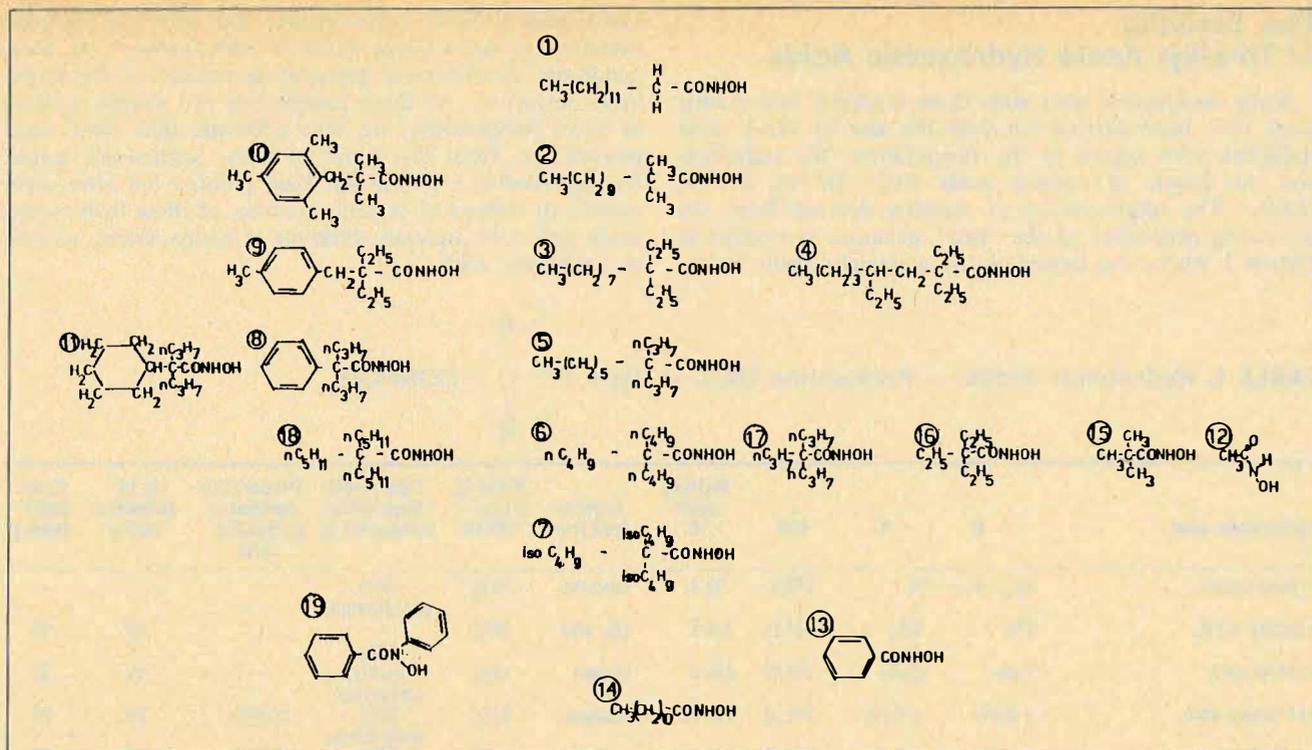


FIGURE 1. Tri-alkyl aceto hydroxamic acids. (Also key to figures)

where R and R' are straight or branched aliphatic chains or less or more substituted aromatic or cyclohexylic rings.

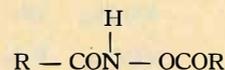
The Preparation of Tri-alkyl Aceto Hydroxamic Acids

All of these new hydroxamic acids are illustrated in Figure 1. The choice of them follows a logical line with the purpose of investigating the properties of these compounds as a function of:

- the molecular weight in the symmetrical series (from the trimethyl to the tri n pentyl aceto hydroxamic acids);
- the molecular structure in the series of acids with the same molecular weight but with straight chains of different length (22' dimethyl dodecano hydroxamic acid, 22' di ethyl decano hydroxamic acid, 22' di propyl octano hydroxamic acid) or with differently branched chains (22'4 tri ethyl octano hydroxamic acid, tri isobutyl aceto hydroxamic acid);
- the substitution of an aromatic or cyclohexylic ring ($\alpha\alpha'$ di propyl phenyl aceto hydroxamic acid, $\alpha\alpha'$ di methyl β (246 tri methyl phenyl) propano hydroxamic acid, $\alpha\alpha'$ di ethyl β (p tolyl) propano hydroxamic acid, $\alpha\alpha'$ propyl cyclohexyl aceto hydroxamic acid).

The Chemical and Physical Properties

The hydroxamic acids prepared are white solids crystallized from heptane or benzene and stable at room temperature. The more branched derivatives, with less elevated melting points, become solids only after some days. The IR and UV spectra of pure compounds are in agreement with the results of similar compounds⁽⁶⁾. Elemental analyses are near to the theoretical values. The principal data on the preparation of these hydroxamic acids are illustrated in Table 1. In the same table are reported the results of potentiometric and colorimetric purity tests. Some differences between the two methods may be attributed to the presence of an acyl hydroxamate:



an acidic secondary compound, not giving the colorimetric iron test, formed during the reaction with hydroxylamine.

The Solubility of Tri-alkyl Aceto Hydroxamic Acids

The effect of the alkyl structure on the solubility of these hydroxamic acids has been examined with different solvents suitable in laboratory or process scale with a wide range of dielectric constant (Table 2). The solubility in non-polar solvent is related to the loading capacity of an extractant; on the other side a low solubility in water prevents losses of extractants during multicyclic extractions. The solubility tests permit us to conclude that:

- The solubility of these tri-alkyl hydroxamic acids in non-polar solvents is higher than that of the corresponding straight-line compounds. At the same time, the solubility in water gives less comparable results; generally a solubility between 10^{-1} — 10^{-2} mols/l is an acceptable value.
- The solubility in water is too high for compounds with a molecular weight < 210 (or a total number of carbons < 12). The following tests have been carried out for compounds with 14 carbon atoms.
- An introduction of an aromatic substituted ring does not seem to improve the solubility;
- A cyclohexyl derivative like the benzyl derivative has a good solubility in chloroform but does not improve the general performances more than the n hexyl derivative.
- In a compound with a long straight chain and two short chains, the solubilities are excessively low (especially in water).
- The best performances are obtained when the aliphatic chains are partially or completely branched. Unfortunately, the preparation of these hydroxamic acids and of their carboxylic derivatives is characterized by low yields and troubles during their synthesis.

The Stability of Tri-alkyl Aceto Hydroxamic Acids

Some comparison tests with these hindered hydroxamic acids have been carried out with the aim to verify their stabilities with regard to the temperature, the radiations and the attack of mineral acids (HCl, HClO₄, HNO₃, H₂SO₄). The improvement of stability derived from the protecting properties of the "neo" structure is evident in Figure 2 where the behaviour of a straight-chain hydro-

xamic acid at 80°C is also shown. The effect of the temperature on hydroxamic acids is well known⁽⁶⁾; at these conditions the principal degradation product is the carboxylic derivative. As these compounds are usually utilized at room temperature, we may conclude that these compounds are, from this point of view, sufficiently stable. No degradation evidence has been pointed out after some months of contact of organic solutions of these hydroxamic acids with 5 M aqueous solutions of hydrochloric, sulfuric or perchloric acids.

TABLE 1. Hydroxamic Acids — Preparation Data — Type $R - \overset{\overset{R'}{|}}{\underset{\underset{R'}{|}}{C}} - CONHOH$

Hydroxamic acid	R	R'	MW	Melting point °C	Crystallized from	Yield % from COOH	Total Yield from initial compound %	Preparation method of carboxylic acid	% by potentiometry	% by colorimetry
n. tetra decano	nC ₁₂ H ₂₅	H	243.4	92-3	benzene	90%	78%	tetradecanoic	—	—
trimethyl aceto	CH ₃	CH ₃	117,15	164-5	eth. acet.	98%	—	—	99	95
tri ethyl aceto	C ₂ H ₅	C ₂ H ₅	159,23	134-5	hexane	92%	72%	triethyl acetic acid	—	98
tri n propyl aceto	n C ₃ H ₇	n C ₃ H ₇	201,31	110-11	benzene	81%	35%	NaNH ₂	98	92
tri n butyl aceto	n C ₄ H ₉	n C ₄ H ₉	243,40	132-3	n hexane	82%	25%	NaNH ₂	97	92
tri i butyl aceto	i C ₄ H ₉	i C ₄ H ₉	243,40	100-101	benzene	70%	10%	NaNH ₂	100	93
tri n pentyl aceto	n C ₅ H ₁₁	n C ₅ H ₁₁	285,47	125-6	n hexane	84%	35%	NaNH ₂	99	96
22' di methyl dodecano	n C ₁₀ H ₂₁	CH ₃	243,40	95-6	benzene	90%	31%	NaH	100	100
22' Diethyl decano	n C ₈ H ₁₇	C ₂ H ₅	243,40	74-5	n heptane	90%	13%	NaNH ₂	98	98
22' Dipropyl octano	n C ₆ H ₁₃	n C ₃ H ₇	243,40	87-8	n heptane	77%	30%	NaNH ₂	97	95
22'4 triethyl octano	See 4 Figure 1	C ₂ H ₅	243,40	61-3	n heptane	80%	24%	NaNH ₂	96	86
αα' di propyl phenyl aceto	See 8	n C ₃ H ₇	235,32	140-1	n heptane	45%	22%	NaNH ₂	100	99
αα' di methyl S (246 trimethyl phenyl propano	See 10	CH ₃	235,32	162-3	benzene	70%	10%	NaH	100	91
αα' di ethyl S (p.tolyl) propano	See 9	C ₂ H ₅	235,32	129-30	benzene	90%	40%	NaH	98	89
αα' din propyl cyclohexyl aceto	See 11	n C ₃ H ₇	241,38	119-20	heptane	64%	20%	NaNH ₂	99	100

TABLE 2. Solubility of the Tri alkyl aceto hydroxamic Acids at 25°C (moles/l) $R' - \overset{\overset{R''}{|}}{\underset{\underset{R''}{|}}{C}} - CONHOH$

R'	R''	n-Heptane	Benzene	Xylene	Mesitylene	Chloroform	Carbon tetrachloride	Trichloro Ethane	Ethanol	Water	HNO ₃ IM
n C ₁₀ H ₂₅	H	0.92	1.6	10	0.92	19.2	0.075	—	314	10 ⁻²	not detect.
n C ₁₂ H ₂₅	H	10	70	—	2.0	30	—	25	110	10 ⁻²	—
CH ₃	CH ₃	0.1	2.5	1.2	1.0	34	0.54	—	10 ³	356	—
C ₂ H ₅	C ₂ H ₅	0.23	18	9	8.2	150	4.0	—	10 ³	50	59
n C ₃ H ₇	n C ₃ H ₇	3.0	80	75	37	800	54	—	10 ³	2.1	0.21
n C ₄ H ₉	n C ₄ H ₉	2.1	76	62	32	440	43	250	10 ³	0.07	not detect
n C ₅ H ₁₁	n C ₅ H ₁₁	1.66	49	23	19	370	23	—	10 ³	1.66	not detect.
i C ₄ H ₉	i C ₄ H ₉	150	370	—	190	10 ³	—	490	10 ³	10 ⁻³	10 ³
n C ₁₀ H ₂₁	CH ₃	6.7	410	—	120	10 ³	—	512	10 ³	16.10 ⁻³	—
n C ₈ H ₁₇	C ₂ H ₅	—	710	—	450	10 ³	—	760	10 ³	6.10 ⁻³	—
n C ₆ H ₁₃	n C ₃ H ₇	2.1	245	—	36	10 ³	—	630	10 ³	1.5	—
See 4											
Figure 1	C ₂ H ₅	—	10 ³	—	103	10 ³	—	10 ³	10 ³	0.45	—
See 8	n C ₃ H ₇	2,0	250	—	40	10 ³	—	630	10 ³	1.3	—
See 10	CH ₃	5	22	—	5	120	—	70	200	0.3	—
See 9	C ₂ H ₅	—	30	—	30	870	—	130	13 ³	1.5	—
See 11	n C ₃ H ₇	10	230	—	40	10 ³	—	290	10 ³	0.45	—

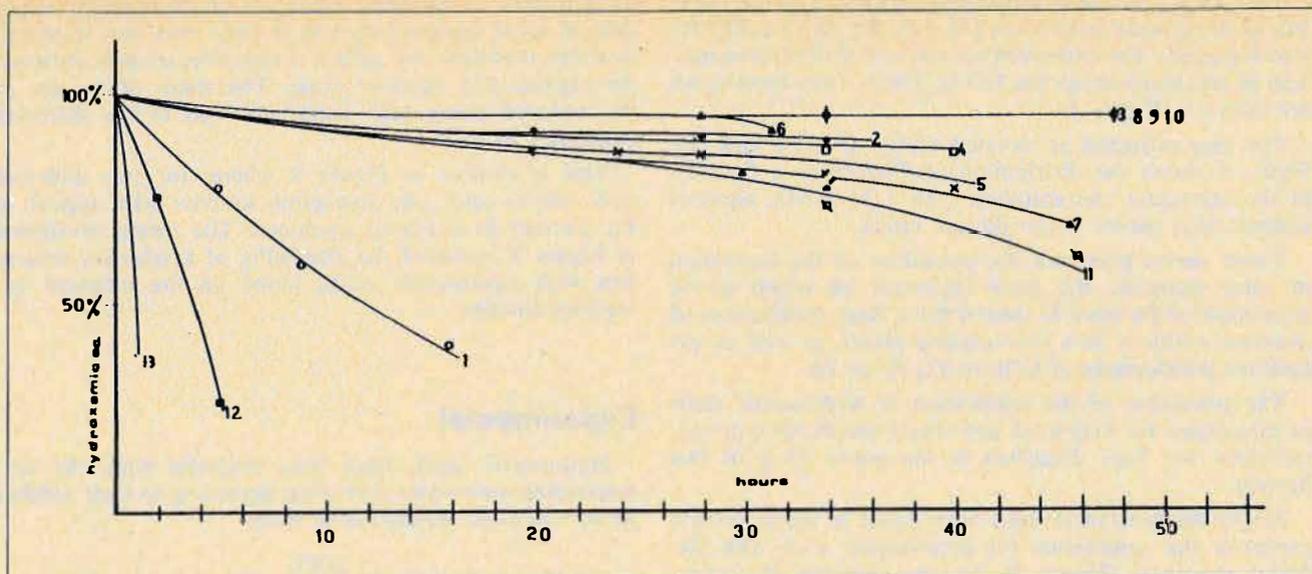


FIGURE 2. Thermal degradation at 80°C.

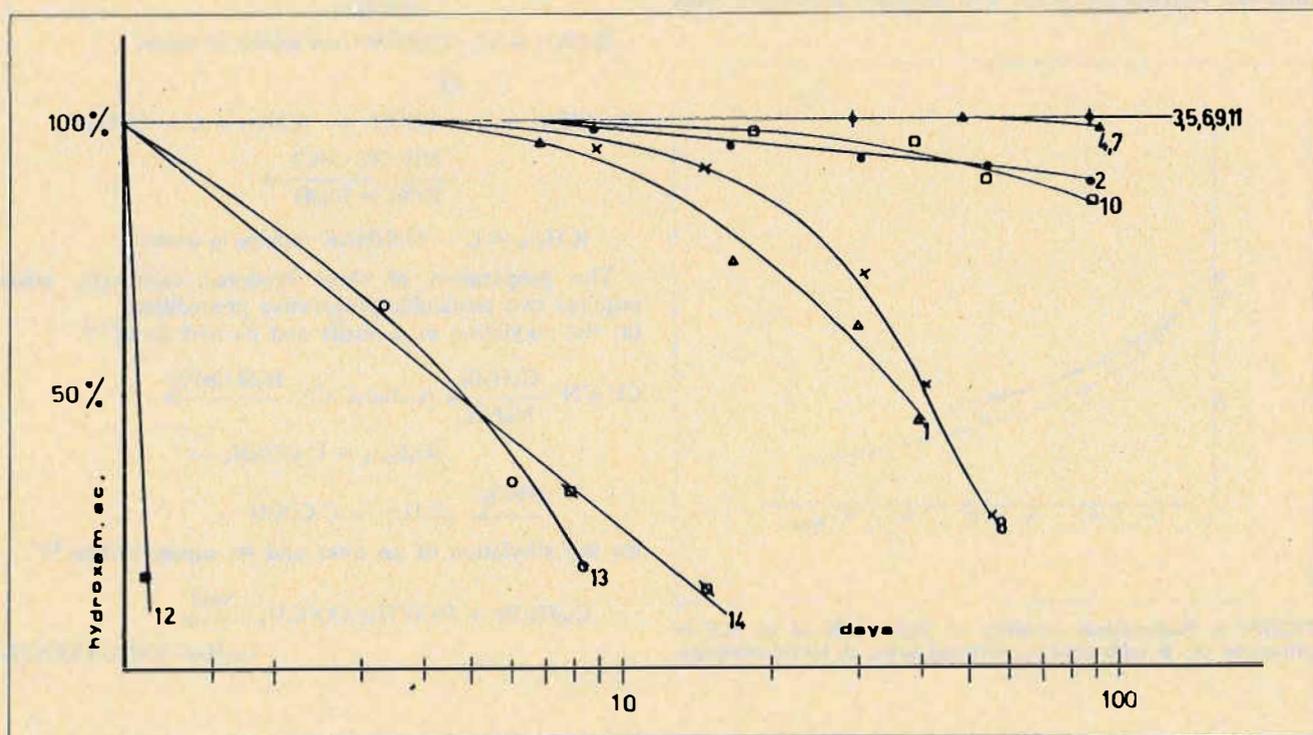


FIGURE 3. Chemical degradation with HNO₃ (urea).

Nitric acid is usually employed in nuclear fuel reprocessing procedures. In Figure 3 the results of the stability tests with this acid are shown; the improvement of the stability given by this neo structure is evident. All tests with nitric acid have been performed in the presence of urea as a nitrous acid suppresser, as hydroxamic acids are not stable with nitrous acid (always present in nitric acid aqueous solutions). There is no information on the action of nitrous acid on the hydroxamic function and we are carrying out some research to investigate the stability of hydroxamic acids. No serious problem is found by the irradiation of the hydroxamic acids if we consider that the more elevated dose of a cycle during a normal reprocessing run may be about 0.2 — 0.3 Mrad. In Figure 4 is illustrated a typical result of an irradiation trial on an hydroxamic acid and on its ferric complex.

The Extracting Capacity.

The particular hindered structure of these acids may introduce some differences in the kinetics of the complex formation and on the extraction rate. A comparative study on the extraction behaviour of these hydroxamic acids for different metal ions as a function of the extractant concentration, of the acidity of the medium, of the time of the contact, and the structure of the hydroxamic acid has been carried out. The diluents used for extraction were xylene, mesitylene, chloroform and trichloroethane, the last being the preferred diluent. One of the most interesting features of the hydroxamic function is its extracting capacity for Pu(IV) from acidic aqueous solutions; Pu(III) and Pu(VI) are not extracted and this fact permits the separation of the different valence states of plutonium.

This subject has been particularly discussed in the paper 33a of the present session. At pH = 0, Zr, Nb, Fe, Mo are also extracted. The extraction curves with 0.05 hydroxamic acid in tri-chloroethane for U(VI), Th(IV) and lanthanides are shown in Figure 5.

For ions extracted at elevated acidity (Pu, Fe and Zr), Figure 6 shows the distribution coefficient as a function of the extractant concentration with 1 M HNO₃ aqueous acidity. Also shown is the diluent effect.

These curves point out the possibility of the separation of some elements, the most important of which is the separation of Pu from U (useful for a final purification of uranium solutions in a reprocessing plant), as well as exhaustive purifications of U from Fe, Zr or Th.

The possibility of the application of hydroxamic acids as extractants for long-lived activities from Purex-type raw raffinate has been described in the paper 33 g of this Session.

Negligible differences have been found in the extraction curves at the equilibrium for hydroxamic acids with different structures (Figure 7). On the contrary, the structure has an important influence on the extraction kinetics. In Figure 8 is shown the extraction kinetics of FeIII with different hydroxamic acids. The different behaviour must

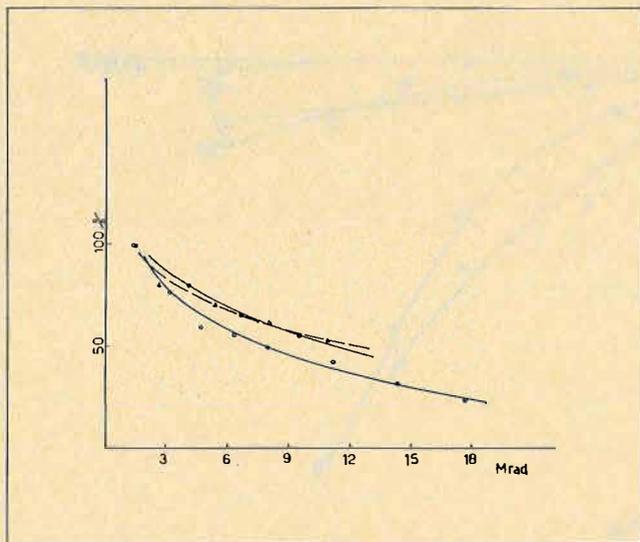


FIGURE 4. Radiolytical stability of TBAH 0.05 M in TCE in presence of: ● with urea, ○ without urea, △ ferric complex.

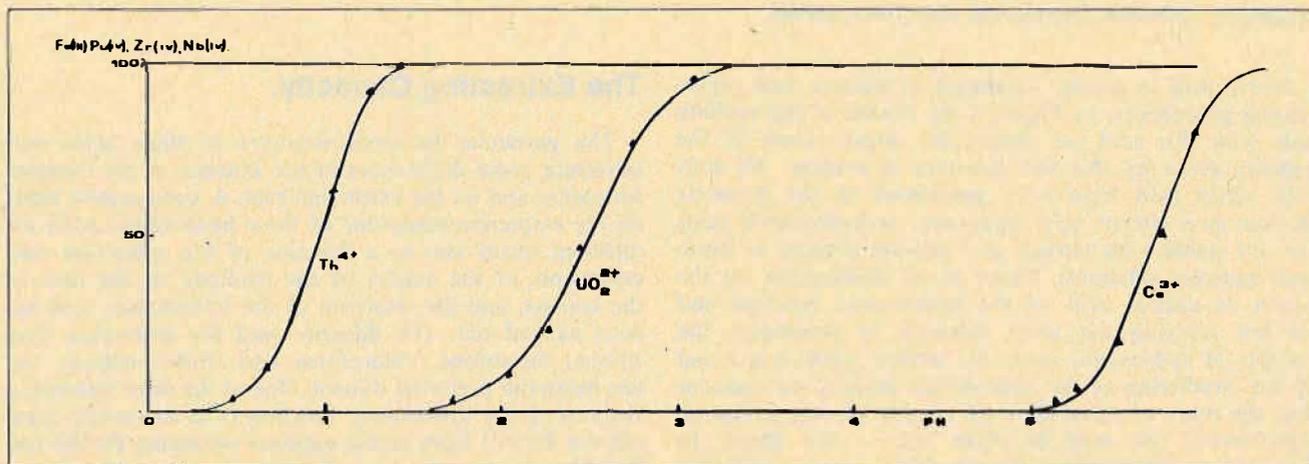


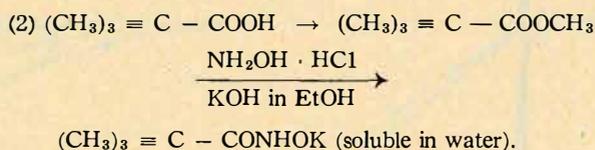
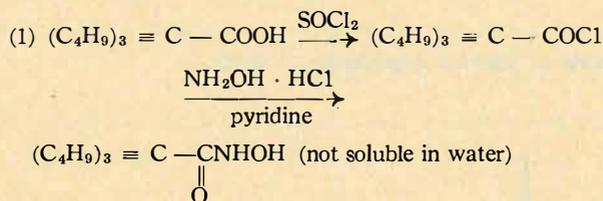
FIGURE 5. Extraction of different ions with TBAH 0.05 M in TCE.

be attributed to the steric hindrance of the aliphatic structure of some compounds, and to their very low solubility in water that does not permit a fast iron transfer between the organic and aqueous phase. The status of the ion in the aqueous phase may contribute also to the different extraction kinetics.

This is evident in Figure 9 where, for two different hydroxamic acids, the extraction kinetics with regard to Pu, Fe and Zr has been examined. The results illustrated in Figure 9 indicated the possibility of a selective separation with hydroxamic acids, based on the different extraction kinetics.

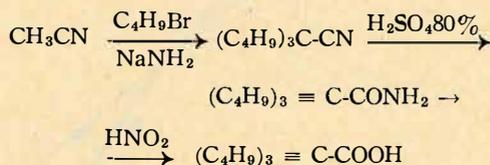
Experimental

Hydroxamic acids have been prepared from the corresponding carboxylic derivative according to their solubility in non-polar solvents or in water.



The preparation of these hindered carboxylic acids requires two particular preparative procedures:

(a) the alkylation of a nitrile and its hydrolysis^(7,8),



(b) the alkylation of an ester and its saponification^(8,9):



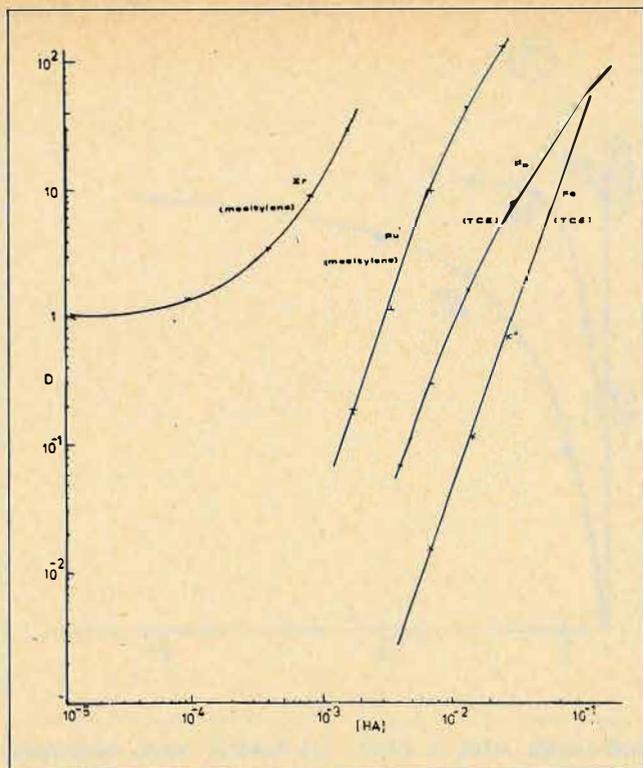
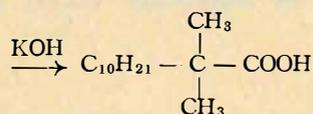


FIGURE 6. Distribution of Pu(IV), Fe(III), Zr(IV) as a function of the hydroxamic acid concentration; HNO_3 1M.



Comparative Tests

The *potentiometric titrations* of hydroxamic acids have been performed with an automatic recording titrator using the following conditions:

Titrant: $(\text{C}_4\text{H}_9)_4\text{N}^+ \text{OH}^-$ 0.1 M in isopropyl alcohol-benzene 1:1,

Solvent: 150 ml of pyridine with 5% of saturated KCl in methanol,

Electrodes: (1) a calomel electrode with a saturated solution of KCl in methanol; (2) a glass electrode conditioned for several hours in pyridine.

Sample: about a milliequivalent.

Delivery rate: 1 ml/min with vigorous stirring.

Colorimetric test: the well known color reaction which takes place between iron and the hydroxamic function in acidic medium has been adopted; for the iron solution 10g of $\text{Fe}(\text{ClO}_4)_3 \cdot 9 \text{H}_2\text{O}$ have been dissolved in 35% ethyl alcohol into a 1 l volumetric flask, cautiously adding 250 ml of 70% perchloric acid and finally diluting with ethyl alcohol.

Procedure: a carefully measured volume of a hydroxamic acid solution (1-10 mmol) was introduced into a 25 ml volumetric flask. Five ml of the iron perchlorate alcoholic solution was added and diluted to 25 ml with ethyl alcohol. The absorbance was measured at 520μ against a blank. The concentration of the hydroxamic acid may be deduced from a standard calibration curve obtained with a pure sample of tri-methyl aceto hydroxamic acid. For the *solubility test*, saturated solutions of hydroxamic acids in different solvents were shaken in a thermostat at 26°C for two hours in glass tubes. After centrifugation, the amount of the hydroxamic acid was determined by iron colorimetry.

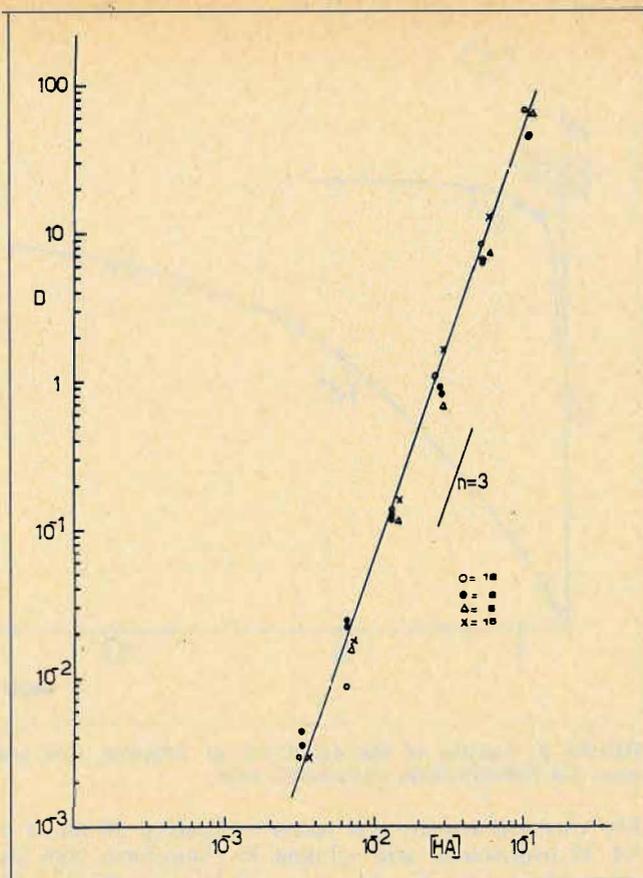


FIGURE 7. Distribution of Fe(III) as a function of the hydroxamic acid concentration; HNO_3 1M; solvent trichloroethane.

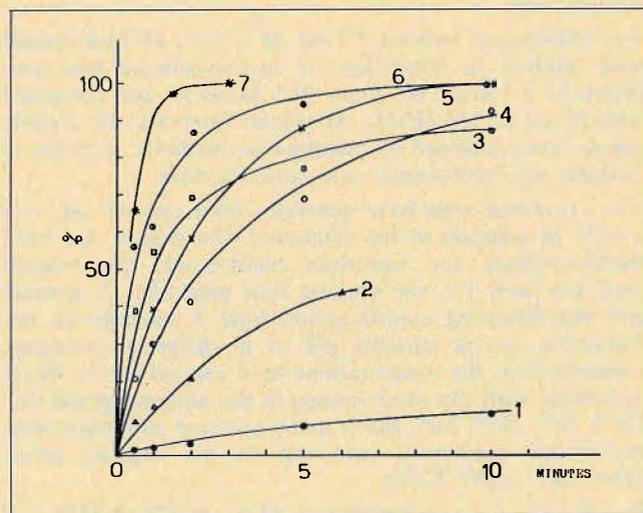


FIGURE 8. Effect of the structure of hydroxamic acids on the kinetics of extraction of Fe(III). Hydrox.ac. 0.1M; HNO_3 2M; solvent CHCl_3 .

The thermal stability was tested as follows: 250 μ l of a 0.1 M solution of hydroxamic acid in chloroform was introduced in ten 25 ml volumetric flasks. After evaporation under vacuum of the chloroform, the flasks were thermostated at 80°C . At regular intervals the remaining hydroxamic acid was determined by iron colorimetry in order to assess the variation of hydroxamic acid concentration as a function of the contact time.

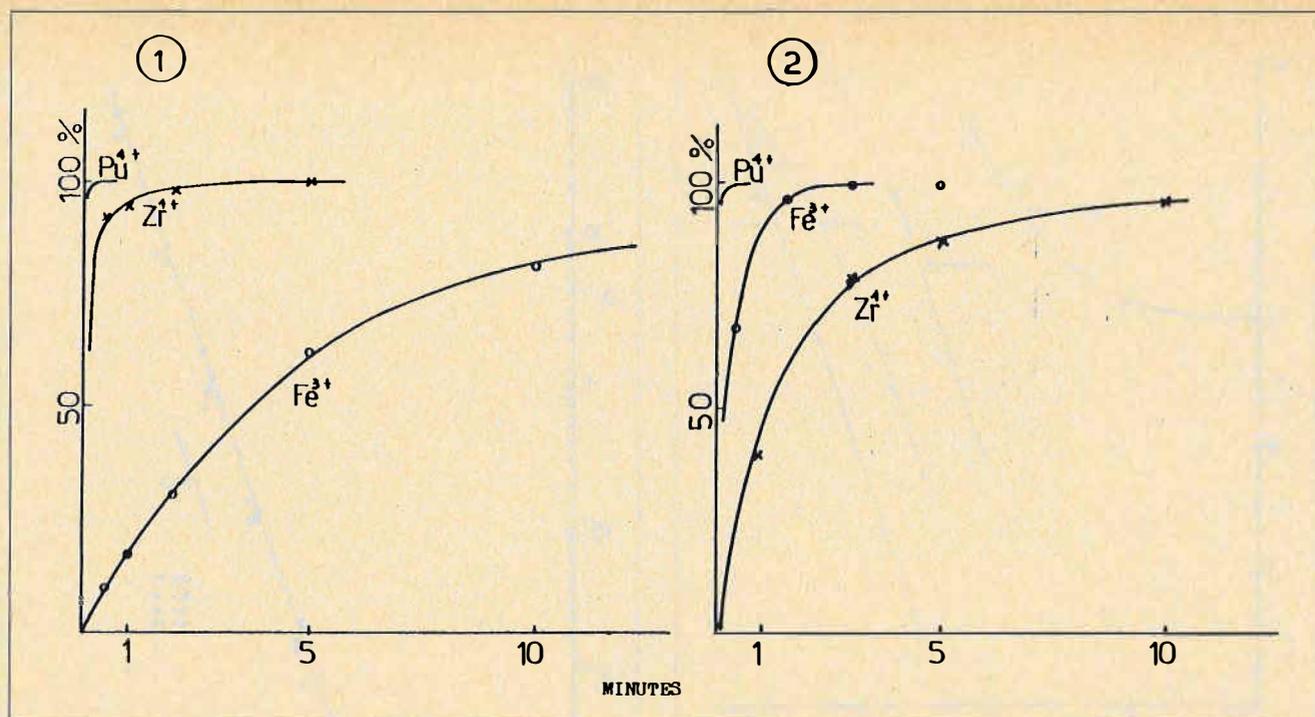


FIGURE 9. Kinetics of the extraction of different ions with hydroxamic acids in CHCl₃. (1) Triethyl octano hydroxamic acid; (2) Tributyl aceto hydroxamic acid.

The chemical stability was tested by shaking 20 ml of a 0.1 M hydroxamic acid solution in chloroform with an equal volume of 3 M nitric acid or 5 M hydrochloric acid in glass tubes; in some experiments with nitric acid hydrazine nitrate (0.02 molar) was also present. At regular intervals aliquots of the organic phases were submitted to colorimetric analysis in order to assess the variation of hydroxamic acid concentration as a function of the contact time.

For radiolytical stability 50 ml of a 0.05 M hydroxamic acid solution in mesitylene or trichloroethane was irradiated in a Cobalt 60 bomb (0.5 Mrad/h) and contacted with 50 ml of 1M HNO₃. At regular intervals, the organic phases were analyzed by colorimetric methods, in order to evaluate the hydroxamic acid concentration.

The extraction tests have generally been carried out with a 0.05 M solution of the extractant; the diluent has been trichloroethane (or sometime mesitylene); the volume ratio has been 1:1, the shaking time generally 15 seconds and the following centrifugation time 5 seconds. In the extraction test at variable pH or at different extractant concentration, the equilibrations were carried out by direct extraction with the trace isotope in the aqueous phase (for Ce¹⁴⁴, Zr⁹⁵, Nb⁹⁵, Fe⁵⁹, Mo⁹⁹) or by reversed extraction with the tracer previously extracted in the organic phase (Th²³⁴, U²³³, Pu²³⁹, Co⁶⁰).

For the kinetic tests Fe(NO₃)₃·9 H₂O, ZrOCl₂·8 H₂O and Pu(NO₃)₄ have been utilized. In five 25 ml test tubes, 10 ml of a 0.1M hydroxamic acid-chloroform solution and 10 ml of 2M nitric acid with 0.25 ml of a 0.01 M aqueous solution of the examined have been shaken for different

times. The concentration of the metal in organic phase has been determined by colorimetry (Fe,Zr) or by α counting (Pu).

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DISCUSSION

K.M. Lewis: What is the effect on the extraction of the various metals when using N-substituted hydroxamic acids? Can you comment on the extractability of chromium and tungsten by the tributyl compound? Do the long-chain derivatives foam in aqueous solution?

G. Gasparini: The effect of the substituted hydroxamic acids may be that the kinetics is less quick. We have not studied tungsten. For the chromium, we do not have positive results because we have not had good reproductivity. No.

Neo-tridecano-hydroxamic Acid as an Extractant of Long-lived Actinides from Purex-type HAW Raffinates

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ABSTRACT

The chemical separation of long-lived actinides from high activity waste (HAW) raffinates originated by the reprocessing of spent fuels could reduce the long-term waste hazard to an acceptable level after a cooling time of about 1000 years, so that problems posed by long-term waste storage can be simplified.

Solvent extraction is one of the actinide separation methods experimentally investigated at J.R.C. laboratories of Ispra Establishment for waste-partitioning purposes. A neo-tridecano hydroxamic acid, patented in 1971 by the CNEN's laboratories of Casaccia (ITALY) and named HX-70, has been tested as an extractant because of its high extractive capacity for Pu, Np, Zr and Nb in highly acidic medium. This paper describes the experimental work performed in order to investigate whether such extractant can be usefully utilized for removing higher valent actinides along with certain fission and corrosion products from acidic HAW raffinates, as well as trivalent actinides from low-acidity solutions obtained by the HAW denitration. Simulated HAW solutions, simulated irradiation conditions and batch-extraction techniques were employed. Results and preliminary conclusions are reported.

Introduction

THE CHEMICAL SEPARATION OF LONG-LIVED ACTINIDES from high-activity waste raffinates, produced by the reprocessing of spent fuels and their subsequent nuclear transmutation, has been proposed as an advanced waste management alternative to reduce to an acceptable level the potential long-term hazard of such wastes, after a cooling time of 1000 years. Many problems posed by the long-term waste storage would be thus simplified.

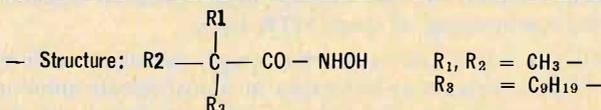
The chemical separation of actinides from liquid wastes is one of the objectives of the "Radioactive Waste Management" Pluriannual Programme of Ispra Joint Research Centre⁽¹⁾. Research activities have been oriented towards highly radioactive waste raffinates (HAW) generated by the reprocessing of LWR spent fuels (more exactly by the 1st extraction cycle of the PUREX Process) and towards partitioning processes operating under low-acidity process conditions⁽¹⁾.

The original idea of investigating the application of the neo-tridecano-hydroxamic acid (HX-70) for partitioning purposes started from the following considerations:

1. The removal of trivalent actinides from HAW raffinates based on the current separation methods (solvent extraction or precipitation) requires the preparation of a low-acidity feed, hence the lowering of the nitric acid content of HAW raffinates.

TABLE 1. Properties of the Neo-Tridecano-Hydroxamic Acid (HX-70)

HX-70 (M./litre)	n-Heptane (D _a ^o)	xylene (D _a ^o)	chloroform (D _a ^o)
0.10	68	220	858
0.25	130	289	985
0.50	218	439	1296



- Molecular Weight (Mean value) = 233 ± 6
- Solubility (H₂O) = 100 ppm
- Ionization constant at 25°C : pK_a = 10
- Distribution coefficient (D_a^o) of neo-tridecano-hydroxamic acid (HX-70) between organic diluents and aqueous solutions as function of total concentration of the hydroxamic acid; pH = 0,1; ionic strength = 0,1; t = 25°C (from ref. 6).

2. The desired pH value may be attained by different treatments of the HAW solution; whatever HAW treatment may be applied, the formation of undesired precipitates cannot be avoided.

It must be pointed out that such precipitates, produced by hydrolysis of certain fission and corrosion products, may irreversibly adsorb or co-precipitate some of the actinides present, so that the non-extractable actinide fraction eventually present in the HAW solution will be increased. Therefore, in order to prevent the formation of α-bearing precipitates during the denitration process, a previous selective extraction of higher-valent actinides (U, Pu, Np) along with some easily hydrolysable metal-ions (Mo, Zr, Fe) could be usefully carried out before lowering the acidity of the HAW solution.

The experimental studies performed on HX-70 were therefore oriented to investigate to what extent such an extractant can be successfully applied to attain this target. The possibility of a further application, namely the extraction of trivalent actinides from low-acidity HAW solution, was also investigated.

The HX-70 Extractant

In 1908 A. Werner⁽²⁾ pointed out the potential ability of the hydroxamic function to give very stable complexes with several metals. The development of the analytical applications (colorimetry, gravimetry and solvent extraction) of hydroxamic acids confirms and emphasizes this ability.

A vast literature has been published on this topic and has been extensively surveyed in a previous study⁽³⁾. Experimental investigations have been started and are being performed at CNEN's laboratories of Casaccia (Roma) in order to characterize and synthesize the most appropriate

alkyl-hydroxamic acids which could be advantageously used as selective extractants in the nuclear separation technology^(3,6). Starting from a neo-tridecanoic acid (a mixture of branched-chain isomer tridecanoic acids produced by Enjay Chemical Company), the corresponding neo-tridecano-hydroxamic acid, named HX-70, (see Table 1) was synthesized⁽⁶⁾ in 1970 and patented in 1971⁽⁷⁾. The HX-70 extractant is therefore a mixture of branched-chain isomer neo-hydroxamic acids of 13 carbon atoms, rather a pure isomer.

This extractant was regarded as a possible candidate for waste partitioning due to its considerable complexing power and rapid extraction kinetics for Pu(IV) and Np(IV) in highly acidic medium (see Tables 2 & 3); HX-70 was in fact successfully utilized at EUREX reprocessing pilot plant of CNEN (Saluggia — Italy) to carry out a thorough decontamination of the uranyl-nitrate product obtained by the reprocessing of spent MTR fuels.

After a single batch-extraction stage, the alpha activity of actinides present as impurities in uranyl-nitrate solution was lowered below the value needed to carry out the subsequent uranium enrichment process by gaseous diffusion⁽⁸⁾.

Experimental

Materials

The HX-70 extractant is a highly viscous yellow oil which tends to transform slowly into a white waxy solid.

TABLE 2. Distribution Coefficients of Some Metal-ions Obtained by 2.5% HX-70 in Aromatic Hydrocarbon Diluent.

Molar ratio (HX-70/metal) 10. Room temperature 9.						
Metal-ion	Distribution coefficient (M. org./M. aq.) at equilibrium pH					
	0	2	4	6	8	10
Am ³⁺	<10 ⁻⁴	<10 ⁻⁴	2	>10 ⁻³	—	→
Cu ²⁺	<10 ⁻²	15	>10 ³	—	—	→
Fe ³⁺	10 ³	>10 ⁻⁴	—	—	—	→
Nb ⁵⁺	>10 ⁴	—	—	—	—	→
Np ⁴⁺	>10 ³	—	—	—	—	→
Ni ²⁺	>10 ⁻³	<10 ⁻²	<1	>10 ²	—	→
Pb ²⁺	>10 ⁻⁴	<10 ⁻³	0.3	>10 ²	—	→
Pu ⁴⁺	>10 ³	>10 ⁴	—	—	—	→
Ce ³⁺ +Eu ³⁺	>10 ⁻⁴	<10 ⁻⁴	2	>10 ³	—	→
Sr ²⁺	>10 ⁻⁴	<10 ⁻⁴	<10 ⁻⁴	<10 ⁻⁴	3·10 ⁻²	40
Th ⁴⁺	0.3	>10 ³	—	—	—	→
UO ₂ ²⁺	>10 ⁻³	1	>10 ³	—	—	→
Zr ⁴⁺	>10 ⁴	—	—	—	—	→
Y ³⁺	<10 ⁻⁴	<10 ⁻⁴	1	>10 ³	—	→

Its solubility in organic diluents is practically complete and the solubility in water is about 10⁻³ M/l⁽⁶⁾. Its chemical stability in mineral acids, even if concentrated, is high. These characteristics are due to the neostructure of the alkyl radical^(6,9). HX-70 is not commercially available for the moment. However it is envisaged by a collaboration contract between the Commission of European Communities and CNEN, that the latter will organize, if needed, through a chemical industry the production of HX-70 or of any other hydroxamic acid on a commercial scale. The product employed in this study was prepared and supplied by the CNEN's laboratories of Casaccia, Rome (Italy); as before mentioned it is a mixture of isomer neo-tridecano-hydroxamic acids with a pure isomer content of about 55%.

Since high loading of metal ions is easily obtained, due to the solubility of HX-70 metal complexes in aromatic hydrocarbons, mesitylene was selected as a diluent for HX-70. A synthetic waste solution, simulating a Purex HAW raffinate was prepared and used for solvent extraction studies. The fission product concentration (Table 4) was fixed according to the composition of a HAW solution generated by the reprocessing of 150-day-cooled LWR fuel elements (UO₂ with 3.3% of ²³⁵U initial enrichment), irradiated at 33,000 MWD/ton and dissolved up to a concentration of 250 grams of fuel per litre (4,000 litres/ton)⁽¹⁰⁾. The chemical composition of the materials other than fission products (Table 5) was fixed assuming that the fuel cladding was not dissolved with the fuel and the waste generated by the first TBP cycle was combined with the wastes of Pu purification cycles⁽¹¹⁾ containing sulphate ions. The concentration of the actinides (U, Pu, Np, Am and Cm), assumed to be present in the simulated HAW raffinates (Table 6), was fixed according to the actinide masses calculated to be present in spent LWR fuels⁽¹⁰⁾ before the reprocessing and to actinide recoveries of 99.5% for uranium and plutonium and of 90% for neptunium. This means that actinide residues corresponding to 10% of neptunium and to 0.5% of uranium and plutonium will be present in HAW raffinates along with the total amount of transplutonium elements produced by nuclear transmutation.

The simulated HAW solution was traced with ⁵⁹Fe, ⁹⁹Mo, ⁹⁵Zr-Nb solutions supplied by the Amersham Radiochemical Centre and with aliquots of a three years' old fission product mixture. This latter solution was also used to add the desired amount of plutonium to the simulated HAW solution. Required amounts of neptunium and americium were added using ²³⁷Np and ²⁴¹Am solutions also supplied by the Amersham Radiochemical Centre. All other chemicals employed were analytical-grade products and were used without further purification.

TABLE 3. Metal-ions Extracted by 2.5-20% HX-70 in Hydrocarbon Diluent from Different Acidic Aqueous Media

Room temperature (9)			
Metal-ions extracted from a highly concentrated acidic medium (1M-10M)	Metal-ions extracted from an acidic medium (0 pH 3)	Metal-ions extracted from a slightly acidic medium (3 pH 7)	Metal-ions extracted from an alkaline medium (7 pH 10)
Fe ³⁺	all the metals of the left column and Cu ²⁺ Th ⁴⁺ UO ₂ ²⁺	all the metals of the left columns and Am ³⁺ rare earths ³⁺ Cr ³⁺ Co ²⁺ Pb ²⁺ Ni ²⁺ Y ³⁺	all the metals of the left columns and Ca ²⁺ Sr ²⁺ Ba ²⁺ Ra ²⁺ Mg ²⁺
Hf ⁴⁺			
Np ⁴⁺			
Nb ⁵⁺			
Pu ⁴⁺			
Po ⁴⁺			
Pa ⁵⁺			
Ta ⁵⁺			
Ti ⁴⁺			
V ⁵⁺			
Zr ⁴⁺			

TABLE 4. Total Masses of Significant Fission Product Elements Present in the Simulated HAW Raffinates.

Calculated from reference⁽¹⁰⁾ assuming a value of 4000 l/ton. U; burn-up = 33 000 MWD/ton.; initial ²³⁵U enrichment = 3.3%

Elem.	Decay time = 150 days		Decay time = 5 years	
	g/ton. × 10 ²	g/l	g/ton. × 10 ²	g/l
Sr	8.96	0.224	8.35	0.208
Y	4.68	0.117	4.65	0.116
Zr	36.6	0.915	37.1	0.927
Nb	0.132	0.003	—	—
Mo	34.4	0.860	34.6	0.805
Ru	22.6	0.565	21.4	0.535
Rh	3.89	0.097	3.9	0.097
Pd	12.9	0.322	14.1	0.352
Ag	0.6	0.015	0.6	0.015
Te	5.65	0.141	5.69	0.142
Cs	27.2	0.680	24.7	0.617
Ba	13.9	0.347	15.48	0.387
La	12.7	0.317	12.7	0.317
Ce	28.8	0.720	26.4	0.660
Pr	12.0	0.300	12.0	0.300
Nd	39.1	0.974	40.76	1.019
Sm	8.08	0.202	8.8	0.22
Eu	1.82	0.045	1.71	0.04

Procedures, Apparatus and Measurement Techniques

Extraction and back-extraction tests were carried out in batch using an organic to aqueous volume ratio equal to 1. Extraction and back-extraction yields of iron, molybdenum, zirconium, niobium and of other fission products have been measured by γ -spectrometry in two separate steps in order to avoid interference between the 740 keV γ -photopeak of ⁹⁹Mo and the 724 keV γ -photopeak of ⁹⁵Zr. In the first step only ⁹⁹Mo and ⁵⁹Fe tracers were added to the simulated HAW solution; in the second one the other fission product tracers were added. A Ge(Li) detector, coaxial type, 20 cm³ volume, was employed for γ -spectrometry measurements.

Plutonium and neptunium extraction yields were measured by α -spectrometry employing a silicon surface barrier detector with a 150 mm² active area. The alpha-sources were prepared by evaporation of suitable aliquots of organic and aqueous phase on tantalum discs placed on a heating block. In the case of sources prepared from aqueous solutions, a technique based on the method proposed by H.W. Kirby and J.J. Dauby was applied⁽¹²⁾. In the case of sources from organic solutions the tantalum discs were cooled at the centre by an air flow.

The concentration of HX-70 in the organic solution of mesitylene was measured by colorimetry utilizing a Beckman DK2 A ratio spectrophotometer⁽¹³⁾. Irradiation tests of the HX-70 extractant were carried out using as an irradiation vessel an open 26 cc glass cell and as a radiation source, a Van de Graaf electron accelerator. Ceric sulphate dosimetry techniques were used^(14,15) to calibrate the dose rates of the electron source as well as the type of glass cells used for irradiation tests. Operating conditions such as an electron energy of 1.5 MeV and current intensity values producing dose rates of 1.25 or 2.5 Mrads per hour were selected.

Irradiation tests were carried out both on the solvent alone and on the solvent in intimate contact (by stirring) with the simulated and suitably traced HAW solution. In both cases the stirring was performed by a magnetic stirrer.

Radiations effects were determined by direct as well as by indirect measurements. When only the solvent was irradiated, the change of the HX-70 concentration was measured directly by spectrophotometry, whereas, when

TABLE 5. Chemical composition of materials other than fission products present in the simulated HAW raffinates.

Calculated from reference⁽¹¹⁾ assuming a value of 4000 l/ton. U

Element	Moles/l	g/l
H	4	—
Fe	0.042	2.35
Cr	0.0023	0.12
Ni	0.001	0.059
Al	0.0001	0.0027
Na	0.164	3.77
NO ₃ ⁻	4.136	—
SO ₄ ²⁻	0.082	—

TABLE 6. Masses of Important Actinides Calculated to be Present in the Spent LWR-Fuel⁽¹⁰⁾ and Assumed to be Present in Simulated HAW Raffinates.

Burn up = 33 000, MWD/ton.; init. ²³⁵U enrich. = 3.3%, decay times = 150 days

Isotopes	Half-life	g/ton ⁽¹⁾	Total Elem.	g/ton ⁽¹⁾	g/l ⁽¹⁾
²³⁴ U	2.47 × 10 ⁵ y	2.42	U	9.55 × 10 ⁵	1.2
²³⁵ U	7.1 × 10 ⁸ y	7.96 × 10 ³			
²³⁸ U	2.39 × 10 ⁷ y	4.08 × 10 ³			
²³⁸ U	4.51 × 10 ⁹ y	9.43 × 10 ⁶			
²³⁷ Np	2.2 × 10 ⁶ y	7.62 × 10 ²	Np	7.62 × 10 ²	2 × 10 ⁻²
²³⁸ Pu	86.4 y	1.66 × 10 ²	Pu	9.08 × 10 ³	1.13 × 10 ⁻²
²³⁹ Pu	2.4 × 10 ⁴ y	5.38 × 10 ³			
²⁴⁰ Pu	4.6 × 10 ³ y	2.12 × 10 ³			
²⁴¹ Pu	13.2 y	1.01 × 10 ³			
²⁴² Pu	3.8 × 10 ⁶ y	3.49 × 10 ²			
²⁴¹ Am	458 y	6.18 × 10 ¹	Am	1.53 × 10 ²	3.8 × 10 ⁻²
²⁴³ Am	7950 y	9.04 × 10 ¹			
²⁴² Cm	163 d	4.52	Cm	3.53 × 10 ¹	9 × 10 ⁻³
²⁴⁴ Cm	19 y	3.07 × 10 ¹			

(1) In a LWR spent fuel

(2) In the simulated HAW raffinates assuming:

- 4000 l/ton of uranium,
- 99.5% of uranium recovery,
- 99.5% of plutonium recovery,
- 90.0% of neptunium recovery.

the simulated and traced HAW solution was also present, the solvent degradation was indirectly detected by gamma-spectrometry. In fact, during the irradiation tests, a decrease of the initially extracted percentage of certain metal-ions, traced with certain gamma-emitter isotopes (⁵⁹Fe, ⁹⁵Zr-Nb), was observed; the behaviour of these metal-ions was thus taken as an indication of the radiation damage on the loaded solvent.

Laboratory Experiments on HX-70 Chemical Stability

The chemical degradation of HX-70, observed when the extractant is contacted with nitric acid, is principally due to the nitrous acid normally present in nitric acid solutions. Its concentration level depends in general on the concentration of nitric acid; in the case of HAW raffinate it will also depend on the radioactivity of the solution. The behaviour of HX-70 in the presence of a simulated HAW solution (4.5 M HNO₃) was investigated in order to determine to what extent its chemical stability can be improved by adding an appropriate anti-nitrite agent. To this purpose a comparative study was carried out on the use of urea and hydrazine. The effectiveness of urea and hydrazine as anti-nitrite agents was determined

by contacting an organic solution of 0.1M HX-70 in mesitylene with equal volumes of the simulated and traced HAW solution to which 0.15 moles per litre of each single anti-nitrite agent was added. To study the effect of the anti-nitrite agents on the extractant stability, the decrease of the initial niobium, zirconium, iron and cerium extraction was determined by gamma spectrometry measurements on tracer isotopes (^{85}Zr -Nb, ^{59}Fe , ^{144}Ce) appropriately added to the simulated waste solution.

It was experimentally observed that hydrazine shows a more evident antagonistic effect towards nitrous acid than urea: in fact within a maximum stirring time of 70 hours (about 3 days) the initial niobium, zirconium, iron and

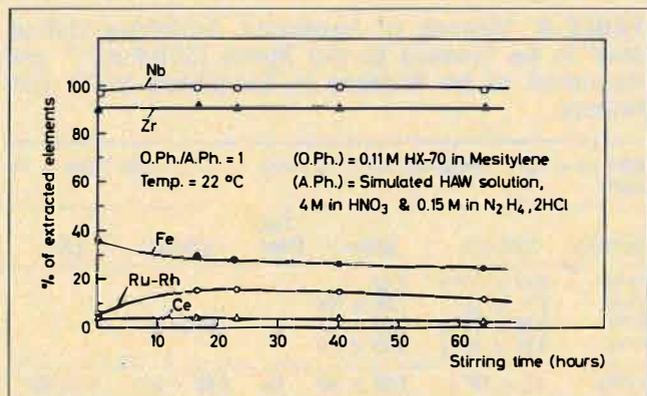


FIGURE 1. Chemical stability of HX-70 in the system HX-70-mesitylene-simulated HAW solution — hydrazine. % extracted elements vs. stirring time.

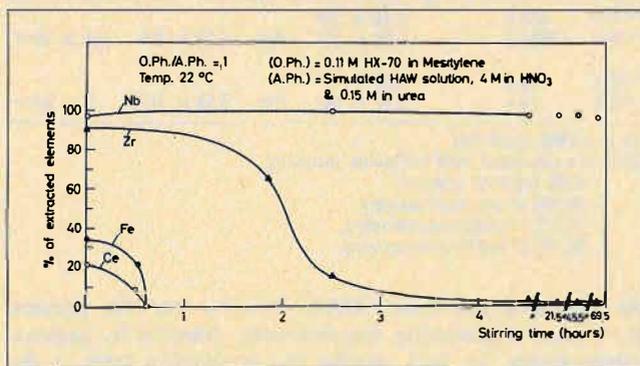


FIGURE 2. Chemical stability of HX-70 in the system HX-70-mesitylene — simulated HAW solution — urea. % extracted elements vs. stirring time.

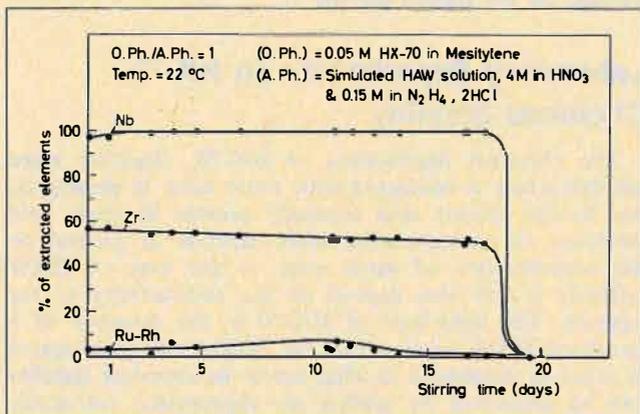


FIGURE 3. Chemical stability of HX-70 In the system HX-70 — mesitylene — simulated HAW solution — hydrazine. % extracted elements vs. stirring time.

cerium extractions remained unchanged (Figure 1) whereas in the case of urea the extraction of zirconium, iron and cerium begins to decrease after only a few hours (Figure 2).

The influence of the hydrazine as well as of the HX-70 concentration on the extraction capacity of the solvent, in intimate contact with a simulated HAW solution (4M in nitric acid), can be easily determined by comparing the curves reported in Figures 3 and 4 and in Figures 4 and 5 respectively.

Using hydrazine and HX-70 concentration of the order of 0.15 and 0.05 moles/litre respectively (Figure 3) the initial niobium extraction did not change over a stirring time of about 17 days. The decrease of the initial zirconium extraction, although not significant, cannot be in any way attributed to a solvent degradation effect.

When the HX-70 concentration was kept constant (0.05M) and the hydrazine concentration was lowered (0.05M, Figure 4), the initial niobium extraction capacity remained constant within a stirring time of about two days, which is considerably smaller than the previous one. Also in the case the decrease of the initial zirconium extraction is of the order of a few percent.

When the HX-70 concentration was increased by a factor of 5, (0.25M) and the hydrazine concentration was kept constant (0.05M, Fig. 5), the niobium extraction remained constant within a stirring time of about 300 hours (12.5 days). Within the same range of time, zirconium and iron extractions decreased from 95 to 65% and from 90 to 75% respectively, whereas the ruthenium-rhodium extraction increased from 5 to 68%.

Nevertheless it is difficult to demonstrate whether the decrease of the zirconium and iron extractions may be entirely ascribed to the chemical degradation of the extractant. In fact, as shown in Figure 5, the increase of ruthenium-rhodium extraction might also explain the observed decrease of the zirconium and iron extraction, provided that a metal extraction mechanism is able to confirm this hypothesis. The extraction capacity of HX-70 decreases suddenly and very rapidly at a certain moment as can be seen from Figs. 3, 4 and 5; this probably occurs when the hydrazine is completely oxidized and the hydroxamic function is thus rapidly destroyed by nitrous acid which is regenerated in a nitric acid solution probably by an autocatalytic effect.

Behaviour under Radiation

As it is possible that the degradation of HX-70 may occur as a consequence of a simultaneous effect of radiation and of nitrous acid, the behaviour of HX-70 under

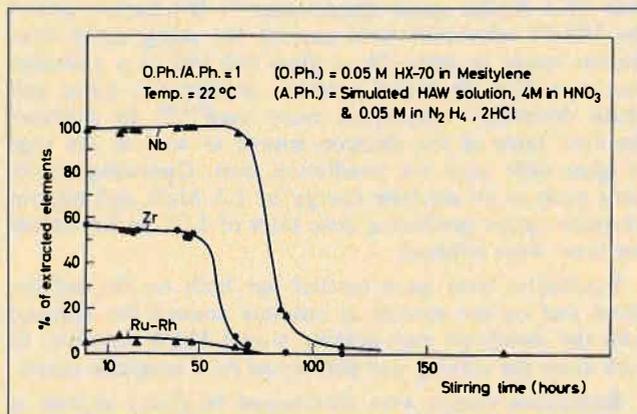


FIGURE 4. Chemical stability of HX-70 in the system HX-70 — mesitylene — simulated HAW solution — hydrazine. % extracted elements vs. stirring time.

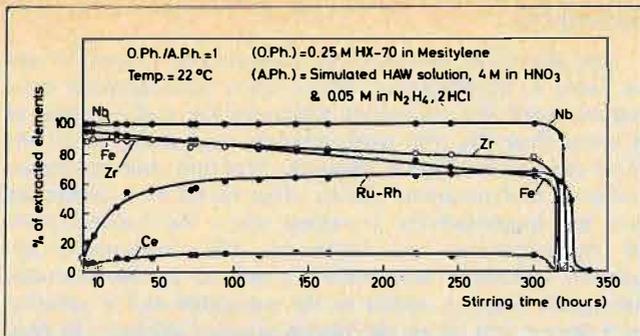


FIGURE 5. Chemical stability of HX-70 in the system HX-70 — mesitylene — simulated HAW solution — hydrazine. % extracted elements vs. stirring time.

radiation was examined after the results on the chemical stability became available.

Theoretical dose rate values of about 0.2, 1 and 2 Mrads per hour were calculated for HAW raffinates assuming 150 days, 1 year and 5 years as minimum, intermediate and maximum waste cooling time. Dose rate calculations were performed using the published data⁽¹⁰⁾ on thermal powers dissipated by fission products and actinides in the HAW raffinate, generated from reprocessed LWR fuels.

In order to reduce the time required by each irradiation test, a higher dose rate value (2.5 Mrads/hour) was used in most of the experiments. Figures 6 and 7 show the stability curves of HX-70 as a function of the irradiation time and HX-70 concentration, in the absence and presence respectively of 4M HNO₃ solution. The variation of the HX-70 concentration was measured in both cases by direct spectrophotometry of irradiated solvent.

It can be seen from Figures 6 and 7 that radiation damage on the HX-70 appears to be more important when the extractant is irradiated in intimate contact with a 4M nitric acid solution. Although in the presence of hydrazine (0.15 M/l), the slopes of the curves obtained in the presence of a nitric acid solution are in fact about a factor 4 greater than those obtained in the absence of an acidic aqueous phase.

The simultaneous effect of radiations and of nitrous acid would give a possible explanation of this increasing of the degradation rate. The increase, however, seems to be minor when a simulated HAW solution is used. In Figure 8, where the stability curves of zirconium, niobium and iron-organo-complexes are reported, it can be seen that the mean slope of the curve, representing the decrease of the iron extraction during the irradiation, is lower than the value reported in Figure 7 for the curve relating to 0.25M HX-70. It must be pointed out that although being two-fold higher than the amount previously used (Figure 7), the indicated overall hydrazine concentration (0.3 M/l, Figure 8) employed in this irradiation test was practically reached by adding twice (at beginning and after 3 hours of irradiation) the amount of hydrazine needed to attain a 0.15M solution. The improved stability of the loaded HX-70 could be explained probably by the substitution of the hydroxamic function as well as by the minor fraction of HX-70 present, at equilibrium, in the aqueous phase and progressively destroyed by nitrous acid.

From the results reported in Figure 8, the stability of metal-organo-complexes does not seem to be greatly affected by the radiations up to an exposure of about 10 Wh./litre. At radiation exposures up to 15-20 Wh./litre only about a 10% decrease of the extracted iron was measured, the extraction of other metal ions remained unchanged.

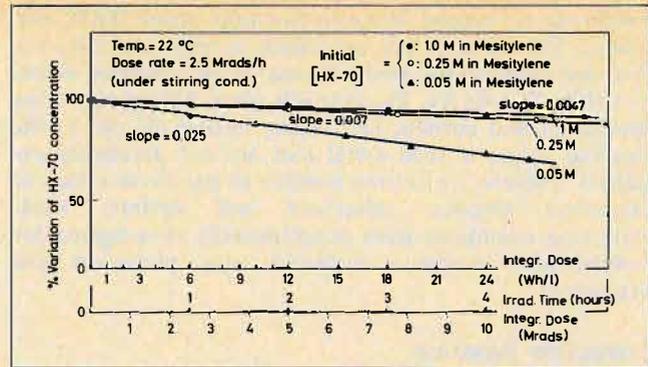


FIGURE 6. Radiolytic behaviour of HX-70 in the system HX-70 — mesitylene. % variation of the HX-70 concentration as a function of the irradiation time and the initial HX-70 concentration.

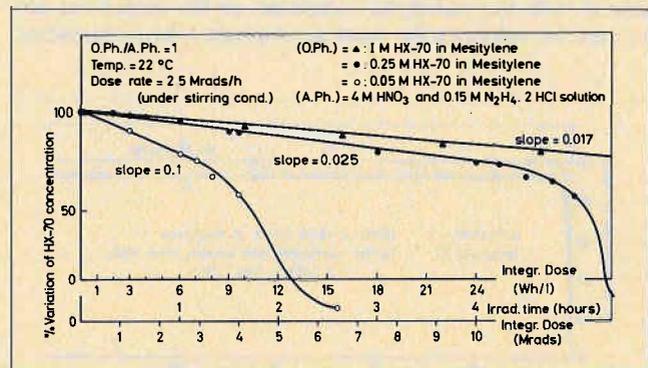


FIGURE 7. Radiolytic behaviour of HX-70 in the system HX-70 — mesitylene — HNO₃ — hydrazine. % variation of the HX-70 concentration as a function of the irradiation time and the initial HX-70 concentration.

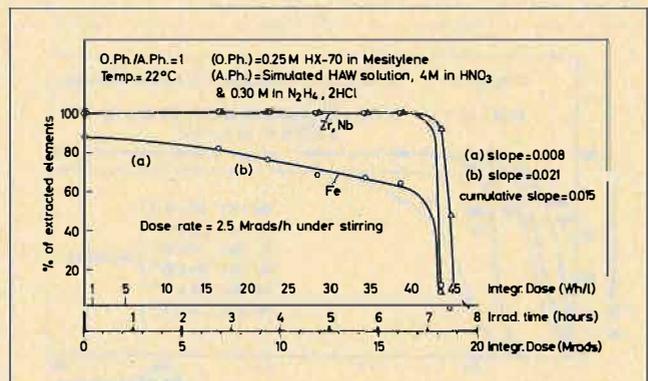


FIGURE 8. Radiolytic behaviour of HX-70 in the system HX-70 — mesitylene — simulated HAW solution — hydrazine. % extracted elements vs. radiation time.

Extraction of Fission Products and Higher-valent Actinides

The neo-tridecano-hydroxamic acid (HX-70) was experimentally investigated to establish whether its extractive properties could be usefully employed in a waste partitioning process. Due to its high complexing power for metal ions, such as zirconium, niobium, iron, plutonium and neptunium, in high acidic medium⁽⁹⁾, HX-70 appears to be a promising candidate for removing these metal ions from HAW raffinates up to the required level.

This type of separation is particularly useful when a solvent extraction process is performed under low-acidity

conditions to remove trivalent actinides from HAW raffinates. The need of this separation is emphasized by the fact that troublesome precipitations of hydrolysable metal-ions (Mo, Zr, Nb, Fe, Pu, Np) will occur before separating americium and curium, i.e., before raising the pH to the required value, if such metal ions are not previously extracted. Therefore a certain number of parameters such as extraction kinetics, selectivity and optimal back-extraction conditions were experimentally investigated for molybdenum, zirconium, niobium, iron, plutonium and neptunium.

Extraction Kinetics

The data concerning the extraction kinetic tests on Mo(VI), Zr(IV), Nb(V), Fe(III), Pu(IV) and Np(IV) reported in Figure 9 indicate that in about one minute the extraction of all the above-mentioned metal-ions reaches the equilibrium conditions. Extraction kinetic data inter-related with the radiolytic behaviour of the extractant can be used for selecting the most appropriate type of extractor.

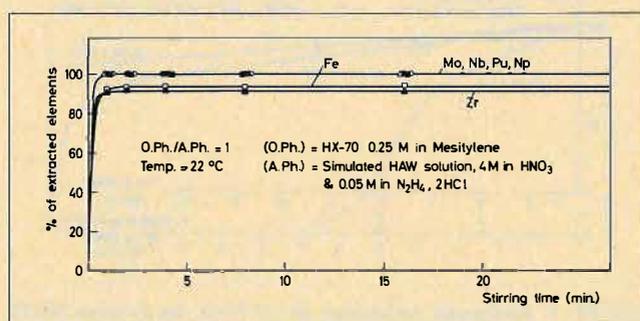


FIGURE 9. Extraction kinetics of Mo(VI), Nb(V), Zr(IV), Np(IV), Fe(III), Pu(IV) by HX-70. % extracted elements vs. stirring time.

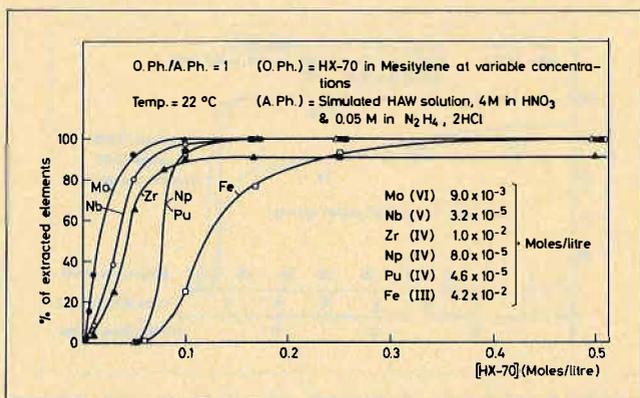


FIGURE 10. Extraction of Mo(VI), Nb(V), Zr(IV), Pu(IV), Np(IV), Fe(III) by HX-70. % extracted elements vs. HX-70 concentration.

TABLE 7. Extraction of Mo, Zr, Nb, Pu, Np and Fe ions. From a Simulated HAW Solution (4M HNO₃, 0.05M hydrazine hydrochloride) as a Function of the Concentration of HX-70 in Mesitylene.

O:Ph/A.Ph = 1, room temperature.

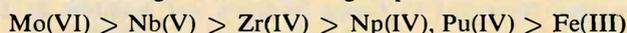
Symbol	Element Conc. (M./l)	% Extraction HX-70 in mesitylene (M./l.)						
		0.01	0.03	0.05	0.1	0.17	0.25	0.5
Mo(VI)	9.0×10^{-3}	33	—	92	99	~ 100	~ 100	~ 100
Nb(V)	3.2×10^{-5}	18	38	80	97	~ 100	~ 100	~ 100
Zr(IV)	1.0×10^{-2}	7	24	65	90	92	92	92
Pu(IV)	4.6×10^{-5}	—	—	1-2	94	~ 100	~ 100	~ 100
Np(IV)	8.0×10^{-5}	—	—	1-2	93	~ 100	~ 100	~ 100
Fe(III)	4.2×10^{-2}	—	—	—	25	77	93	~ 100

Selectivity

The selectivity of HX-70 is illustrated in Figure 10 and in Table 7. Molybdenum, which has a concentration comparable with the zirconium concentration and a factor of 4 lower than the iron concentration, was found to be the most extractable fission product. Niobium and zirconium followed molybdenum. Unlike other metal-ions, zirconium was not quantitatively extracted when the concentration of the extractant was increased. This unexpected zirconium behaviour was probably due to an inextractable zirconium fraction added to the simulated HAW solution as a component of an old fission product mixture. In fact, when only pure ⁹⁵Zr tracer solution was added to simulate waste solution, a quantitative extraction was obtained.

When HX-70 concentrations higher than 0.05M were employed (Figure 10), neptunium, plutonium and iron were also extracted; for neptunium and plutonium however, HX-70 exhibits a selectivity higher than that for iron, in spite of the fact that the concentration of the latter is about a factor 10³ higher.

From the results obtained one can conclude, therefore, that the metal-ions considered above may form metal-organo-complexes with HX-70, the stabilities of which increase according to the following sequence:



If HAW raffinates, sufficiently cooled and reasonably free from non-radioactive chemicals, will be produced in the future, the previous separation of easily hydrolysable metal-ions from the HAW could in practice be limited to molybdenum, zirconium, neptunium and plutonium, since niobium and iron will be present in negligible and very low quantities, respectively.

Back-extraction of Metals-ions

Ammonium carbonate and oxalate solutions at different initial pH values were tested to strip molybdenum, zirconium, niobium, iron, plutonium and neptunium ions from HX-70. The results of stripping tests (expressed as percentage of the stripping metal-ion) are reported in Table 8 as a function of the different stripping conditions and HX-70 concentrations. The percentages of the metal-ions extracted by a previous extraction step are also indicated. Table 8 results indicate that zirconium, iron, plutonium and neptunium are almost quantitatively stripped from 0.25M HX-70 by a 0.4M ammonium oxalate solution at pH = 2.5.

A subsequent back-extraction step was carried out by contacting the loaded HX-70 organic solution with a 1M ammonium carbonate solution at pH = 8.8; 63% of the initially extracted molybdenum was stripped from 0.25M HX-70. Under the same conditions niobium appeared to be inextractable. Molybdenum and niobium stripping percentages increase to about 98% and 30% respectively if the concentration of HX-70 used to extract them is

TABLE 8. Back-extraction of Mo, Zr, Nb, Pu, Np and Fe ions from Loaded HX-70 by Different Stripping Solutions at Different pH Value.

O.Ph/A.Ph = 1, room temperature.

Element	HX-70 (M/l)	% Extr.	(NH ₄) ₂ C ₂ O ₄ , 0.4M pH = 2.5	% Back — Extraction (NH ₄) ₂ C ₂ O ₄ , 0.4 M pH = 4	(NH ₄) ₂ CO ₃ , 1 M pH = 8.8
Mo(IV)	0.01	33	27	43	98
	0.05	92	1.3	7	98
	0.25	99	1.0	5	63
Nb(V)	0.05	80	31	42	31
	0.25	~ 100	7	5	n.m.
Zr(IV)	0.05	65	~ 100	99	99
	0.25	92	94	58	n.m.
Pu(IV)	0.05	0	—	—	—
	0.25	~ 100	~ 100	n.m.	n.m.
Np(IV)	0.05	0	—	—	—
	0.25	~ 100	~ 100	n.m.	n.m.
Fe(III)	0.25	92	93	71	n.m.
	0.50	~ 100	81	72	n.m.

n.m. = Not measured

lowered to 0.05 M/l. However, niobium will not be a problem because its quantity in a sufficiently cooled waste solution is negligible. It must be mentioned that after the equilibrium back-extraction conditions were reached, a certain decrease of the initial pH of aqueous solutions used for stripping was observed; this was probably due to the presence in the loaded HX-70 of some nitric acid previously extracted along with metal-ions.

Extraction of Trivalent Actinides

From data in Table 2 and 3 we can see that americium ions begin to be extracted by 0.1M HX-70 in aromatic hydrocarbon diluent at an equilibrium pH value of 3 and that the maximum distribution coefficient is obtained at a pH value of 6. Similar extraction tests were performed on a nitric acid solution of ²⁴¹Am (27-30 micrograms per millilitre) adjusted at different pH values. Using a mesitylene solution 0.5M in HX-70, the formation of a persistent emulsion and a considerable increasing of the initial pH were observed at equilibrium. This latter observation must be taken as a further proof of the fact that nitric acid is also extracted by HX-70. Further experiments were performed by extracting americium from a simulated HAW solution at different pH values. To this purpose the HAW solution was previously conditioned by the following steps:

- (i) selective extraction of hydrolysable metal-ions (Mo, Zr, Nb, Fe) by 1M HX-70 in mesitylene,
- (ii) denitration by a concentrated solution of HCOOH up to a pH value of about 0.85,
- (iii) addition of an aliquot of ²⁴¹Am solution to obtain an americium concentration of about 30 mg/litre and subsequent acidity adjustment (performed separately on various fractions of the denitrated HAW solution) to obtain the desired pH value. Each aqueous fraction was contacted by stirring with an equal volume of 1M HX-70 in mesitylene. Before being stirred with the aqueous phase, each organic phase was pre-equilibrated with a nitrate solution having the same acidity as the HAW fraction to be extracted. Neither appreciable pH variation nor emulsion were thus observed. The results of these extraction tests are reported in Figure 11.

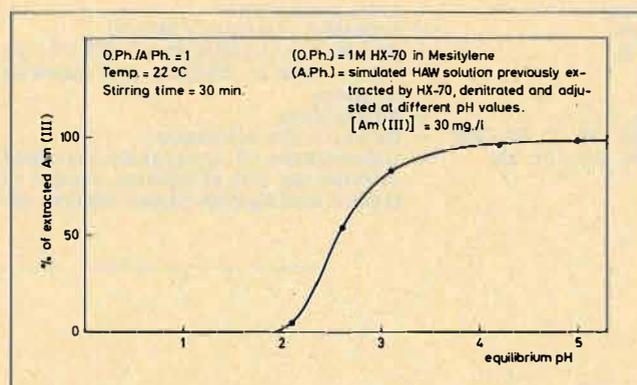


FIGURE 11. Extraction of Am(III) by HX-70 as a function of equilibrium pH.

Conclusions

The experimental results thus far obtained by using a simulated HAW solution show that:

- (i) The remarkable extractive properties (rapid extraction kinetics and high extraction capacity) of HX-70 for Pu(IV), Np(IV), Zr(IV) Nb(V) and Mo(VI) in highly acidic solutions have been experimentally confirmed using a simulated HAW solution.
- (ii) With the exception of niobium, all the metal-ions extracted by HX-70 under acidic conditions can be quantitatively stripped. For molybdenum however, the optimum back-extraction conditions are different from those required for other metal-ions.
- (iii) Although chemically degraded by nitrous acid, the chemical stability of HX-70 appears to be acceptable when a suitable anti-nitrite agent is needed.
- (iv) Although in general less resistant to radiations than other conventional organic solvents, the HX-70/mesitylene system does not seem to be greatly affected by the radiation up to an exposure of 15-20 Wh/litre. Only a 10% decrease of the extracted iron was in fact measured, the extraction percentages of other metal-ions remained unchanged.
- (v) An extraction yield of about 96% can be attained by extracting americium from a simulated HAW solution

under low-acidity process conditions ($\text{pH} = 4$). The required pH value seems, however, rather high in comparison with the value required by other extractants at the same operating conditions.

Therefore according to these results, this type of extractant could be, in principle, usefully employed for removing Pu(IV), Np(IV), Zr(IV), Mo(VI) and Fe(III) from acidic HAW solutions. This removal would prevent the polymerization of plutonium and the formation of alpha-bearing precipitates during the preparation of a low-acidity HAW solution, required for removing trivalent actinides. It is evident, nevertheless, that more extended laboratory-scale experiments on *real* HAW solutions are needed before drawing any definite conclusion on the applicability of this extractant for partitioning purposes.

Acknowledgements

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NOTATIONS

ppm	= parts per million
$\text{p}K_a$	= ionization constant of HX-70
D_a	= distribution coefficient of HX-70 between organic diluents and aqueous solutions
t	= temperature
M., M./l., M./litre	= moles per litre of solution
M. org., M. aq.	= concentration of a metal-ion expressed in moles per litre of solution, present in organic and aqueous phases respectively

HAW	= High Activity Wastes
l./ton. U	= litres of solution per tonne of uranium
MWD/ton.	= Mega-watt-day per tonne of uranium
g/l or ml	= grams per litre or millilitre
g/ton. $\times 10^2$	= grams per tonne of uranium; all the listed values are 1/100 of the true value
(O. Ph), (A. Ph)	= Organic and aqueous phases
O.Ph/A.Ph	= Organic to aqueous volume ratio
[]	= Concentration expressed in moles per litre of solution
Wh/l	= watt-hour per litre, integrated dose

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Extraction of Cyclohexanone Oxime and Cyclohexanone with Toluene in a Pulsed Packed Column (PPC)

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SUMMARY

In the industrial application of the HPO process (production of cyclohexanone-oxime without formation of unwanted ammonium sulphate) use is made of a Pulsed Packed Column (PPC) for extracting cyclohexanone-oxime and cyclohexanone almost quantitatively from the recycling organic process liquor with the aid of toluene. This extraction process is complicated by a chemical reaction. The PPC scaled up from experimental 0.1 m dia laboratory columns offers the advantage that the column length needed for achieving a given efficiency is independent of the diameter. Further, for optimizing the extraction of oxime and anone, a process engineering model (PEM) has been developed on the basis of the 'stage model'.

The extraction of oxime and anone, chosen as the subject of this paper, clearly demonstrates the usefulness of the PEM for extraction calculations and PPC for industrial extraction operations.

Introduction

DSM IS ONE OF THE WORLD'S LEADING PRODUCERS of caprolactam (licensed by Stamicarbon BV), the basic material for Nylon 6. The conventional caprolactam processes yield about 4.5 tons of ammonium sulphate per ton of product. To reduce byproduct formation DSM developed a low sulphate route to caprolactam, the so-called HPO (Hydroxylamine Phosphate Oxime) process^(1,2,3,4).

The key steps in this process are: selective catalytic reduction of nitrate to hydroxylamine *hyam*⁽⁵⁾ in a buffered solution and conversion of the latter with cyclohexanone *anone* to cyclohexanone-oxime *oxime* without byproduct formation. A simplified diagram of the process is shown in Figure 1. The inorganic process liquor *i.p.l.* containing *hyam* is contacted countercurrently in a multi-stage reactor with a solution of *anone* in toluene. The *anone* reacts with the *hyam* to form oxime, and this product is extracted by the toluene phase (extractive reaction).

The *i.p.l.* flow from the oximation section which, owing to the reaction in the *first* oximation stage, contains some oxime and *anone* must be freed of these components before being recycled to the *hyam* reactor. This is done by extraction with toluene from the distillative toluene-oxime separation. So in the HPO process two recycle loops can be distinguished — the *i.p.l.* loop and the toluene loop — as well as two operations in which immiscible liquids exchange material:

- the extractive oximation reaction, and
- the extraction of oxime and *anone* from the *i.p.l.*

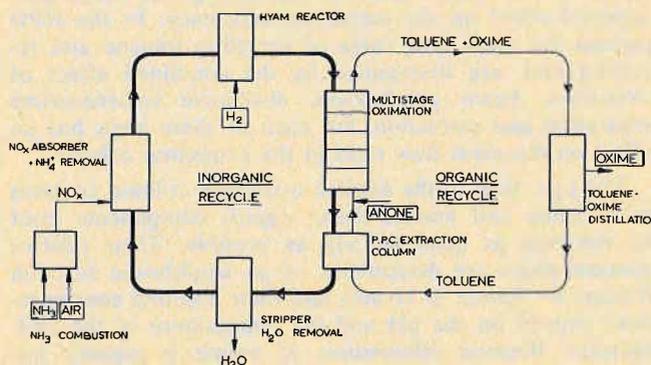


FIGURE 1. Simplified flow diagram of HPO process.

This paper deals with the latter extraction step, which in plant practice is carried out in a Pulsed Packed Column (PPC*). The PPC consists of a vertical shell filled with packing, e.g. Raschig rings, and has a pulsator at the base of the column which produces an up and down movement of the total liquid content in the column.

Scaling-up of a PPC

In the HPO pilot plant, which had a capacity of about 50 tons oxime per year, a PPC of 3 in. dia was used. After all necessary chemical, physical and technological data had been assembled in the pilot plant, an industrial HPO plant (capacity of 70,000 tons oxime per year) and the PPC were directly scaled up from pilot plant level.

An obvious advantage of the PPC is that the column length needed for achieving a given extraction efficiency is independent of the diameter. Even for an extraction combined with a chemical reaction the PPC can be correctly scaled up on the basis of results of experiments in smaller diameter columns. These pilot columns should be sufficiently long that the desired efficiency is reached; then, complete understanding of the transfer processes and reaction kinetics is not necessary for designing large scale equipment. For physical extractions, scaling-up can be done on the basis of the process engineering model for the PPC. Should there be some doubt about the correctness of the process parameters, a few additional (standard) experiments can be carried out. So, in constructing a PPC, one has to apply: (1) chemical engineering know-how for determining the main dimensions of the column (diameter D_c and column height H);^(6,7) (2) mechanical engineering know-how for designing the column and its pulsator.

To determine the column diameter one needs information about the volumetric flow rates and the maximum allowable linear velocities of the phases; the latter are de-

*In three continents, since 1971, Pulsed Packed columns have been operational in plants of Stamicarbon design.

fined by the characteristic velocity of the droplets and the dispersed phase hold-up. The column length is defined by the required separation efficiency as well as by *basic data* like: distribution coefficients, kinetics of the reaction, physical properties of the liquids, and *process conditions* like: linear velocities of the phases, frequency and amplitude of the pulsation, and packing characteristics. DSM have developed substantial know-how about the scaling-up of PPC's and about special pulsation mechanisms^(6,7,8). A diagram of a PPC is shown in Figure 2.

Toluene Extraction Column

It is clear that the ratio between the mass flow rates of the extract phase and the raffinate phase has a pronounced effect on the extraction efficiency. In the HPO process the mass flow rates of recycling toluene and recycling i.p.l. are determined by the combined effect of oximation, hyam preparation, distillative toluene-oxime separation and extraction. So, each of these steps has an effect on the mass flow ratio in the extraction column.

The i.p.l. feed to the toluene extraction column contains both oxime and anone; these organic components must be removed as quantitatively as possible. Their relative concentrations are determined by an equilibrium reaction ($\text{Oxime} \rightleftharpoons \text{Anone} + \text{Hyam}$) and their absolute concentrations depend on the pH and the temperature of the i.p.l. solution. Because elimination of oxime is equally important as that of anone, we introduce the concept ' Σ carb' denoting the sum of the concentrations of oxime and anone. By analogy we introduce the concept ' Σ hyam', denoting the sum of the concentrations of oxime and hyam. If the conditions of the i.p.l. feed are such that the Σ carb consists of oxime only, then, at the *chosen* mass flow ratio, far too little toluene is available for physical

extraction of this oxime. If, however, the Σ carb consists of anone only, then, the amount of toluene suffices for physical extraction. Figure 3 shows the ratios between the applied and minimum toluene mass flow rates needed for achieving a given Σ carb extraction efficiency (Σ carb being considered to consist of oxime or anone only). The differences between the ratios in the A and B band are due to the differences between the values of the physical distribution coefficients of oxime and anone. It can be concluded from the figure that to obtain an extraction efficiency of over 90%, transformation of oxime into anone is desirable.

Now, in the toluene extraction column, the following overall processes take place simultaneously:

- physical extraction of oxime; the distribution of oxime between toluene and i.p.l. is a function of e.g. the pH and temperature of the solution;
- transformation of oxime into anone; the reversible reaction rate constants are a function of the pH and the temperature;
- physical extraction of anone; the distribution of anone between toluene and i.p.l. is a function of e.g. the pH and temperature of the solution;
- association of oxime in the toluene phase; this reaction is considered to be infinitely fast;
- protonation of oxime and hyam in the i.p.l. phase; these reactions are also considered to be infinitely fast.

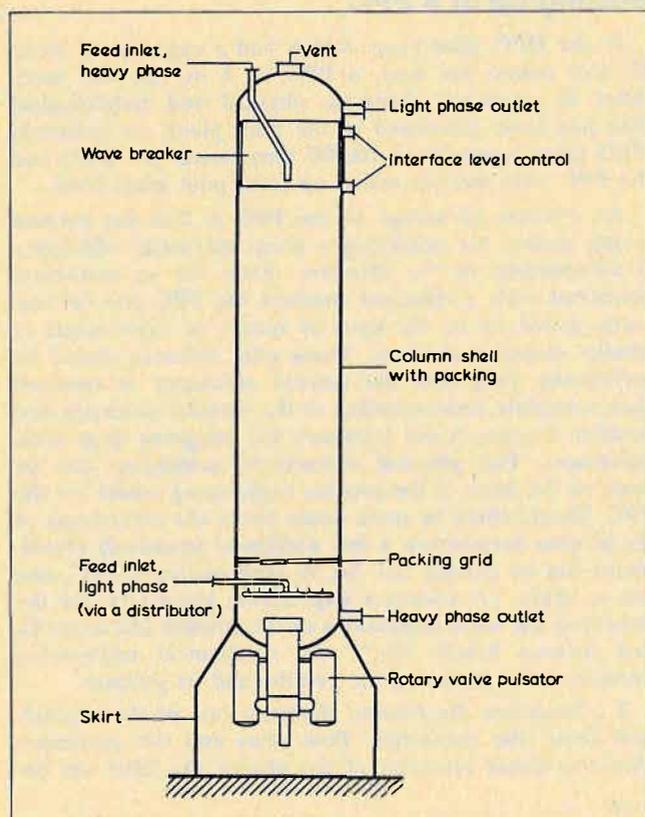


FIGURE 2. Diagram of the PPC.

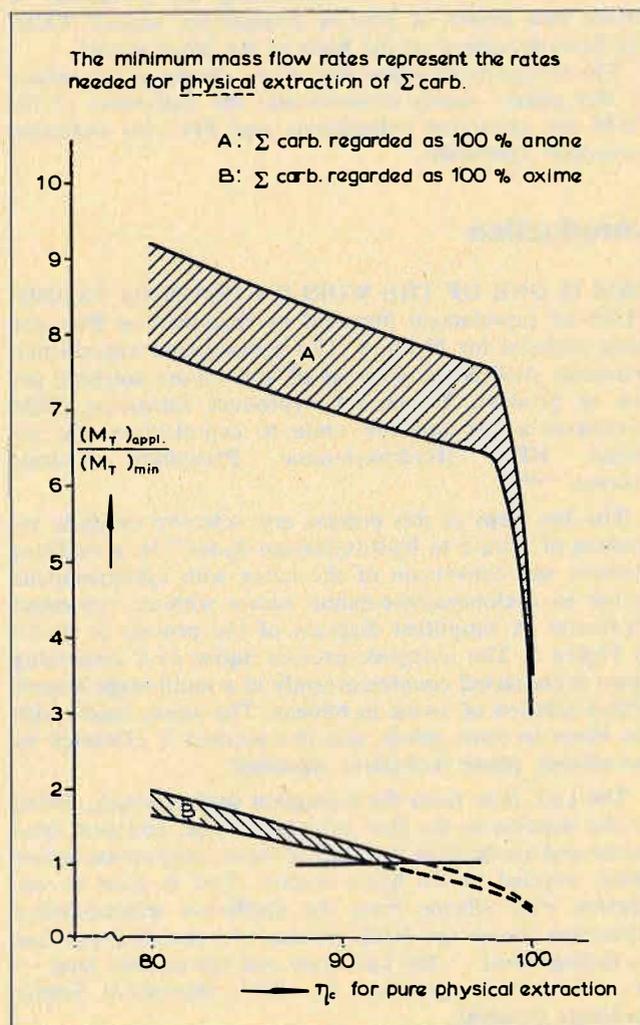


FIGURE 3. Ratios of applied and minimal mass flow rates of toluene vs. extraction efficiency η_c .

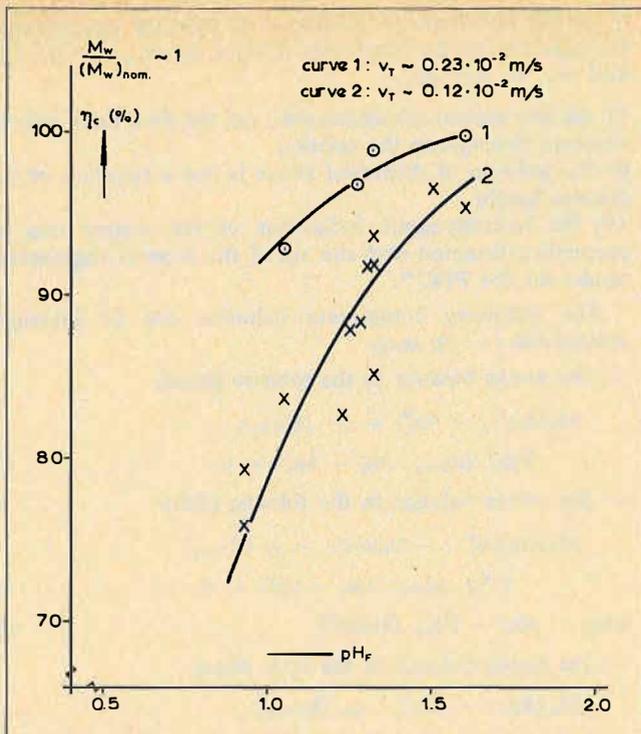


FIGURE 4. Relation between the extraction yield η_c and the pH of the i.p.l. feed. (all other conditions being kept constant).

Influence of Process Variables on the Extraction Efficiency

The extraction efficiency η_c is here defined by the following equation:

$$\eta_c = \frac{\Sigma \text{carb}_F - \Sigma \text{carb}_R}{\Sigma \text{carb}_F} \cdot 100\% \dots \dots \dots (1)$$

The drastic influence the pH of the i.p.l. has on the extraction efficiency is schematically shown in Figure 4; the magnitude of this influence depends also on the mass flow ratio. The pH of the i.p.l. feed to the extraction column normally has a certain constant value; fluctuations in pH are caused by irregularities in the i.p.l. recycle loop.

A likewise great influence on the extraction efficiency is exerted by the Σhyam_F content of the i.p.l. feed, as is schematically illustrated in Figure 5; the magnitude of this influence depends also on the mass flow ratio.

If the pH, the Σhyam_F and Σcarb_F contents are constant, then three parameters have a pronounced effect on η_c :

- the (dispersed) toluene load
- the (continuous) i.p.l. load
- the pulsation velocity.

Both the mass flow rate of the dispersed phase and the pulsation velocity determine the mass transfer interfacial area:

$$S = \frac{6 \epsilon \cdot \varphi'}{d_{vs}} \text{ i.e. } \frac{\text{surface area of dispersed phase}}{\text{volume of the column}} \dots \dots \dots (2)$$

The velocity of the continuous phase, together with the height of the column, determine the residence time τ_w of the phase in which the reaction takes place:

$$\tau_w = \frac{H'}{v_c} \text{ i.e. } \frac{\text{volume of the column}}{\text{flow rate of the cont. phase}} \dots \dots \dots (3)$$

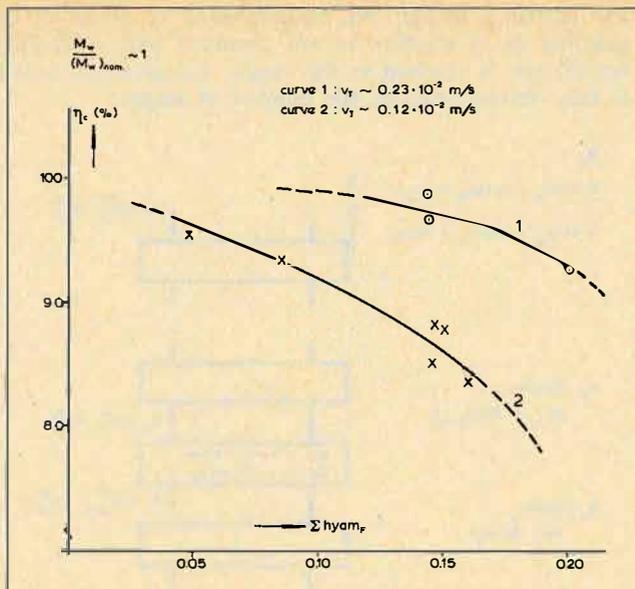


FIGURE 5. Influence of Σhyam_F content on the extraction yield η_c . Nominal values for pH, temperature, Σcarb_F , and pulsation velocity; 4 in. diam column, 1 in. ceramic Raschig rings.

An increase of both S and τ_w improves the extraction efficiency η_c ; the product $\tau_w \cdot S$, therefore, also has a strong influence on the value of η_c . From equations 2 and 3 it is seen that the product $\tau_w \cdot S$ is defined as follows:

$$\tau_w \cdot S = \frac{\text{surface area of dispersed phase}}{\text{flow rate of the continuous phase}} \dots \dots \dots (4)$$

Plotting η_c vs $\tau_w \cdot S$ for constant Σhyam_F (Figure 6) and comparing the resulting curve with those holding for other feed conditions, we gained an insight into the variables that have the greatest impact on the extraction efficiency. For optimizing the extraction of oxime and anone we developed a process-engineering-model (PEM) on the basis of a 'stage model'.

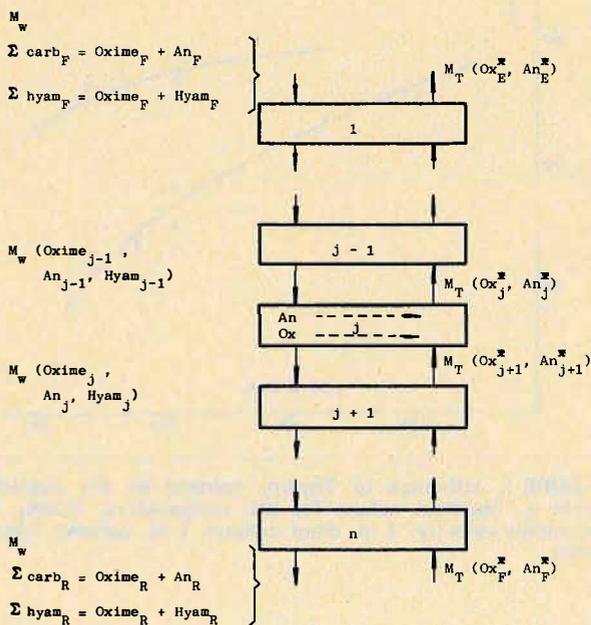
Process Engineering Model for the Extraction of Oxime and Anone

Reliable prediction of the efficiency of an extraction column has always been considered a difficult proposition because of the effect longitudinal mixing has on the mass transfer driving force. A reasonable design calculation of an extraction column must be based on a description of the elementary mass transfer process between the phases. In describing this process use is made of mathematical models with which the chemical-physical behaviour of actual systems is compared. The closer the mathematical description ('the model') approaches physical reality, the more accurate the design calculation will be. Of course, the values of the parameters used must be known.

Several models, describing axial mixing have been published⁽⁹⁾. For the extraction of oxime and anone a model based on the 'stage model' was chosen because this is one of the simplest models for describing mass transfer with longitudinal mixing in counter-current extraction columns and longitudinal mixing in the liquid phases in a PPC usually is slight, which implies that it has only little effect on mass transfer in a PPC.

The figure below shows the relation between the concentrations of components in the flows to and from several stages. It is assumed that in each stage the phases

are perfectly mixed. No consideration is given to the question as to whether or not chemical and/or physical equilibrium is reached in the stages. Longitudinal mixing is only characterised by the number of stages.



If a column has n stages, the height l of one mixing stage equals:

$$l = \frac{H}{n}$$

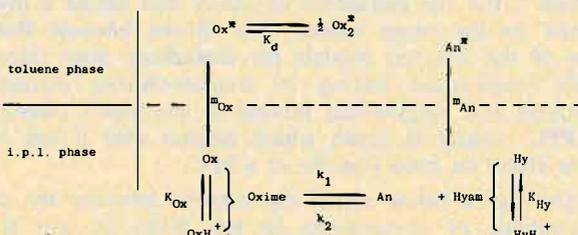
The main objection to this model is that no distinction is made between longitudinal mixing in the raffinate and longitudinal mixing in the solvent phase. In a PPC longitudinal mixing in the dispersed phase is practically always less than in the continuous phase and often negligible.

In arranging the component balances around the stages the following assumptions have been made:

- 1) the reaction takes place in the i.p.l. phase,
- 2) oxime and anone are both extracted by the toluene phase,
- 3) oxime dimerizes in the toluene phase (equilibrium being assumed established infinitely fast),
- 4) oxime and hyam are partly protonated in the i.p.l. phase (equilibrium being assumed to establish infinitely fast),
- 5) the behaviour of the components on both sides of the interface can be represented by the following scheme:

P' power per unit cross-sectional area of column (hp(metric)/m²)
 s_{nf} pulsation velocity (m/s)

curve	packed height(m)
a	6
b	12
c	24



6) at the interface the system is in physical equilibrium; the equilibrium constants are defined by $m_{\text{Ox}} = \text{Ox}_i^*/\text{Ox}_i$ and $m_{\text{An}} = \text{An}_i^*/\text{An}_i$,

7) the two phases are immiscible, i.e. the flow rates remain constant throughout the column,

8) the hold-up of dispersed phase is not a function of the column height,

10) the hydrodynamic behaviour of the system can be correctly calculated with the aid of the process engineering model for the PPC⁽⁶⁾.

The following component balances can be arranged around the j — th stage:

— the anone balance in the toluene phase:

$$M_T(\text{An}_{j+1}^* - \text{An}_j^*) + \rho_T \cdot (K_{T,\text{An}})_j \cdot \text{F.S.I.} (m_{\text{An},j} \cdot \text{An}_j - \text{An}_j^*) = 0 \dots \dots \dots (5)$$

— the oxime balance in the toluene phase:

$$M_T(\text{Oxime}_{j+1}^* - \text{Oxime}_j^*) + \rho_T \cdot (K_{T,\text{Ox}})_j \cdot \text{F.S.I.} (m_{\text{Ox},j} \cdot \text{Ox}_j - \text{Ox}_j^*) = 0 \dots \dots \dots (6)$$

with: $\text{Ox}_j^* = f(K_d, \text{Oxime}_j^*) \dots \dots \dots (7)$

— the anone balance in the i.p.l. phase:

$$M_w(\text{An}_{j-1} - \text{An}_j) - \rho_T \cdot (K_{T,\text{An}})_j \cdot \text{F.S.I.} (m_{\text{An},j} \cdot \text{An}_j - \text{An}_j^*) + r_{\text{An},j} (1 - \phi) \cdot \epsilon \cdot \text{F. I.} \cdot \rho_w = 0 \dots \dots \dots (8)$$

— the oxime balance in the i.p.l. phase:

$$M_w(\text{Oxime}_{j-1} - \text{Oxime}_j) - \rho_T \cdot (K_{T,\text{Ox}})_j \cdot \text{S.F.I.} (m_{\text{Ox}} \cdot \text{Ox}_j - \text{Ox}_j^*) + r_{\text{Ox},j} (1 - \phi) \cdot \epsilon \cdot \text{F. I.} \cdot \rho_w = 0 \dots \dots \dots (9)$$

with: $\text{Ox}_j = f(\text{pH}, K_{\text{Ox}}, \text{Oxime}_j) \dots \dots \dots (10)$

— the hyam balance in the i.p.l. phase:

$$M_w(\text{Hyam}_{j-1} - \text{Hyam}_j) + r_{\text{Hy},j} \cdot (1 - \phi) \cdot \epsilon \cdot \text{F. I.} \cdot \rho_w = 0 \dots \dots \dots (11)$$

The boundary conditions are:

$$\begin{aligned} \text{Hyam}_0 &= \text{Hyam}_F & \text{Hyam}_1^* &= \text{Hyam}_F^* = \text{zero} \\ \text{Oxime}_0 &= \text{Oxime}_F & \text{Oxime}_1^* &= \text{Oxime}_F^* \\ \text{An}_0 &= \text{An}_F & \text{An}_1^* &= \text{An}_F^* \\ \text{Hyam}_n &= \text{Hyam}_R & \text{Hyam}_{n+1}^* &= \text{Hyam}_R^* = \text{zero} \\ \text{Oxime}_n &= \text{Oxime}_R & \text{Oxime}_{n+1}^* &= \text{Oxime}_R^* \\ \text{An}_n &= \text{An}_R & \text{An}_{n+1}^* &= \text{An}_R^* \end{aligned}$$

The following equations are also valid:

$$- r_{\text{Oxime},j} = - k_2 \cdot \text{An}_j \cdot \text{Hyam}_j + k_1 \text{Oxime}_j \dots \dots (12)$$

$$- r_{\text{Oxime},j} = + r_{\text{An},j} = + r_{\text{Hyam},j} \dots \dots \dots (13)$$

$$\frac{1}{\rho_T \cdot (K_{T,\text{An}})_j} = \frac{1}{\rho_T \cdot k_{T,\text{An}}} + \frac{m_{\text{An}}}{\rho_w \cdot k_{w,\text{An}}} \dots \dots \dots (14)$$

$$\frac{1}{\rho_T \cdot (K_{T,\text{Ox}})_j} = \frac{1}{\rho_T \cdot \phi_T \cdot k_{T,\text{Ox}}} + \frac{m_{\text{Ox}}}{\rho_w \cdot \phi_w \cdot k_{w,\text{Ox}}} \dots \dots (15)$$

It is further assumed that

$$\begin{aligned} k_{T,\text{An}} &= k_{T,\text{Ox}} \\ k_{w,\text{An}} &= k_{w,\text{Ox}} \end{aligned}$$

The partial mass transfer coefficients for oxime in the i.p.l. phase and the toluene phase are influenced by the protonation and association reactions, respectively. The magnitudes of the reaction factors ϕ_T and ϕ_w depend on

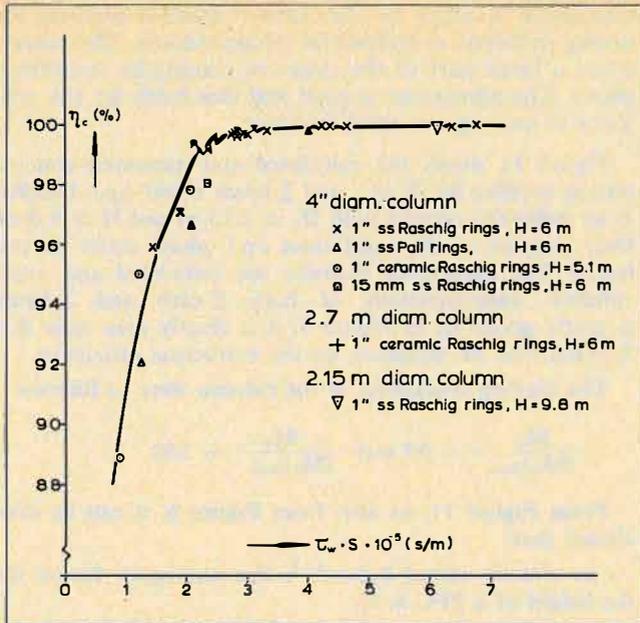


FIGURE 6. Relation between extraction yield η_c and parameter $\tau_w \cdot S$. Nominal values for pH, temperature, Σhyam_F and Σcarb_F .

the pH of the i.p.l. solution, the values of K_{Ox} and K_A , the difference in mobility between the components in question, and on the concentration level.

Equations 5 through 15 contain the following unknowns: $Oxime_j$, $Oxime_j^*$, An_j , An_j^* and $Hyam_j$. The physical parameters, which also include the interfacial area, are known, as are the kinetic parameters.

On the basis of the above model a computer program has been set up by the mathematical department of the Central Laboratory of DSM.

Digital simulation of the countercurrent column was carried out with the aid of relaxation methods. The concentration profiles assumed in the phases are modified by iterative calculations to fit in with the overall balances.

To fit the stage model to the real equipment, suitable values have to be chosen for l ($= \frac{H}{n}$). The usual

way of finding such values is by equating the respective variances of residence time distribution (σ_r^2) of the model and the equipment. In the case of high values for n and for Pe ($\frac{v \cdot H}{E} = Pe > 10$) it can be shown that:

$$\sigma_r^2 = \frac{1}{n} = \frac{2}{Pe}$$

Calculations with the process engineering model have shown that in an industrial PPC we normally have $Pe > 50$, meaning that the PPC operates under nearly piston flow conditions. It has also been found that a variation in n ($15 < n < 50$) has hardly any effect on the calculated results. The principal advantage of the stage model is that it facilitates design calculations as well as evaluation of experimental data.

Comparison of Calculations with Experimental Results

The variables in the PEM can be divided into:

System variables : $\rho_w, \rho_T, m_{Ox}, m_{An}, k_1, k_2, K_d, K_{Ox}, K_{Hy}$

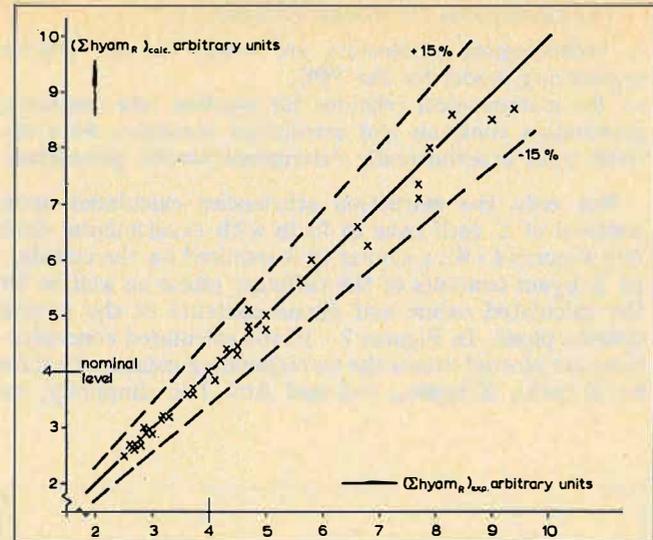


FIGURE 7. Calculated and experimental Σcarb contents of the raffinate phase. 4 in. diam column, 1 in. ss Raschig rings, H: 6 and 9 m.

Column variables : H, D_c , D_p , ϵ

Process variables : $M_w, M_T, \Sigma \text{carb}_F, \Sigma \text{hyam}_F, Ox_F^*, An_F^*, pH_F$

Technological variables : s, f, ϕ , d_{vs} , k_w , k_T , ϕ_w , ϕ_T , T

Iterative variables : 'assumed concentration profiles' number of iterations, etc.

The range over which the model variables were experimentally varied was as follows:

H : 2.5 to 9 m
 D_c : 3", 4", 2.15 and 2.7 m
 D_p : 15 mm and 25 mm ceramic Raschig Rings
 15 mm and 25 mm s.s. Raschig Rings
 25 mm s.s. Pall rings
 25 mm carbon rings
 ϵ : 0.65 to 0.95

$$M_w / (M_w)_{nom.} : 0.2 < \frac{v_c}{v_{c1, nom}} < 2$$

$$M_T / (M_T)_{nom.} : 0.35 < \frac{v_d}{v_{d, nom}} < 3$$

$$\Sigma \text{carb}_F : 0.5 < \frac{\Sigma \text{carb}_F}{\Sigma \text{carb}_{F, nom}} < 2$$

$$\Sigma \text{hyam}_F : 0.5 < \frac{\Sigma \text{hyam}_F}{\Sigma \text{hyam}_{F, nom}} < 3$$

Ox_F^* : not varied because oxime has never been detected in the extracting toluene phase under plant conditions

$$An_F^* : 0 < \frac{An_F^*}{An_{F, nom}^*} < 2$$

$$pH_F : 0.6 < \frac{pH}{pH_{nomi}} < 1.3$$

$$s.f. : 0.5 < \frac{s.f.}{(s.f.)_{nom}} < 2.0$$

system variables: varying in dependence on temperature
 The curves drawn in Figures 4 - 6 were calculated with the aid of the PEM.

The calculations are straight-forward, i.e.:

- technological parameters are based on the process engineering model for the PPC,
- the mathematical relations for reaction rate constants, protonation constants and association constants, were derived from experimentally determined kinetic parameters.

Not only the extraction efficiencies calculated upon removal of Σ carb have to fit in with experimental data (see Figures 4 - 6); a similar fit is required for the calculated Σ hyam contents of the raffinate phase as well as for the calculated oxime and anone contents of the issuing toluene phase. In Figures 7 - 10 the calculated concentrations are plotted versus the corresponding measured values for Σ carb_R, Σ hyam_R, Ox_E^{*} and An_E^{*}. For simplicity, no

distinction is made in the figures between symbols denoting different experimental circumstances. The results cover a large part of the range of conditions mentioned above. The agreement is good and this holds for the majority of our experimental findings.

Figure 11 shows the calculated and measured concentration profiles for Σ carb and Σ hyam in the i.p.l. handled in an industrial column with $D_c = 2.15$ m and $H = 9.8$ m. Only samples of the continuous i.p.l. phase could be collected. The agreement between the calculated and experimental concentrations of both Σ carb and Σ hyam is pretty good. As in Figure 5, it is clearly seen here that Σ hyam_F has an influence on the extraction efficiency.

The loading conditions of the column were as follows:

$$\frac{M_w}{(M_w)_{nom.}} \sim 0.7 \text{ and } \frac{M_T}{(M_T)_{nom.}} \sim 1.25$$

From Figure 11, as also from Figure 6, it can be concluded that:

- as already stated before^{6,7,8}, the scaling-up factor for the height of a PPC is 1,
- the simple stage model, supplemented with the process engineering model for the PPC, provides a suitable aid for calculating extraction efficiencies in a PPC, even if the extraction is complicated by a chemical reaction.

LIST OF SYMBOLS

- An(one) = Concentration of anone in i.p.l. phase moles/kg
- An^{*} = Concentration of anone in toluene phase moles/kg
- D_c = Column diameter m
- D_p = Packing diameter m
- d_{vs} = Average drop diameter acc. to Sauter m
- E = Longitudinal mixing coefficient m²/s
- F = Cross-sectional area m²
- f = Frequency s⁻¹
- H = Height of packed column section m
- Hy = Concentration of 'hyam' in its single definite form in i.p.l. phase moles/kg
- Hyam = Concentration of Hy + HyH⁺ in i.p.l. phase moles/kg

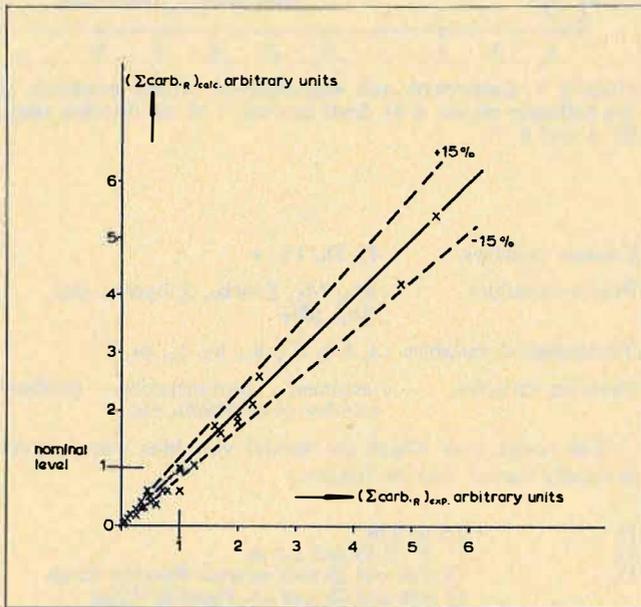


FIGURE 8. Calculated and experimental Σ hyam contents of the raffinate phase. 4 in. diam. column, 1 in. ss Raschig rings, H: 6 and 9 m.

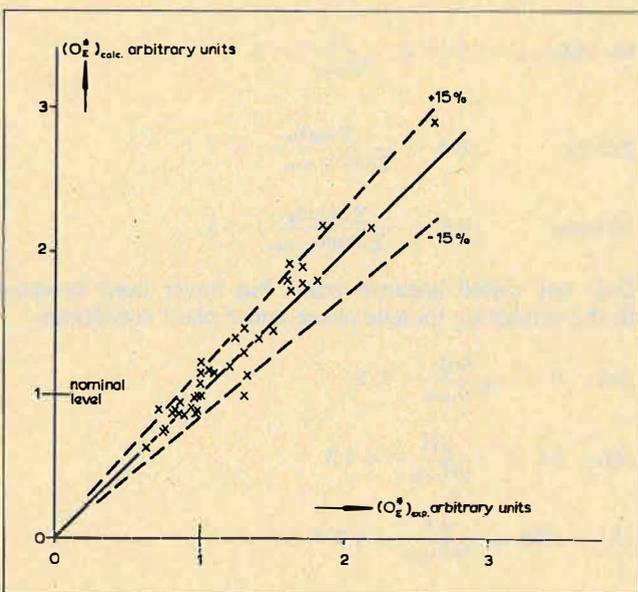


FIGURE 9. Calculated and experimental oxime contents of the issuing toluene phase. 4 in. diam. column, 1 in. ss Raschig rings, H: 6 and 9 m.

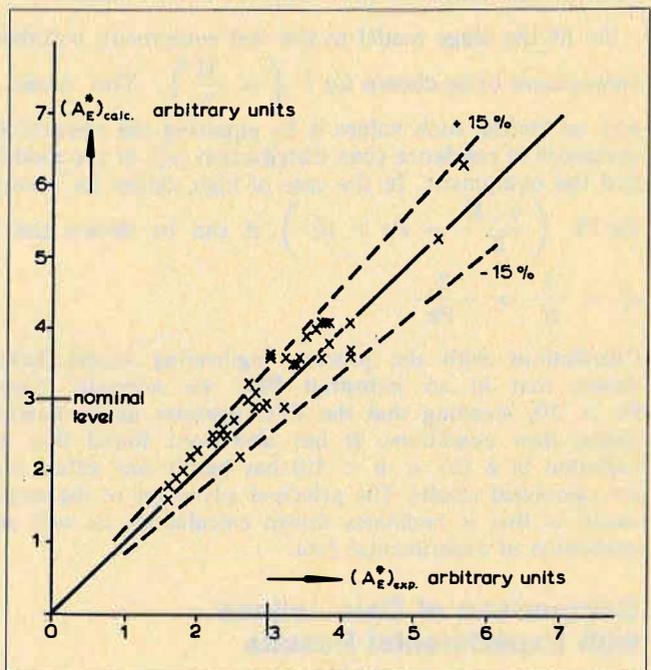


FIGURE 10. Calculated and experimental anone contents of the issuing toluene phase. 4 in. diam. column, 1 in. ss Raschig rings, H: 6 and 9 m.

i.p.l.	= Inorganic process liquor —
j	= Stage number —
K	= Overall mass transfer coefficient m/s
K_{ox}, K_{Hy}	= Protonation constants for oxime and hyam moles/kg
K_d	= Association constant for oxime in the toluene phase moles/kg
k_1, k_2	= Reaction rate constants s^{-1} , $\frac{kg}{mole \cdot s}$ resp.
k_w, k_T	= Partial mass transfer coefficients in i.p.l. phase and toluene phase m/s
l	= Height of a mixing stage m
m_{ox}	= Distribution coefficient of oxime between toluene and i.p.l. with $m_{ox} = Ox^*/Ox_i$
m_{An}	= Distribution coefficient of anone between toluene and i.p.l. with $m_{An} = An_i^*/An_i$
M	= Mass flow kg/s
n	= Number of mixing stages —
Ox	= Concentration of 'oxime' in its single definite form in i.p.l. phase moles/kg
Oxime	= Concentration of $Ox + OxH^+$ in i.p.l. phase moles/kg
Ox^*	= Concentration of 'oxime' in its single definite form in toluene phase moles/kg
Oxime*	= Concentration of $Ox^* + Ox_2^*$ in toluene phase moles/kg
Pe	= Peclet number: $Pe = \frac{v \cdot H}{E}$
r	= Reaction rate $\frac{moles}{kg \cdot s}$
S	= Specific interfacial area: $S = \frac{6 \cdot \epsilon \cdot \phi}{d_{vs}}$
s	= Pulse amplitude: total stroke length in empty column section m
T	= Temperature °C
v	= Superficial velocity m/s
$\Sigma carb$	= Oxime + Anone moles/kg
$\Sigma hyam$	= Oxime + Hyam moles/kg
ϵ	= Bed porosity
η_e	= Extraction efficiency referred to the carb content of the i.p.l., defined by eq. 1
ρ	= Liquid density kg/m^3
σ_r^2	= Variance of residence time distribution
τ_w	= Residence time of the continuous i.p.l. phase s
ϕ	= Reaction factor
φ	= Hold-up of dispersed phase

INDICES

An	= Anone
appl.	= applied
c	= continuous phase
d	= dispersed phase
E	= extract phase
F	= feed phase
i.p.l.	= inorganic process liquor
i	= interface
j	= stage number
min	= minimal
n	= last mixer
n + 1	= imaginary mixer after the n-th (for the toluene feed phase only)

DISCUSSION

G. Aly: You mentioned that a scale-up factor of 1.0 was used in the HPO-process; what would this factor be for a physical extraction process?

A.J.F. Simons: The scale-up factor for a physical extraction process carried out in a PPC is 1, provided certain conditions are fulfilled. Some of these conditions are given somewhere else in the discussion. These conditions also hold for the HPO process.

P.J. Bailes: You have shown a comparison of theoretical and practical results for a large-scale column. Could you clarify for me whether you determined your mass transfer co-efficients directly from fundamental considerations or whether you used those values which gave a

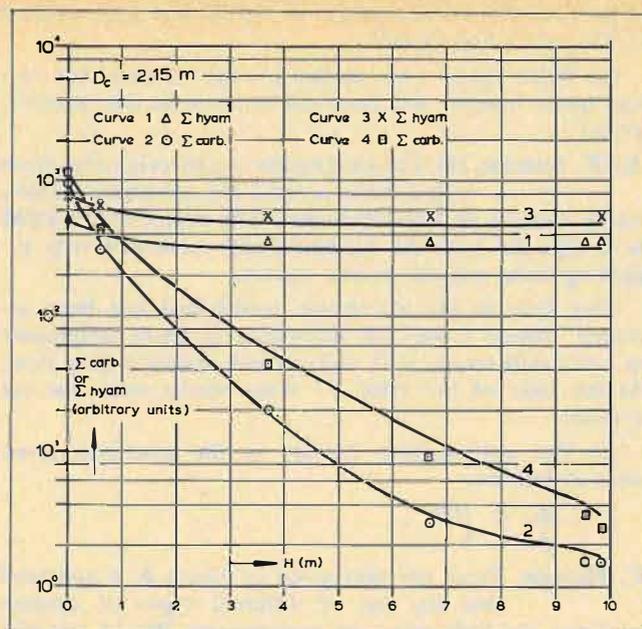


FIGURE 11. Calculated and experimental concentration profiles.

nom.	= nominal (design conditions)
$Ox(ime)$	= oxime
o	= imaginary mixer preceding the first one (for the i.p.l. feed phase only)
R	= raffinate phase
T	= toluene phase
w	= aqueous phase
1	= first mixer

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concentration profile (as calculated by the model), the same as that measured experimentally on the small 3 in. column?

A.J.F. Simons: Concentration profiles as measured in the smaller columns have only been used to compare with calculated results.

The values of the mass transfer co-efficients have been based on the process engineering model for the PPC. The enhancement factor for the mass transfer plus chemical reaction were estimated directly from fundamental considerations.

S. Bruin: (1) The axial dispersion in the PPC's is small as the author stated in the model. A cascade of mixers is used to take dispersion effects into account. Could the author comment on what deviations between experimental conc. profiles and calculations would occur

if pure counter-current plug flow would have been assured in the calculation model?

(2) What values were needed for the enhancement factors (mass transfer and chemical reaction) in the examples given?

A.J.F. Simons: (1) The calculation model originates from calculations around the oximation section which consists of 5 mixer-settlers. The object of the PEM is to describe both the oxidation and extraction step, regarding these sections as one reactor.

Plug flow in the calculation model had not been assumed. Indeed it was felt interesting to know differences in calculated results with and without assumed plug flow. At the time of the ISEC 77 these results were not yet available.

(2) The enhancement factors in the examples given were as follows:

$$5 < \phi_w < 100$$

$$1 < \phi_T < 5$$

C. Hanson: From the data given in Figure 6, it appeared that the use of different types of column packings had little effect on performance. Would you like to comment on the influence of packing type on column performance?

A.J.F. Simons: It needs no showing that the performance of an extraction column is determined by, e.g., the (specific) interfacial area and the degree of backmixing.

The specific interfacial area S , as given by equation 2 of the paper, contains three parameters, i.e. ϵ , φ , and d_{vs} . As may be known from other publications on the PPC, the packing diameter, within a certain range, has hardly any effect on the droplet diameter. But the hold-up of dispersed phase φ decreases with increasing ϵ , if due to the pulsation velocity, droplets with a same diameter are produced for different types of packing, the net result being a smaller S . To get the same interfacial area with different types of packing, then different pulsation velocities must be applied, provided superficial velocities are kept constant. So, it can be concluded that, on the condition all other parameters are kept constant, different types of packing have an influence on performance. Figure 6 of the paper contains the dependency of the parameter, S , which implies also the dependency of the pulsation velocity.

In general, higher pulsation velocities mean an increase in backmixing. The degree of backmixing in a PPC is determined mainly by the pulsation velocity, the characteristic dimensions of the packing and the bed porosity. The backmixing in a PPC is of minor importance and it does not differ materially for the different types of packing provided these are of the same order of magnitude. Figure 6 demonstrates this as well as does the PEM.

S. Hartland: How do you reconcile the fact that there is little backmixing in your column with your stagewise model which inherently introduces backmixing into both phases when considered as being in differential flow?

A.J.F. Simons: In estimating the performance of real equipment, like pipe reactors or counter-current columns, use is often made of a representation (description) of this equipment by a series of perfectly mixed compartments. For pure piston flow, the number of compartments should be great.

In a PPC, normally the degree of backmixing in the continuous phase is greater than that in the dispersed phase. At the same time the backmixing in the continuous phase of an industrial PPC is so small that, in a stagewise representation, it is not necessary to make a distinction between

the backmixing in both phases. The number of stages is so great that the stagewise results approach differential ones. Besides this mathematical concept reduces the amount of computation considerably.

T.C. Lo: Your paper is very interesting to me. I'd like to raise the following two questions:

(1) You have scaled up your commercial column based on a 3 in. diameter pilot scale test; what is the scale-up factor on HEHS or HTU?

A.J.F. Simons: As known from the literature, there exists a theory which states:

$$HTU_{\sigma} = (HTU_{\sigma})_p + HDU \dots \dots \dots (1)$$

If the transfer units are based on, e.g., the dispersed phase then:

$$(HTU_{\sigma_d})_p = \frac{v_d}{K_{\sigma_d} \cdot S} = \frac{v_d \cdot d_{vs}}{K_{\sigma_d} \cdot 6 \cdot \epsilon \cdot \varphi} \dots \dots \dots (2)$$

- $(HTU_{\sigma_d})_p$ = overall height of a transfer unit, based on the dispersed phase, for piston flow.
- HDU = height of a diffusion unit
- v_d = superficial velocity of the dispersed phase
- d_{vs} = Sauter mean droplet diameter
- K_{σ_d} = overall mass transfer coefficient for the dispersed phase
- ϵ = bed porosity
- φ = fractional hold-up of dispersed phase

If two columns with different diameters are compared with regard to $(HTU_{\sigma_d})_p$, then the transfer units have the same value, provided, e.g.:

- the same packing is applied,
- the same pulsation velocity is applied,
- the same superficial velocity and mass flow ratio are applied,
- the distribution of the dispersed phase over the cross sectional area in both cases is uniform.

The diffusion unit (HDU), under the conditions above and in general, is **not** a function of the column diameter.

The result is an HTU_{σ_d} which is independent of the column diameter, i.e. the scale-up factor on HTU is 1.

T.C. Lo: (2) From an energy conservation point of view, did you ever evaluate the column construction cost vs. operating cost for your commercial-scale column?

The energy consumption for a large pulsed column could be ten times than that of a similar-sized mechanical agitated column, e.g. RDC, ARD, Scheibel column, Oldshue Rushton column and reciprocating-plate column.

A.J.F. Simons: From a point of view of construction costs and operating cost the commercial Pulsed Packed Columns have been compared with other types of columns. In general, for the different systems for which the PPC is applied, the investment costs are lower because commercial Pulsed Packed Columns have smaller volumes (scale-up factor = 1) than columns which have a scale-up factor greater than 1. Operating costs are of the same order as other columns that use mechanical agitation.

The energy consumption for large-scale Pulsed Packed Columns is also of the same order as other mechanical agitated columns. In Figure D 1 the net-drive power requirements for a PPC are given as a function of the pulsation velocity.

M.R. Resetarits: Why was a pulsed packed column chosen as the contactor for this extraction application?

A.J.F. Simons: During the period that the HPO process was investigated on a pilot-plant scale, DSM had already a substantial know-how on Pulsed Packed Columns. Scaling-up of the pilot plant PPC was

believed to cause no problems, even if the complex reaction mechanism would not yet be understood completely. As stated in the paper, a correct scale-up of a PPC can be done just on the basis of results of experiments in smaller diameter columns.

M.R. Resetarits: Were other contactors considered?

A.J.F. Simons: For every kind of extraction different types of contactors have to be considered.

A final decision, in general, is made on factors like capital investment costs and operating costs, provided one has been able to estimate the dimensions of these contactors from results in smaller columns (often only of one kind).

M.R. Resetarits: Why was it felt necessary to employ any form of mechanical agitation in the contactor?

A.J.F. Simons: Mechanical agitation was necessary because (a) the kinetics of the hydrolysis reaction was not (very) fast, (b) the mass flow rate of the extract phase (toluene) available for extraction was not only determined by the extraction as stated in the paper; this means that without agitation (too low interfacial area) the column length would become much too large, (c) scaling up of a complicated system, as is the case for the oxime and anone extraction, handled in a PPC is much easier and much more reliable than any other type of contactor, (d) the mechanical agitation also can be considered as a 'free parameter' with which the extraction efficiency practically always can be adjusted within a certain range of column operation.

M.R. Resetarits: Might a non-agitated column such as a packed, a spray, or a trayed column have sufficed?

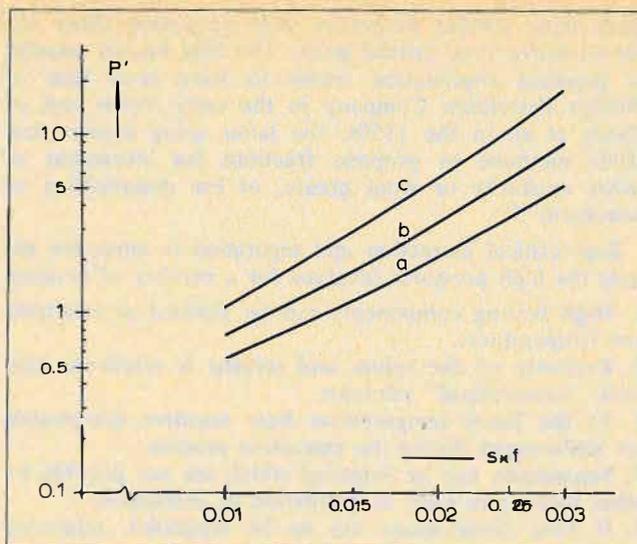


FIGURE D1. Nett drive-power requirements for PPC. Column diameter 1 — 4 M, pulsation frequency $f = 1.5 \text{ (s}^{-1}\text{)}$, ceramic Raschig rings 25 mm.

A.J.F. Simons: Let's start from the point of view that a certain kind of extraction can meet the requests in a battery of mixer-settlers. As a general rule one can say then that this extraction can also be carried out in any type of counter-current column. The question as to whether such an application is justified is a matter of economics.

ORGANIC PROCESSES

The Extraction and Separation at Near Critical Conditions of Components in Some Natural Products

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SUMMARY

It has been demonstrated that n-pentane, near and above its critical point, acquires unusually high solvent power for asphaltenes, in some cases surpassing that of benzene. Such solutions were found to be easily separated by contact with active carbon, while the lower molecular weight hydrocarbons and compounds remained in solution, passed through the carbon bed without being adsorbed, and thus were separated from the asphaltenes retained on the carbon. It has been further observed that the yield of oils is practically independent of the degree of demetallization, and therefore higher yields of oil should be obtained than in the conventional propane deasphalting. Asphaltenes are recovered from the carbon by benzene, for economic reasons preferably under the extraction conditions.

Introduction

THE PROCESS OF EXTRACTION WITH A SOLVENT above its critical point is variably described as vapour phase or supercritical extraction or, as some authors prefer, supercritical distillative extraction⁽¹⁾, or even a "solvent-free" extraction⁽²⁾. It is one of the more recent extraction and separation techniques; its main features and practical applications have been discussed by Ellis⁽³⁾, Peter⁽⁴⁾, Zosel⁽⁵⁾ and others. So far, most interest has been directed to theoretical aspects of this problem as seen from the number of papers dealing with the vapour-liquid equilibria in the neighbourhood of the critical point of the solvent and their prediction by different equations of state.

The phenomenon itself has been known for about one hundred years, though mainly because of the complications and interference it was causing in some high pressure systems, such as the salt deposits on the blades of high pressure steam turbines, or the blockage of pipelines by hydrates of hydrocarbons. Supercritical steam and

gases have solvent properties well surpassing those observed below their critical point. The first known attempt at practical exploitation seems to have been that of Phillips Petroleum Company in the early 1940s and of Zhuze et al. in the 1950s, the latter using supercritical crude methane or propane fractions for extraction of either ozokerite or wool grease, or for deasphalting of petroleum^(3,6).

Supercritical extraction and separation is attractive despite the high pressures involved for a number of reasons:

1. High boiling components can be gasified at relatively low temperatures.
2. Recovery of the solute and solvent is relatively easy from "supercritical" solutions.
3. At the lower temperatures heat sensitive compounds are undamaged during the extraction process.
4. Separations can be achieved which are not possible by other techniques such as distillation or extraction.
5. If food components are to be separated, non-toxic solvents, such as carbon dioxide, may be used which leave no harmful residues⁽⁷⁾.
6. In general terms compressed gases are relatively cheap solvents.

In its supercritical state, the dense gas phase represents a very mobile fluid. Compared with the corresponding liquid phase, it has a density up to one-third and more, yet its viscosity could be as low as one-fifth and less, depending on the pressure and temperature excess above the critical point. Therefore, the dense gas phase will manifest solubilities approaching those of the liquid phase, yet will penetrate faster and deeper into the matrix of natural substances to be extracted, or would progress faster through a densely packed fixed bed, or column, such as in high pressure exclusion chromatography⁽⁸⁾, than corresponding liquid solvents.

The high solvent power of the supercritical gas phase has been used also for analytical purposes, especially for the separation of high boiling and high molecular weight compounds in supercritical fluid-liquid chromatography (FLC)⁽⁹⁾. A very interesting method suitable for analytical scanning of supercritical extractions has been suggested by Stahl, who originated thin layer chromatography (TLC); he developed an analytical supercritical micro-extractor coupled to a TLC plate for direct spotting of the extract⁽²⁾.

The main interest of the present work was in simultaneous extraction and separation effects, and in extraction rates and yields, mainly of systems where there is a need for a new technology, more effective than the existing methods. The standard supercritical solvent used was *n*-pentane, in addition to mixed solvents or benzene. The examples show broadly the scope of the interest in complex systems, though two-components systems, both liquid and solid, were also studied.

It became obvious that the desired separation effects in multicomponent systems cannot be achieved by the selection of extraction conditions and solvents alone, so adsorption under supercritical conditions was examined and found most useful. It ensured a minimum energy loss during the separation stage, and a good selectivity. Adsorption coupled with supercritical extraction has been used before for scrubbing the recycle CO₂ in the deodorisation of edible oils⁽¹⁰⁾, or in the removal of minor components (e.g. caffeine from coffee beans⁽¹¹⁾, or nicotine from tobacco⁽¹²⁾), but not for the actual separation of major components, as far as is known.

The systems described here included glycerides, tar sands and peat. With glycerides, the problem was separation of individual glycerides of a single fatty acid on a preparative scale; a chromatographic adsorption effect

under supercritical conditions was tried with a degree of success. With tar sands and peat, the emphasis was on obtaining fractions of commercial interest, such as a deasphalted and demetallized oil fraction of tar sand bitumen, or a light pre-refined peat wax fraction separated from the rest of the bitumen. In all cases the adsorbate had to be readily recoverable by desorption.

During the course of research, a special gauge was developed to "sense" the criticality of the dense gas phase because the supercritical state is easily lost as more solute is taken up into the gas phase, resulting in the loss of its solvent power.

This paper may be regarded as a preliminary communication describing the state of research at the end of the first phase of the studies.

Experimental

Supercritical Extraction Unit (Figure 1)

The apparatus was designed to operate at up to 400°C and 140 bar (2000 psig) max. The extraction unit consisted of a pressure feed vessel, holding 7 litres of liquid, a preheater, a hot-air bath containing a temperature equilibrating coil with the extractor (and carbon columns, if used), a cooler, a split-flow double valve, a sampling arrangement (made of glass) and the LC detector for monitoring of the concentration of the extract.

Two types of extraction vessel were used in the experiments. The larger vessel, an autoclave, was originally used for the extraction of liquids and later modified to reduce its volume so that smaller samples could be extracted in some form of cylindrical cartridge; the cup cartridge (with 8 cups on a central stem) was used for soft solids and liquids; a static bed extractor of 76 ml capacity for high-melting solids. A small tubular extractor made from a 20 mm I.D. stainless steel tube 23 cm long, was used in later test runs, its extraction volume being 80 ml.

The two carbon adsorption columns were of 15 mm I.D. pipe 25 cm and 12 cm long respectively.

Continuous sampling and monitoring of the extract concentration was achieved using a liquid chromatograph detector (PYE System 2 with an FID detector).

A sensor indicating the actual physical state of the fluid during the extraction in the critical region was developed in the form of a heat and pressure-resistant Cerl-Planer strain gauge, based on a micro air-capacitor. The strain gauge was attached to a 1 in. OD plug to fit in the 1 in.-port of the large extractor. Its normal capacitance was 1 pF (measured to 10⁻³ pF by the Wayne-Kerr Universal Bridge and recorded).

Procedure

The supercritical extraction was operated as a semi-continuous process, in which the stream of a preheated and gasified solvent under pressure was fed to the extractor. The feed rate was determined by the rate of the extract withdrawal, the driving force being the nitrogen pressure in the headspace above the liquid solvent in the pressure feed vessel; it was kept constant by a Hale Hamilton pressure controller L15. The solvent was not continuously recovered and recirculated as it would be on a pilot plant or commercial scale.

The extract was cooled under pressure and, after expansion to atmospheric pressure, liquid samples were collected in volumetric flasks in fractions of 50, 100 and 250 ml (depending on the dilution indicated by the LC detector). A small portion of the extract stream was continuously diverted to the coating block of this detector, and from there returned to the main sample (see Figure 1).

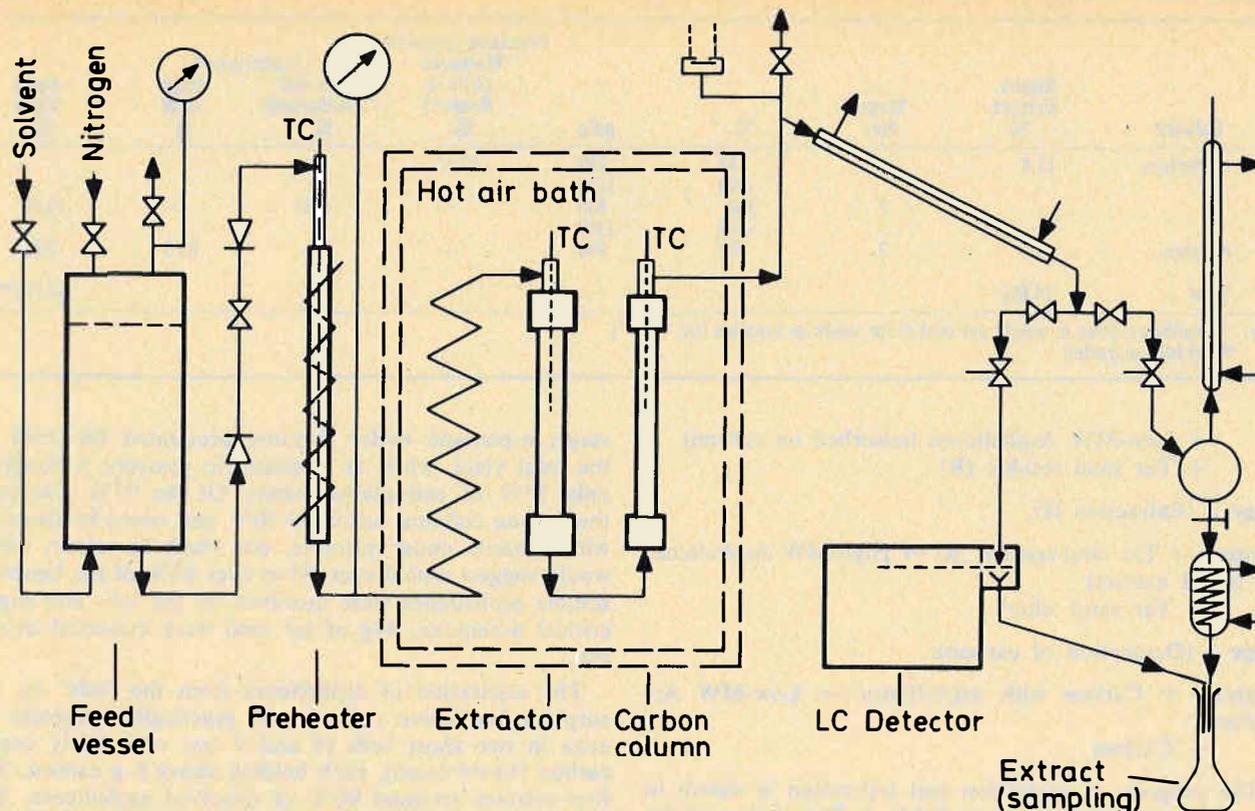


FIGURE 1. Sub and super-critical extraction with separation by adsorption.

The glycerides were first dissolved and then supported on a particulate solid, packed in a sample cartridge and inserted into the large extractor. Peat was packed as a fixed bed directly into the small tubular extractor. In all cases, a shallow layer of celite followed downstream from the main fixed bed to prevent any losses due to the exuding solute during the heating-up period. Tar sands, with their putty-like consistency, could not be packed in a fixed bed because the molten bitumen was then mechanically and unselectively displaced by gases out of the tar sand bed; this could be prevented by packing the tar sand round a central porous core made of several layers of a fine wire gauze wound round the central thermocouple pocket.

Flow Conditions

The average space velocity of the solvent was 12-14 litres per litre of extraction volume per hour. The linear vapour velocities were of the order of 1-3 mm/second. The residence time of the solvent in the fixed bed was from about 30 to 60 seconds (for beds 6-18 cm long). During the separation runs with the di- and tri-glyceride mixtures on silica, the flowrates were increased 2-3 times, corresponding to average space velocities of 20-35 l/h/l, vapour velocities up to 8 mm/sec, and residence time of 15-25 seconds.

Adsorption Stage — Operation of Carbon Columns

When the extraction was combined with simultaneous separation by adsorption on carbon, the carbon column followed downstream of the extractor as used with tar sands and peat (see Figure 1). The preferred sequence of extraction stages was then as follows:

Stage 1: Extractor and carbon column (in series). Solvent: n-pentane (sub- and supercritical).

Stage 2: Carbon column (isolated); separately eluted with solvents under pressure to desorb adsorbed asphaltenes etc. Solvents: benzene followed by benzene/ethanol (9:1) (subcritical, liquid).

Stage 3: Extractor (isolated).

Solvents: benzene, followed by benzene/ethanol (9:1) in the extraction of peat; benzene only was used (sub- and supercritical) in the case of tar sands.

Each stage needed one day (for cooling and reconnecting of the columns) as heat-resistant valves were not available to isolate either the column or the extractor. In the three stages of a run about 40 fractions were collected.

Results

Extraction of Tar Sands

The Athabasca tar sands contain a soft bitumen nearly completely soluble in benzene, or toluene, at atmospheric pressure. The bitumen contains 18-25% asphaltenes, 29-35% resins and 45-49% oils, and is associated with fine-grained sand (and some clay) at an average concentration of only 12%, though this can vary from 1 to 18% bitumen⁽¹³⁾. Resins with oils, known as maltenes, are soluble in n-pentane at atmospheric pressure, while asphaltenes are not. However, in the sub- and supercritical extraction most of the asphaltenes could be dissolved in n-pentane. When the hot extract was passed, under the extraction conditions, through two carbon columns, the dissolved lower-MW asphaltenes were adsorbed, while maltenes passed through. Thus maltenes and asphaltenes were extracted, and separated, and partly fractionated, in a single operation. The mode of this pressure extraction was as follows:

Stage 1 (Extraction 1):

n-Pentane + Tar sand + Carbon → Maltenes (passed through carbon)

TABLE 1. Extraction of Tar Sands*

Solvent	Atmos. Extract %	Stage No.	°C	psig	Pressure Extraction			Total Yield %
					Maltenes (Oils + Resins) %	Asphaltenes Low-MW (Adsorbed) %	Asphaltenes High-MW %	
n-Pentane	11.4	1	140	280	10.63			
			-240	-1200				
		2	260	830	—	2.84	—	13.47
Benzene	3.4	3	-290	-1100	—	—	0.73	0.73
			360	280	—	—	—	—
Total	14.8%							14.2%**

Note: *Results are given in weight per cent of tar sands as supplied (i.e. "wet")
 **Not fully extracted

- + Low-MW Asphaltenes (adsorbed on carbon)
- + Tar sand residue (R)

Stage 2 (Extraction II):

Benzene + Tar sand residue (R) → High-MW Asphaltenes (as liquid extract)
 + Tar sand 'char'

Stage 3 (Desorption of carbon):

Benzene + Carbon with asphaltenes → Low-MW Asphaltenes
 + Carbon

The progress of extraction and separation is shown in Figure 2, and summarised in Table 1. The design of the extractor and the mode of packing tar sands did not allow for a complete recovery of the bitumen from the middle of the fixed bed, along the porous core; this accounts for a lower yield (by 4%) when compared with the atmospheric extraction. The residue was free flowing (except for the partly extracted core in the centre).

The most striking difference between the atmospheric and pressure extractions was observed in the pentane

stage; n-pentane under pressure accounted for 95% of the total yield, while at atmospheric pressure it dissolved only 75% of extractable matter. Of the 95% extracted, the carbon columns adsorbed 20% and could be desorbed with benzene under pressure, was black in colour, which would suggest asphaltenes. Thus over 80% of the benzene-soluble asphaltenes were dissolved by the sub- and super-critical n-pentane; 44g of tar sand were extracted in one run.

The separation of asphaltenes from the "oils" by adsorption on active carbon was practically complete — even in two short beds (8 and 9 cm) of a fairly coarse carbon (14-44 mesh), each holding about 8 g carbon. The first column retained 90% of dissolved asphaltenes. The asphaltenes were obtained as solids on carbon, partly fractionated by molecular weight, with the possibility of further fractionation, e.g. on several carbon columns at different temperatures; since metals (and sometimes sulphur) are to a large extent associated with asphaltenes, it seems possible that these could be, at least partly, removed and concentrated by adsorption — this would go a long way towards up-grading of the tar sand bitumen.

In one experiment, the results shown in Table 2 were obtained.

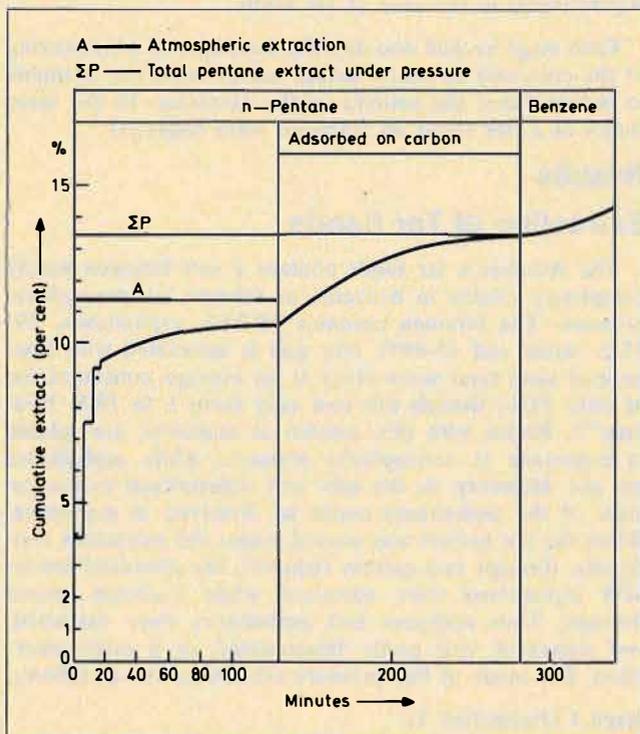


FIGURE 2. Sub and super-critical extraction of Tar Sand with separation by adsorption.

TABLE 2. Iron and Nickel Removal

	Iron		Nickel*	
	ppm	%	ppm	%
Benzene extract (Soxhlet).....	290	(100)	180	(100)
Asphaltenes adsorbed on Carbon (pentane extract).....	30	(14)	110	(61)
Deasphalted oils (passed through carbon bed) (pentane extract)...	0.3	(0.1)	6	(3.3)

*Vanadium could not be estimated

Since it is known that in propane deasphalting the relative removal of vanadium and nickel is very similar, it could be expected that it would also occur in these experiments. The demetallisation of the deasphalted oil was practically complete at a 95% yield of oil, even with the short carbon beds, and could most likely be improved by using longer carbon beds.

Extraction of Peat

In contrast to tar sands, not more than 15% of the organic matter of peat can be extracted with n-pentane and benzene, or a mixture of benzene with ethanol (the usual peat solvents). The chemical composition of the

pentane extract is entirely different from that of tar sands — the latter consisting basically of hydrocarbons, while peat yields mostly “waxes” (esters of long-chain fatty acids with long-chain alcohols, free acids, alcohols, resins, etc.). This “peat wax” is the most valued of the peat extracts.

The pressure and increased temperature had a very positive effect on the yield of the peat wax and of other components of the peat bitumen, when compared with atmospheric extraction (see Table 3 and Figure 3). Being of a more polar nature, peat responds especially well to polar solvents, or their mixtures with benzene or toluene, such as nine parts of benzene with one part of ethanol; the crude wax represents less than one-half of the atmospheric extract, and requires a thorough refining.

Peat is a particularly suitable raw material for a pressure extraction with separation by adsorption; in a single operation, with a non-polar solvent, it is possible to obtain a high yield of the pre-refined peat wax besides high yields of partly fractionated asphaltenes (dewaxed bitumen).

The mode of drying the peat affects the yield of extract, therefore both oven-dried and air-dried peat were used in pressure extractions. When the pressure extraction of peat was combined with separation by adsorption, the extraction scheme was as follows: —

Stage 1 (Extraction 1):

n-Pentane + Peat + Carbon column → Peat wax (passed through carbon column)
+ Asphaltenes (adsorbed on carbon)

Stage 2 (Desorption of Carbon):

Desorption I:

Benzene → Low-MW Asphaltenes (A₁) (as liquid extract)

Desorption II:

Benzene/Ethanol (9:1) → Medium-MW Asphaltenes (as liquid extract)

+ Carbon + trace polymers

Stage 3 (Dewaxed Peat):

(Extraction II):

Benzene → High-MW Asphaltenes (as liquid extract)

(Extraction III):

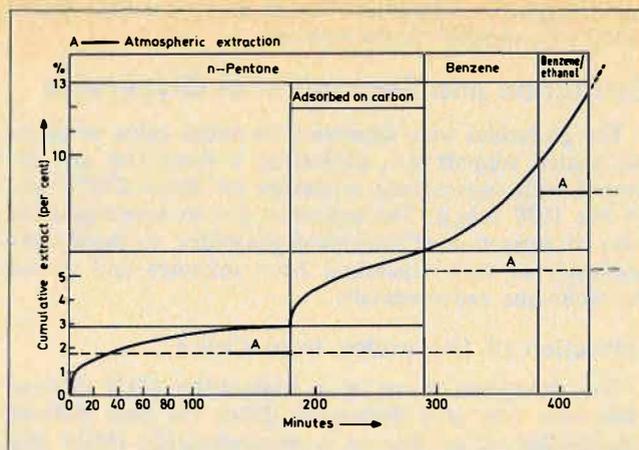


FIGURE 3. Sub and super-critical extraction of Peat with separation by adsorption.

Benzene/Ethanol (9:1) → Very High-MW Asphaltenes + Extracted Peat Residuum

In a straight pressure extraction without separation, the extraction Stage 1 was with n-pentane, Stage 2 with benzene and Stage 3 with a benzene/ethanol mixture.

These two extraction schemes are represented diagrammatically in Figure 4. The results (see Table 3) show that the sub- and super-critical extraction of peat yielded from 50% to 90% more in total extracts than could be obtained in atmospheric extractions with identical solvents. The strongest effect was observed with n-pentane as solvent — the yields were more than three times higher than at atmospheric pressure; actually it was more than benzene and pentane combined can dissolve at atmospheric pressure at their boiling point.

When pressure extraction was combined with separation by adsorption on carbon, the product was a pre-refined peat wax, with a yield about 35% higher than that of the crude wax obtained in the atmospheric extraction with n-pentane (Table 3).

Increased yields were observed with all solvents used under the sub- and supercritical conditions. The sample of peat available was not typical; it was a young peat with a very low wax content (2% instead of the usual 6% in

TABLE 3. Extraction of Peat

Solvent	Atmos. Extract		Stage No.	°C	psig	Pressure Extraction				Total Yield %
	%	Total Yield %				Peat Wax %	Low -MW (Adsorbed) %	Asphaltenes Medium -MW %	High -MW %	
Oven-dried Peat:										
n-Pentane	1.4		1	222	830	(-----)	4.4	(-----)		
Benzene	2.5		2	281	822			(-----)	4.6	
Benzene + Ethanol	3.3	7.2	3	277	805				4.6	13.6
				-250						
				-288						
Air-dried Peat:										
n-Pentane	1.8		1	161	815	2.8				
			2	-218	-846		2.5			
				158	830					
				-170						
			2a	180	820			0.75		6.05
Benzene	3.4		3	160	790				3.8	
				-270	-846					
Benzene + Ethanol	3.2	8.4	3a	282	785				2.8*	12.7
				-823						

Note: *Extraction interrupted (not exhaustive).

the atmospheric extraction). The air-dried peat gave higher yields with pentane under pressure.

Extraction and Separation of Glycerides

The glycerides were supported on either celite or silica, the coated support was packed as a fixed bed and extracted with supercritical n-pentane (at about 230°C and 56 bar (800 psig.)). The intention was to investigate the rates of extraction of individual glycerides, to predict the feasibility of their separation from mixtures and to test the technique experimentally.

Extraction of Glycerides from Celite

The desorption curve of a triglyceride (TG) differed little from that of a diglyceride (DG), but both differed considerably from that of a monoglyceride (MG) (the glycerides being derived from the same fatty acid). This would suggest that MG could be separated from TG + DG on celite, and that under favourable conditions (longer columns and optimum flowrates) even TG and DG could possibly be separated. No hydrolysis of glycerides was observed. Time did not permit study of the separation of mixtures.

Extraction of Glycerides from Silica

The extraction rates for TG supported on silica were about five times faster than those for DG or MG. This strongly suggested the feasibility of separating TG from partial glycerides. It was decided, therefore, to study the separation effect on a 50/50 mixture of TG + DG. In the first separation run, the LC detector trace and the gravimetric fractionation curve showed unexpectedly four peaks instead of two. The TLC confirmed deep hydrolysis of glycerides (and contamination by "waxes" from the silica support — lastpeak). After two more separation runs with a thoroughly dried and conditioned silica in situ (under pressure), it became obvious that a high-surface silica was not a suitable support for glycerides, even if elaborate precautions were taken to prevent hydrolysis.

DISCUSSION

Extraction and Separation of Bitumen

Solvent Power of n-pentane

The results show a great increase in the solvent power of n-pentane for asphaltenes under the sub- and supercritical conditions. This is true both for tar sand and peat, though it was especially prominent in the case of peat. By dissolving asphaltenes, n-pentane behaved more like a cycloparaffinic or even aromatic compound⁽¹⁴⁾, because only these compounds can dissolve asphaltenes, which are normally quite insoluble in lower paraffins such as n-pentane. Benzene, with its high solvent power even at atmospheric pressure, shows a smaller increase due to pressure. For this reason it is tentatively suggested that n-pentane undergoes a temporary change in character under the sub- and supercritical conditions, becoming similar to that of a cyclo-paraffinic compound. The extraction conditions were not severe enough to lead to a ring closure of the n-pentane chain, so a simple cyclopentane configuration is not only unlikely but impossible. The association of the n-pentane molecule with the asphaltene molecule seems a likely way of "closing" or forming a hetero-cyclo-paraffinic "ring" — perhaps an arch or bridge would be a better description. Since propane and butane do not dissolve asphaltenes under supercritical conditions, it seems that the length of the paraffinic molecule is crucial, a five-carbon chain being the minimum length. This could point to a bridging effect

between the basic units (sheets) of the asphaltene molecule.

Given the size of the asphaltene molecule, it is likely that more than one molecule of n-pentane will associate with a single asphaltene molecule. Judging by the behaviour of the n-pentane solution of asphaltenes in contact with active carbon under the sub- and supercritical conditions, such aggregates seem to be held together by weak linkages, which are easily broken during the adsorption; the asphaltene molecule would then be preferentially adsorbed by virtue of its large molecular weight and n-pentane desorbed. The existence of such weak aggregates seems therefore, to be an essential requirement for a successful separation by adsorption during sub- and supercritical extraction.

There is another possibility which should be mentioned, that is the effect of oils dissolved in pentane; such a solution has a higher solvent power than n-pentane itself. Mitchell and Speight⁽¹⁴⁾ investigated the solubility of the tar sand asphaltenes in mixtures of n-pentane with different amounts of the tar sand bitumen and found that, at atmospheric pressure, about 20% of bitumen in pentane would be required to increase the solubility of asphaltenes by about 5-8% only. During the extractions of tar sands with n-pentane, the highest average concentration of "oils" in the first and second fraction was 1.7% (with a possible maximum of about 5% for a minute or so). With peat it was only 0.3%. Since the increase in solubility was more than 300%, it seems unlikely that the "solution" effect contributed substantially to the solvent power of n-pentane. Because such a solution would contain lower aromatics, its effect would be more likely negative in the sense that it could redissolve some of the asphaltenes adsorbed in the carbon bed; this may explain traces of asphaltenes in the first five fractions.

The pressure and increased temperature assist the solvent to penetrate better into the lattices and the fine structure of the solids to be dissolved or extracted. It is known that strong, high-boiling solvents benefit from it considerably, but not weak, low-boiling solvents. Another effect of pressure and increased temperature concerns paraffinic solvents themselves — the self-association of paraffinic molecules is reduced, which imparts to them higher dispersion forces and therefore higher solvent power⁽¹⁴⁾. If this were the case with n-pentane, at least to any large extent, it would interfere with the separation of asphaltenes on carbon by redissolving them.

n-Pentane, under sub- and supercritical conditions, does not dissolve all the asphaltenes present. According to Mitchell and Speight⁽¹⁴⁾, the asphaltene molecules of different size form aggregates (micelles) having a high molecular weight core of a more polar character, while the outer zone of the micelles is formed by lower molecular weight asphaltenes with aliphatic moieties. This makes the outer zone less polar and less aromatic in character and obviously more easily dissolved in the sub- and supercritical pentane. The high molecular weight resins tend to associate with the core of the micelle. Thus the solubility of asphaltenes in n-pentane under the sub- and supercritical conditions can be a measure of their molecular size and association; with the tar sands, the high-MW cores seem relatively small, because n-pentane dissolved 95% + of the benzene-soluble extract; with peat, they are much bigger, since only 32% and 48% could be dissolved.

Rates of Extraction of Bitumen

With the easily soluble and extractable bitumen of tar sands, the differences in the extraction rates between

atmospheric and pressure extraction were not significant in the experimental arrangement. With peat, however, and its less accessible and less soluble bitumen, the differences were highly significant in favour of the pressure extraction, especially with n-pentane.

The yield obtained with boiling n-pentane in the atmospheric extraction of peat after one hour could be reached in 7 minutes under supercritical conditions. When the extract was simultaneously "refined" by absorption on carbon, it took only 35 minutes under pressure to collect the same amount of the refined peat wax as against 5.35 hours required with atmospheric extraction (to obtain crude wax). The pressure extraction rates with pentane were, therefore, approximately ten times higher. With benzene, and benzene/ethanol mixture, the differences in the extraction rates of peat were smaller, yet the pressure extraction was still twice to three times faster than atmospheric extraction. The solvent flowrates, expressed as space velocities, were between 12 and 16 litres of solvent per hour per litre of the extraction volume; and increase in flowrates would undoubtedly improve the extraction rates, especially for tar sands.

Separation Effects in Bitumen Extractions

Temperature Programming

The sub- and supercritical extraction was not operated isothermally (see Tables 1 and 3), though in some cases the benzene stage was more or less isothermal. The pentane stage, including the adsorption stage, was always temperature programmed. In the tar sand extractions, the pressure was also partly programmed, but with peat it was kept more or less constant, well above the critical pressure of the solvent.

The advantage of temperature programming — and perhaps the main reason for it — was that the extraction was progressive and the heat-sensitive compounds were not exposed to high temperatures from the beginning of the extraction. The other advantage was fractionation of the extracts by their boiling points— in the case of the pentane extracts this applied both to the deasphalted product and to the adsorbed asphaltenes.

Although the actual separation effect was not determined so far analytically, changes in colour of individual fraction residues and changes in odour could be observed. The temperature programming would reduce considerably the need for distillation of extracts. In other words, in a single operation it would be possible to extract, deasphalt and fractionate simultaneously.

Fraction of asphaltenes

Given considerable differences in the size and complexity of asphaltene molecules⁽¹³⁾, consisting of several basic units (aromatic sheets), each unit having at least 6 condensed aromatic rings with side-chains, and held together by alkyl chains (or even by electrostatic association), it is not surprising that the asphaltenes can be fractionated by their molecular weight using differences in solubility. The more soluble low molecular weight asphaltenes have molecular weights from about 2,500 to 4,000, the less soluble and insoluble ones have a molecular weight up to 10,000 and more⁽¹⁴⁾. Fractions have been obtained which are soluble in sub- and supercritical n-pentane (which are described as the low-MW asphaltenes), and those either soluble in benzene under pressure (medium to high-MW), or requiring a more polar solvent, like benzene with ethanol (very high-MW asphaltenes).

Mitchell and Speight⁽¹⁴⁾ recently separated tar sands asphaltenes into two fractions by a two-stage precipitation, and found that the first fraction contained 91% of all

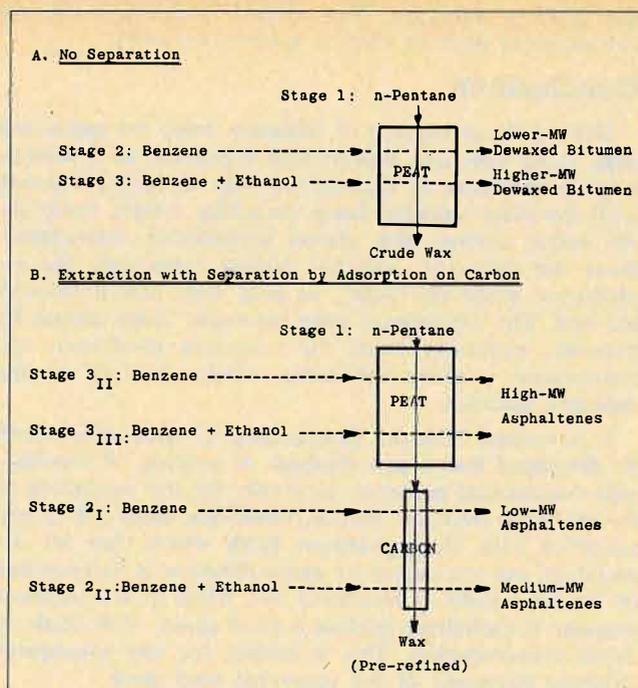


FIGURE 4. Peat extraction.

mineral matter present in the original bitumen, while the second fraction had only 7%; about 2% were found in the deasphalted oil. They speak about the "implications of such a process being far-reaching insofar as it allows the removal of mineral matter, which has an adverse effect on catalysts, in conjunction with a fraction relatively enriched in hetero-atoms (nitrogen, oxygen and sulphur) and allows the preparation of low-mineral cracking stocks which are also lower in hetero-atom content".

The temperature-programmed pressure extraction with separation by adsorption seems especially suitable for such a fractionation as it could provide several asphaltene fractions with pentane; and several benzene-fractions as well, if this were desirable. The adsorption train should then have several carbon columns, one for each temperature range of the pentane stage; in the benzene stage, adsorption could not be used, only the difference of solubility changing with temperature. Each carbon column would be separately extracted to recover the asphaltene fractions.

Resins could be separated from the pentane extract by adsorption on bleaching earth simultaneously with deasphalting, using a bleaching earth column downstream of

TABLE 4. Metal Content of Tar Sands Fractions

	Vanadium (ppm)	Nickel (ppm)	Iron (ppm)
Pressure extract with n-pentane (de-asphalted by adsorption) on active carbon	20	6	0.3
Atmospheric extract with n-pentane	40	*	*
Low-MW asphaltenes (desorbed from active carbon by benzene)	415	110	40
High-MW asphaltenes (from the residue after the pressure extraction with n-pentane)	79.5	*	*
Atmospheric extract with benzene of the residue after the atmospheric extraction with n-pentane (Soxhlet)	630	180	290

*Not estimated

the carbons columns. This would be desirable in the extraction of peat (to recover a resin-free wax).

Conclusions

During the extraction of bitumens from tar sands and peat, using sub- and supercritical n-pentane as a solvent, large proportions of asphaltenes were extracted together with the more valuable lower molecular weight materials. An active carbon bed, placed immediately downstream from the extractor, adsorbed almost completely the asphaltenes, while the "oils", or peat wax, passed through the bed. The asphaltenes were recovered from carbon by benzene, preferably under the extraction conditions, and represented a lower molecular weight fraction of the asphaltic materials.

It is realised that the deasphalting by adsorption could be developed into a new method, or process, of considerable commercial potential, especially for the upgrading of the tar sands bitumen. Metals (vanadium, nickel, iron) are adsorbed with the asphaltenes (with which they are associated), but the degree of demetallization is independent of the total yield of recovered oils, while in the standard propane deasphalting process a yield above 75% leads to metal contamination. This is critical for any subsequent catalytic treatment of the recovered feed stock.

In the extraction of peat, a pre-refined peat wax was obtained at a yield 35% higher than in the atmospheric extraction (before refining). The total pressure extract, with n-pentane and benzene, was up to 90% higher.

Patent Application

A new deasphalting process is proposed based on adsorption of asphaltenes, and permitting a practically complete recovery of "oils" from a bitumen, or a vacuum residue, while maintaining a high degree of demetallization and deasphalting. A provisional patent application has been filed⁽¹⁶⁾.

Acknowledgement

We wish to thank the Science Research Council, London, for the research grant, and Unilever Limited for their support and help with analyses of glyceride mixtures.

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DISCUSSION

S. Bruin: Do you have any experience with using carbon dioxide as a supercritical solvent in, e.g., food applications?

T.R. Brott: We have a limited experience in food application. We have studied the solubilities of glycerides using supercritical carbon dioxide as a carrier gas at pressures at 80 to 100 bars. At these pressures the solubility of glycerides in the dense gas phase was very low; pressure several times higher is required to obtain commercially interesting solubilities (see references 7, 10-12). The solubility of glycerides in carbon dioxide at 100 bar increased considerably when a second solvent was added (often spoken of as an entrainer) (see reference 4). Good separations were obtained.

J. Rendall: RTL is involved in tar sands with a solvent extraction. Your figure for pre-refined, demetallized, non-asphaltic material as 93% of the organic extract from the sand seems very high compared to other published results. Can you please comment?

T.R. Brott: The yields of deasphalted oils (maltenes) were expressed in percent of the recoverable oils (such as obtained by the atmospheric extraction in a Soxhlet with n-pentane, which is considered to be an exhaustive recovery of oils). Because asphaltenes in our process cannot appear in the deasphalted oils — unlike in the conventional deasphalting with propane — we did not include asphaltenes in the calculation of yields. Using Table 1, the total organic extractable matter contained 77% of the pentane extract and 23% asphaltenes. The 93% yield of adsorption-deasphalted oils (based on total pentane extract) would correspond to 75% of the total charge. The asphaltenes separated by adsorption (and those left in the residue) contained no oils. By careful temperature programming it is considered possible to recover all soluble matter contained in the original tar sand sample.

Since the paper was prepared, further work on the analysis of the fractions has been carried out by thin layer chromatography. The results demonstrate more thorough removal of asphaltenes in samples deasphalted by adsorption on carbon than in pentane deasphalted samples at atmospheric pressure.

In addition, the analysis of the metal content in various samples has been extended. The results are shown in Table 4 which supplements the data contained in Table 2.

G.H. Beyer: Extraction under super-critical conditions may offer intriguing possibilities for obtaining aromatic feed stocks from coal on its way to a conventional boiler. This approach strikes me as a good way to divert part of the coal to higher-grade uses as a potential hedge against dwindling supplies of petroleum.

Are you aware of any plans for using super-critical extraction on a larger pilot-plant scale for selective removal of a fraction of the coal prior to the combustion of the remainder as a boiler fuel?

T.R. Brott: As far as I am aware the National Coal Board in the U.K. has extensive plans for the liquefaction of coal which, I believe, include extraction near critical conditions. It is likely that any ultimate adoption of the technique will form part of an integrated, optimized 'complex' overall process producing a range of fuels and chemicals.

Selectivity and Solvency Properties of Extraction Solvents and their Mixtures

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ABSTRACT

We have studied the selectivity and solvency properties of eight commercially used, or proposed, BTX (benzene-toluene-xylene) extraction solvents. Four binary mixtures of some of these solvents were investigated over the whole concentration range. The selectivity and solvency were defined in terms of limiting activity coefficients. For 14 hydrocarbons we determined the limiting activity coefficients, in the temperature range 30 - 80°C, by means of a GLC technique.

For the mixture of *N*-methylpyrrolidone and ethylene glycol we found a maximum in selectivity. The results show sulfolane to be the most selective solvent.

Introduction

SINCE THE INTRODUCTION OF THE LIQUID-LIQUID extraction process for the purification of benzene-toluene-xylene (BTX) aromatics, numerous extraction solvents have been proposed. Due to the variety of properties involved, no satisfactory answer had hitherto been found to the question — what is the optimum solvent. The overall performance of a solvent is governed by solvency and selectivity and to a lesser extent by properties such as thermal stability, viscosity, boiling point, density and corrosivity.

Surveys of extraction solvent properties presented in the literature, e.g.^(1,2), are inconsistent in their definitions, especially with regard to solvency and selectivity; also, they do not cover the complete range of today's solvents or lack the required accuracy. As a result it has been difficult to make a reliable comparison between the various solvents proposed. We have therefore felt the need to investigate the solvency and selectivity of commercially used, or proposed, BTX-extraction solvents. In addition, we have studied the properties of solvent mixtures to investigate whether their use would have any advantages over that of pure compounds. The present study does not cover other (less) relevant extraction solvent properties such as vapour pressure, density, viscosity, thermal stability, etc.

Measures of Solvency and Selectivity

Comparison between solvents has been hampered by the large number of definitions of solvency and selectivity used over the past two decades. In our study we have followed the example of Deal and Derr⁽²⁾, who did scouting work on aromatics-extraction solvents and, just as Gerster⁽³⁾ had done for the pentane-pentene separation, introduced as a measure of solvency the reciprocal value of the infinite dilution or limiting activity coefficient γ_i^∞ of hexane in the solvent. As a measure of the selectivity they chose the ratio of the limiting activity coefficients of hexane and benzene in the solvent. These choices have their basis in the thermodynamic equilibrium relation for

a component distributed over two phases, namely the equality of fugacities f_i :

$$f_i = f_i' \dots \dots \dots (1)$$

For the case of a hydrocarbon distributed over a solvent and a hydrocarbon phase, this relation reduces to an equality of activities:

$$\gamma_i^h x_i^h = \gamma_i^s x_i^s \dots \dots \dots (2)$$

where x is the mole fraction and the superscripts h and s stand for hydrocarbon and solvent phase, respectively. From eq. (2) it can be seen that the distribution coefficient k_i , defined as

$$k_i = x_i^h/x_i^s \dots \dots \dots (3)$$

can also be expressed as $k_i = \gamma_i^s/\gamma_i^h \dots \dots \dots (4)$

Now, if we define the selectivity $\beta_{i,j}$ as the ratio of the distribution coefficients, we find:

$$\beta_{i,j} = k_i/k_j = (\gamma_i^s/\gamma_j^s) \cdot (\gamma_j^h/\gamma_i^h) \dots \dots \dots (5)$$

As the ratio of the activity coefficients in the hydrocarbon phase is close to unity, with a maximum value of about 1.5, and as it will be almost the same for different solvents, the ratio of the activity coefficients in the solvent phase can be adopted as a measure of selectivity.

Since the activity coefficient is highly dependent on the composition, we can only use this quantity to compare solvents if the coefficients are measured at equal concentrations. Measurements at finite concentrations are difficult and time consuming, so we chose the infinitely dilute state as the reference. Limiting activity coefficients can accurately be determined by measuring the retention volume of a hydrocarbon as it passes through a GLC column where the solvent is used as the stationary phase. Applying this technique and following the definitions of solvency and selectivity, we can compare extraction solvents in a thermodynamically consistent way. Furthermore, the limiting activity coefficient data will be of value for a complete description of the phase equilibria for a given extraction system based on methods such as the ASOG method⁽⁴⁾ or the NRTL⁽⁵⁾ or UNIQUAC⁽⁶⁾ equation.

Measurements of Limiting Activity Coefficients

Theory (See Notation)

According to a review by Young⁽⁷⁾, the relation between the net retention volume V_N and the limiting activity coefficient is given by

$$\ln V_N = \ln \left[\frac{n_3 RT}{p_1^0 \gamma_{13}^\infty} \right] - \frac{(B_{11} - v_1^0) p_1^0}{RT} + \\ + \tilde{p} \left[\frac{2 B_{12} - \bar{v}_{13}^\infty}{RT} + \lambda \left\{ 1 - \left(\frac{\gamma \ln \gamma_{13}^\infty}{\gamma x_2} \right)_0 \right\} \right] \dots \dots \dots (6)$$

when \tilde{p} is a mean column pressure given by.

$$\tilde{p} = \frac{3}{4} \left[\frac{(p_i/p_o)^4 - 1}{(p_i/p_o)^3 - 1} \right] p_o \dots \dots \dots (7)$$

$$\gamma_{i3}^{\infty} = \frac{n_3 R T_{f1} p_o J_2^3}{(R_i - R_a) p_1^0 F} \dots \dots \dots (9)$$

The three outer right terms in eq. (6) are corrections for, respectively, the influence of pressure on the fugacity of the pure solute, the influence of pressure on the fugacity of the solute under column conditions and the influence of the solubility of the carrier gas in the stationary phase. As in our experiments we used hydrogen as the carrier gas and the pressure never exceeded 2 bar, it will be clear that the third effect is sufficiently small for us to leave out the third correction term. Under our experimental conditions, even if we assume conservative values for $B_{1,2}$ and \bar{v}_{13}^{∞} , the second correction term will always be smaller than 0.5%. The first correction term only contributes significantly for the very light solutes (e.g. pentane) and at the highest temperatures (100°C).

The net retention volume can be found from experimental conditions through

$$V_N = \frac{(R_i - R_a) F T_{co}}{p_o J_2^3 T_{f1}} \dots \dots \dots (8)$$

where R_i and R_a are the retention times of the solute and of air, respectively. F is the flow of the carrier gas, $p_o J_2^3$ is the mean column pressure defined by eq. (7) and T_{co} and T_{f1} are the temperatures of the column and of the flow measurements, respectively. So, if we combine eqs. (6) and (8) and ignore the correction terms in eq. (6), the limiting activity coefficient can be calculated from

This equation demonstrates the linear dependence of the activity coefficient on the five main experimental variables: the mass of the stationary phase, the pressure, the temperature, the flow and the retention time. In consequence, limiting activity coefficients can be measured accurately by the GLC technique, once the proper determination of all the five main variables is guaranteed.

Experimental

General

Beside the above five main variables, two other factors can significantly affect the validity of the results, viz.

- (a) adsorption of the solute at the liquid and/or the solid surface,
- (b) the influence of the sample size on the retention time.

(a) In the early days of measuring γ 's by GLC, adsorption of the solute at the solid phase did occur. However, it was soon found that this was easily suppressed by choosing the proper, "inert" solid support and by increasing the ratio of the stationary phase to the solid support. Ashworth and Everett⁽⁸⁾ measured the vapour pressure of solutes as a function of composition both in bulk solvent and in solvent spread on Celite. Even in cases where the accuracy of their measurements corresponded to 0.001 in γ 's they were unable to detect any systematic difference between the two series of measurements.

TABLE 1. Limiting Activity Coefficients in Sulfolane, Ethylene Glycol and Dimethyl Sulfoxide

Hydrocarbon	Sulfolane			EG			DMSO	
	30°C γ^{∞}	60°C γ^{∞}	80°C γ^{∞}	30°C γ^{∞}	60°C γ^{∞}	80°C γ^{∞}	30°C γ^{∞}	80°C γ^{∞}
n-Pentane	48.8	33.2	27.7	311.0	229.0	197.0	48.8	25.9
n-Hexane	69.5	47.0	37.9	522.0	384.0	536.0	72.5	35.4
n-Heptane	96.0	65.3	51.4	831.0	610.0	806.0	107.0	47.8
n-Octane	132.0	88.8	66.0	1250.0	915.0	1170.0	156.0	63.9
n-Nonane	181.0	119.0	87.3	1840.0	1360.0	1710.0	229.0	83.6
n-Decane	252.0	161.0	115.0	2620.0	1970.0		334.0	108.0
Cyclohexane	34.9	24.3	19.3	238.0		148.0	36.6	20.7
Methylcyclohexane	51.1	34.9	27.4	410.0		276.0	54.5	29.1
Ethylcyclohexane	71.6	47.6	37.1	674.0	311.0	429.0	78.5	39.4
n-Propylcyclohexane	107.0	67.8	50.9	1140.0	485.0	705.0	117.0	54.1
n-Butylcyclohexane	160.0		69.4	1970.0		25.1	181.0	74.9
Benzene	2.61	2.46	2.38	31.1	27.4	45.7	3.27	2.67
Toluene	4.19	3.72	3.51	58.7	50.4	76.9	5.04	3.92
Ethylbenzene	6.00	5.22	4.93	105.0	86.7		7.76	5.41

TABLE 2. Limiting Activity Coefficients in N-Formylmorpholine, 3-Methylsulfolane and N-Methylpyrrolidone

Hydrocarbon	N-formylmorpholine			3-Methylsulfolane			NMP	
	30°C γ^{∞}	60°C γ^{∞}	80°C γ^{∞}	30°C γ^{∞}	60°C γ^{∞}	80°C γ^{∞}	30°C γ^{∞}	80°C γ^{∞}
n-Pentane	26.0	19.1	15.5	21.8	16.7	14.1	12.3	8.26
n-Hexane	35.2	25.4	20.5	30.0	22.4	18.3	15.6	9.91
n-Heptane	47.5	33.1	26.3	41.2	28.8	23.7	19.9	11.8
n-Octane	63.4	42.2	33.1	55.6	37.8	30.3	25.1	14.3
n-Nonane	85.2	53.6	40.6	75.8	49.0	38.6	31.1	16.5
n-Decane	114.0	69.5	49.9	103.0	62.3	45.6		20.1
Cyclohexane	17.9	13.9	11.5	16.4	12.3	10.4	9.53	6.55
Methylcyclohexane	24.7	18.6	15.0	22.8	16.8	13.7	11.5	7.70
Ethylcyclohexane	33.0	23.8	19.1	30.7	21.8	17.8	14.4	9.41
n-Propylcyclohexane	46.7	31.7	24.6	42.6	29.0	23.1	18.4	14.1
n-Butylcyclohexane	66.2	42.7	32.3	62.1	39.8	30.8	24.2	11.1
Benzene	1.96	1.99	1.93	1.82	1.80	1.83	1.09	1.44
Toluene		2.75	2.62	2.56	2.51	2.53		1.82
Ethylbenzene		3.66	3.42	3.53	3.32	3.30		1.81

Adsorption at the gas-liquid interface has been proved experimentally. For several systems, the retention volumes have been known to vary with the ratio of the stationary phase to support. Martin⁽⁹⁾ showed that adsorption at the liquid surface can play a role especially for systems with apolar solutes and polar stationary phases. However, the effects he mentioned were very small (less than 0.5%) compared with the effect of dissolution in the liquid phase. Furthermore, the ratio of stationary phase to solid support has been much higher in our work than in Martin's experiments. Therefore, we are certain that liquid surface adsorption did not influence our results in a significant way.

(b) Since, in most systems, the activity coefficients depend very much on their concentration in the liquid phase, it will be clear that the retention time is dependent on the size of the sample. It is therefore important to use small samples. Cruickshank⁽¹⁰⁾ found that in a column containing 2 g of stationary liquid and 8 g of solid support, the effect was negligible for samples less than 2 μ mol. In our work the column loading was generally about 10 g and the samples were 2 μ mol.

We used an air thermostat, which was regulated to within 0.1°C. The flow was controlled by a Zambra & Negretti type valve and the flow rate was measured by a soap-film gas meter. The pressures were read from Bourdon-type gauges to an accuracy of 0.5%. The detector was a standard heat conductivity cell. The retention time was measured to within 0.5 s with a stopwatch. The columns were stainless steel, with an internal diameter of 6 mm. The solid support consisted of Chromosorb P which we coated with 30 %w of liquid phase. All liquid phases were purified by distillation before use and analysed by GLC to a purity of 99.9% or better. The solutes were purchased as regular A.R. material and used without any further purification.

To test the accuracy of the method we measured the activity coefficients of 14 hydrocarbons in sulfolane at 60°C on two different columns. One column was twice as long as the other, so that except for the temperature all experimental variables were changed. The average between the measured activity coefficients in the two experiments was 0.6%, while the largest difference was 1.3%. The outcome indicated that limiting activity coefficients can be measured by this GLC technique to an accuracy of approx. 1%.

Results and Discussion

Pure Compounds

The following solvents were studied:

Diglycolamine	(DGA)
Dimethyl sulfoxide	(DMSO)
Ethylene glycol	(EG)
3-methylsulfolane	
N-formylmorpholine	
N-methylpyrrolidone	(NMP)
Sulfolane	
Tetraethylene glycol	(TTEG)

Numerous other extraction solvents have been proposed but for reasons of chemical instability or high corrosivity they have never found application in actual plant operation; therefore, we did not include them in the present study. N-methylpyrrolidone and ethylene glycol are not in fact pure extraction solvents, but we included them because mixtures of the two solvents are used in the Arosolvan process⁽¹¹⁾.

We measured the limiting activity coefficient for each of the following 14 hydrocarbons in every solvent at 30, 60, and 80°C.

Paraffins	Naphthenes	Aromatics
n-pentane		
n-hexane	cyclohexane	benzene
n-heptane	methylcyclohexane	toluene
n-octane	ethylcyclohexane	ethylbenzene
n-nonane	n-propylcyclohexane	
n-decane	n-butylcyclohexane	

TABLE 3. Limiting Activity Coefficients in Diglycolamine and Tetraethylene Glycol

Hydrocarbon	DGA		30 °C γ^∞	TTEG	
	30 °C γ^∞	70 °C γ^∞		60 °C γ^∞	80 °C γ^∞
n-Pentane	65.5	36.6	27.6	20.0	15.4
n-Hexane	97.8	50.6	36.0	27.4	21.1
n-Heptane	144.0	70.7	49.5	35.6	28.7
n-Octane	212.0	98.2	67.5	46.7	38.1
n-Nonane	315.0	135.0	91.1	61.5	51.6
n-Decane	464.0	184.0	120	82.0	67.9
Cyclohexane	45.4	26.1	17.9	13.2	11.1
Methylcyclohexane	69.2	37.2	25.7	18.7	15.4
Ethylcyclohexane			35.5	24.8	20.8
n-Propylcyclohexane			51.4	34.7	29.1
n-Butylcyclohexane			74.4	47.8	39.9
Benzene	5.53	5.03	2.41	2.33	2.26
Toluene	8.26	7.68	3.71	3.54	3.34
Ethylbenzene	12.6	11.1	5.50	5.16	4.77

We did not include higher homologues of the aromatic series because the low activity coefficients and vapour pressures would result in excessive retention times (> 1 hour).

As an example, the results of our measurements for sulfolane at 60°C are presented in Figure 1, where the log of the activity coefficient is plotted as a function of the carbon number. It is striking how very nearly this system, like all the systems we measured, shows the well-known linear relationship, indicating that the concept of group or segment-wise additivity of log γ is very closely obeyed in these systems. Of course, benzene and cyclohexane do not follow this relationship exactly. The complete results are listed in Tables 1-3. Figure 2 gives the solvency-selectivity plot. Here every solvent is represented by a line plotting its selectivity and solvency as a function of temperature, between 30 and 80°C. This diagram shows that sulfolane is far and away the most selective solvent, followed by DMSO and N-formylmorpholine. EG obviously has too low a solvency and can only be used in combination with another solvent. The opposite is true for NMP which solvent has a rather high selectivity in view of its solvency level. However, its enormous solvency prevents its use as a BTX-extraction solvent because it will be completely miscible with most feeds. Since in liquid-liquid extraction the number of theoretical equilibrium stages is rather limited (6-10), methylsulfolane and N-formylmorpholine clearly do not reach the desired level of selectivity. However, their higher solvency makes them suitable for use as extractive distillation solvents. DMSO has both a lower selectivity and a lower solvency than sulfolane, which is even more true of DGA.

TABLE 4. Limited Activity Coefficients in Mixtures of Sulfolane (sulf.) and 3-Methylsulfolane

Hydrocarbon	γ^∞ at 30°C					γ^∞ at 60°C					γ^∞ at 80°C				
	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w
n-Pentane	48.8	37.2	31.1	26.3	21.8	33.2	26.8	22.6	19.4	16.7	27.7	22.3	18.6	16.4	14.1
n-Hexane	69.5	53.2	43.7	36.6	30.0	47.0	37.7	31.4	26.1	22.4	37.9	31.0	25.7	21.7	18.3
n-Heptane	96.0	74.8	60.3	50.1	41.2	65.3	52.1	42.8	35.1	28.8	51.4	42.1	35.0	28.1	23.7
n-Octane	132.0	103.0	82.3	67.2	55.6	88.8	70.0	56.5	45.3	37.8	66.0	55.5	45.0	36.4	30.3
n-Nonane	181.0	143.0	114.0	92.2	75.8	119.0	93.4	73.7	58.1	49.0	87.3	72.2	58.2	46.2	38.6
n-Decane	252.0	197.0	197.0	122.0	103.0	161.0	125.0	98.3	76.3	62.3	115.0	93.4	74.2	58.1	45.6
Cyclohexane	34.9	27.9	23.0	19.5	16.4	24.3	20.1	17.1	14.6	12.3	19.3	16.6	14.3	12.2	10.4
Methylcyclohexane	51.1	40.4	32.9	27.4	22.8	34.9	28.4	23.8	20.0	16.8	27.4	23.4	19.7	16.6	13.7
Ethylcyclohexane	71.6	56.6	45.1	36.9	30.7	47.6	38.2	31.4	25.9	21.8	37.1	30.6	25.5	21.2	17.8
n-Propylcyclohexane	107.0	83.2	65.5	52.5	42.6	67.8	53.7	43.1	34.9	29.0	50.9	41.8	34.3	27.9	23.1
n-Butylcyclohexane	160.0	124.0	96.0	75.8	62.1		75.5	60.3	47.9	39.8	69.4	56.5	46.4	37.0	30.8
Benzene	2.61	2.29	2.09	1.95	1.82	1.46	2.24	2.09	1.95	1.80	2.38	2.23	2.08	1.93	1.83
Toluene	4.19	3.48	3.10	2.83	2.56	3.72	3.32	3.01	2.73	2.51	3.51	2.21	2.95	2.69	2.53
Ethylbenzene	6.00	5.00	3.92	3.92	3.53	5.22	4.59	4.09	3.67	3.32	4.93	4.33	3.93	3.51	3.30

TABLE 5. Limiting Activity Coefficients in Mixtures of Sulfolane (Sulf.) and Ethylene Glycol

Hydrocarbon	γ^∞ at 30°C					γ^∞ at 60°C					γ^∞ at 80°C				
	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w	Sulf. 100 %w	Sulf. 75 %w	Sulf. 50 %w	Sulf. 25 %w	Sulf. 0 %w
n-Pentane	48.8	76.0	115.0	184.0	311.0	33.2	50.9	65.2	140.0	229.0	27.7	42.6	53.0	113.0	197.0
n-Hexane	69.5	119.0	159.0	300.0	522.0	47.0	76.6	103.0	222.0	384.0	37.9	63.3	82.1	177.0	
n-Heptane	96.0	180.0	257.0	476.0	831.0	65.3	109.0	155.0	340.0	610.0	51.4	89.0	120.0	274.0	536.0
n-Octane	132.0	263.0	372.0	732.0	1250.0	88.8	160.0	232.0	525.0	915.0	66.0	124.0	176.0	415.0	806.0
n-Nonane	181.0	379.0	545.0	1100.0	1840.0	119.0	223.0	338.0	781.0	1360.0	87.3	172.0	253.0	613.0	1170.0
n-Decane	252.0	542.0	783.0	1610.0	2620.0	161.0	310.0	484.0	1140.0	1970.0	115.0	235.0	357.0	892.0	1710.0
Cyclohexane	34.9	57.6	72.6	140.0	238.0	24.3	38.8	50.2	103.0		19.3	31.4	40.5	83.0	
Methylcyclohexane	51.1	89.8	122.0	230.0	410.0	34.9	58.3	78.1	168.0		27.4	46.4	62.7	135.0	148.0
Ethylcyclohexane	71.6	136.0	192.0	374.0	674.0	47.6	84.4	118.0	263.0	311.0	37.1	65.4	91.0	205.0	276.0
n-Propylcyclohexane	107.0	214.0	309.0	618.0	1140.0	67.8	125.0	183.0	419.0	485.0	50.9	94.7	137.0	324.0	429.0
n-Butylcyclohexane	160.0	330.0	494.0	999.0	1970.0		185.0	282.0	674.0	1050.0	69.4	136.0	205.0	507.0	705.0
Benzene	2.61	4.70	6.70	14.7	31.3	2.46	4.18	5.96	13.6	27.4	2.38	4.05	5.51	12.6	25.1
Toluene	4.19	7.66	11.4	26.2	58.7	3.72	6.54	9.78	23.3	50.4	3.51	6.26	8.86	21.2	45.7
Ethylbenzene	6.00	11.7	18.5	43.6	105.0	5.22	9.65	15.1	37.7	86.7	4.93	9.00	13.4	33.7	76.9

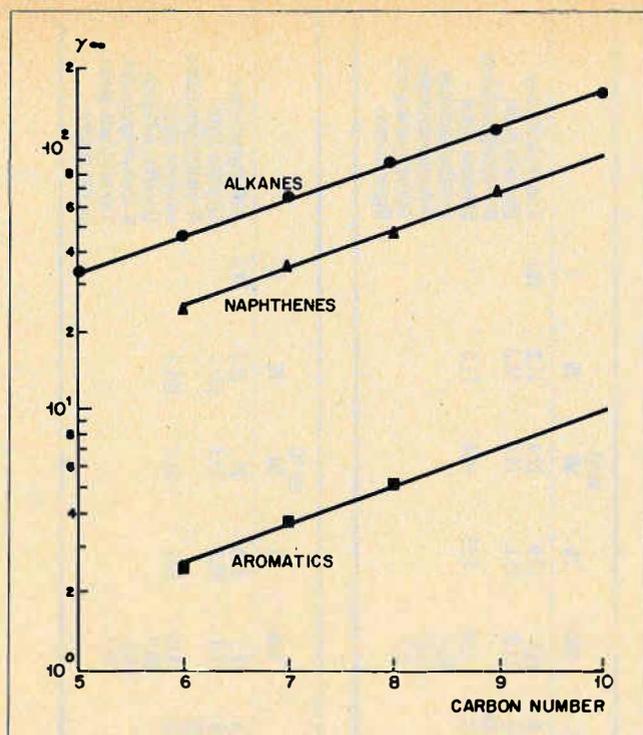


FIGURE 1. Limiting activity coefficients in sulfolane at 60°C.

Mixtures of Solvents

Mixed extraction solvents were first commercially applied by Lurgi, who use mixtures of NMP and EG in their Arosolvan process. They stated⁽¹¹⁾ that such mixtures show a synergistic effect, the pair having a significantly higher selectivity than either of the pure components. The basic data on which they base this conclusion were chosen in such a way that a straightforward comparison with existing data on sulfolane is impossible. We therefore measured the selectivity and solvency of NMP-EG mixtures in exactly the same way as we had done for sulfolane. For purposes of comparison we also collected data on the following combinations:

- Sulfolane-EG, to see whether this system, too, would exhibit a synergistic effect.
- Sulfolane-NMP and sulfolane-methylsulfolane as examples of combinations of two solvents having each at its own solvency level, a relatively high selectivity.

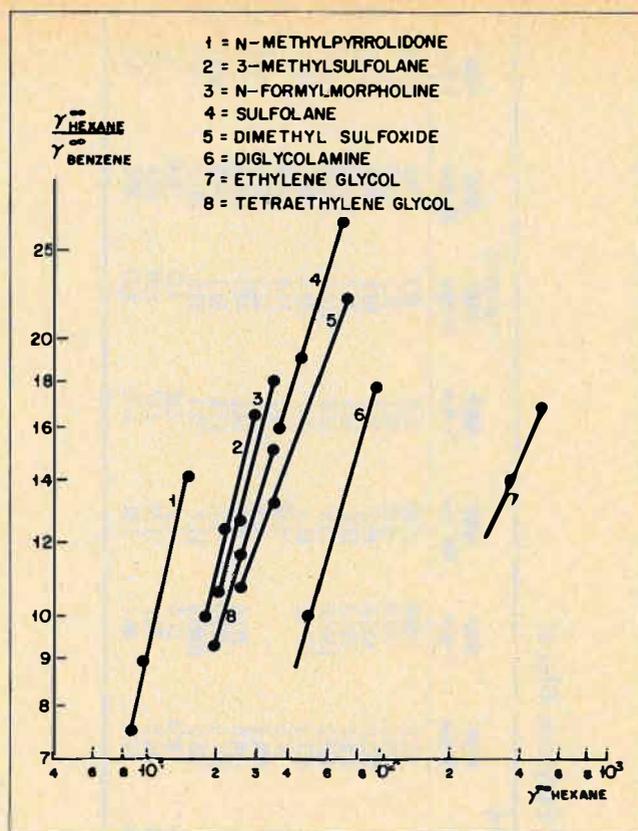


FIGURE 2. Selectivity-solvency of pure solvents at 30, 60, 80°C.

The limiting activity coefficient of the same 14 hydrocarbons as used before was measured at 30 and 60°C in each of the four above-mentioned solvent combinations, at three compositions (25, 50, 75 %w). The results of our measurements are listed in Tables 4-8. The relation between solvency, selectivity and composition is given in Figures 3-6 and Table 8. Figure 7 shows the solvency-selectivity diagram for the four mixtures at 60°C. From this diagram it can be concluded that going from NMP or 3-methylsulfolane to sulfolane there is a continuous increase in selectivity and a decrease in solvency. These mixtures behave in accordance with all the existing solution theories.

For the system NMP-EG we do find a maximum in the selectivity, but this maximum is located in such a low sol-

TABLE 6. Limiting Activity Coefficients in Mixtures of Sulfolane (Sulf.) and N-Methylpyrrolidone

Hydrocarbon	γ^∞ at 30°C					γ^∞ at 60°C				
	Sulf. 100 %m	Sulf. 75 %m	Sulf. 50 %m	Sulf. 25 %m	Sulf. 0 %m	Sulf. 100 %m	Sulf. 75 %m	Sulf. 50 %m	Sulf. 25 %m	Sulf. 0 %m
n-Pentane	48.8	30.2	21.0	13.9	12.3	33.2	26.3	17.1	12.4	8.26
n-Hexane	69.5	41.8	28.3	18.1	15.6	47.0	35.3	23.0	15.1	9.91
n-Heptane	96.0	58.2	37.6	23.2	19.9	65.3	46.8	29.5	18.6	11.8
n-Octane	132.0	78.4	49.1	29.6	25.1	88.8	61.0	37.2	22.6	14.3
n-Nonane	181.0	110.0	65.3	37.8	31.1	119.0	79.9	46.4	27.5	16.5
n-Decane	252.0	147.0		48.1		161.0	104.0		33.3	20.1
Cyclohexane	34.9	22.1	15.4	10.5	9.53	24.3	18.9	12.9	9.08	6.55
Methylcyclohexane	51.1	30.2	20.5	13.0	11.5	34.9	26.0	16.7	11.2	7.70
Ethylcyclohexane	71.6	42.5	28.6	16.8	14.4	47.6	34.2	21.3	13.6	9.41
n-Propylcyclohexane	107.0	62.7	38.6		18.4	67.8	48.2	28.1		11.7
n-Butylcyclohexane	160.0	90.6	53.4	29.9	24.2		66.0	36.6	21.9	14.1
Benzene	2.61	1.91	1.53	1.20	1.09	2.46	2.13	1.68	1.32	1.11
Toluene	4.19	2.88	2.19	1.63		3.72	3.10	2.33	1.77	1.44
Ethylbenzene	6.00	4.12	3.00	2.14		5.22	4.19	3.04	2.24	1.82

TABLE 7. Limiting Activity Coefficients in Mixtures of N-Methylpyrrolidone (NMP) and Ethylene Glycol

Hydrocarbon	γ^∞ at 30°C					γ^∞ at 60°C					γ^∞ at 80°C				
	NMP 100 %w	NMP 75% w	NMP 50 %w	NMP 25 %w	NMP 0 %w	NMP 100 %w	NMP 75 %w	NMP 50 %w	NMP 25 %w	NMP 0 %w	NMP 100 %w	NMP 75 %w	NMP 50 %w	NMP 25 %w	NMP 0 %w
n-Pentane	12.3	25.0	57.0	129.0	311.0	8.26	17.7	39.6	92.4	229.0	7.40	15.0	30.2	74.9	197.0
n-Hexane	15.6	34.2	76.7	196.0	522.0	9.91	22.2	55.0	138.0	384.0	8.83	19.2	41.7	101.0	
n-Heptane	19.9	45.9	111.0	301.0	831.0	11.8	28.8	78.3	212.0	610.0	10.5	24.2	59.4	155.0	536.0
n-Octane	25.1	60.0	155.0	444.0	1250.0	14.3	36.3	107.0	305.0	915.0	12.2	30.1	77.2	218.0	806.0
n-Nonane	31.1	80.0	220.0	650.0	1840.0	16.5	45.9	146.0	438.0	1360.0	13.9	36.8	101.0	305.0	1170.0
n-Decane		111.0	301.0	943.0	2620.0	20.1	58.1	198.0	627.0	1970.0	15.9	45.7	132.0	425.0	1710.0
Cyclohexane	9.53	18.9	399.0	95.5	238.0	6.55	13.1	29.4	67.5		5.92	11.5	22.9	50.5	
Methylcyclohexane	11.5	24.7	56.6	147.0	410.0	7.70	16.7	41.3	104.0		6.98	14.7	31.5	72.6	148.0
Ethylcyclohexane	14.4	33.1	81.0	229.0	674.0	9.41	21.5	57.0	154.0	311.0	8.18	18.5	42.7	109.0	276.0
n-Propylcyclohexane	18.4	45.1	121.0	365.0	1140.0	11.7	28.6	81.7	237.0	485.0	9.73	23.5	58.1	162.0	429.0
n-Butylcyclohexane	24.2	67.7	184.0	591.0	1970.0	14.1	37.2	117.0	365.0	1050.0	11.7	30.3	80.0	237.0	705.0
Benzene	1.09	2.12	4.45	10.8	31.1	1.11	2.03	4.34	9.59	27.4	1.17	2.08	4.01	8.47	25.1
Toluene		3.04	6.88	18.2	58.7	1.44	2.82	6.53	15.8	50.4	1.50	2.87	5.94	13.4	45.7
Ethylbenzene		4.24	10.4	29.8	105.0	1.82	3.74	9.35	24.6	86.7	1.81	3.72	8.23	20.1	76.9

TABLE 8. Solvencies (γ^∞ Hexane) and Selectivities ($\frac{\gamma^\infty \text{ Hexane}}{\gamma^\infty \text{ Benzene}}$) in Solvents and Solvent Mixtures

Solvencies	30 °C					60 °C					80 °C					
	100	75	50	25	0	100	75	50	25	0	100	75	50	25	0	
Sulfolane %w	26.6	23.2	20.9	18.8	16.5	19.1	16.8	15.0	13.4	12.4	15.9	13.9	12.4	11.2	10.0	3-Methylsulfolane
Sulfolane %m	26.6	25.3	23.7	20.4	16.8	19.1	18.3	17.3	16.3	14.0	15.9	15.6	14.9	14.0		Ethylene glycol
Sulfolane %m	26.6	21.9	18.5	15.1	14.3	19.1	16.6	13.7	11.4	8.93						N-methylpyrrolidone
N-Methylpyrrolidone %w	14.3	16.1	17.2	18.1	16.8	8.93	10.9	12.7	14.4	14.0	7.55	9.23	10.4	11.9		Ethylene glycol
Dimethyl sulfoxide	22.2					13.3					10.7					Dimethyl sulfoxide
N-Formylmorpholine	18.0					12.8					10.6					N-formylmorpholine
Tetraethylene glycol	14.9					11.7					9.3					Tetraethylene glycol
Diglycolamine	17.7					10.1*										Diglycolamine

Selectivities	30 °C					60 °C					80 °C					
	100	75	50	25	0	100	75	50	25	0	100	75	50	25	0	
Sulfolane %w	69.5	53.2	43.7	43.7	30.0	47.0	37.7	31.4	26.1	22.4	37.9	31.0	25.7	21.7	18.3	3-Methylsulfolane
Sulfolane %w	69.5	119.0	159.0	300.0	522.0	47.0	76.6	103.0	222.0	384.0	37.9	63.3	82.1	117.0		Ethylene glycol
Sulfolane %m	69.5	41.8	28.3	18.1	15.6	47.0	35.3	23.0	15.1	9.91						N-methylpyrrolidone
N-methylpyrrolidone %w	15.6	34.2	76.7	196.0	522.0	9.91	22.2	55.0	138.0	384.0	8.83	19.2	41.7	101.0		Ethylene glycol
Dimethyl sulfoxide	72.5					35.4					25.3					Dimethyl sulfoxide
N-formylmorpholine	35.2					25.4					20.5					N-formylmorpholine
Tetraethylene glycol	36.0					27.4					21.1					Tetraethylene glycol
Diglycolamine	97.8					50.6*										Diglycolamine

*measured at 70°C

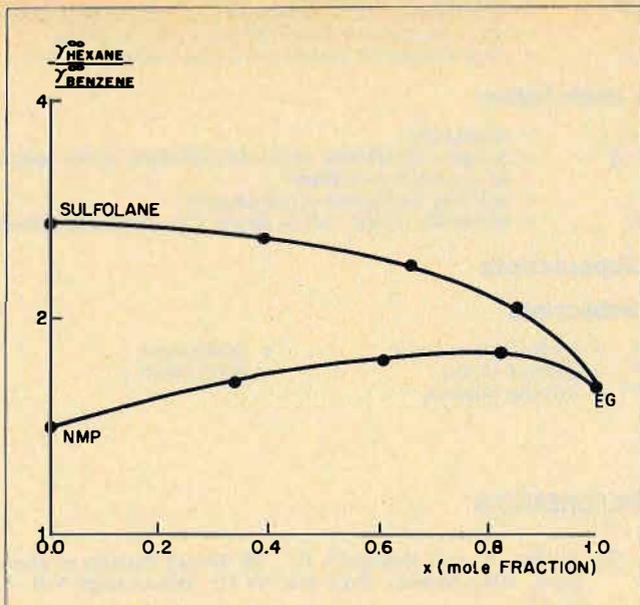


FIGURE 3. Selectivity in mixtures of solvents at 30°C.

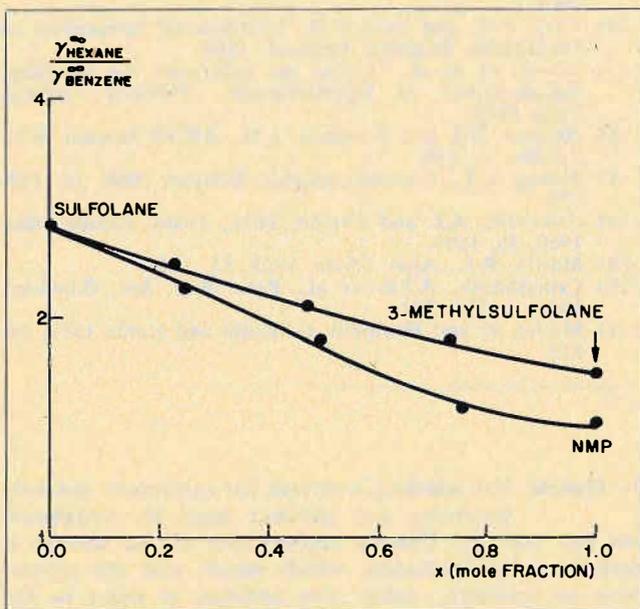


FIGURE 4. Selectivity in mixtures of solvents at 30°C.

vency range that mixtures with that specific composition can hardly be used as an extraction solvent.

The selectivity pattern of the system EG-NMP becomes clear if one realizes that highly polar molecules like ethylene glycol are potentially excellent extraction solvents. Their high degree of hydrogen bonding, however, prevents them from reaching a high selectivity. Used as a component in a mixture they have a less pronounced tendency to hydrogen bonding and act as solvents of a higher selectivity level. This synergistic effect is only observed if the selectivity of the diluents is the same as or lower or only slightly higher than that of the hydrogen-bonding solvents. If the diluent has a distinctly higher selectivity, as with mixtures of sulfolane and EG, its addition does cause a sharp increase in selectivity but no maximum is reached. The fact that the addition of small amounts of water to sulfolane causes a slight increase in selectivity follows from this same principle.

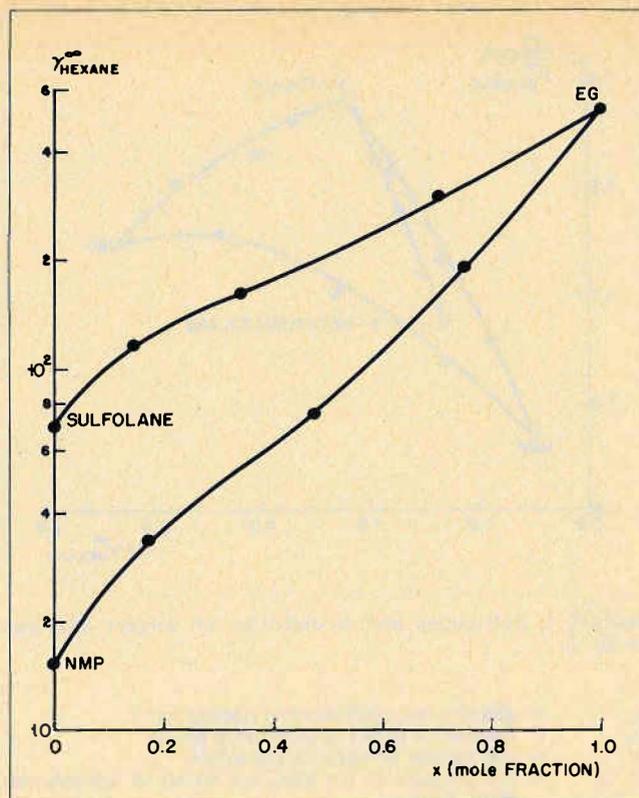


FIGURE 5. Solvencies in mixtures of solvents at 30°C.

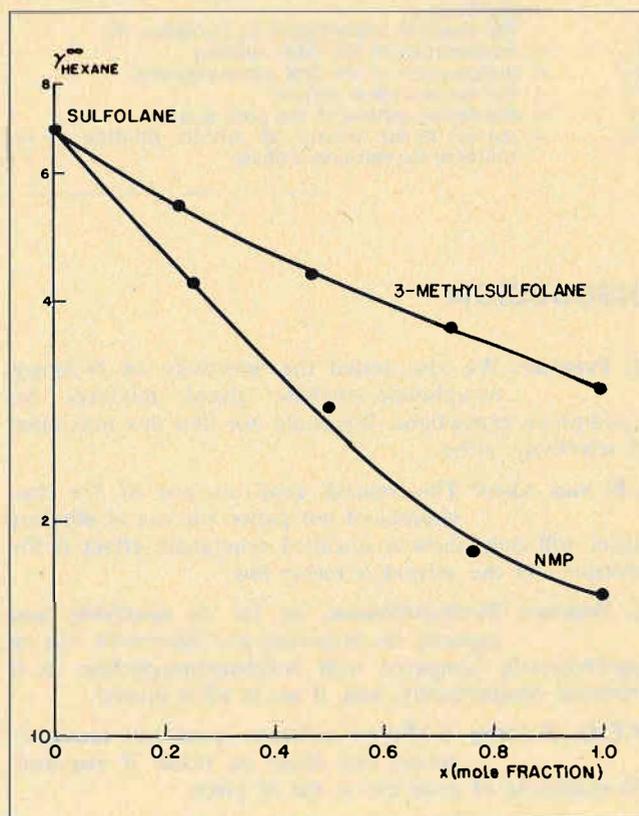


FIGURE 6. Solvencies in mixtures of solvents at 30°C.

NOTATION

- B_{11}, B_{12} = second virial coefficients in Equation (6)
- f_i = fugacity of component i
- F = flow of the carrier gas in Equation (8)

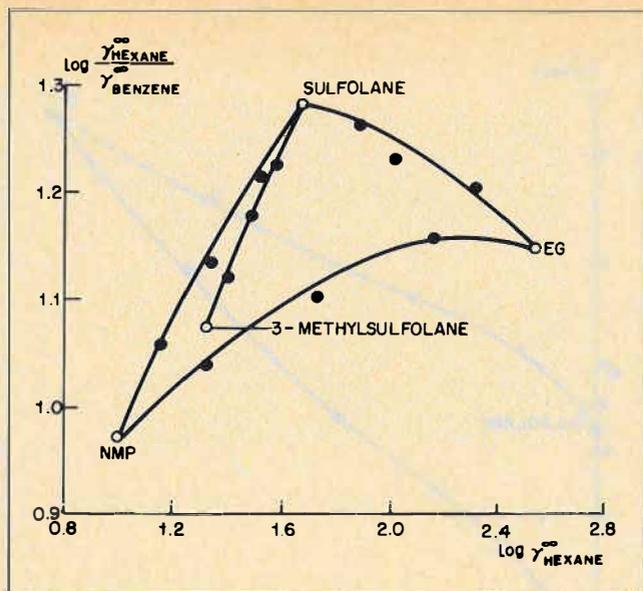


FIGURE 7. Solvencies and selectivities of solvent mixtures at 60°C.

k_i	= distribution coefficient of component i
n_s	= number of moles of stationary phase
p_i^0	= the vapour pressure of the solute
p_o, p_a	= the pressure at the inlet and outlet of the column, respectively
\bar{p}	= the mean column pressure in Equation (7)
$p_o J_2^3$	= the mean column pressure in Equation (8)
R	= the gas constant
R_i, R_a	= the retention times of the solute and of air, respectively.
T	= the absolute temperature in Equation (6)
T_{co}	= temperature of the GLC-column
T_{f1}	= temperature of the flow measurements
V_N	= the net retention volume
v_i^0	= the molar volume of the pure solute
\bar{v}_{i3}^∞	= partial molar volume at infinite dilution of the solute in the stationary phase

x_i^h	= mole fraction of component i in a hydrocarbon phase
x_i^s	= mole fraction of component i in a solvent phase
x_2	= mole fraction of carrier gas in the stationary phase

Greek Letter

$\beta_{i,j}$	= selectivity
γ_{i3}^∞	= activity coefficient at infinite dilution of the solute in the stationary phase
γ_i	= activity coefficient of component i
λ	= solubility of the carrier gas in the stationary phase

Superscripts

Subscripts

h	= hydrocarbon phase	i	= component i
s	= solvent phase	j	= component j
∞	= infinite dilution		

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DISCUSSION

G. Preusser: We also tested the selectivity of N-formyl morpholine/ethylene glycol mixtures for liquid-phase extractions. We could not find any maximum of selectivity, either.

A.B. van Aken: This remark confirms one of the conclusions of our paper: the use of ethylene glycol will only show a so-called synergistic effect if the selectivity of the solvent is rather low.

G. Preusser: Methylsulfolane, as far as selectivity and capacity for aromatics are concerned, can be approximately compared with N-formylmorpholine. Is it produced commercially, and, if so, at what prices?

W.C.G. Kosters: 3 Methyl sulfolane is not yet manufactured, but could be made if required. No indication of price can as yet be given.

U. Onken: For selecting a solvent for extraction, not only selectivity and solvency must be considered, but also stability. Usually regeneration of the solvent is performed by distillation, which means that the solvent must be thermally stable. The addition of water to the solvent in order to increase selectivity as suggested in the paper may lead to hydrolysis and formation of acid compounds having corrosive properties. Would you comment on this point?

A.B. van Aken: I agree that stability is certainly an important property in judging the merits of an extraction solvent. In this paper, however, we only considered commercially used, or proposed, solvents which have shown, some of them for many years, to be quite stable. Their stability in the presence of water is an added virtue which gives the engineer new degrees of freedom in designing the process. Especially the glycols and sulfolane are known for their good stability in the presence of water, even at elevated temperatures.

Performance of ARD-Extractors in the Purification of Caprolactam

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ABSTRACT

ARD-extractors with diameters of 1800 mm and 2800 mm are used in a process for the purification of caprolactam consisting of extraction, re-extraction and regeneration of solvent. An optimization model of the process permits the selection of solvent circulation rate for minimal product losses. A mathematical model is shown to apply for prediction of the separation performance for ARD-extractors in two industrial plants.

Introduction

MODERN CAPROLACTAM (CL) PRODUCTION PROCESSES include liquid extraction as an important step in the purification of the crude product.

In the SNIA Viscosa process, toluene is used both as the starting material for the synthesis of CL and as the extraction solvent. The extractive purification is performed in asymmetric rotating disc (ARD) extractors. Two industrial plants based on this process are in operation. The plant designated as T contains two ARD-extractors with a diameter of 1800 mm, the plant D four machines with a diameter of 2800 mm arranged in two lines.

The availability of fairly complete operating results from these units of different size offers a unique chance to check and extend the theoretical analysis of the process and

equipment used. It is the purpose of this communication to present and compare with measured data an optimization model of the extraction process on one side and a mathematical model of the ARD-extractor on the other.

Caprolactam Extraction Process

Description

Figure 1 shows a simplified flow diagram of the CL extraction process consisting of extraction, re-extraction and solvent regeneration.

Crude feed of CL and impurities in water solution is introduced at an intermediate point into the first ARD-extractor and is countercurrently contacted with toluene. CL is preferentially extracted into the solvent phase and roughly separated from ionic and polar components which are discharged together with some residual CL in the raffinate stream. The extract is washed in the upper part of the extractor with a reflux stream of product solution to remove entrained feed droplets and coextracted impurities.

The CL-toluene extract is fed to a second ARD-extractor and is countercurrently contacted with water. CL is reextracted into the water phase and roughly separated from nonpolar impurities which remain in the toluene stream. The product solution of purified CL in water is used to a small part as reflux in the extraction stage; the main stream is sent to concentration and further purification.

The solvent toluene loaded with impurities and residual CL is partially regenerated by distillation. The unregenerated and clean streams are combined and recycled to the

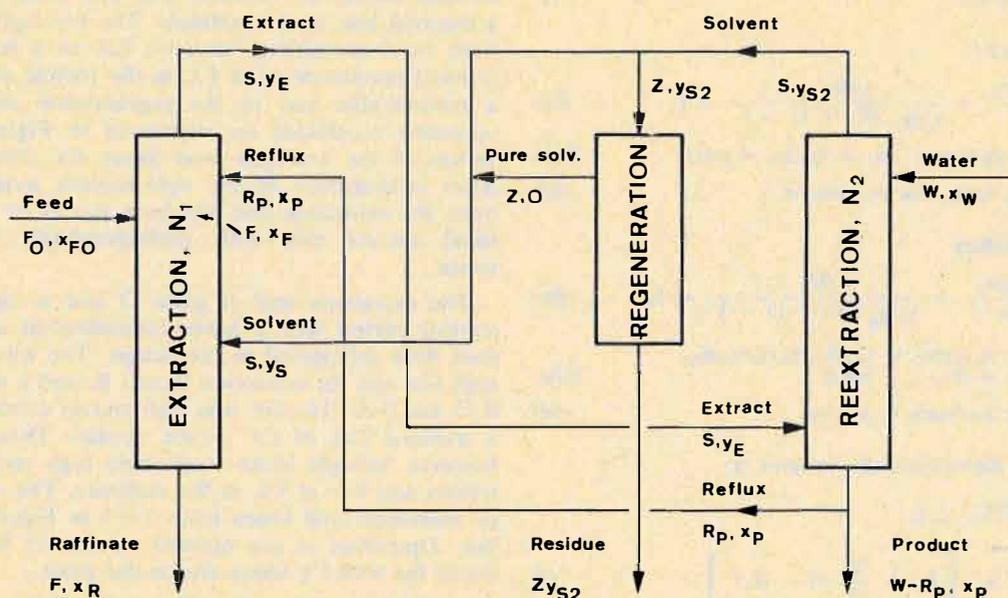


FIGURE 1. Caprolactam extraction process.

extraction stage. The residue consisting of impurities and some CL is sent to further treatment.

The aim of this process is the separation of CL from the bulk of impurities present in the crude feed. The unit should obviously be run with minimal CL losses in the raffinate and the residue.

Optimization Model

The function of the extraction unit at steady state can be described by a set of mass balance equations and relations for the extraction effect. These are shown together with the simplifying assumptions valid for this particular case in Table 1.

The relative losses of CL in the raffinate and in the residue are described by the following relations.

$$L = \frac{F x_R + Z y_{S2}}{F x_F} = f_1 + f_2 \quad \left[R_1 + \frac{Z}{S} (1 - R_1) \right] \dots \dots \dots (7a)$$

$$f_1 = \frac{1/R_1 - 1}{1/R_1 (N_1 + 1) - 1}, \quad f_2 = \frac{1/R_2 - 1}{1/R_2 (N_2 + 1) - 1} \dots \dots \dots (7bc)$$

TABLE 1. Relations for Losses of Solute

Extraction mass balance

$$F = F_0 + R_P, \quad x_F = (F_0 x_{F0} + R_P x_P)/F \quad (1ab)$$

$$F (x_F - x_R) = S (y_E - y_S) \quad (2a)$$

$$F/S = y_E/x_F \quad \text{for } x_R \ll x_F, y_S \ll y_E \quad (2b)$$

Re-extraction mass balance

$$S (y_E - y_{S2}) = W (x_P - x_W) \quad (3a)$$

$$W/S = y_E/x_P \quad \text{for } y_{S2} \ll y_E, x_W \ll x_P \quad (3b)$$

Regeneration mass balance

$$S/(S - Z) = y_{S2}/y_S \quad (4)$$

Extraction effect⁽¹⁾

$$\frac{x_R/x_F - y_S/x_F m_1}{1 - y_S/x_F m_1} = \frac{1/R_1 - 1}{1/R_1 (N_1 + 1) - 1} = f_1 \quad (5a)$$

$$R_1 = F/Sm_1 \doteq y_E/x_F m_1, \quad m_1 = (y/x)_e = \text{const} \quad (5bc)$$

$$x_R/x_F = f_1 + y_S/x_F m_1 \quad \text{for } y_S/x_F m_1 \ll 1 \quad (5d)$$

Re-extraction effect

$$\frac{y_{S2}/y_E - x_W/y_E m_2}{1 - x_W/y_E m_2} = \frac{1/R_2 - 1}{1/R_2 (N_2 + 1) - 1} = f_2 \quad (6a)$$

$$R_2 = S/Wm_2 \doteq x_P/y_E m_2 = (1/R_1) x_P/x_F m_1 m_2, \quad m_2 = (x/y)_e = \text{const} \quad (6bc)$$

$$y_{S2}/y_E = f_2 \quad \text{for } x_W/y_E m_2 \ll y_{S2}/y_E \quad (6d)$$

CL losses from Equations (5), (6) and (4)

$$L = \frac{F x_R + Z y_{S2}}{F x_F} \doteq f_1 + f_2 \left[R_1 + \frac{Z}{S} (1 - R_1) \right] \quad (7)$$

$$R_1 = \frac{F}{S m_1} \doteq \frac{y_E}{x_F m_1}, \quad R_2 = \frac{S}{W m_2} \doteq \frac{x_P}{y_E m_2} \doteq \frac{1}{R_1} \cdot \frac{x_P}{x_F m_1 m_2} \dots \dots \dots (7de)$$

The losses depend on certain fixed parameters, i.e. the distribution coefficients, m_1, m_2 (properties of the liquid system), boundary concentrations of CL, x_F, x_P (determined by the preceding and following operations) and theoretical stages, N_1, N_2 (related to the performance of the ARD-extractors), and on two parameters which can be freely varied within certain limits, i.e. the regeneration ratio, Z/S , and solvent to feed ratio, S/F (contained in the extraction factor R_1).

The regeneration ratio can lie between 0 (no regeneration) and 1 (complete regeneration). The actual operating value is selected on the basis of an acceptable level of impurities in the recycle solvent. The losses of CL increase with growing regeneration ratio. The solvent to feed ratio can be varied from a minimal value for $R_1 = 1$ to a maximum value for $R_2 = 1$ (total losses in both cases). The losses of CL show a minimum at an intermediate value of this ratio, i.e. of the extraction factor, R_1 . This minimum can be determined from a graphical representation of Equation (7).

Plant Results

The extraction units of both plants T and D are normally operated at conditions which correspond to an average value, $x_P/x_F m_1 m_2 = 0.214$. The ARD-extractors are designed for a nominal efficiency of 8 theoretical stages. Some solid deposits are formed in the second extractor and influence the throughput capacity. To compensate for this the rotor speed is successively reduced in the period between two washing operations with a resulting decrease in re-extraction effect. An average value of 7 theoretical stages is therefore assumed in re-extraction.

Figure 2 shows the relationship between the CL losses, extraction factor, R_1 , and regeneration ratio, Z/S , calculated from Equation (7) with the above parameters. The optimal value of the extraction factor, R_1 , lies between 0.45 and 0.49.

The extraction unit of plant T was operated in the period after start-up at a high solvent rate, i.e. with the extraction factor, R_1 , between 0.26 and 0.34. The aim was a minimal loss in the raffinate. The corresponding conditions in re-extraction, however, led to a relatively high residual concentration of CL in the recycle solvent and to a considerable loss in the regeneration residue. These operating conditions are illustrated in Figure 2 by two values of the averaged total losses for 1969 and 1971. After introduction of the optimization model described here, the extraction unit has been run at or near the optimal solvent rate with correspondingly reduced CL losses.

The extraction unit of plant D had to operate in the starting period with a lower concentration of CL in the feed than anticipated in the design. The solvent rate was kept low and the extraction factor, R_1 had a value between 0.55 and 0.61. The aim was high extract concentration and a minimal loss of CL in the residue. These conditions, however, brought about a relatively high residual concentration and loss of CL in the raffinate. The two examples of measured total losses from 1975 in Figure 2 illustrate this. Operation at the optimal solvent to feed ratio reduced the total CL losses also in this plant.

An analysis of Equation (7) for the relative losses of CL indicates that when the extraction unit is operated at a

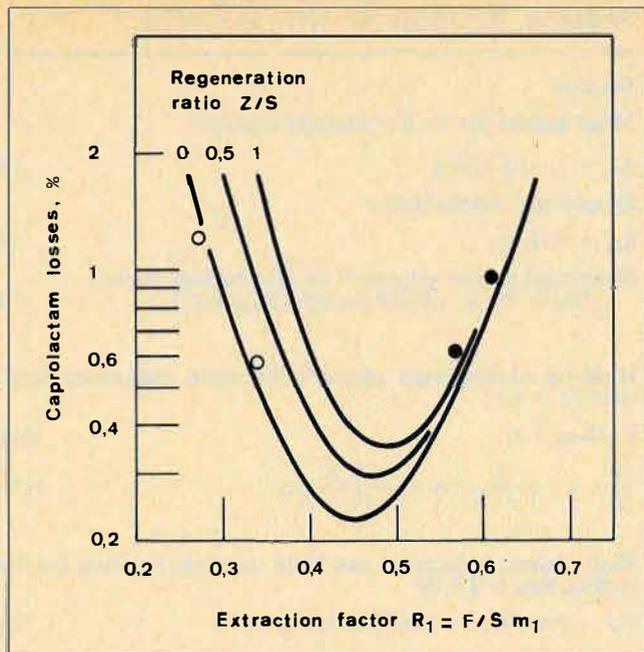


FIGURE 2. Caprolactam losses.
 — theoretical; ○ actual, plant T 1969/71; ● actual, plant D 1975.

solvent to feed ratio above the optimal value, i.e. with the extraction factor, R_1 , below 0.45, the loss in the residue becomes increasingly more significant than the loss in the raffinate. In this case the number of theoretical stages in the second ARD-extractor plays a more important role than the corresponding value of the first extractor. When operating with a solvent to feed ratio below the optimal value, i.e. with the extraction factor, R_1 , above 0.49, the situation is reversed.

Figure 3 illustrates the conditions at plant T in 1971. It shows the theoretical and actual relationship between the total and individual losses, residual concentration of CL in the solvent from re-extraction and rotor speed of the second ARD-extractor. The theoretical calculation is based on Equation (7) and a relationship between the rotor speed and the number of theoretical stages of the extractor which is described later. As the solvent rate was at that time higher than the optimal value, the loss in the residue was considerably higher than in the raffinate and the influence of the reextraction efficiency, i.e. of the rotor speed of the second ARD-extractor, quite significant.

The agreement between the theoretical and actual values illustrated in Figures 2 and 3 indicates that the optimization model represented by Equation (7) can be used with confidence not only for the selection of optimal solvent circulation rate but also for the prediction of CL losses under actual conditions.

ARD — Extractor

Description

The ARD-extractor shown in Figure 4 is an agitated column consisting of a cylindrical shell, a baffled stator and a rotor. The column shell houses the extraction section and the top and bottom settling sections. The extraction section is divided by a vertical stator baffle into a mixing zone and a separation zone. The horizontal stator baffles interdivide both zones into a set of staggered closed chambers which communicate with each other only through openings between the shell and the vertical baffle.

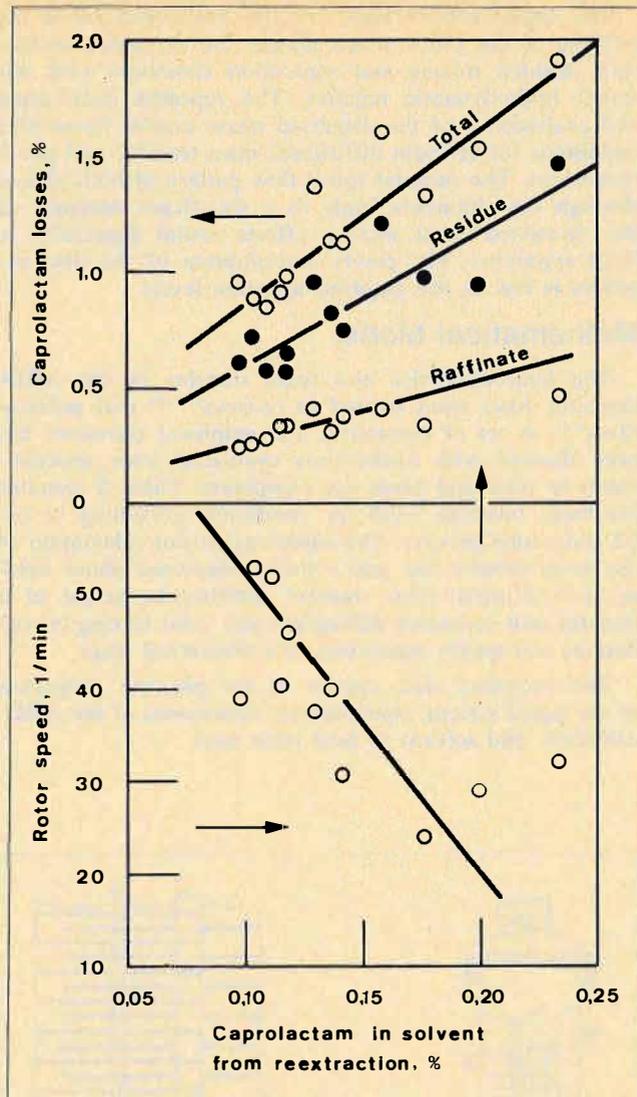


FIGURE 3. Individual losses at plant T.
 — theoretical; ○ ● actual, 1971.

The rotor shaft, which passes off-center through the mixing zone, carries disc impellers placed in each chamber. The variable-speed rotor top bearing is mounted on the shell cover and the bottom bearing is placed below the extraction zone.

The light phase is introduced at the lower end and the heavy phase at the upper end of the extraction section. The phases flow by gravity countercurrently, one continuous and the other dispersed, past the vertical stator baffle in a spiral flow pattern alternatively from the mixing to the separation zone and back. In each mixing chamber the agitation effect of the impeller redistributes the droplets of the dispersed phase. In each separation chamber, which is shielded from the impeller effect by the vertical baffle, the droplets coalesce and the phases separate to a certain extent and pass on the neighbouring mixing chambers. As a result of the phase contact, solute is transferred from the feed into the solvent. The raffinate and extract streams pass from the extraction section into the respective top and bottom settling sections. The droplets of the dispersed phase combine at the phase interface which is kept in one of these. Entrained particles of the other phase are settled out in the settling sections and the product streams leave from the top and bottom of the apparatus.

The characteristic feature of the ARD-extractor is the baffling of the stator which divides the extraction section into shielded mixing and separation chambers with different hydrodynamic regimes. The repeated distribution and coalescence of the dispersed phase creates favourable conditions for efficient diffusional mass transfer and phase movement. The ordered spiral flow pattern of both phases through the chambers leads to a significant decrease of the unwanted axial mixing effects found especially in large apparatus. The power consumption of the disc impellers is low at the required agitation levels.

Mathematical Model

The hydrodynamics and mass transfer in the ARD-extractor have been treated in reviews^(1,2,12) and publications⁽³⁻⁹⁾. A set of theoretical and empirical equations has been derived with coefficients evaluated from measurements in pilot and plant size equipment. Table 2 contains the basic relations valid for conditions prevailing in the CL extraction process. The equations permit calculation of the mean droplet size and velocity, dispersed phase hold-up, power input, mass transfer coefficients, height of a transfer unit including diffusional and axial mixing contributions and height equivalent of a theoretical stage.

The necessary data consist of the physical properties of the liquid system, characteristic dimensions of the ARD-extractor, and solvent to feed ratio used.

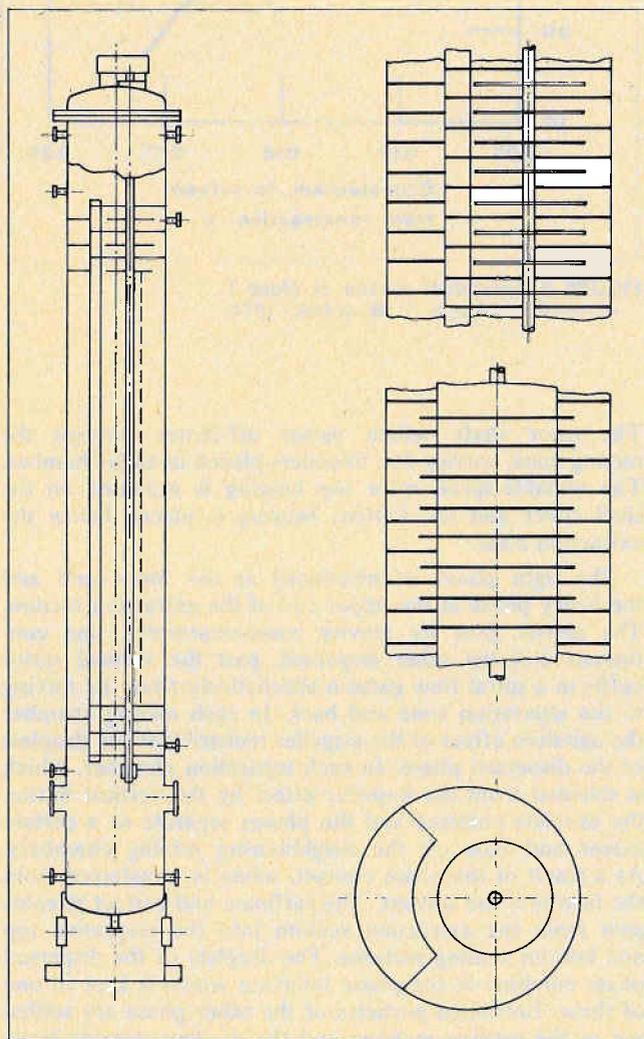


FIGURE 4. ARD-extractor.

TABLE 2. Relations for HTU and HETS

Droplet

Mean droplet size for low intensity mixing⁽³⁾

$$d_{43} = c_a \sqrt{\delta_i / \Delta \rho g} \quad (8)$$

Droplet size distribution⁽⁴⁾

$$d_{32} = 0,75 d_{43} \quad (9)$$

Mean axial droplet velocity⁽⁵⁾ for intermediate region, $Re_d > 10$, $u = 0,249 d_{43} (g^2 \Delta \rho^2 / \rho_c \eta_c)^{1/3}$

$$Re_d > 10, u = 0,249 d_{43} (g^2 \Delta \rho^2 / \rho_c \eta_c)^{1/3} \quad (10)$$

Hold-up of dispersed phase⁽⁶⁾ (for mean coalescence coefficient $z = 4,1$)

$$U_d / X \epsilon \chi = u \quad (11a)$$

$$\frac{1}{z} = \frac{1}{1-X} + \frac{U_c X}{U_d (1-X)^2} \quad (11b)$$

Power input from rotor disc⁽⁸⁾ for turbulent flow near the disc surface, $Re_M > 6,7 \cdot 10^4$

$$N_P = P / n^3 D^5 \rho_c = 0,069 (n D^2 \rho_c / \eta_c)^{-0,155} \quad (12)$$

Mass transfer coefficient in dispersed phase for low intensity mixing and oscillating and circulating droplets^{11,7}

$$1/k_d = (1 + \eta_d / \eta_c) / 0,00375 u \quad (13)$$

Mass transfer coefficient in continuous phase^(10,6)

$$1/k_c = 7,69 (0,785 D_c^2 h_m / P)^{1/4} \rho_c^{1/2} \eta_c^{5/12} / D_i^{2/3} \quad (14)$$

Overall mass transfer coefficient

$$1/K_d = 1/k_d + m_{dv} / k_c \quad (15)$$

where for extraction $m_{dv} = 1/m_{v1}$ and for re-extraction $m_{dv} = m_{v2}$

Height of a diffusional transfer unit

$$HTU_{0d} = d_{32} u \epsilon \chi / 6K_d \quad (16)$$

Longitudinal mixing contribution to HTU in continuous phase⁽⁹⁾

$$\xi_c / U_c h_m = 0,5 + c_b n D / U_c \quad (17a)$$

$$c_b = c_c N_P^{1/3} \epsilon D^{2/3} / h_m^{1/3} D_c^{2/3} \quad (17b)$$

Longitudinal mixing contribution to HTU in dispersed phase⁽⁹⁾

$$\xi_d / U_d h_m \doteq 0,5 \quad (18)$$

Overall height of a transfer unit⁽¹²⁾

$$HTU = HTU_{0d} + \frac{R_{dv} \xi_c \alpha}{U_c} + \frac{\xi_d \beta}{U_d} \quad (19a)$$

$$\alpha = \frac{1}{1 - (1 - R_{dv}) \xi_c / U_c \cdot HTU} \quad (19b)$$

$$\beta = \frac{1}{1 + (1 - R_{dv}) \xi_d / U_d \cdot HTU} \quad (19c)$$

where for extraction $R_{dv} = 1/R_{v1}$ and for re-extraction $R_{dv} = R_{v2}$

Height equivalent of a theoretical stage for extraction and re-extraction

$$\begin{aligned} HETS_1 &= h_1 / N_1 = HTU_1, \\ HETS_2 &= h_2 / N_2 = HTU_2 \cdot R_2 \end{aligned} \quad (20ab)$$

TABLE 3. Basic Data

Average physical properties	Extraction	Re-extraction
Density cont. phase, g/cm ³	0,88	0,89
Density disp. phase, g/cm ³	1,11	1,00
Viscosity cont. phase, poise.....	0,0059	0,0059
Viscosity disp. phase, poise.....	0,010	0,010
Interfacial tension, dyne/cm.....	4,0	5,8
ARD-extractor dimensions	Plant T	Plant D
Diameter, mm.....	1800	2800
Disc diameter, mm.....	880	1370
Chamber height, mm.....	190	258
Free cross-section, %.....	25	25

Plant Results

Actual flow-rate and concentration data from the extraction units of both plants served as a basis for evaluation of the number of theoretical stages reached in the ARD-extractors at the given rotor speed. Equations (5) and (6) (Table 1) were used for this purpose. The actual HETS, HTU and HTU_{od} values were then calculated from Equations (20) to (17) in Table 2.

Basic physical properties of the liquid systems and characteristic dimensions of the ARD-extractors shown in Table 3 were used for the theoretical calculation of HTU_{od}, HTU and HETS from the relations (8) to (20) in Table 2.

Figure 5 shows the theoretical relationship between the height of diffusional transfer unit and the power input per unit volume, and the actual values for ARD-extractors in plant T. Figure 6 contains the theoretical and actual results for plant D in the form of a direct correlation of the height equivalent of a theoretical stage and rotor speed. It can be seen that there is a difference between the HTU_{od} and HETS values in extraction and re-extraction. This is due to the different directions of solute transfer between the aqueous and organic phase in the two stages.

Both Figures 5 and 6 show as good an agreement between theoretical and actual HTU_{od} and HETS values as can be expected with process data from industrial units. This is an indication for the applicability of the mathematical model of the ARD-extractor even for large diameter apparatus.

Conclusions

The two-stage extraction of CL with partial regeneration of solvent is an efficient method from the point of view of both the purification and the CL yield. The optimization model of the process described in this communication and confirmed by plant results is a useful means for rational selection of the solvent circulation rate leading to minimal CL losses in the extraction raffinate and in the regeneration residue. Plant data indicate that a mathematical model of the ARD-extractor can be used with confidence for prediction of the separation performance of this apparatus in the extraction and re-extraction stage.

Acknowledgement

The authors are indebted to SNIA Viscosa for permission to use their plant data as a basis for this communication.

NOMENCLATURE

- c = constant
- d = mean droplet size, cm
- D = disc diameter
- D_e = extractor diameter, cm
- D_i = diffusion coefficient, cm²/s

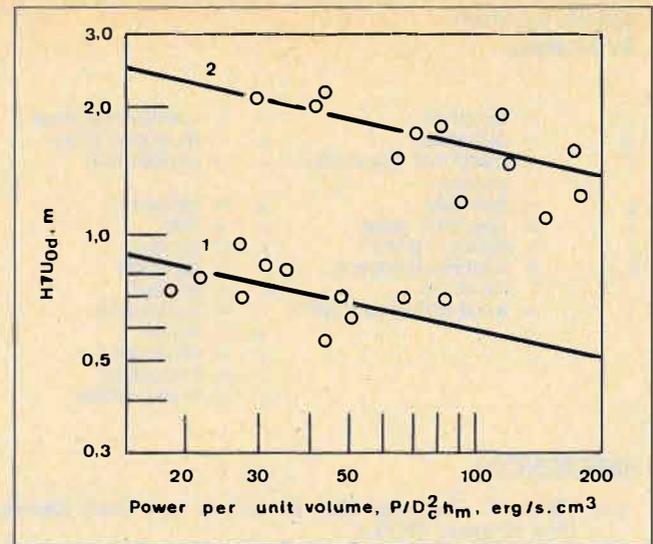


FIGURE 5. HTU_{od} in ARD-extractors at plant T. — theoretical; ○ actual; 1 extraction; 2 re-extraction.

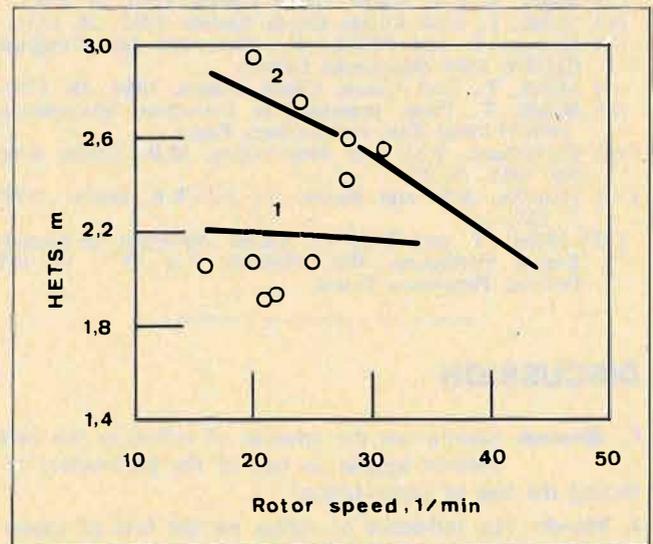


FIGURE 6. HETS in ARD-extractors at plant D. — theoretical; ○ actual; 1 extraction; 2 re-extraction.

- f = nonextractable fraction
- F = feed (including reflux), solute-free, kg/h
- g = gravitational constant, cm/s²
- h = height of extraction zone, cm
- h_m = height of chamber, cm
- HETS = height equivalent of a theor. stage, cm
- HTU = overall height of a transfer unit, cm
- HTU_{od} = height of diffusional transfer unit, cm
- k = mass transfer coefficient in one phase, cm/s
- K = overall mass transfer coefficient, cm/s
- L = relative losses of solute
- m = distribution coefficient
- n = rotor speed, 1/s
- N = number of theoretical stages
- N_p = power number
- P = power input from rotor disc, erg/s
- R = extraction factor
- Re = Reynolds number
- R_p = reflux, solute-free, kg/h
- S = solvent, solute-free, kg/h
- u = mean axial droplet velocity, cm/s
- U = specific phase flow-rate, cm³/cm² · s
- W = water, solute-free, kg/h
- x = mass ratio of solute in water phase, kg/kg
- X = fractional hold-up of dispersed phase
- y = mass ratio of solute in solvent phase, kg/kg
- z = coalescence coefficient
- Z = solvent to regeneration, solute-free, kg/h

Greek symbols Subscripts

α, β	= function	c	= continuous phase
Δ	= difference	d	= dispersed phase
ϵ	= fractional free cross-section	e	= equilibrium
χ	= function	E	= extract
η	= viscosity, poise	F	= feed
ρ	= density, g/cm ³	P	= product
δ_i	= interfacial tension, dyne/cm	R	= raffinate
ξ	= axial diffusivity, m ² /s	S	= solvent
		v	= volumetric
		w	= water
		0	= crude feed
		1	= extraction
		2	= re-extraction

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DISCUSSION

C. Hanson: Should not the amount of reflux in the first column appear as one of the parameters affecting the loss of caprolactam?

J. Marek: The influence of reflux on the loss of caprolactam is negligible in comparison with the effect of main parameters.

R.R.S. Bruin: In the listing of fixed and variable parameters you mentioned the number of stages (i.e. column length and HETS) as a fixed parameter while solvent/feed ratio is listed as a variable. Can you explain this?

J. Marek: In an existing plant, ARD-extractors of a certain height are installed. The active length and, in the first approximation, also the number of theoretical stages are thus fixed. On the other hand, the solvent to feed ratio can be varied within certain limits during operation.

A.J.F. Simons: (1) What are the heights of the columns?
(2) Which phase is dispersed in the different extractors?

(3) What are typical ratios between diffusional HTU's and overall HTU's?

(4) How does the "overall" HETS change with column height, due to the fact that there exists a strong concentration gradient in the columns?

(5) Is it possible to give designed dimensions for the columns in the new SNIA process?

(6) What are typical values for the physical parameters in the extractions of the new SNIA process?

J. Marek: (1) The ARD-extractors in Plant T have an active height of 12 m, in Plant D-16 m.

(2) The water phase is dispersed in both the extraction and the reextraction unit.

(3) Typically, the active height of a diffusional transfer unit amounts to 85 - 60% of overall HTU in industrial-size ARD-extractors.

(4) HETS is by definition a mean value obtained by dividing the active height of the extractor by the number of theoretical stages calculated for the concentration range from feed to raffinate. Local HETS values could be obtained if concentrations were measured along the height of the extractor. These values would be concentration dependent. Such an evaluation is not available for the described units.

(5) Plant specification for the new SNIA process and dimensions of the ARD-extractors are not yet fixed.

(6) Physical properties of the mixtures in the new SNIA process cannot be quoted here.

J.W. Portzer: With reference to your Figure 6, line 1 is approximately horizontal showing very little effect of agitator speed on HETS. Thus, it would seem that even with 0 rotor speed, an acceptable HETS could be achieved. Why is agitation necessary? Why not use a simpler, less mechanically complex device, i.e. a stationary contacting device, (packed tower, spray tower) for this particular separation?

J. Marek: The dependence of HETS on rotor speed shown in Figure 6 for the extraction unit at plant D is relatively flat only within the range of 15-30 rpm. Below 15 rpm the separation effect drops and HETS rises sharply. An excessively long extraction column without agitation would be needed to perform the same separation.

U. Onken: In Figure 6 of your paper, the height equivalent to a theoretical stage (HETS) is shown as a function of rotor speed. Can you give an explanation why for column 1 the HETS is practically independent of rotor speed, whereas in column 2 it is decreasing with rotor speed considerably?

J. Marek: Different conditions, such as dispersed phase, direction of mass transfer and physical properties, in the extraction and re-extraction unit account for the different dependence of HETS on rotor speed.

A.E. Karr: Dr. Marek, how would you characterize the caprolactam extraction system? Is it easy or difficult? What are the interfacial tensions and density differences at both ends of the column?

J. Marek: The extraction of caprolactam can be characterized as fairly difficult. The physical properties of the liquid system are given in Table 3 of the paper.

The Recovery of Pure Aromatics from Hydrocarbon Mixtures by Extractive Distillation and Liquid-Liquid Extraction using Morpholine-Derivates as Solvents

Gerhard Preusser and Johannes Franzen,
Krupp-Koppers GmbH, Essen, Federal Republic of Germany.

SUMMARY

The paper describes the specific advantages of *N*-substituted morpholines when used as solvents in the recovery of pure aromatics by extractive distillation, alone or in combination with preceding liquid phase extraction. Test results from laboratory and pilot-scale investigations are reported, as well as process details and economical data of several large-scale commercial installations.

Introduction

FOR SEVERAL YEARS there has been an ever-increasing demand for a higher purity of aromatics as feedstock for chemical synthesis. Non-aromatic impurities of not more than 50 - 600 ppm in the final product are now generally required for benzene and toluene. The requirements for C_8 aromatics are normally not quite so high, and are somewhere in the region of about 1000 ppm.

The customary methods, today, of attaining higher purities⁽¹⁾ are liquid phase extraction and extractive distillation. The first method is preferred when more than one aromatic compound, such as benzene and/or toluene and/or xylenes, is to be recovered from aromatic feed-stocks which contain relatively large quantities (more than 30% wt.) of non-aromatics, as is the case with the gasoline fraction from reformers. Extractive distillation, however, offers economic advantages when only one aromatic is to be removed from a corresponding cut if its content in non-aromatics is relatively small (below 30% wt.). The latter is particularly the case with feedstocks like hydro-refined coke-oven benzole and hydrogenated pyrolysis gasoline from steam-crackers. Such feedstocks predominantly contain benzene, while toluene and xylenes form only small fractions so that only benzene is recovered, while the cuts containing toluene and xylenes are frequently admixed with motor fuels in order to increase the octane number.

Aromatic Feedstocks

The main sources for the production of aromatics are black coal and petroleum. Whilst the volume of aromatics derived from coal has remained constant over the last 20 years, with a tendency to decrease in most countries, petroleum fractions have taken over the role of main feedstocks to cope with the rapid and considerable increased need for aromatics. In Germany, for instance, nowadays only about 25% of the consumption of benzene is covered by coal carbonisation, and toluene and the xylenes are totally produced from petroleum feedstocks.

TABLE 1. Typical Distribution of Aromatic Compounds in Industrial Feedstocks.

	Coke Oven Benzole (refined)	Pyrolysis Gasoline (hydrogenated)	Reformate
Benzene	65	40	3
Toluene	18	20	13
Xylenes	6	4.5	18
Ethylbenzene	2	2.5	5
Higher Aromatics	7	3	16
Aromatics Total	98	70	55
Non-aromatics	2	30	45
	100	100	100

At present three main sources of aromatics exist:

- (1) Condensate from catalytic reforming of gasoline.
- (2) Condensate from steam cracking (pyrolysis gasoline).
- (3) Coke oven light oil.

The separation of very pure aromatics from these industrial feedstocks is performed in a sequence of process steps. In the first step, steam-cracker condensate and coke-oven light oil are hydro-refined under pressure in one or more stages, whereby nitrogen compounds and sulfur compounds are converted into easily removable products. Simultaneously, the olefines in the feedstock are converted into paraffins and cyclo-paraffins. This pre-treatment is necessary in order to meet the present very high requirements for pure aromatics with regard to bromine number and sulfur. Reformates, however, do not need such pre-treatment in most cases.

Table 1 shows typical figures for the portions of individual aromatic compounds in various feedstocks⁽²⁾. From this Table, it can be seen that coke oven benzole and pyrolysis gasoline are the most important sources for benzene, whilst the xylenes are enriched in the reformat fraction. Toluene is of less importance, and appears at a similar concentration in all three feedstocks. In order to meet the high demand for benzene, often toluene and C_8 -aromatics are hydrodealkylated to produce additional quantities of benzene.

The pre-treated feedstock, containing only aromatics, paraffins and naphthenes, is normally predistilled to form fractions which contain one or more of the essential aromatics depending on the specific feedstock. The higher boiling portions (boiling point above 150°C) are separated and treated as a distinct cut. As the components which boil lower than benzene do not interfere with the recovery of the aromatics, they can be left in the feedstock.

With coke oven benzole and pyrolysis gasoline as feedstocks, predistillation is performed to produce a narrow-

cut benzene fraction, leaving toluene and xylenes in the form of an anti-knock additive for auto motor fuels. If reformates or a mixture of reformat and pyrolysis gasoline are used as feedstock, predistillation is performed to produce a broad aromatic fraction, including benzene, toluene, and the xylenes, from which fraction all three types of aromatics are commonly recovered in a pure form.

Extractive Distillation

This paper deals with a special development in the extractive recovery of pure aromatics, which has been performed during the last ten years by Krupp-Koppers, initially under its former name of Heinrich Koppers GmbH. The aim of this development was primarily an extractive distillation using certain types of morpholine derivatives for the recovery of aromatics from suitable feedstocks. Later we combined this special type of extractive distillation with a preceding liquid phase extraction, for which a simple process scheme was designed. In both extraction steps of the combination, N-substituted morpholines are used as extracting solvents, including N-formyl morpholine (NFM) and N-acetyl morpholine (NAM). It should be mentioned that liquid-phase extraction of aromatics, using morpholine and its derivatives as solvents, was first proposed some thirty years ago⁽³⁾. However, the special advantages of the use of this class of compounds as solvents in extractive distillation systems, whether as such or in combination with liquid-phase extraction, were discovered by KRUPP-KOPPERS only recently^(4,5,6).

As is known, extractive distillation is based on the selective changing, especially increasing, of the vapour pressures of the individual components by the presence of a solvent, flowing down in the column in such a way as to allow distillative fractionation of the feedstock into aromatic and non-aromatic fractions which otherwise, due to overlapping boiling ranges and/or the formation of azeotropes, could not be achieved⁽⁷⁾. The vapour pressures must be altered in such a way that the non-aromatics will almost completely be discharged at the top of the column, while the aromatic fraction is withdrawn at the bottom together with the solvent. Altering the vapour pressure through the presence of a polar solvent becomes less effective in the sequence n-paraffins, isoparaffins, naphthenes⁽¹⁾. Thus, naphthenes are the most difficult non-aromatics to separate, particularly if they boil considerably higher than the aromatics to be recovered. Methylcyclohexane (MCH) has (a) a naphthenic structure and (b) its

boiling point is 21°C higher than that of benzene. Therefore, it is most difficult to separate MCH from benzene by extractive distillation. This is the reason why MCH is looked upon as a key compound for this extractive distillation.

In other extractive distillation processes known up to now, it is necessary to remove at least most of the MCH in the predistillation to enable recovery of the benzene cut. In order to achieve this, either more distillation equipment has to be provided, i.e. a larger number of trays and higher reflux ratios, which results in increases in the investment costs and heat consumption, or corresponding benzene losses have to be accepted.

NFM Selective Solvent

After carrying out numerous tests, we have found certain morpholine derivatives to be admirably suited as solvents in extractive distillation, particularly for separating naphthenes, so that expensive pre-separation of methylcyclohexane from the benzene cut is no longer necessary⁽⁸⁾. In particular, NFM has an almost ideal combination of characteristics which are essential for the recovery of aromatics by extractive distillation. On the one hand, the selectivity for aromatics versus naphthenes is very good. Selectivity here means the attainable increase in the relative volatilities of the accompanying non-aromatic components versus the aromatics in the presence of the solvent. On the other hand, NFM has also sufficient solvency for the non-aromatics at operating temperature in the extractive distillation column⁽⁹⁾. This is important, because the non-aromatics concentration in the top part of the extractive distillation column should be as high as possible to achieve a good yield of aromatics. With too low a solvency of the solvent for the non-aromatics, a phase separation of the liquids takes place on the trays in the top section of the column. Of the two liquid phases formed there, one would be practically free of solvent. In this phase, the influence of the solvent on the vapour pressures is lacking. Thus the possibility of maximum separation of the aromatics would again be neutralized. This is the reason why well-known solvents, which have a high selectivity in liquid-phase extraction, are not necessarily suitable for the recovery of aromatics by extractive distillation because they do not have sufficient solvency for the non-aromatics and therefore, cause difficulties in the top of the extractive distillation column. Other solvents, which have a better solvency for non-aromatics but, simultaneously, an essentially lower selectivity, allow the separation of methylcyclohexane from benzene, for example, to be carried out only to a certain degree. Since selectivity and solvency for non-aromatics oppose each other in the case of polar solvents, a suitable solvent must be employed to attain an optimum compromise between selectivity and solvency. The morpholine derivatives, particularly N-formylmorpholine, possess these characteristics to a high degree.

A reasonable and practical method to evaluate the effect of different solvents when used in extractive distillation of aromatic feedstocks is comparison of the initial boiling points (IBP) of mixtures consisting of hydrocarbons and solvents^(10,11). Figure 1 shows the Initial Boiling Points of a mixture of 85 mol % solvent and 15 mol % of a hydrocarbon, as prevailing in practice in the top part of an extractive distillation column at various pressures. The differences in the boiling points of benzene/methylcyclohexane and benzene/n-heptane, shown at the right-hand side of the Figure, indicate the selectivity and relative volatilities. The larger the difference in the boiling points, (Δt) , the higher the selectivity and, thus, the relative volatility. At a pressure of 1 atmosphere the value

Hydrocarbons B.P.	Solvents B.P.	pressure psi	Benzene	Methyl-	n-Heptane	Δt Benzene/ Methyl-	Δt Benzene/ n-Heptane
			80°C	cyclohexane 101°C	98°C	cyclohexane	n-Heptane
N-Formyl- morpholine 243°C	14.7	136°C	110°C	100°C	26°C	36°C	
	44.0	203°C	174°C	157°C	29°C	46°C	
N-Methyl- pyrrolidone 206°C	14.7	140°C	126°C	113°C	14°C	27°C	
	14.7	146°C	120°C	105°C	26°C	41°C	
Sulfolane 276°C	14.7	128°C	insoluble	insoluble			
	74.9	255°C	184°C	insoluble	61°C		
Triethylene- glycol 286°C	14.7	98°C	insoluble	insoluble			
	91.0	250°C	194°C	insoluble	66°C		

FIGURE 1. Initial boiling points (85 Mol. % solvent/15 Mol. % hydrocarbon).

of Δt for benzene/methylcyclohexane is approximately 26°C with NFM, about 14°C with N-methylpyrrolidone, and about 26°C with N-acetylmorpholine as solvent. Similar differences in the boiling points are shown for benzene/n-heptane. The Figure also indicates that, under these conditions, sulfolane and triethylene glycol have an excellent selectivity but only a limited solvency for non-aromatics, which is impractical for extractive distillation.

Figure 2 shows some data of properties and characteristics of NFM, the production of which is based on commercially produced ethylene oxide, ammonia and formic acid. The flash and ignition points are such that, from a safety point of view, no special measures are necessary.

Due to its boiling point (243°C) and the fact that no azeotropes between NFM and C₆ - C₉ hydrocarbons occur, NFM can be used in extractive distillation for purifying aromatics up to the C₉-range, without expensive distillation being necessary for subsequent separation for the aromatics from the solvent. The yielded aromatics obtained are practically free of solvent, and subsequent washing is not necessary. The non-aromatics after separation, (often called raffinate), however, contain residual amounts of the solvent which, in order to avoid losses, should be recovered. Due to the complete miscibility of the solvent, both with the aromatics and water, the solvent can be recovered with low expenditure by extraction with water and counter-extraction with the aromatics to be recovered. In many cases, recovery of the solvent from the raffinate by distillation, using cheap waste heat, is economical.

The price of NFM is favourable compared to other highly selective solvents. NFM is produced today on a commercial scale and is supplied by several chemical producers.

NFM is weakly basic. When mixed with water at a ratio of 1:1, the pH-value of the mixture is 8.6, so no corrosive effects are to be expected. Thermal decomposition, which would lead to high molecular polymerization or polycondensation products, is negligible, even at temperatures up to 230°C and heat transfer rates up to 18,000 kcal/m²/h..

For extractive distillation, NFM is normally used without the addition of water. Even in certain process variations, where NFM is diluted with up to 10% water in order to further increase the selectivity, practically no hydrolytic effects of NFM occur, provided certain conditions are met. Due to the good thermal and chemical stability of NFM, it is possible to manufacture the commercial equipment for extractive distillation and liquid-phase extraction plants totally from normal carbon steel without danger of corrosion, even with extended periods of operation.

Our first large-scale plant for the recovery of 220,000 tons/year benzene from hydro-refined coke oven benzole by extractive distillation⁽⁸⁾ was made completely of carbon steel, including the reboilers. It has now been operating trouble-free for 9 years. Up to date, no damage through corrosion has been found. Since start-up, the quality of the solvent has been supervised for an uninterrupted operating period of two years, by checking the pH value and the resins formed. Figure 3 shows the results of this checking. The continuous curve shows the amount of resin or pitch, respectively (left-hand ordinate), plotted against the duration of operation or throughput (abscissa). After two years of continuous operation without any regeneration of the solvent, the amount of resins formed has gradually reached 1.7% wt. If the amounts of resins are related to the total throughput of feedstock during that period, the broken-line curve is obtained, which shows the quantity of resins formed per ton of throughput (right-hand ordinate). It can be seen that, after the initial impurities left

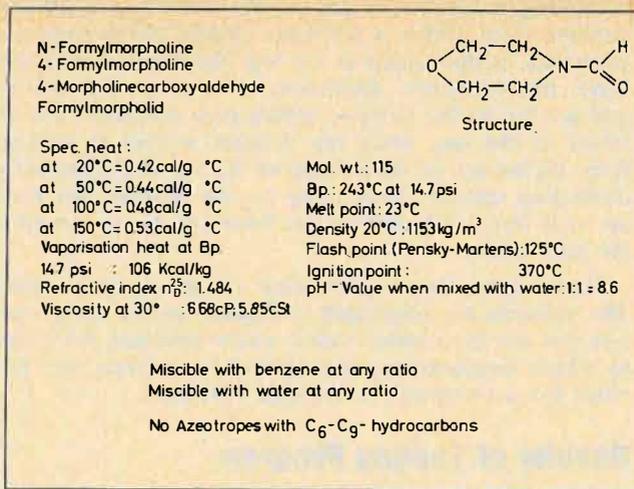


FIGURE 2. Characteristics of N-formylmorpholine (NFM).

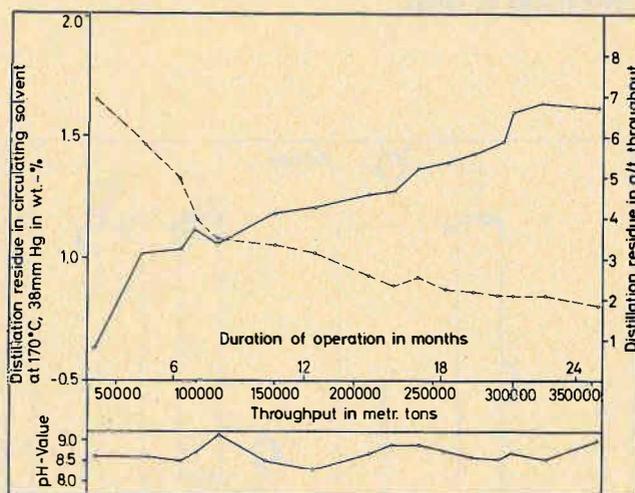


FIGURE 3. Solvent stability control in a commercial plant.

from the erection of the equipment are removed, this figure drops to about 2 g/ton of feed. In this plant, the solvent is heated to a maximum temperature of 190°C in the bottom of the stripper. A drop in effectiveness of the solvent, in spite of this slight formation of resins, has not been observed. We would recommend, however, regeneration of the recirculated solvent — either the whole quantity batchwise from time to time, or a small side stream continuously — by distillation under reduced pressure, in order to avoid precipitation and deposition of gum-like condensation products within the columns, heat-exchangers, pipes etc.

Pilot Plant

Before designing commercial plants, we operated an extensively automated pilot plant in which various process parameters were studied and optimized in advance and then used as a basis for commercial plants. Figure 4 shows a simplified flowsheet of this pilot plant which incorporates all essential features of a typical extractive distillation unit. The extractive distillation column at the left, and the stripper column at the right, are made up of individual sections which are provided with bubble cap trays and are fitted together according to requirement. The principle of operation is quite simple. The feedstock

containing aromatics is fed to the extractive distillation column, from which a raffinate, chiefly comprising non-aromatics, is discharged at the top. Solvent and aromatics leave the extractive distillation column at the bottom, and are fed to the stripper, where pure aromatics are obtained at the top, while the stripped solvent is returned from the bottom of the stripper to the top of the extractive distillation column. Depending on the feed/solvent ratio, up to 6 litres of feedstock per hour can be processed in the pilot plant.

Figure 5 shows the pilot plant at our research centre. The columns are suspended in frames. In the foreground one can see the control board which indicates the extent to which measurement and control instruments are provided for a completely automated operation.

Results of Testing Program

From the numerous test results only a few process parameters, which are of special interest to extractive distillation, will be discussed here:

(a) The residual content of aromatics in the stripped solvent and its effect.

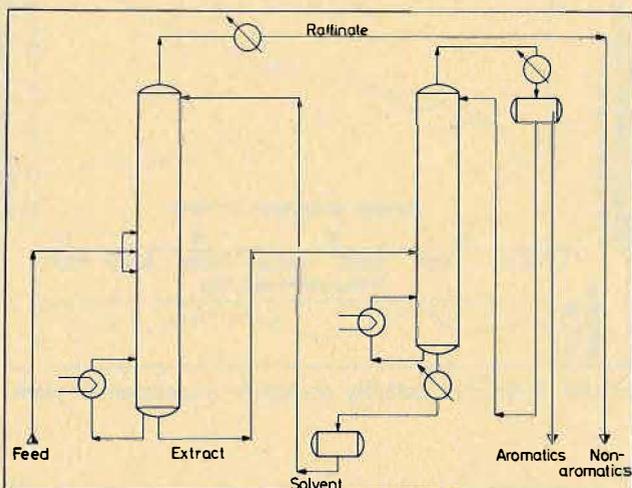


FIGURE 4. Flowsheet of extractive distillation pilot plant.

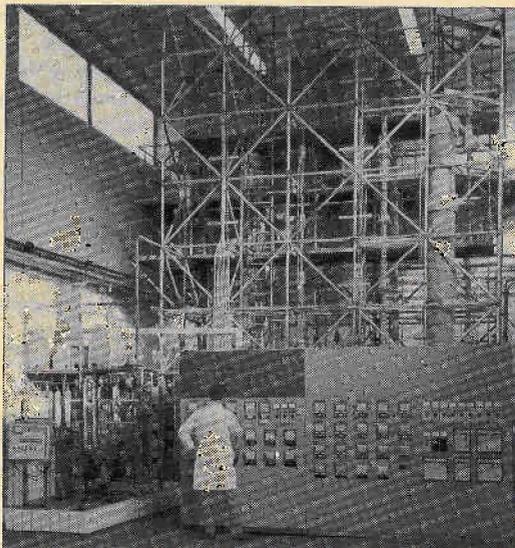


FIGURE 5. Pilot plant.

(b) Influence of solvent/feed ratio on product purity and yield of final product.

Stripping

Figure 6 shows how poor stripping will be noticed. The weight ratio of solvent to feed is shown on the ordinate, plotted against the aromatics content in the top product on the abscissa. The two curves refer to the same feed and to final products of the same purity, but different benzene contents — 1.5% and 5%, respectively, in the stripped solvent. At the same solvent/feed ratio, there are considerable differences regarding the unavoidable benzene content in the top product of the extractive distillation column — about 3% benzene in the top product with solvent stripped to 1.5%, and about 20% benzene in the top product with solvent stripped to 5% — if the purity of the aromatics in the bottom product is kept constant. This effect has negative influences on the yield in aromatics which, when processing hydro-refined coke oven benzole, would not be of such great importance as in the case of other industrial benzene fractions, such as those obtained from steamcracker condensate, due to their higher content of non-aromatics.

From this statement it follows that a good stripping effect should be obtained in order to avoid lower yields or lower purity of the product, or both. The somewhat higher heat requirement, due to the higher temperature level for better stripping, is negligible, considering the advantages of a good stripping effect, especially since, in large scale plants, this heat requirement can be economically recovered by an optimum heat exchange.

Solvent/feed Ratio

Figure 7 shows the effect of variations in the solvent/feed ratio on yield and purity of the product. The solvent/feed ratio (ordinate) for various industrial feedstocks is plotted against the aromatic content of the top product, which is decisive for yield (abscissa). All other process parameters are kept unchanged. The two lower curves refer to hydro-refined coke oven benzole fractions with different purity requirements. When maintaining relatively low solvent/feed ratios — 2.2 for a non-aromatic content of 650 ppm; 3.4 for a non-aromatic content of 150 ppm in the final product, practically 99.9% yield can be attained which corresponds to a benzene content of about 3% in the top product (raffinate). If no great value is placed on a maximum yield, the same purities can

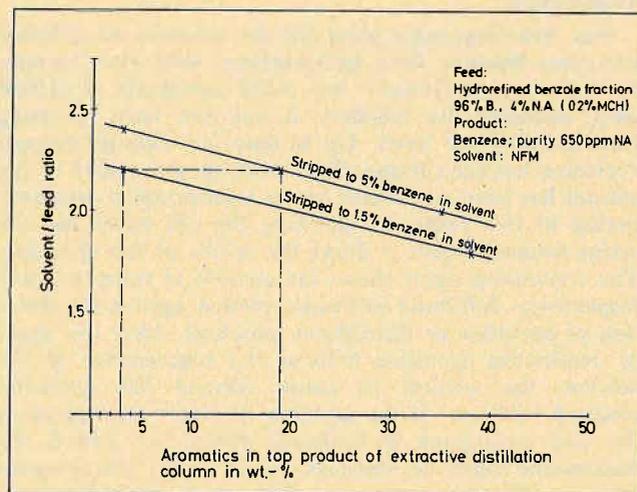


FIGURE 6. Effect of stripping efficiency on aromatic yield.

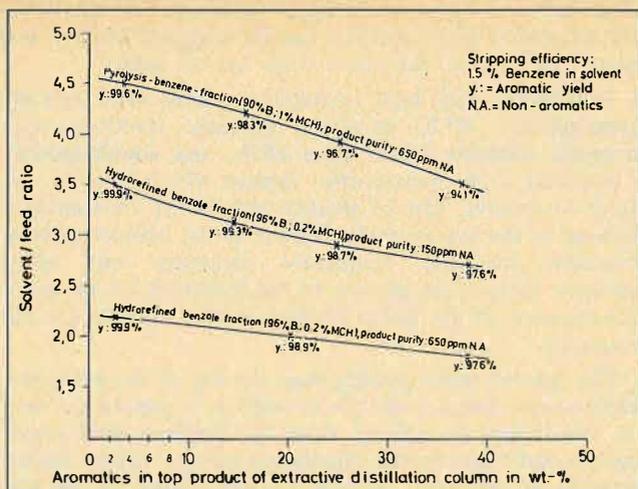


FIGURE 7. Influence of solvent/feed ratio on aromatic yield and purity.

be obtained with lower solvent/feed ratios (1.8 for 650 ppm non-aromatics at a yield of 97.6%; 2.7 for 150 ppm non-aromatics at a yield of 97.6%). In this case, the energy requirement would be less.

The top curve in Figure 7 shows the results of purifying a steam cracker condensate fraction containing 90% benzene and 10% non-aromatics, of which one tenth is methylcyclohexane. At a conventional and economical solvent/feed ratio of 3.5 to 4.5, yields of 94% to well above 99% can be obtained, if a maximum non-aromatics content of 650 ppm is permitted.

Figure 8 as an example of a benzene fraction from a hydrogenated steam cracker condensate, illustrates how the benzene content in the top product (raffinate) affects the purity of the final aromatic product when the other process conditions are kept unchanged. The benzene content in the top raffinate and the aromatic yield, respectively, (ordinate) are plotted against the content of non-aromatics in the pure benzene (abscissa). From Figure 8 it can be seen that, at quite an economical solvent/feed ratio of 4.5, the entire purity range of 1000 to 50 ppm non-aromatics in the final product, of which the lower figure is profitable today, can be controlled without having to increase the benzene content in the top product above 10%. This is equivalent to benzene yields of 98.8 to 99.7%, and indicates the excellent selectivity of NFM.

Figure 9 shows concentration profiles for a number of typical hydrocarbons over the length of the extractive distillation column of the pilot plant using the benzene fraction of a steam cracker condensate as an example, which again demonstrates the good selectivity of NFM. For instance, at the 53rd tray, the methylcyclohexane level reaches 14% wt. with a feed containing 2% wt. methylcyclohexane while, in the reboiler, practically 100 ppm methylcyclohexane can be attained.

Where pure BTX aromatics are to be recovered simultaneously from adequate feedstocks, such as reformates or pyrolysis gasolines, we pretreat the feedstock in a liquid-phase extraction step before feeding the resulting aromatic fraction to the extractive distillation step.

When developing this process variant, we were guided by the fact that the higher boiling non-aromatics could be very easily removed by liquid-phase extraction, because their solubility in a selective solvent is less than that of the lower boiling non-aromatics. Contrary to this, the removal of lower boiling non-aromatics in extractive distillation is particularly good for reasons already explained.

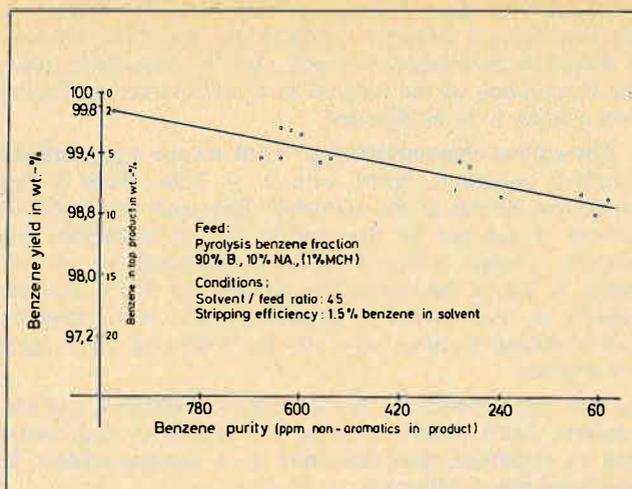


FIGURE 8. Benzene yield depending on benzene purity.

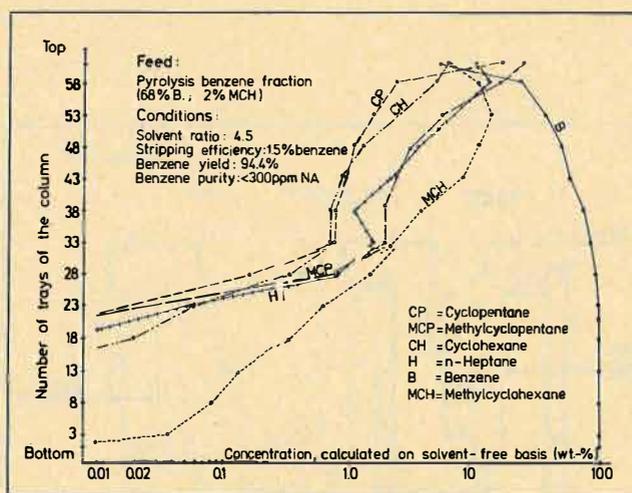


FIGURE 9. Concentration profile in the extractive distillation column.

However, a prerequisite for such a combination is that, with both liquid phase extraction and extractive distillation, an optimum effect of the solvent can be attained which, when using solvents other than morpholine substitutes, has been possible only to a limited extent.

We have found that, when using NFM, the selectivity and solvency characteristics can be adjusted in such a way that an optimum effect can be achieved in both the liquid-phase extractor and the extractive distillation unit when operated in combination. In particular, water can be used as a selectivity intensifier. For the liquid-phase extraction step, a low solvency for non-aromatics is desired, in addition to a good absorption for the aromatics, which can be achieved by water contents of 4 - 10% wt. in NFM. In the extractive distillation step, a certain solvency for non-aromatics, particularly in the top section of the column, can be realised by water contents of up to 3% wt. in NFM.

Figure 10 shows a simplified flowsheet of liquid-phase extraction combined with extractive distillation, when NFM is used as solvent and BTX aromatics are to be recovered simultaneously from adequate feedstocks. With conventional solvents other than substituted morpholines, similar flowsheets are often used but without feeding a separate stream of stripped solvent at the top of the

extractive distillation column^(12,13). Instead, as indicated by the broken line, enriched solvent from the bottom of the liquid-phase extractor is fed at the top of the column. It should be mentioned, however, that, in these other cases, the functioning of the column as a real extractive distillation column is to be doubted.

The unique characteristics of NFM favour a particularly effective operation. NFM with 4 — 10% water is fed at the top section of the extractor. The aromatics-enriched solvent is charged in the middle of the extractive distillation column. Stripped solvent, containing up to 3% water, is fed at the top of this column, so that it is operated as a real extractive distillation unit with stripping and enriching sections, whereby the following advantages are attained:

1. The top product of the extractive distillation column contains much smaller portions of aromatics than usual and is, therefore, very effective as a counter-solvent in the liquid-phase extractor.
2. Because of the low aromatics content in the counter-solvent the load on the liquid-phase extractor is considerably reduced, since far less aromatics are recirculated.

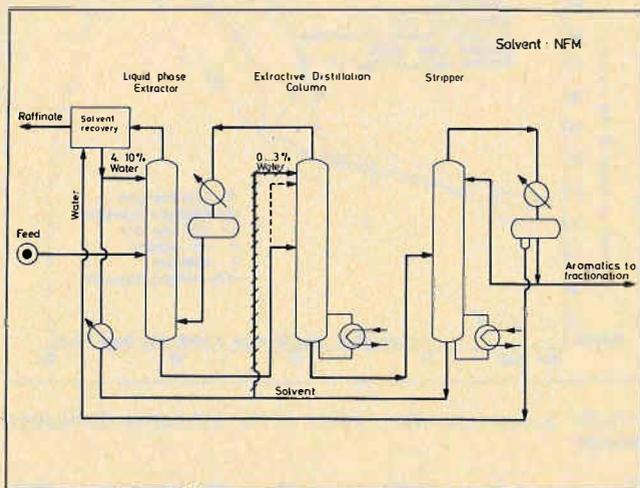


FIGURE 10. Liquid phase extraction combined with extractive distillation.

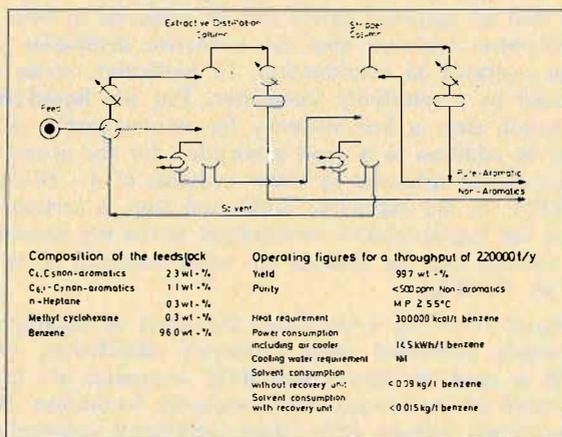


FIGURE 11. Recovery of pure benzene from a fraction of hydro-refined coke oven benzole.

Furthermore, with a real extractive distillation as second step, only a minimum of energy is necessary for vaporizing the aromatics. The extractor can be designed smaller and more simplified so that sieve trays can be used.

3. Feedstocks with high aromatic contents, such as fully hydrogenated BTX pyrolysis gasoline fractions with aromatic contents higher than 80%, and simultaneously a relatively high cycloparaffin content which is often difficult to remove, can be treated with NFM economically because of the low aromatic content in the counter-solvent. Remedial measures frequently necessary with other solvents, such as predilution of the feedstock or an essential increase of the water content in the solvent, are not necessary.

The surplus water passing over the top of the extractive distillation column with the aromatics is separated, used for recovering the solvent from the raffinate and subsequently fed again to the circulating solvent stream before entering the extractor, so that a water content of the solvent of 4 - 10%, necessary for optimum liquid-phase extraction, is attained again. In that way the water circuit in the entire plant is self-sustaining and no effluents are discharged from the process.

Commercial Plants

Up to the present, 5 commercial plants have been designed, supplied and commissioned by us, in which NFM is used as a solvent for the recovery of pure benzene, toluene and orthoxylene in a total quantity of 580,000 metric tons per year. No operational problems have been reported so far. Four plants use the extractive distillation step only, whilst the fifth uses a combination of a liquid-phase extraction and an extractive distillation. In two plants, a hydro-refined coke oven benzole fraction is extracted; two more plants process hydrogenated pyrolysis gasoline fractions and, in one plant, a reformate fraction is used as feedstock. So with substituted morpholines, experience gained on commercial-scale extractive recovery of pure aromatics from the most interesting feedstocks is now available and applied in our design offices. Two more plants, one for the recovery of 150,000 tons/year of benzene and one for 120,000 tons/year of toluene, are under design. In both cases, pyrolysis gasoline fractions are used as feedstocks for extractive distillation.

Figure 11 shows the flowsheet with production and consumption data of the first extractive distillation plant supplied by us in 1968 for the extraction of 220,000 tons per year benzene from hydro-refined coke oven benzole. This

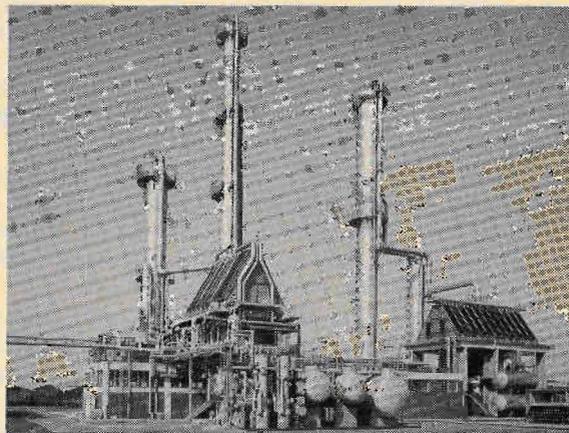


FIGURE 12. Plant for recovery of pure benzene from hydro-refined coke oven benzole.

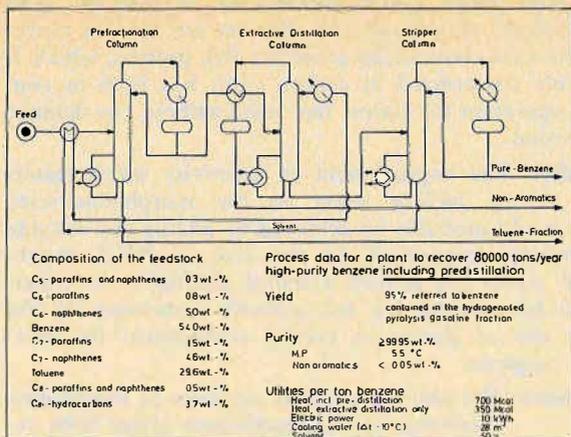


FIGURE 13. Recovery of high-purity benzene from a hydrogenated pyrolysis gasoline fraction.

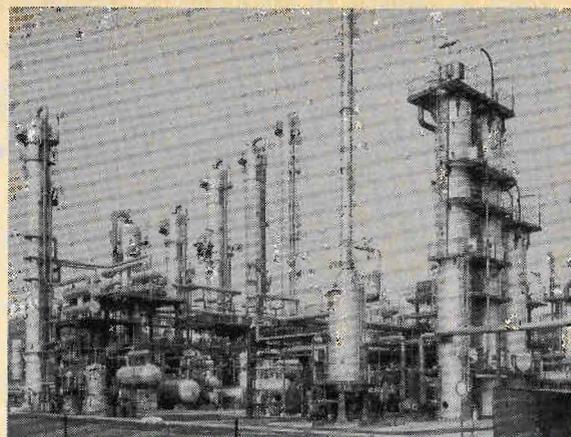


FIGURE 14. Installation for the hydrogenation of pyrolysis gasoline, fractionation and recovery of pure benzene by extractive distillation.

plant, a picture of which is shown in Figure 12, has now been in continuous, trouble-free operation for nine years. The column at the right side of the picture serves to distill a benzene fraction — the feed for the extraction step — from hydro-refined coke oven benzole. In the tall column in the middle of the picture, an extractive distillation, with NFM as solvent, is performed to separate benzene from the non-aromatics in the feed. The column on the left serves as stripper column to separate the pure benzene units in the foreground are aircoolers. This special shape from the solvent, which is recirculated. The roofshaped was designed at the request of the customer.

Figure 13 shows the flowsheet and the production data of a commercial plant for the recovery of 80,000 tons per year pure benzene from a suitable cut of a pyrolysis gasoline fraction, including pre-fractionation. Figure 14 shows a picture of this plant, which itself forms an integrated part of a larger plant for the working-up of steam cracker condensates. Arranged from right to left are: 3 reactors for the partial and complete hydrogenation of the crude pyrolysis gasoline; a furnace for start-up purposes (with high stack); the extractive distillation column; 2 columns for the production of the crude cut for the hydrogenation step and of the benzene cut for the extraction step, respectively; the stripper column for the aromatic enriched NFM-solvent; 2 columns for the separation of the low-boiling and high-boiling fractions of the crude pyrolysis gasoline.

Figure 15 shows the flowsheet of a plant, commissioned five years ago, for the recovery of about 170,000 tons benzene and toluene from 520,000 tons per year reformat fraction. In this case, the extractive distillation step is preceded by a liquid-phase extraction step using a simple sieve-tray extractor. The aromatic products show a very high purity, less than 150 ppm non-aromatics. Figure 16 is a picture of this plant. The short and thick column immediately left of the big tank is the liquid-phase extractor; the bright tall column close to the extractor is the extractive distillation column; on the far right, is the column for stripping the aromatics-enriched solvent; the two tall columns further left of the stripper serve as fractionation columns to split the pure aromatics fraction into its components benzene and toluene.

Conclusion

The new process, in all its variations, has been given the Registered Tradename "MORPHYLANE", in order to indicate that morpholines play a key role in this process.

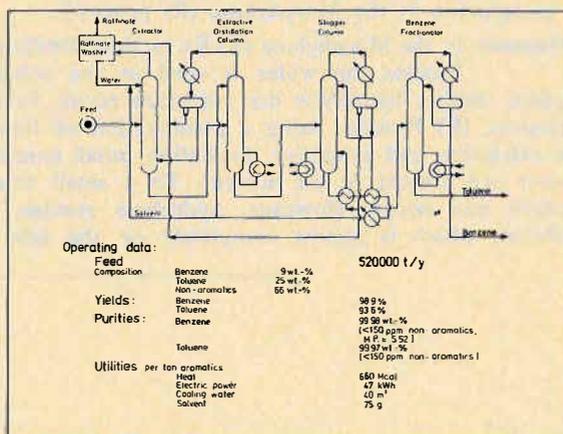


FIGURE 15. Recovery of pure benzene and toluene from a reformat fraction.

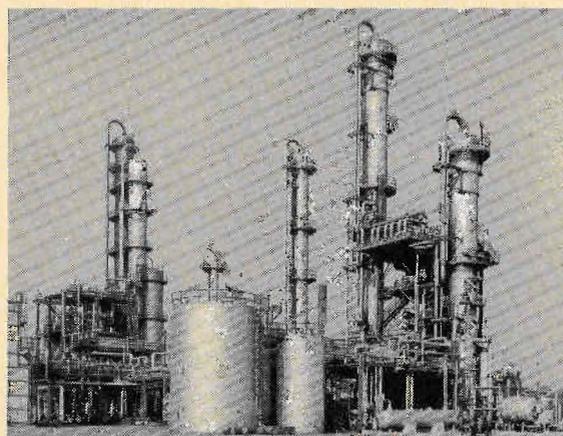


FIGURE 16. Installation for the recovery of pure benzene and toluene from a reformat fraction.

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DISCUSSION

U. Onken: Referring to my remark to the paper by Dr. Van Aken, I should like to say that I know of a case of hydrolysis of a solvent in an absorption process where dimethylformamide was used for selective absorption of acetylene. In this process, formation of formic acid was observed, leading to corrosion. Does this also happen with morpholine in the Morphylane (R) process?

G. Preusser: In the Morphylane (R) Extraction Distillation Process, no water is used in the solvent. Therefore, neither hydrolysis nor corrosion occur. In the Morphylane (R) Process, using a combination of liquid-phase extraction and extractive distillation, small amounts of water are present in the solvent. To a small extent hydrolysis can occur. However, hydrolysis reaches an equilibrium which is almost completely on the side of

solvent and water. The concentrations of acid and base are, therefore, very small and they do not lead to corrosion. The first commercial plant for this process, which is completely constructed in carbon steel, has been in continuous operation for almost five years without any damage by corrosion.

P.J. Bailes: The improvement in selectivity which results by adding water to the morpholine-based solvents could probably be achieved by adding any suitable polar mixing component. In the case of NMP, monoethylene glycol has proved a useful alternative to water. I would be grateful for the author's comments on the possible use of glycols as mixing components for morpholine reagents.

G. Preusser: We also have tested mixtures of morpholine derivatives and monoethylene glycol with respect to their selectivity in liquid-liquid extraction of aromatics. We did not find a maximum selectivity due to a synergistic effect as can be found with mixtures of N-methylpyrrolidone and monoethylene glycol.

W.C.G. Kusters: In the flow scheme water comes into the aromatic/solvent distillation column. Is good removal of xylenes, etc. still achieved when water is more volatile than xylenes?

G. Preusser: In the aromatics/solvent distillation column, the water dissolved in the solvent acts as a stripping aid. By this fact, very good stripping of the aromatics, including the xylenes, is achieved at low temperatures which are required for the careful thermal treatment of the solvent. It is not necessary to operate the column under vacuum.

Solvent Extraction of Coal

G.H. Beyer, Virginia Polytechnic Institute and State University.

ABSTRACT

A loop reactor system operated at 400°C on ground coal slurried in mineral oil, shows promise for utilizing the prompt decomposition products of coal. Coupled with solvent extraction, it should be possible to separate higher value products — such as aromatic feedstocks — from coal without excessive hydrogen consumption. Partial sulfur removal was accomplished using hydrogen indigenous to the coal itself.

Introduction

THE USE OF SOLVENT EXTRACTION TO ANALYZE COAL is attested to by the voluminous literature, summarized in Lowry⁽¹⁾ by Dryden. A description of the Pott-Broche process⁽²⁾ details efforts in Germany some thirty years ago to use solvent extraction for converting coal to higher value products. There is yet little evidence that the potential of solvent extraction has been realized to produce commercial products from coal in the quantity that will be necessary in the future as oil and gas reserves are depleted.

The overwhelming reason why we have not made more intelligent use of coal is that we haven't had to. Oil and gas will continue to be preferred raw materials for chemical manufacture, but it is high time that we began to expend the necessary effort to learn what can be done with coal.

Processes

The organic chemical industry has long made use of solvent extraction in processing coal tars and — in much larger volume — in separating aromatics from aliphatics as described in Hanson⁽³⁾ by Coleby. These applications foreshadow what might be done with coal if it can be adeptly depolymerized, desulfurized and de-ashed.

In recent years efforts to solvent-refine coal have resulted in a number of different variations on a central theme: exemplified by the Consol process⁽⁴⁾ (shallow extraction), the Pittsburgh-Midway process⁽⁵⁾ (deep extraction) and the Exxon process⁽⁶⁾ (separate catalytic hydrogenation of the solvent).

Typical of current technology are solvent-refined coal (SRC) pilot plants operated by Pittsburgh-Midway at Tacoma, Washington (50 tons/day) and by Southern and Catalytic at Wilsonville, Alabama (6 tons/day). As shown in Figure 1, the Southern Refined Coal (SRC) process uses a slurry of ground coal in a coal-derived solvent. This slurry is combined with hydrogen, heated to 800°F at 1500 psia in a preheater, followed by an adiabatic dissolver in which exothermic reactions raise the temperature to 850°F. Most of the coal is dissolved and depolymerized to products of lower molecular weight. Sulfur is removed as hydrogen sulfide gas. The separation train recycles unused hydrogen, filters out a mineral residue and recovers solvent from a vacuum column. The column bottom product is solvent-refined-coal, a low-ash,

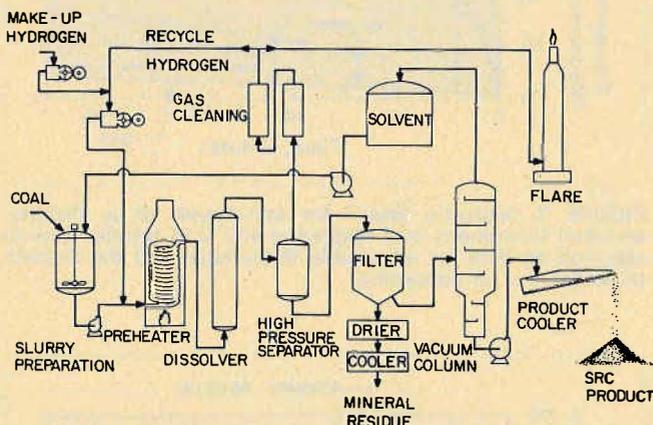


FIGURE 1. Solvent refined coal process.

low-sulfur material with a solidification point of 350-400°F and a heating value of some 16,000 Btu per pound.

Although the SRC process represents a considerable advance in technology, it has some serious limitations: excessive hydrogen consumption; long residence times in the dissolver; and slow filtration rates. There is a continuing need for improved processes for making coal a more environmentally acceptable fuel, and for making chemical feedstocks from coal.

Chemistry

How does coal come apart? The destructive treatment of coal has been widely practiced for years; the constructive treatment of coal has only just begun.

Pioneering work by Neavel⁽⁷⁾ suggests that coal undergoes rapid change in both donor solvents (such as tetralin) and nondonor solvents (such as naphthalene). Within five minutes pyridene-solubility reaches high levels. Conversion — as measured by pyridene-solubility, at least — does not seem to depend on the availability of hydrogen.

Work by Beyer and Mason⁽⁸⁾ has confirmed that important changes take place quickly even in the presence of other nondonor solvents such as decalin. Experiments were run using small tubing bombs, 3/8 in. diameter, 5 in. long. Such bombs, loaded with approximately 1 gram of coal and 2-3 grams of solvent, were quickly heated to 440°C by immersion in a fluidized sand bed, and quickly quenched by immersion in water. Mason used thermogravimetric analysis, calculating dry ash-free yields at reaction times up to 300 sec at nominal solvent-to-coal ratios of 2.0 and 3.0. Figures 2 and 3 afford a general picture of our interpretation of how coal may come apart at short residence times.⁽⁹⁾

The chemistry and structure of coal converted to soluble products under typical solvent refining conditions has benefited from new analytical techniques developed by Whitehurst and co-workers at Mobil.⁽¹⁰⁾ Using a fast-dump reactor they have been able to make and to analyze the early decomposition products of coal and identify the systematic changes that take place both in the coal and in the solvent.

It seems that one effect of hydrogen availability may

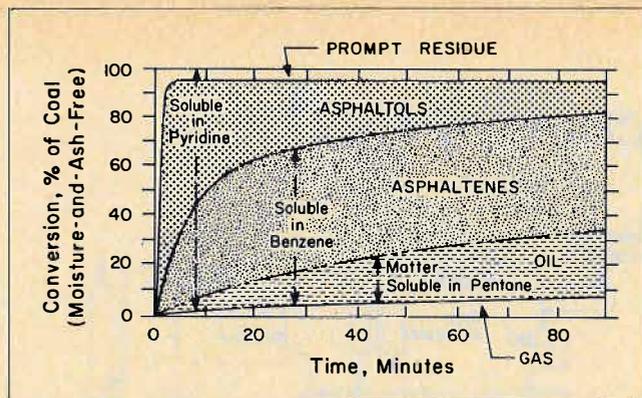


FIGURE 2. Neavel's data⁽⁷⁾ for conversion of a vitrinite-enriched bituminous coal reacted at 400°C in tetralin. Neavel reported no data for oil soluble in pentane, and the dashed-triple-dot line is conceptual.

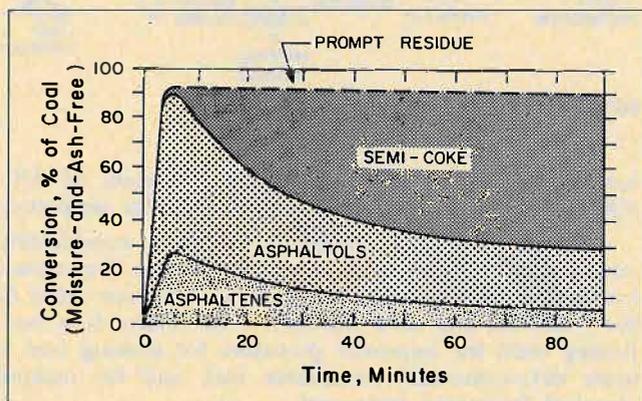


FIGURE 3. Neavel's data⁽⁷⁾ for conversion of the coal of Figure 2 at 400°C in naphthalene.

be to encourage the production of asphaltenes and oils, while inhibiting semicoke formation. But the fact that pyridene-solubility rises to peak values in both donor and nondonor environments lends credence to the theory that local coal-contained hydrogen may be surprisingly effective. In fact, one can make a case that coal may often be "overcooked". The products obtained are sometimes as unattractive as cafeteria-line vegetables subjected to similar treatment.

Test Work

These data encouraged us to design and build a loop reactor, to explore the properties of short-exposed coal — which we refer to as "prompt coal". Taken from a reactor at a propitious time, "prompt coal" may represent a whole new raw material worthy of careful study. Such study may help reveal how coal comes apart, as well as providing relatively unspoiled perasphaltenes for further processing.

Under ERDA sponsorship, we have designed and built a loop reactor system⁽⁸⁾. Figure 4 shows our continuous reactor system and some of its peripheral equipment. The coil of 3/8-in. diameter tubing, and a recycle pump operated in an autoclave (Figure 5), form a loop reactor with the high recirculation conducive to good heat and mass transfer. Pumping coal slurry to, and overflowing coal slurry from, this loop reactor gives control of residence time and produces "prompt coal" of known thermal history.

A great deal remains to be learned about the best conditions for depolymerizing coal, while avoiding semicoke formation and the unproductive use of hydrogen to produce gas and destroy solvent. Preliminary results with a Monterey coal containing 4.25% sulfur, slurried in a paraffinic white mineral oil, indicates that a product containing 3.4% sulfur can be produced using only the hydrogen indigenous to the coal itself.

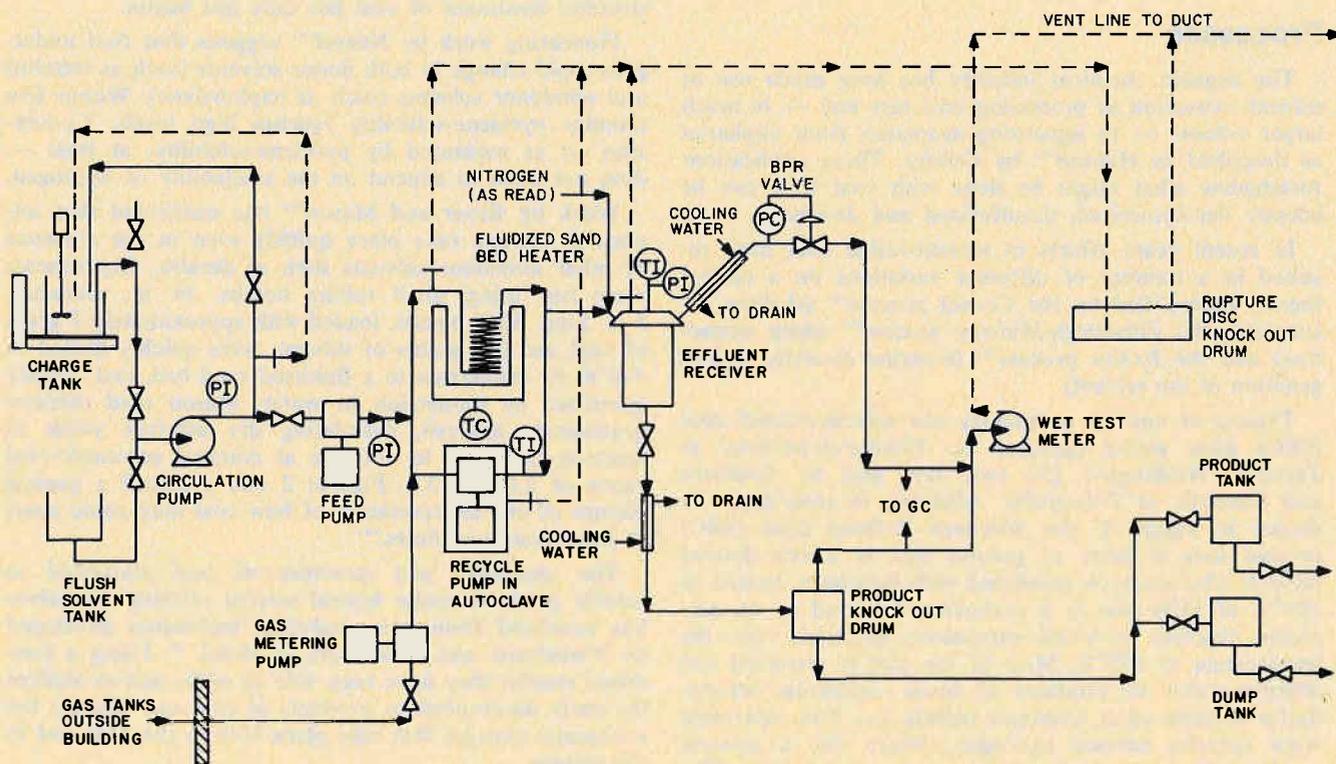


FIGURE 4. Continuous reactor system.

Role of Solvent Extraction

The role of solvent extraction in coal processing is far from clearly defined. At one end of the spectrum there is a search for a "complete" solvent which dissolves virtually all of the coal. Such a solvent would presumably be coal-derived, high in aromatics content and most likely a commercial plant would have to operate in solvent balance — with no appreciable amounts of solvent purchased. These constraints may seriously conflict with the necessity to digest a variety of coals, without excessive hydrogen consumption and at short enough residence times to keep capital expenditures for high temperature, high-pressure reaction space within reasonable bounds.

In the center of the solvent spectrum are "temporary" solvents such as supercritical gases⁽¹¹⁾, which attempt to dissolve only a select fraction of the coal to produce, for example, aromatic feedstocks for chemicals manufacture. After removal of lower-molecular weight aromatics, the major portion of the coal might simply be used to fire conventional boilers equipped with scrubbers.

At the other end of the solvent spectrum one can envision the use of antisolvents primarily to expedite separation of solids and liquids⁽¹²⁾, a separation that is embarrassingly slow and costly, using conventional filtration equipment. In this role the solvent serves to wash, leach and/or settle the unreactive coal, after being carefully depolymerized in a reactor operated at conditions uniquely suitable to the coal being processed.

The fact that these vastly different solvent functions have not yet been synthesized into a viable process attests to our inadequate understanding of how coal can best be taken apart and efficiently separated into products of greater value.

Summary

In summary, it seems likely that solvent extraction will certainly be involved in the more intelligent utilization of coal, just as it has been involved in making oil more useful. Who would have predicted, several decades ago, that millions of pounds of polyester fibers would be manufactured from naphtha, a mixture of hydrocarbons whose complexity is attested to by a boiling range of 250 to 450°F?

One of our current goals is to process coal under relatively mild conditions in the hope of reducing heteroatom content — particularly sulfur — without excessive hydrogen consumption. The addition of gross amounts of hydrogen to coal seems essential to producing fuel oil and gasoline; but such costly treatment can hardly be justified for coal destined for utility boilers.

Another goal is to devise new ways to un-do or depolymerize coal, followed by solvent extraction to remove valuable feed-stock fractions before the coal is burned. Supercritical extraction may offer opportunities for separation by simple pressure reduction after contacting.

To accomplish these goals will require a much better understanding of how coal comes apart. Perhaps the removal of sulfur will prove less important in the long run, than the "creaming" of coal to remove valuable feedstocks, rich in aromatics. Certainly a versatile reactor, with good heat and mass transfer, coupled with a versatile separation train, for truly continuous solid-liquid separation, will be essential components.

Solvent extraction may well turn out to be the key to unlocking the complex material known simply as "coal".

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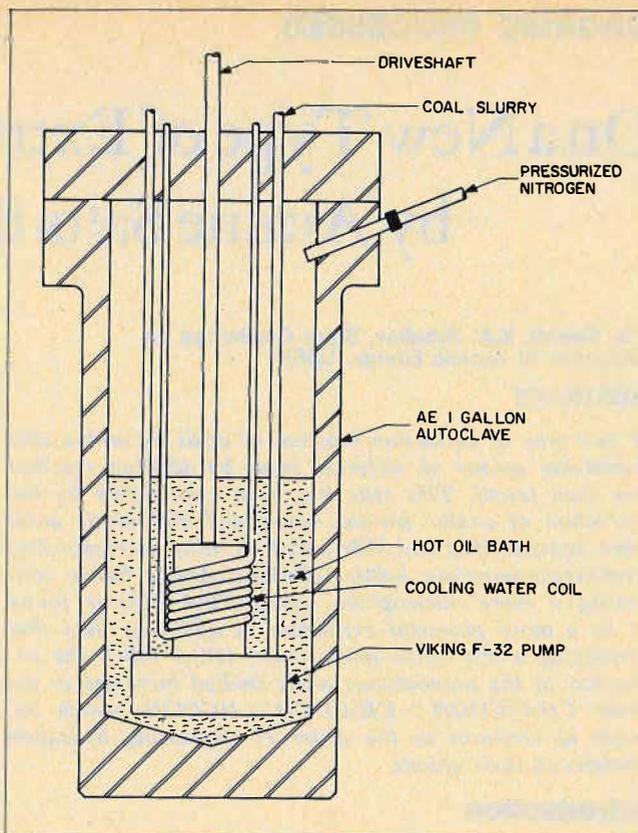


FIGURE 5. Loop reactor cycle pump.

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DISCUSSION

H.M. Stoenner: What is the suggested operating pressure?

G.H. Beyer: The "best" solvent is open to question, as yet. The solvent we are currently using is a white mineral oil which is paraffinic, quite stable and generally thought to be a non-donor solvent. We chose the solvent to see what can be accomplished using just the hydrogen in the coal itself. Our operating pressure of 400-500 psia is maintained by nitrogen, using a back-pressure-regulator. Later we plan to add reactive gases to our loop reactor system, at which point we may well change the operating pressure.

On a New Type of Extraction Reaction of Acids by Amine Salts through Addition

V.S. Shmidt, K.A. Rybakov, State Committee on Utilization of Atomic Energy, USSR

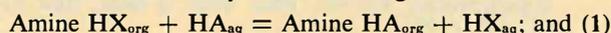
ABSTRACT

A new type of extraction reaction of acids by amine salts containing anions of different acids by addition reaction has been found. This type has been exemplified by the extraction of oxalic, formic, acetic and chloroacetic acids from aqueous HCl and HBr solutions using corresponding tri-n-octylammonium halide solutions. Amine halide containing a more nucleophilic anion (TOA-HCl) is found to be a more powerful extractant in additions than that containing a less nucleophilic anion (TOA-HBr); the extraction of the monoatomic acids studied increases in the order $CH_2ClCOOH > CH_3COOH > HCOOH$, which appears to conform to the order of decreasing hydration energies of their anions.

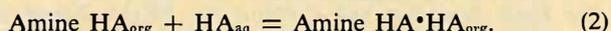
Introduction

AT PRESENT TWO TYPES OF EXTRACTION REACTIONS of acids by amine salts are known⁽¹⁾:

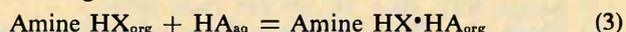
(a) the extraction of HA acid with amine salt containing different HX acid by anion exchange:



(b) the extraction of HA acid with amine salt containing the same acid due to adduct formation:



Anions of amine salts having nucleophilic properties⁽²⁾ can, in principle, add molecules of any electrophilic compound. Thus another type of extraction (c) seems to be feasible, i.e.: the extraction of HA acid with amine salt containing a different HX acid due to adduct formation:



The (c) reactions do not seem to occur widely since they demand a peculiar compromise between the properties of HX acid entering into the salt composition and HX acid extracted in addition. Clearly, HA acid must be relatively weak as the formation of adducts such as amine $\text{HX} \cdot \text{HA}$ must be favoured by the presence of undissociated HA molecules. HX acid, a part of the amine salt, has to meet the most specific requirements. The acid must be relatively strong and the X^- must have a relatively low hydration energy to have little or no substitution from the salt by the A^- anions available. But the X^- nucleophilicity must not be too high to prevent a significant formation of amine $\text{HX} \cdot \text{HX}$ by the (b) type reaction. However, it must be above zero, otherwise amine HX could not add electrophilic substances including HA.

Evidence for the feasibility of the (c) type reactions was first found in studying the extraction of oxalic acid with tri-n-octyl-ammonium (TOA) nitrate from nitric acid solutions⁽³⁾. In the HNO_3 high concentration range where the anion exchange extraction of $\text{H}_2\text{C}_2\text{O}_4$, typical of the system studied^(3,4), is ruled out, the distribution factors ($D_{\text{H}_2\text{C}_2\text{O}_4}$), if small (~ 0.05), did not decrease to zero with increasing the HNO_3 concentration in the aqueous phase. A small amount of $\text{H}_2\text{C}_2\text{O}_4$ extracted

with $\text{TOA} \cdot \text{HNO}_3$ under these conditions is conceivably bound by addition; the low value of $D_{\text{H}_2\text{C}_2\text{O}_4}$ is ascribed to most amine $\text{HNO}_3 \cdot \text{HNO}_3$ being in the non-extracting form (amine $\text{HNO}_3 \cdot \text{HNO}_3$) due to a significant nucleophilicity of NO_3^- .

Among anions of considerable nucleophilicity, but less than nitrate, is Cl^- . Our previous study has shown that oxalic acid is actually extracted in marked quantities with TOA chloride in organic solvents from hydrochloric solutions so high in concentration (2-4M) that the anion-exchange extraction of $\text{H}_2\text{C}_2\text{O}_4$ appears to be impossible. In this system, oxalic acid can be expected to be extracted by the (c) reaction under the conditions described.

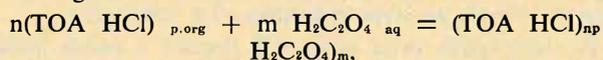
This paper is aimed at a more detailed study of the extraction of oxalic and other acids from HCl and HBr solutions.

Experimental

The tri-n-octylamine used in the study was 98% pure. O-xylene pure and chloroform medicinal were used as diluents. The phase ratio was equal to 1:1. Stirring for 5 minutes was sufficient to reach equilibrium. The phases were separated by centrifugation for 5 minutes. Before and after extraction the oxalic acid concentration was determined by titration with 0.1N KMnO_4 ⁽⁶⁾. Its equilibrium concentration in the organic phase was estimated as the difference between the total concentration and that in the equilibrium aqueous phase.

Results and Conclusions

The most interesting results were obtained with o-xylene as diluent* and at relatively low concentrations of oxalic acid in aqueous solutions (Figure 1). It is seen from Figure 1 that with the HCl concentration above 0.2M, the extraction of $\text{H}_2\text{C}_2\text{O}_4$ decreases sharply as might be expected with the anion-exchange extraction because of the $\text{H}_2\text{C}_2\text{O}_4$ displacement from the amine salt by chloride ions. However, at HCl concentrations exceeding 1.0M the $\text{H}_2\text{C}_2\text{O}_4$ distribution coefficients tend to increase. This could only be attributed to the fact that along with the anion-exchange displacement of $\text{H}_2\text{C}_2\text{O}_4$ from the organic phase the process of oxalic acid extraction with TOA begins to manifest itself due to the addition reaction:



where P is the amount of association of amine chloride. Within this concentration range, an increase in $D_{\text{H}_2\text{C}_2\text{O}_4}$ is perhaps explained by the salting-out effect of HCl. At HCl concentrations above 4M, the values of $D_{\text{H}_2\text{C}_2\text{O}_4}$ begin to decrease probably as a result of a partial formation of amine $\text{HCl} \cdot \text{HCl}$ salt due to the competitive "b" - type reaction which is known to take place to an appreciable extent at high concentrations of HCl ⁽¹⁾.

*Check experiments have shown that this diluent does not extract oxalic acid under the conditions studied ($D_{\text{H}_2\text{C}_2\text{O}_4} \sim 0.005$); the extraction of HCl is also negligible (5).

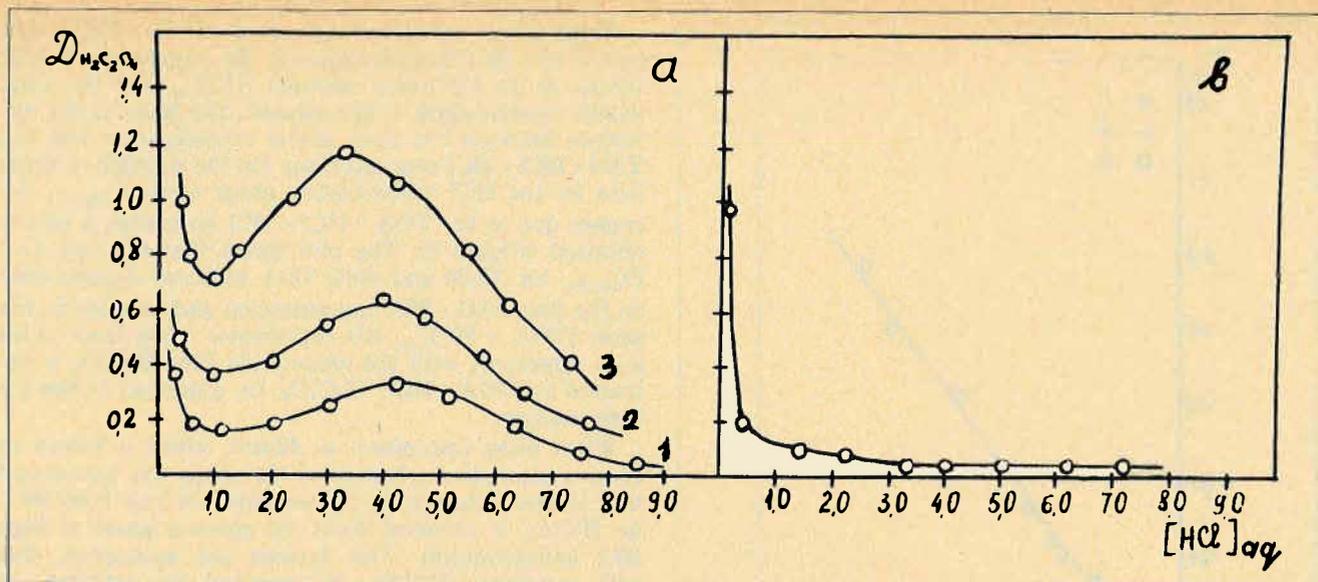


FIGURE 1. Dependence of distribution coefficients of oxalic acid between HCl aqueous solutions and TOA solutions in diluents on HCl concentration in the aqueous phase. Initial $H_2C_2O_4$ concentration in the aqueous phase — 0.12M; $V_{org} : V_{aq} = 1:1$; diluents: (a) o-xylene; (b) chloroform; TOA concentrations (vol. %): 1-10; 2-20; 3-40.

The supposed extraction mechanism is in agreement with data on the co-distribution of hydrochloric and oxalic acids (and the distribution of HCl alone) (Table 1). One can see from Table 1 that extraction of HCl at concentrations up to 3.5M is practically unaffected by the presence of $H_2C_2O_4$. At the 0.5-3.5M HCl concentration in the aqueous phase, its concentration in the organic phase is essentially equal to that of amine indicating the existence of amine in the form of $TAO \cdot HCl$ under these conditions. At the same time, over this concentration range, the extraction of $H_2C_2O_4$ is considerable and supports the assumption of the formation of the product of the $H_2C_2O_4$ and $TAO \cdot HCl$ addition. Comparison of the $D_{H_2C_2O_4}$ values at various amine concentrations (Figure 1)

shows linear dependence between them. This suggests that a molecule of $H_2C_2O_4$ in the extract is bound with a molecule of the amine salt associate. Assuming⁽⁷⁾ the amine chloride associate takes the form of cyclic trimers, both $-COOH$ groups of oxalic acid can add to two different chlorine anions of the trimer to form a relatively stable cycle.

At HCl concentrations $> 3M$ in the aqueous phase, an appreciable additional extraction of HCl results from the $TOA \cdot HCl \cdot HCl$ formation; this leads to a decrease in the free $TOA \cdot HCl$ concentration. It is interesting that in this HCl concentration range the extraction of $H_2C_2O_4$ also tends to decrease, supporting the assumption of $TOA \cdot HCl$ being an extractant.

TABLE 1. Hydrochloric and Oxalic Acid Equilibrium Concentrations in the Extraction with TOA Solutions in O-xylene

$H_2C_2O_4$ initial concentration in the aqueous phase — 0.12 mole/l, $V_{org} : V_{aq} = 1:1$.

Total Amine Concentration, M	$[HCl]_{aq}$	$[HCl]_{org}$	$[HCl]_{org}$ (without $H_2C_2O_4$)	$[H_2C_2O_4]_{org}$	$[TOA \cdot HCl - HCl]$	$[TOA \cdot HCl]$	$D_{H_2C_2O_4}$
0.240	1.10	0.24	0.24	0.018	—	0.24	0.17
	2.06	0.24	0.24	0.020	—	0.24	0.20
	3.10	0.25	0.25	0.024	0.01	0.23	0.25
	4.24	0.25	0.27	0.030	0.01	0.23	0.33
	5.20	0.27	0.30	0.028	0.03	0.21	0.30
	6.27	0.32	0.33	0.019	0.08	0.16	0.18
	7.50	0.37	—	0.009	0.13	0.11	0.081
	8.50	0.40	0.40	0.006	0.16	0.08	0.05
0.50	1.00	0.51	0.50	0.032	0.01	0.49	0.36
	2.00	0.52	0.51	0.034	0.02	0.48	0.40
	3.00	0.52	0.52	0.042	0.02	0.48	0.54
	4.10	0.56	0.57	0.047	0.06	0.44	0.64
	4.80	0.59	0.62	0.041	0.09	0.41	0.52
	5.80	0.65	0.066	0.036	0.15	0.35	0.43
	6.60	0.75	0.73	0.026	0.25	0.25	0.28
	7.70	0.80	0.78	0.018	0.30	0.20	0.175
0.93	0.48	0.95	—	0.06	0.02	0.91	1.00
	1.47	0.97	—	0.054	0.04	0.89	0.82
	3.37	1.03	—	0.065	0.10	0.83	1.18
	4.28	1.09	—	0.060	0.16	0.77	1.00
	5.55	1.27	—	0.054	0.34	0.59	0.82
	6.33	1.37	—	0.46	0.44	0.49	0.62
	7.40	1.54	—	0.034	0.61	0.32	0.40

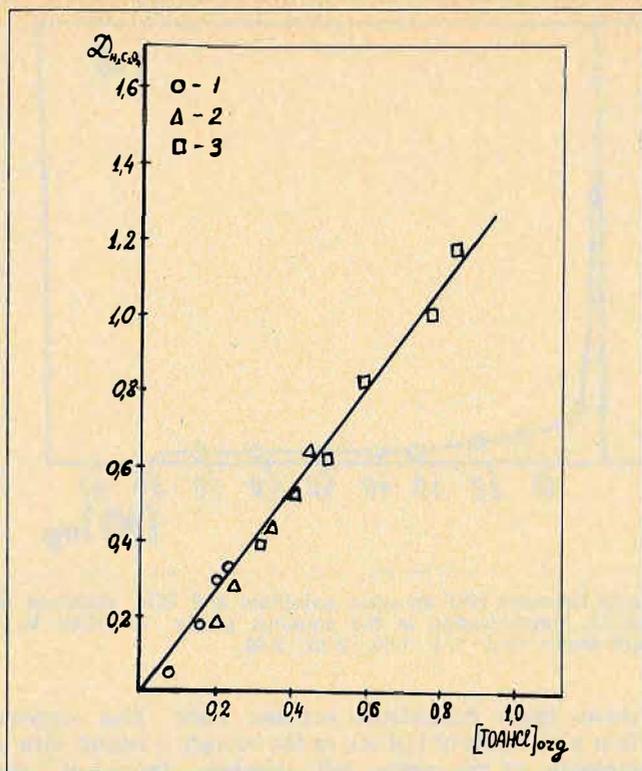


FIGURE 2. Dependence of oxalic acid distribution coefficients on free TOA HCl concentration. Initial $H_2C_2O_4$ concentration in the aqueous phase — 0.12M; $V_{org}:V_{aq} = 1:1$; extractants: 1 — 0.24M TOA in o-xylene; 2 — 0.5M TOA in o-xylene; 3 — 0.93M TOA in o-xylene.

Table 1 lists calculated data on the TOA · HCl · HCl and TOA · HCl concentrations in the organic phase. The former is the difference between $[HCl]_{org}$ and the total amine concentration in the extract. The latter is the difference between the total amine concentration and the TAO · HCl · HCl concentration. On the strength of these data for the HCl concentration range where $D_{H_2C_2O_4}$ decreases due to the TOA · HCl · HCl formation, a plot is obtained (Figure 2). The plot shows that the values of $D_{H_2C_2O_4}$ for 10,20 and 40% TOA solutions depend only on the free TAO · HCl concentration and coincide at the same $[TOA \cdot HCl]_{org}$, the dependence being linear. This is in agreement with the assumption that $H_2C_2O_4$ is extracted as (TOA · HCl) $H_2C_2O_4$, i.e. a product of the (c) type reaction.

When using chloroform as diluent, which is known to cause a significant solvation of the amine salt anions and thus to lower sharply the concentration of free TOA · HCl, no $H_2C_2O_4$ is extracted from the aqueous phase at high HCl concentrations. This favours the assumption that with o-xylene, $H_2C_2O_4$ is extracted by addition to TOA · HCl which has a weakly solvated anion.

The above-mentioned extraction mechanism is favoured by our recognition of the failure of the quaternary ammonium compound — tri-n-alkylbenzylammonium chloride in o-xylene — to extract $H_2C_2O_4$ at HCl concentrations of > 1.2M. In connection with the much higher nucleophilicity of Cl^- in this extractant (compared to TOA · HCl) at the concentrations given, the total tri-n-alkylbenzyl-ammonium chloride is the adduct^(9,19), which seems to prevent the addition of $H_2C_2O_4$ to R_3BzHCl .

Previous experiments have shown that besides $H_2C_2O_4$,

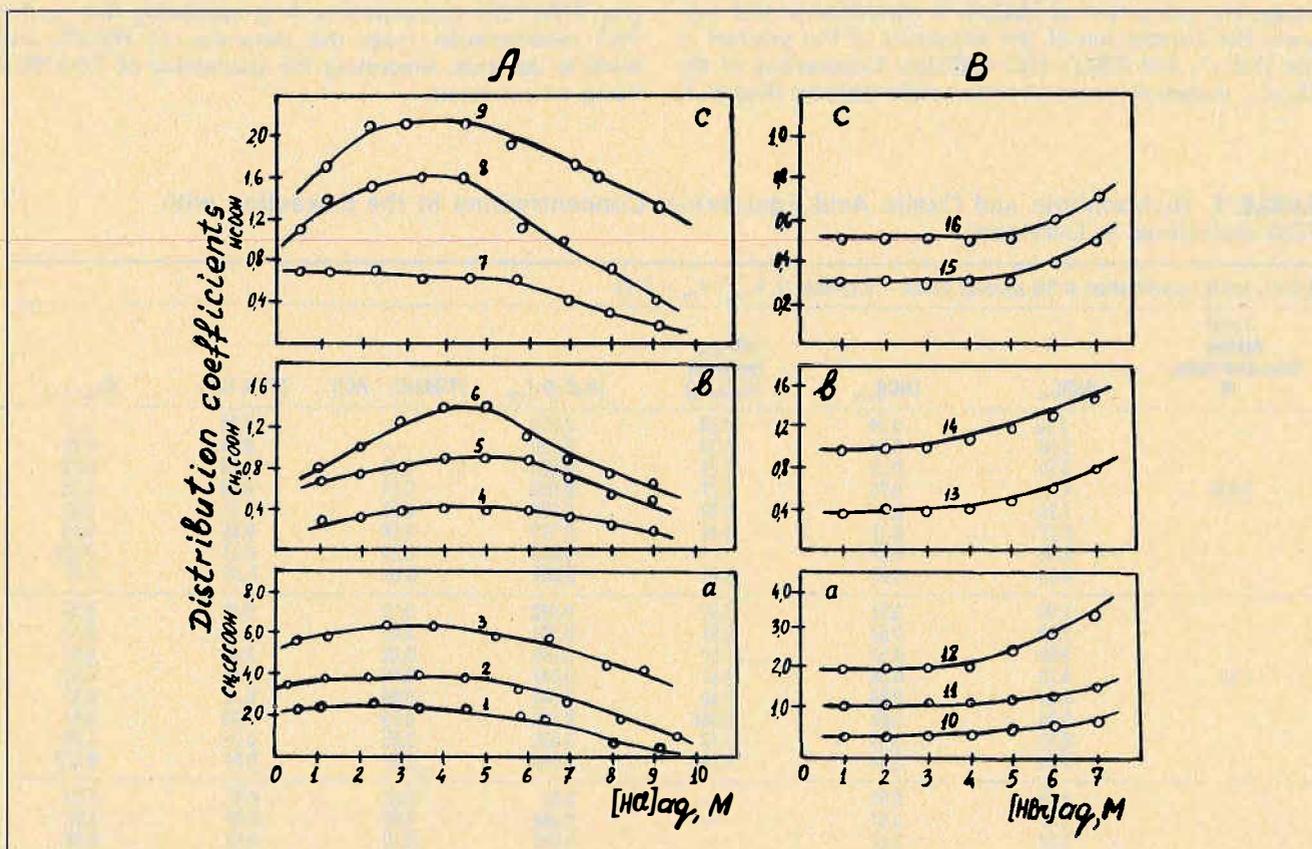


FIGURE 3. Dependence of distribution coefficients of (a) monochloroacetic, (b) formic and (c) acetic acids between halide acid solutions and TOA solutions in o-xylene on halide acid concentration in the aqueous phase; halide acids: A — HCl; B — HBr; Initial TOA concentrations in xylene; 1a — 0.45M; 2a — 0.81M; 3a — 1.26M; 1b — 0.50M; 2b — 0.95M; 3b — 1.37M; 1c — 0.22M; 2c — 0.48M; 3c — 1.00M;

TABLE 2. Equilibrium Concentrations of HCl, CH₂ClCOOH, CH₃COOH and HCOOH (mole/l) in the Co-extraction with TOA Solutions in o-xylene

(a) Extraction of CH ₂ ClCOOH, [HX] _{aq} = 0.1M				(b) Extraction of HCOOH [HX] _{aq} = 0.1M			(c) Extraction of CH ₃ COOH [HX] _{aq} = 0.16M				
Amine Conc. mole/l	[HCl] _{aq}	[HCl] _{org}	[CH ₂ ClCOOH] _{org}	Amine Conc. mole/l	[HCl] _{aq}	[HCl] _{org}	[HCOOH] _{org}	Amine Conc. mole/l	[HCl] _{aq}	[HCl] _{org}	[CH ₃ COOH] _{org}
0.45	0.50	0.45	0.22	0.50	0.48	0.50	0.07	0.22	1.00	0.22	0.05
	1.00	0.45	0.23		0.16	0.51	0.07		2.00	0.22	0.05
	2.32	0.45	0.25		2.27	0.53	0.07		3.00	0.22	0.06
	3.40	0.45	0.24		3.40	0.55	0.06		4.00	0.23	0.06
	4.50	0.46	0.23		4.45	0.59	0.06		5.00	0.24	0.06
	5.50	0.49	0.20		5.59	0.63	0.06		6.00	0.26	0.06
	6.42	0.52	0.18		6.90	0.72	0.04		7.00	0.29	0.05
	8.08	0.63	0.06		7.90	0.82	0.03		8.00	0.32	0.04
	9.15	0.73	0.04		9.00	0.91	0.016		9.00	0.37	0.03
0.81	0.55	0.81	0.34	0.95	0.47	0.95	0.11	0.48	1.00	0.48	0.11
	1.15	0.81	0.38		1.13	0.95	0.14		2.00	0.48	0.12
	2.18	0.81	0.39		2.20	0.95	0.15		3.00	0.49	0.13
	3.43	0.83	0.40		3.40	0.97	0.16		4.00	0.51	0.15
	4.53	0.86	0.38		4.40	1.02	0.16		5.00	0.53	0.14
	5.75	0.93	0.32		5.77	1.20	0.11		6.00	0.56	0.14
	6.90	1.04	0.27		6.75	1.36	0.10		7.00	0.56	0.11
	8.15	1.20	0.18		7.90	1.47	0.07		8.00	0.72	0.09
	9.50	1.42	0.09		8.90	1.63	0.04		9.00	0.79	0.08
1.26	1.20	1.26	0.59	1.37	1.12	1.07	0.17	1.00	1.00	1.00	0.13
	2.58	1.26	0.64		2.14	1.07	0.21		2.00	1.00	0.17
	3.67	1.32	0.63		3.00	1.44	0.21		3.00	1.00	0.20
	5.23	1.42	0.53		4.37	1.55	0.21		4.00	1.00	0.22
	0.47	1.58	0.57		5.45	1.73	0.19		5.00	1.08	0.23
	7.87	1.80	0.44		7.00	1.96	0.17		6.00	1.18	0.18
	8.73	1.95	0.42		7.58	2.03	0.16		7.00	1.31	0.14
					9.00	2.29	0.13		8.00	1.42	0.12
									9.00	1.56	0.10

some other organic acids such as monochloroacetic, formic and acetic are also extracted to an appreciable extent with tri-n-octylammonium chloride and bromide from solutions of appropriate halide acids. From the above considerations of the effect of the acid nature on the feasibility of the third type of reaction, one can expect the extraction to follow the same addition scheme in these systems. Another object of our work was examination of the validity of this assumption and the effect of the nature of the acid contained in the amine salt and that extracted from aqueous solution on extraction equilibrium.

The Cl⁻ and Br⁻ concentrations in the organic phase were determined by the titration with 0.08M AgNO₃ by the method of Folhard⁽⁶⁾ in the presence of excess isopropyl alcohol, while the CH₂ClCOOH, HCOOH and CH₃COOH concentrations were determined by titration of all the acids with 0.1M NaOH in phenolphthalein, followed by subtraction of the inorganic acid content*. Data on the acid distribution are presented in Figures 2 and 3 and in more detail in Tables 2 and 3. The most interesting result is that over the HCl and HBr concentration range 1-4M in the aqueous phase, which is characterized by a significant extraction of acids studied (especially CH₂ClCOOH), no displacement of halide ions from the organic phase is observed (Tables 2, 3). Under these conditions the HCl and HBr concentrations are constant and equal to the amine concentration, i.e. TOA·H(hal) available in the organic phase remains unaltered. This suggests that these organic acids are not extracted by anion exchange. Then the only possible explanation of the extraction is their addition to TOA·H(hal) according to the "c" type reaction.

*The value [CH₂ClCOOH]_{org} has been corrected by subtraction of the acid extracted by the diluent. Formic and acetic acids in the concentration range studied are extracted by o-xylene with the distribution coefficient of < 0.005.

The shape of the curves illustrated in Figure 3 is similar to that of relevant relationships found for the extraction of H₂C₂O₄ with TOA·HCl solutions from HCl solutions in addition. As in the case of monoatomic HA acids studied, the increase in the distribution coefficients with increasing HCl_{aq} concentration up to 4-6M can be explained by the salting-out effect of halide acid in the aqueous phase. The decrease in the HX distribution coefficient with increasing [HCl]_{aq} up to 5-10M can be attributed to the HCl competition. At these concentrations the acid is markedly extracted (Table 2) and links to TOA·HCl, an extractant for HX acid, to form the adduct TOA·HCl·HCl⁽¹⁾. With HBr which forms complexes such as TOA·HCl·HCl⁽¹⁾ with difficulty, no decrease is observed in the HX extraction at high halide acid concentrations as opposed to HCl.

Based on the data from Tables 2 and 3 the CH₃COOH and HCOOH distribution coefficients vs the free TOA·H(hal) concentration are plotted (Figure 4). The [TOA·H(hal)]_{org} was calculated assuming that each molecule of halide acid extracted above the quantity necessary to form TOA halide acid links a molecule of TOA·H(hal) and that each extracted molecule of organic acid also links a molecule of TOA·H(hal) in the organic phase. Figure 2 shows linear dependence of the distribution coefficients on [TOA·H(hal)] for formic and acetic acids. This is in line with an initial assumption that each molecule of TOA·H(hal) corresponds to a molecule of HX. For monochloroacetic acid a linear dependence of D_{HX} on [TOA·HCl]_{org} is not apparent. This can be explained by a different HX:TOA ratio in the compound being extracted and results from different amounts of association of linking groups (TOA·HCl)_n and (CH₂ClCOOH)_m.

Comparison of Figures 3a and 3b shows that TOA·HCl is a more powerful extractant for HX acids than TOA·HBr. This corresponds to higher nucleophilicity of Cl⁻ compared to Br⁻. As with TOA·HA·HA⁽⁵⁾, the

TABLE 3. Equilibrium Concentrations of HBr, CH₂ClCOOH, CH₃COOH and HCOOH in the Extraction with TOA in o-xylene

a) Extraction of CH ₂ ClCOOH, [HX] _{aq} = 0.1 M				b) Extraction of CH ₃ COOH, [HX] _{aq} = 0.1M				c) Extraction of HCOOH, [HX] _{aq} = 0.1M			
Amine Concentra-	[HBr] _{aq}	[HBr] _{org}	[CH ₂ ClCOOH] _{org}	Amine Concentration	[HBr] _{aq}	[HBr] _{org}	[CH ₃ COOH] _{org}	Amine Concentration	[HBr] _{aq}	[HBr] _{org}	[HCOOH] _{org}
0.24	1.00	0.24	0.06	0.40	1.00	0.40	0.04	0.40	1.00	0.40	0.03
	2.00	0.24	0.06		2.00	0.40	0.04		2.00	0.40	0.03
	3.00	0.24	0.06		3.00	0.40	0.04		3.00	0.40	0.03
	4.00	0.24	0.06		4.00	0.40	0.04		4.00	0.40	0.03
	5.00	0.24	0.07		5.00	0.41	0.04		5.00	0.41	0.03
	6.00	0.25	0.08		6.00	0.42	0.05		6.00	0.42	0.04
	7.00	0.25	0.08		7.00	0.44	0.06		7.00	0.44	0.05
0.55	1.00	0.55	0.13	0.88	1.00	0.88	0.10	0.88	1.00	0.88	0.05
	2.00	0.58	0.13		2.00	0.88	0.10		2.00	0.88	0.05
	3.00	0.55	0.13		3.00	0.88	0.10		3.00	0.88	0.05
	4.00	0.55	0.13		4.00	0.88	0.10		4.00	0.88	0.05
	5.00	0.56	0.14		5.00	0.90	0.11		5.00	0.90	0.05
	6.00	0.58	0.15		6.00	0.98	0.12		6.00	0.93	0.06
	7.00	0.61	0.17		7.00	1.01	0.13		7.00	1.01	0.07
0.88	1.00	0.88	0.22	0.88	1.00	0.88	0.10	0.88	1.00	0.88	0.05
	2.00	0.88	0.22		2.00	0.88	0.10		2.00	0.88	0.05
	3.00	0.88	0.22		3.00	0.88	0.10		3.00	0.88	0.05
	4.00	0.88	0.22		4.00	0.88	0.10		4.00	0.88	0.05
	5.00	0.90	0.22		5.00	0.90	0.11		5.00	0.90	0.05
	6.00	0.93	0.26		6.00	0.98	0.12		6.00	0.93	0.06
	7.00	1.01	0.30		7.00	1.01	0.13		7.00	1.01	0.07

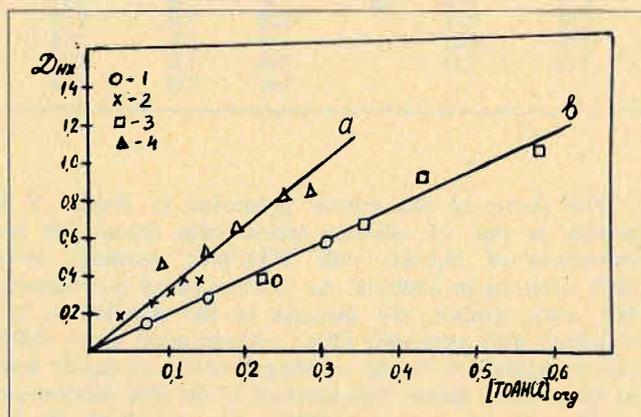


FIGURE 4. Dependence of distribution coefficients of formic (β) and acetic (α) acids on free TOA halide acid concentration. Initial TOA concentrations: 1 — 0.50M; 2 — 0.22M; 3 — 0.95M; 4 — 0.48M.

strength of TOA·HA·HX complexes is likely to be primarily affected by the nucleophilicity of the anion involved in the amine salt being an extractant. At the same time Figure 3 shows that the sequence of extractability of organic acids with TOA·H (hal) by the (c) type reaction is CH₂ClCOOH > CH₃COOH > HCOOH. This sequence

does not correlate with the order of increasing nucleophilicity. The extractability of HX acids seems to be affected primarily by the hydrophobic behaviour dependent on the anion hydration energy rather than the nucleophilicity.

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Dissociation Extraction

— Economic Optimization of a Separation Process for Meta- and Para-Cresols

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ABSTRACT

A dissociation extraction process for the separation of mixtures of *m*- and *p*-cresols is described involving reaction with the weak base: aqueous tri-sodium orthophosphate. The various unit operations within the process are mathematically modelled and the important design variables established by a parametric survey. The overall process is optimized to produce minimum costs for the separation of a feed of 400 tons/year of mixed cresols (40% meta) into isomers of purities ranging from 85% to 99%. The use is outlined of a combination of dynamic programming and direct search optimization techniques in a procedure which may be advantageously applied to other separations.

Introduction

THE CHEMICAL INDUSTRY CONSUMES LARGE QUANTITIES of raw materials and energy in processes that are predominantly capital intensive. Since the world's supplies of minerals and fuels are becoming increasingly scarce it is vital that these commodities are used efficiently and, therefore, that the design of chemical processes is optimized. Common sense and good engineering expertise often allow selection of design parameters that represent approximately an optimum arrangement both for financial profitability and also for resource and energy conservation. In areas where expertise is lacking or where processes are complex, the question of optimization merits detailed analysis and modern computer methods provide a practical means of finding optimum solutions. To date, the art of optimization applied to whole processes is still in its infancy, certainly in its application to solvent extraction technology, and there is a need for optimization studies, not only to design particular processes but also to provide models capable of more general application. As a contribution in this direction, this paper describes the modelling and economic optimization of a particular solvent extraction process: the separation of mixtures of *m*- and *p*-cresol by dissociation extraction.

Dissociation Extraction of Cresols

Dissociation extraction is a type of separation process which has been used chiefly for the separation of mixtures of organic acids or bases which are isomeric or chemically similar. Much work has been devoted at the University of Bradford in recent years⁽¹⁻⁴⁾ to the theoretical understanding of dissociation extraction and a new form of this process has been developed. An application which has been studied⁽³⁾ is for the separation of the isomeric tar acids *m*- and *p*-cresol. This separation is of commercial significance, as these compounds are intermediates currently used in the manufacture of resins, plasticizers, dis-

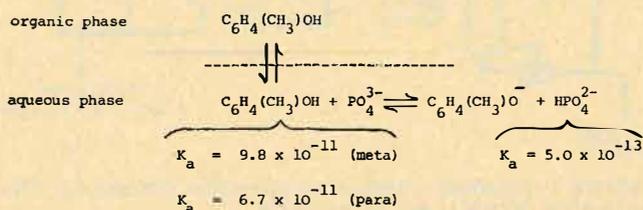
infectants, anti-oxidants and agricultural chemicals. The chemical similarity of the isomers makes impractical simple methods of separation such as distillation or solvent extraction, but a separation by dissociation extraction, which exploits the differences in the acidic strength of the isomers, is possible. This difference in strength as acids (or bases) of a mixture of organic compounds to be separated can be considerable, even for isomers, and results in a difference in affinity for a neutralization (dissociation) reaction, which may form the basis of a separation.

The traditional or 'classical' type of dissociation extraction process for the separation of cresols would involve the reaction of the organic acids with a stoichiometric deficiency of an aqueous base, such as caustic soda. As there is insufficient base for complete reaction of the cresols, there must be competition between the two isomers to react and the stronger organic acid, *m*-cresol, having the higher dissociation constant, will tend to react to form a salt, soluble in the aqueous phase, while the weaker acid, *p*-cresol, will tend to be left in its undissociated form and will be soluble in an organic solvent. If the cresol mixture is thus distributed between an aqueous base and an organic solvent, a partial separation will result and a multi-stage counter-current process can yield separate isomers of high purity. The aqueous phase containing the dissociated *m*-cresol salt could be treated with mineral acid to displace the *m*-cresol product and the *p*-cresol separated from its solution in organic solvent by a simple distillation.

A disadvantage of this 'classical' type of dissociation extraction process is that it involves the continuous consumption of strong base and acid. Therefore, it inevitably has high operating costs and will only be considered for products which have a high value in comparison with the chemicals consumed.

The modification to the 'classical' process developed at the University of Bradford is based upon the principle that, in an extraction process, the interaction between the separating reagent and the component being separated should be fairly weak, for otherwise much chemical or thermal energy will be necessary to break down the link between them and liberate the separated product and the reagent for recycle.

Consider the use of an aqueous solution of tri-sodium orthophosphate as a weakly basic reagent for the separation of *m*- and *p*-cresols by dissociation extraction. The equilibria established are:



The three dissociation constants of ortho-phosphoric acid are: 7.5×10^{-3} (1st); 6.2×10^{-8} (2nd) and 5.0×10^{-13} (3rd), so the cresols, with dissociation constants of the order of 10^{-11} , are acidic compared with the HPO_4^{2-} ion. The dissociation equilibrium for the aqueous phase will tend to proceed from left to right, reaction with the m-isomer being favoured as the tri-sodium phosphate will be present in stoichiometric deficiency compared with the cresols. The undissociated cresols will also distribute themselves between the organic and aqueous phases, as indicated, but while the isomer separation is proceeding in a multi-stage contact process, a high concentration of cresols will be maintained in the organic solvent, which should be one which does not have a particularly high affinity for cresols, such as a hexane/benzene mixture. This allows a relatively high concentration of dissociated cresol in the aqueous phase, and the separation of the two cresol isomers to a high degree of purity can be achieved. The separated aqueous phase, containing the salt of the purified m-cresol, is then contacted with a fresh solvent not laden with cresols and which should have a high affinity for cresols, such as benzene or chloroform. There is, therefore, a strong tendency for undissociated cresol to pass to the organic phase, and this pull is transmitted to the dissociation equilibrium, in the direction of reaction from right to left. Undissociated m-cresol tends to be reformed and pass to the organic phase at the same time that phosphate ion, PO_4^{3-} , is being regenerated and so may be recycled. The purified cresol isomers may then be recovered from their solutions in organic solvents by simple distillations. The separation is therefore achieved without the continuous consumption of chemicals. This modified process could be economically advantageous compared with the classical process, due to the saving in operating costs. It was a

purpose of the work described in this paper to achieve an economic assessment and optimisation of the process for cresols separation using tri-sodium phosphate as reagent.

General Procedure

The unit operations within the process were described through the formulation of mathematical models. These permitted computer calculation of the associated operating and capital costs. The important design variables in each section of the process were established by means of a parametric survey, in which the input variables to the process models were discretely varied and the effect computed on both the output process state variables and cost variables.

The arrangement of unit operations in the process results in an acyclic flow of information, so the sub-systems could be sub-optimised by dynamic programming with respect to their feeds from the cresols separation unit. Handling of the sub-optimal solutions was facilitated by linear-regression analysis so that the sub-optimal solution of a sub-system could be linked easily to the solution of the next sub-system, saving computer storage space and computation time. The overall optimal solution for the process was then achieved by a version of the Hooke and Jeeves direct search method. The objective function which was minimized was the overall costs of the process, at 1972 prices, for a plant handling 400 tons per year of a mixed cresol feed consisting of 40% meta cresol to produce separate isomers of purities between 85% and 99%.

Before the mathematical modelling of the process could be achieved, further experimental data had to be collected, and is described first, for the distribution of cresols between the organic and aqueous phases to be used for the isomer separation and m-cresol recovery stages.

Space does not permit a fully detailed description of the experimental tests made to confirm the mathematical models of the process, nor for the full listing of computer programs, equipment design procedures and cost data used. These are, however, fully described elsewhere in thesis form⁽⁵⁾.

Description of Process to be Modelled and Optimized

The process to be considered for the separation of m- and p- cresols is sketched in Figure 1.

The mixed cresols feed (40% m-cresol) is dissolved in the mixed organic solvent, 70% v/v, n-hexane, 30% benzene, a solvent composition which avoided third-phase formation encountered at lower benzene proportions. The feed solution enters the middle of the cresols separator where it is contacted with an aqueous solution of 0.5M Na_3PO_4 , this strength being 80% of saturation solubility at 20°C, the normal operating temperature envisaged. Following multi-stage contact, the cresol isomers are separated to the required degree of purity, the p-cresol concentrating in the organic solvent phase and the m-cresol as its dissociated salt in the aqueous phase. Earlier experimental work⁽³⁾ has shown that the addition of a small proportion of phosphoric acid to the aqueous phase greatly facilitates the recovery of m-cresol, although the phosphoric acid requires subsequent neutralization and purge of excess phosphate salt. The effect of phosphoric acid addition was therefore considered in the process evaluation. In the m-cresol recovery extractor, the aqueous m-cresol solution is contacted with benzene or chloroform. The cresol dissociation reaction is reversed and m-cresol is extracted into the organic solvent. The tri-sodium

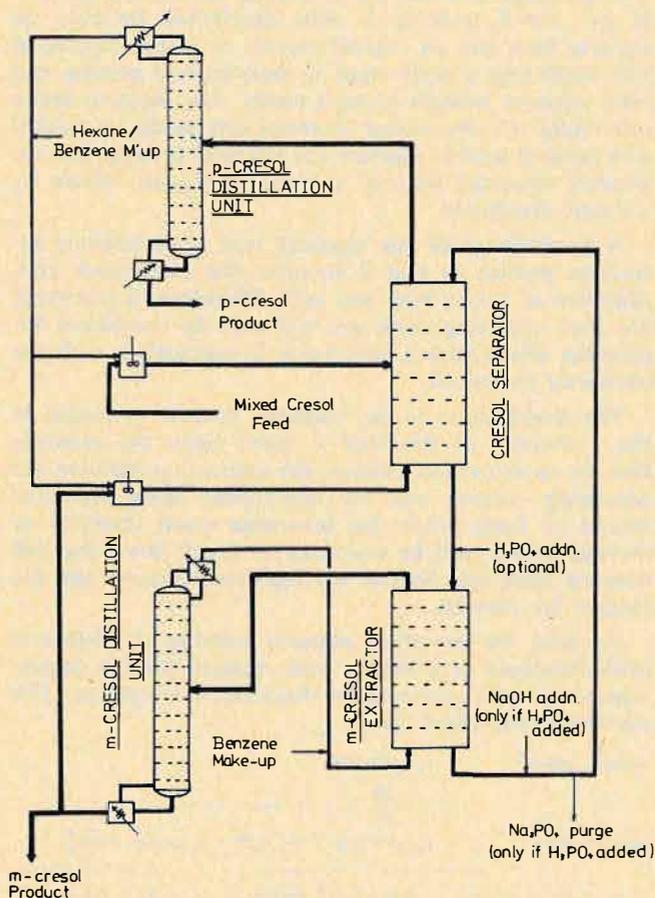


FIGURE 1. Modified dissociation extraction process for the separation of meta- and para-cresols.

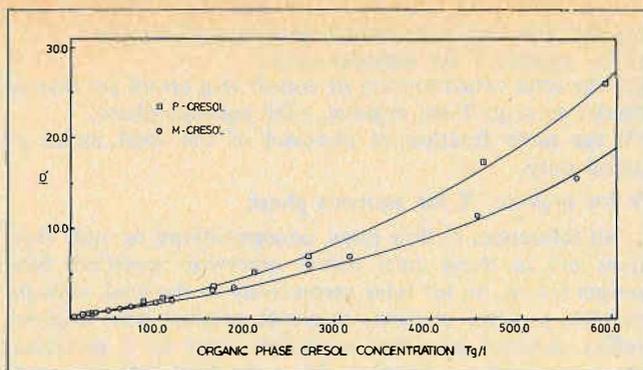


FIGURE 2. Overall distribution coefficients of m- and p-cresol between hexane-benzene (70%/30% v/v) and 0.5M tri-sodium orthophosphate at 20°C.

phosphate reagent is regenerated in the aqueous phase, which may be recycled to the cresols separator. This m-cresol recovery reaction is unlikely to be complete, so the effect of varying concentrations of unrecovered m-cresol in the aqueous recycle was considered. The purified m- and p- cresol products of the process are recovered from their solution in organic solvents by distillation and the solvents recycled, any losses being made up. Part of the m-cresol product is dissolved in the hexane/benzene solvent and recycled to the main cresol separator as a reflux stream.

The Measurement and Modelling of Cresols Distribution

For the modelling of the cresols separation and m-cresol recovery contactors, it is vital to know both the separation factor of the cresol isomers and also their overall distribution between the organic and aqueous phases over the whole working range of cresol concentrations.

For dissociation extraction systems in which reaction in the aqueous phase is complete, separation factors may be calculated⁽¹⁾. In systems such as the cresols separation, in which reaction in the aqueous phase is incomplete, the basis for the theoretical calculation of separation factors has been initiated⁽⁴⁾ but not yet verified for the cresols system. Experimentally measured values for cresols distribution had to be used, therefore, but since previous work was not extensive, it was necessary to undertake a new experimental programme to provide the necessary data.

Measurement of Overall Distribution of Individual Isomers

The overall distribution coefficients were measured of the individual cresol isomers between a 0.5 M aqueous solution of tri-sodium phosphate and the three organic solvent systems used: 70% hexane/30% benzene; benzene; and chloroform. In the case of chloroform, results were also obtained with varying proportions of phosphoric acid present in the aqueous phase.

A known weight of the cresol isomer was distributed between 25 ml of the aqueous phosphate solution and 25 ml of the organic solvent. The mixture was shaken in a thermostated bath at 20°C ± 0.5°C and 25 mins were allowed for equilibrium to be attained. After separation, the cresol concentration in the aqueous phase was determined by measurement of its refractive index by an Abbé refractometer, using a previously determined calibration curve of refractive index versus cresol concentration in the aqueous phase, saturated with the organic solvent

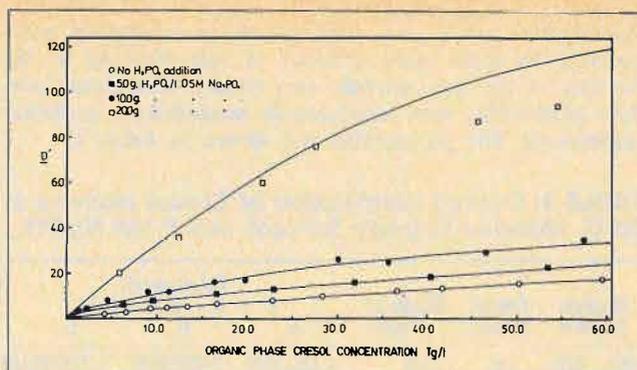


FIGURE 3. Overall distribution coefficients of m-cresol between chloroform and 0.5M tri-sodium orthophosphate (containing various quantities of orthophosphoric acid) at 20°C

to be used. The cresol concentration in the organic phase was calculated by difference from the known original total weight of cresol present. Then, the overall distribution coefficient D' for the cresol isomer could be found from the relation $D' = T/t$, where T and t are the total cresol concentrations of organic and aqueous phases respectively in g cresol per litre of cresol-free solvent. As this calculation depends upon the assumption of phase immiscibility, it was checked that this persisted up to high cresol concentrations (200 g/l in the organic phase and 40 g/l in the aqueous phase).

The graphs of overall distribution coefficient versus organic phase concentration for the separate isomers and hexane/benzene solvent are shown in Figure 2, and for m-cresol and chloroform solvent, with various proportions of phosphoric acid added, in Figure 3.

Determination of Isomer Separations

Measurement of the distribution of mixtures of m- and p-cresols was achieved by the equilibration in a similar manner of known weights of the mixed isomers between 25 ml each of the aqueous phosphate and the mixed hexane/benzene phases. The phases were then separated and the relative amount of each isomer in both phases measured by GLC analysis. A Pye series 104 Gas-Liquid Chromatograph was used at 115°C with a 5ft glass column, supplied by Pye Unicam, containing 2,4 xylene phosphate on 100-120 celite. The peaks produced by the cresols leaving the column were recorded on a Kent recorder and the area under each peak measured by a Kent Chromalog Integrator. It was confirmed experimentally that the ratio of peak areas was equal to isomer ratio with an average error of 2%.

In Figure 4 are shown the equilibrium mole fractions of m-cresol as a proportion of the total cresols in the aqueous phase, X , and organic phase, Y , at 20°C. The results cover organic phase total cresol concentrations ranging from 20 to 300 g/l, but the variation in distribution with concentration was less than the experimental error, so the single curve was taken as being applicable over the whole range of cresol concentrations used. The (average) error in measuring an equilibrium mole fraction of cresol was estimated to be ± 0.02.

Modelling the Distribution data

(1) For the individual isomers:

The overall distribution coefficients, D' , were modelled as polynomial functions of the organic phase cresol concentration, T , using the ICL computer subroutine F4CFORPL, which fits a

least-squares curve to a data set using orthogonal polynomials. In some cases, a better fit was obtained by the division of the data set into two ranges. Non-linear portions of the data were satisfactorily modelled by quadratic expressions. The polynomials are shown in Table 1.

TABLE 1. Overall Distribution of Cresol Isomers at 20°C between Organic Solvent and 0.5M Na₃PO₄

Organic Solvent	Cresol Isomer	Range of T g/l	Polynomial: D' = A + B.T + C.T ²		
			A	B	C
70% : 30% n-hexane: benzene	m	< 119	0.12574997	0.01989498	-0.00002169
	m	≥ 119	0.04664144	0.01666096	+0.00001915
	p	< 119	0.03823411	0.02377035	-0.00001395
	p	≥ 119	0.9250395	0.00618614	+0.00006274
benzene	m	< 80	0.10371637	0.03321977	-0.00011416
	m	≥ 80	0.31596575	0.02140618	0
	p	< 100	0.10930405	0.03118023	-0.00005648
	p	≥ 100	0.55406369	0.02082274	0
chloroform	m	0	0.10633504	0.03338581	-0.00007701
		5	0.19666303	0.06030066	-0.00042675
		10	0.23962496	0.09671730	-0.00074351
		20	0.16701365	0.33685281	-0.00236636

(2) For mixtures of the cresol isomers:

The equilibrium mole fractions of m-cresol in the aqueous and organic phases, shown in Figure 4, were modelled by the polynomial:

$$X = 1.55024019Y - 0.87511348Y^2 + 0.32487328Y^3$$

Model of the Cresol Separation Unit

The modelling of the cresol separator is considered first, as it is the main source of information flow for the variables in the process as a whole. The process streams entering, leaving and within the unit are sketched in Figure 5, their place within the overall process being indicated in Figure 1. Each stream is defined by three variables:

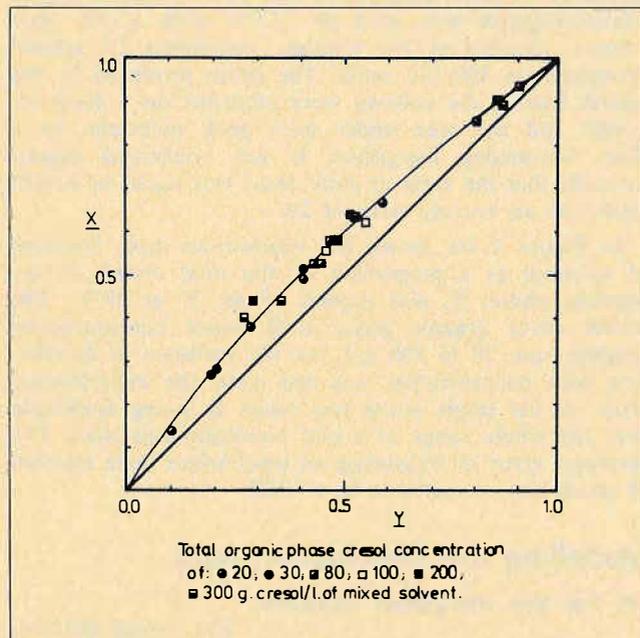


FIGURE 4. Equilibrium mole fractions of m- and p-cresol in hexane-benzene (70%/30% v/v) and 0.5M tri-sodium ortho-phosphate at 20°C.

- (1) the flow in l/h of solvent *exclusive* of cresols: Q for organic, Z for aqueous phase;
- (2) the total concentration of cresols in g cresol per litre of carrier solvent: T for organic, t for aqueous phase;
- (3) the mole fraction of m-cresol of the total moles of cresol only: Y for organic, X for aqueous phase.

All references to flow rates, concentrations, or mole fractions are in these units unless otherwise specified. Subscripts f, o, p, m, mr refer respectively to the feed, aqueous recycle, p-cresol product, m-cresol product and m-cresol reflux streams; all other subscripts refer to a particular stage within the contractor. M_f is the feed rate of cresols in g/h.

The definition of all symbols used is given in the Notation List at the end of paper.

The important sub-system variables have been allocated to one of three categories:

(i) Externally Fixed Variables. The first of these categories contains variables fixed by external conditions and may be regarded as constraints on the system, e.g. the purity of the feed from another plant.

(ii) Design Variables. These are variables which may, within certain limits, be freely varied. A typical example is the concentration of cresol in the aqueous recycle stream or the flow ratio of organic to aqueous carrier liquid. Where optimization is an objective, design variables are the optimising parameters.

(iii) State Variables. The design variables and externally fixed variables may be linked by the design relationships of the system to produce a state variable which is the result of a mathematical manipulation of the externally fixed and design variables.

Allocations of variables to categories (i) and (ii) are somewhat arbitrary, and some of the externally fixed

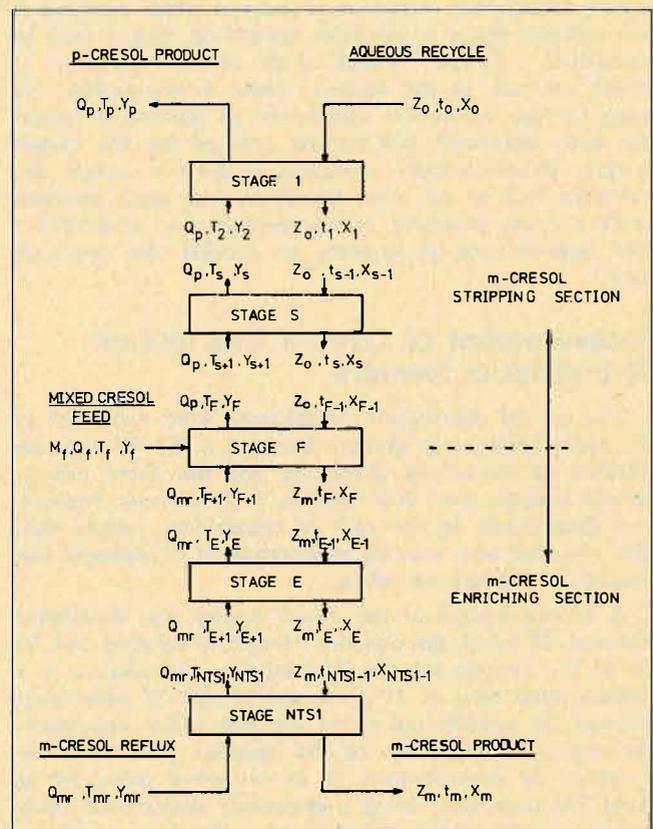


FIGURE 5. Notation for cresol separator.

variables could have been given design variable status. As an example, if it had been desired to optimize the cresol feed, then the feed mass flow rate and cresol mole fraction would have become design variables.

A number of produce purities have been evaluated, but these purities have been considered as discrete cases, i.e. product purity is assigned as an externally fixed variable, and therefore the variables X_o and Y_{mr} are also included in this category. This is possible on the assumption that $X_o = X_m$ and $Y_{mr} = X_m$. This is justifiable because it is unlikely that any appreciable cresol separation will occur during the recovery of m-cresol or its distillation. This is particularly so if the m-cresol product is of a high purity, and for m-cresol products of 0.98 mole fraction or better the calculated mole fraction of m-cresol in the reflux stream will rarely differ from the product mole fraction by an amount greater than 0.005.

The allocation of important variables in the sub-system is shown in Table 2.

TABLE 2. Variables

Externally fixed Variables	Design Variables	State Variables
1. M_f	7. T_f	11. Q_f
2. Y_f	8. Q_{mr}	12. Q_p
3. X_m	9. Z_o	13. Z_m
4. Y_p	10. t_o	14. PR_s
5. Y_{mr}		15. PR_E
6. X_o		16. t_m
		17. T_p
		18. T_{mr}
		19. NTSSI
		20. NTSEI
		21. NTSI
		22. RRS
		23. RRE

Table 2 includes only variables which are of fundamental importance to the variable subsystem. It does not include cost variables because the performance of the separator is being modelled as a function of the design variables and, until any form of optimization is initiated, costs are irrelevant. Equipment capital cost for instance will be calculated via an equipment size parameter, which is a function of solvent flow rate and number of theoretical stages, variables which are of importance at this stage. By using this approach, the list of variables does not become unnecessarily large.

Design Relationships

The design relationships relating to the variables are listed in the order of their evaluation:

- $Q_f = M_f/T_f$
- $Q_p = Q_f + Q_{mr}$
- $Z_m = Z_o$
- $PR_s = Z/Q_p$
- $PR_E = Z/Q_{mr}$
- $t_m = f(T_{NTSI}, Y_{NTSI})$
- $$T_p = \frac{Q_f \cdot T_f \cdot (Y_f - Y_{mr}) + Z_m \cdot t_m \cdot (Y_{mr} - X_m)}{Q_p \cdot (Y_p - Y_{mr}) + Z_o \cdot t_o \cdot (X_o - Y_{mr})}$$
- $T_{mr} = (Q_p \cdot T_p + Z_m \cdot t_m - z_o \cdot t_o - Q_f \cdot T_f)/Q_{mr}$
- $NTSSI = f(Q_f, Q_p, Z_m, Z_o, T_p, t_o, Y_p, X_o, Y_f)$
- $NTSEI = f(Q_{mr}, Z_m, X_m)$
- $NTSI = NTSSI + NTSEI$
- $RRE = Q_{mr} \cdot T_{mr}/(Z_m \cdot t_m - Q_{mr} \cdot T_{mr})$
- $RRS = Z \cdot t_1/Q_p \cdot T_p$

The number of degrees of freedom for this sub-system (i.e. the numerical difference between the variables in the sub-system and the design relationships) is ten, which allows the independent selection of all externally fixed and design variables.

Design relationships 2 and 3 assume immiscibility of the two carrier liquids, and relationships 7 and 8 are derived from the total and m-cresol mass balance over the cresol separator. The calculation of t_m by design relationship 6 creates a temporary problem because, at this point in the evaluation of design equations, the concentration and mole fraction of cresols in the organic stream leaving the last stage of the contractor (T_{NTSI} , Y_{NTSI}) are unknown. This concentration is calculated via a stage-to-stage computation procedure, described below, which requires T_p as an initial condition. T_p , however, is calculated through a knowledge of t_m !

Stage to Stage Calculation Procedures for the Cresol Separator

One method of overcoming this difficulty is to assume an initial value of t_m and then to calculate T_p . Using Q_p , Z_o , T_p and t_o as initial conditions, the number of stages required to obtain a given separation of the feed is calculated (using the procedure to be described). During this, new values of t_m and T_{mr} are calculated. The initial and new values are compared and a new initial value of t_m chosen. The calculation is repeated until the difference between the initial and new values of t_m and T_{mr} has satisfied some previously specified convergence criterion. A short series of trials showed that successive substitution produced rapid convergence within three iterations and nearly always within two.

Non-iterative Method

A non-iterative method is possible through the assumptions already made that $x_o = Y_{mr} = X_m$. Design relationship 7 then reduces to $T_p = Q_f \cdot T_f \cdot (Y_f - Y_{mr})/Q_p \cdot (Y_p - Y_{mr})$. The initial condition, T_p , is now independent of t_m and so the solution of the state variables may be achieved in a single iteration.

The differences in stage-to-stage computations for the iterative and non-iterative methods are difficult to assess for all cases, but are unlikely to be significant if product purities of 80% or greater are required. In such instances X_o , Y_{mr} and X_m will be approximately equal for the reasons given before, so the assumption regarding these three variables will be reasonably valid. In addition, this assumption will only affect one initial condition to the calculation, i.e. T_p . When high-purity products are designed, the error between calculating T_p by design relationship 7 or by the shortened relationship above will be negligible, so the stage-to-stage computation for each case will be very similar.

Procedure for Non-iterative Method

- Values of the externally fixed and design variables are specified.
- The flow rate of each cresol-free carrier liquid is calculated by design relationships 1-3.
- T_p is calculated using the expression above and a check made to ensure that it is positive. If not, calculation may be stopped or restarted with new variable values.
- Instead of immediately commencing the stage-to-stage calculations with Q_p , T_p , Y_p , Z_o , t_o , X_o as initial conditions, T_{mr} is first calculated using an assumed value of t_m .

Not all combinations of externally fixed and design

variables give feasible solutions to the state variables. T_{mr} may, for instance, be calculated to be negative, after solution of design relationship 8, which is impossible in a real process.

This is more likely to occur when t_m is small and, as an initial check, T_{mr} is calculated using the largest expected value of t_m , i.e. the most favourable value, to see if the former remains positive. (For the system hexane/benzene — 0.5M tri-sodium ortho-phosphate, the maximum expected value of t_m is 54 g/l.)

If T_{mr} is zero or negative, the calculation is taken no further and the new variable values chosen for any further calculations. At the end of the calculation procedure, the actual value of T_{mr} will correspond to the concentration of cresols in the organic stream entering the last stage of the contactor. This value will have been calculated from an overall stage mass balance of cresols using the latest calculated value of t_m .

(e) Calculation of theoretical stages may now proceed using the initial conditions, Q_p , T_p , Y_p and Z_o , t_o , X_o . The counter for total theoretical stages and for theoretical stages in the stripping section of the contactor is set to 1.

(f) The concentration of cresols and mole fraction of m-cresol in the aqueous stream leaving stage 1, t_1 and X_1 , are calculated from T_p and Y_p , using equilibrium data in the method described below.

(g) the total concentration of cresols and the mole fraction of m-cresol entering stage 1 in the organic phase, T_2 and Y_2 , are determined by solution of the two stage mass balances: One for total cresols; the other for m-cresol:

$$\text{i.e. } T_2 = (Q_p \cdot T_p + Z_o \cdot t_1 - Z_o \cdot t_o)/Q_p$$

$$Y_2 = \frac{(Q_p \cdot T_p \cdot Y_1 + Z_o \cdot t_1 \cdot X_1 - z_o \cdot t_o \cdot X_o)}{(Q_p \cdot T_2)}$$

T_2 is checked to ensure that it is positive and Y_2 is also checked to ensure its value is greater than zero but less than unity. If either of these conditions is not satisfied, calculation ceases or new variables are chosen and the procedure restarted.

(h) The leaving aqueous and entering organic stream of stage 1 now become the initial conditions for stage 2. The theoretical stage counters are set to 2 and the procedure repeated for all stages in the stripping section of the contactor.

(i) The optimum location of the feed plate is obtained by comparing the value of Y_{s+1} with Y_f . Values of Y increase as the computation proceeds and the stage at which Y_{s+1} first exceeds Y_f will be the feed stage. Thus values of T_{s+1} and Y_{s+1} must be recalculated to account for the effect of the feed entering at this point.

$$\text{i.e. } T_{f+1} = \frac{(Q_p \cdot T_F + Z_m \cdot t_f - Z_o \cdot t_{f-1} - Q_f \cdot T_f)/Q_{mr}}{(Q_p \cdot T_F \cdot Y_F + Z_m \cdot t_f \cdot X_F - Z_o \cdot t_{f-1} \cdot X_{F-1} - Q_f \cdot T_f \cdot Y_f)}$$

$$Y_{f+1} = \frac{Q_{mr} \cdot T_{F+1}}{Q_{mr} \cdot T_{F+1}}$$

Again T_{F+1} and Y_{F+1} are checked to see if they violate the constraints $0 < T_{F+1}$; $0 < Y_{F+1} < 1$

(j) Calculation of the enriching section of the contactor now begins. Recording of the total number of theoretical stages continues, but the counting of enriching stages replaces counting of stripping stages. The total number of stripping stages automatically records the optimum location of the feed plate from the top of the contactor.

(k) Calculation of enriching stages continues in an identical manner to that for the stripping stages and the repetitive calculation of stages ceases when the mole fraction of m-cresol in an equilibrium aqueous phase, X_E , is greater than or equal to the desired m-cresol product purity, X_m . The

final operation, to calculate T_{E+1} and Y_{E+1} for the last stage, using the stage material balances, also determines the values of T_{mr} and Y_{mr} that satisfy the total cresol and m-cresol mass balances for the unit as a whole.

Calculation of Aqueous Stream Equilibrium Conditions from a Given Organic Stream

For a theoretical stage N , it is required to obtain the total aqueous phase cresol concentration, t_N , and the mole fraction of m-cresol, X_N , in equilibrium with the given organic stream concentration and mole fraction, T_N and Y_N , using the experimentally measured and modelled equilibrium data.

First, the mole fraction of m-cresol in the aqueous phase, X_N , is calculated directly from Y_N using the modelled expression relating the two variables. The loading of cresols in the aqueous phase is then found from the loadings applicable if the individual isomers existed at a concentration T_N in the organic phase and on the assumption that the contribution of each isomer to the actual aqueous phase cresol concentration is in direct proportion to its organic phase mole fraction: — $t_N = (T_N/D_m') Y_N + (T_N/D_p') (1 - Y_N)$ where D_m' and D_p' are the overall distribution coefficients modelled for m- and p-cresol respectively at an organic phase concentration of T_N .

Experimental verification of this relation was obtained for the system m- and p- cresols: hexane/benzene: 0.5M Na_3PO_4 . The average difference between experimentally measured and predicted aqueous phase cresol loadings was less than 5%.

A Parametric Survey of the Important Design Variables

To investigate the relative sensitivity of the functioning of the cresols separator to changes in the externally fixed, design and state variables, a parametric survey was conducted. This used the non-iterative stage-to-stage calculation procedure, transcribed into a Fortran computer module⁽⁵⁾.

The equilibrium relationships for the separator are concentration dependent and, for a given set of initial concentrations, the state variables will be independent of absolute flow rates if constant flow ratios of the carrier liquids are used in both the stripping and the enriching sections. The absolute flow rates affect only the physical size of the contactor and so its cost, but these two variables were not included in the parametric survey so that its scope would be as broad as possible and also, so that the amount of calculation would be reduced.

The effect of this reclassification of variables is to introduce as design variables the flow ratios in the stripping and enriching stages, respectively $PR_s = (Z_o/Q_p)$ and $PR_E = (Z_m/Q_{mr})$. The mass of cresols fed to the separator, M_f , then becomes irrelevant. For ease of computation, dummy values of 1000 were assigned to Z_m and Z_o ; Q_p and Q_{mr} calculated from the given flow ratios and computation completed by the non-iterative procedure.

For the survey, flow ratios in each section of the contactor were varied from 0.1:1 to 10:1 in twenty equal logarithmic proportions, thus covering the practical range. Plotting the phase ratios of the two sections, as in Figure 6, the total possible number of solutions to the operating conditions of the contactor will be 20^2 , lying within the area ACBD.

However, as Q_p must always be greater than Q_{mr} in any practical process in which the cresol feed is dissolved in organic solvent, no feasible solutions will exist in area ABC

and the amount of computation may be reduced by one half. The remaining area, ABD, of the typical solution domain shown in Figure 6 also contains non-feasible solutions. The portion AED covers attempted solutions which fail at the step in the stage-to-stage calculation at which it is checked that T_{mr} is positive when t_m is assumed to be at its maximum value. Above this, the area AFE contains those solutions which require more than 100 theoretical stages for the separation. These indicate that a 'pinch-point' has been encountered in the calculation and the enrichment per stage is negligible, so that practical operation in this area may be ruled out. In the relatively narrow region GFH, the stage-to-stage calculation failed because a non-positive mole fraction of m-cresol was indicated in the organic phase.

The remaining area, AHGB, is the section of the domain containing valid solutions. The greater this area, the more freedom there is in selection of operating phase ratios for the separator under the given values of the other operating variables and so the more practical will be the design of a working process. The variables investigated in this parametric survey were T_r , Y_f , Y_p , X_m and t_o . A total of 64 different sets of values of these variables was surveyed to show the relative sensitivity of the design of the process to changes in them.

Results and Discussion of Parametric Survey

(i) Variation in the Feed Cresol Concentration, T_r

The effect of increase in T_r , shown in Figure 7, is a reduction in the area of the feasible separation domain for the region in which T_{mr} is non-positive is increased. The lower T_r , therefore, the easier the design of a practical separator.

(ii) Variation in the Feed Cresol Mole Fraction, Y_f

Increase in the mole fraction of m-cresol in the feed from 0.4 to 0.6 has a negligible effect on the solution domain, showing that the design of the separator is insensitive to this variable.

(iii) Variation in Product Purities

The effect of variation in the cresol product purities is shown in Figure 8. The area of the solution domain increases as the degree of product purity decreases. This is in accord with the general principle applying to chemical separation processes, that the ease of achieving a successful process increases when the extent of separation required is reduced.

(iv) Variation in t_o

The number of valid solutions, shown by the area of the valid solution domain, always decreases rapidly with increase in t_o , the cresol concentration in the aqueous recycle to the separator. Figure 9 shows the maximum allowable value of t_o to obtain a given purity of p-cresol when $X_m = 0.99$ and $Y_f = 0.4$. Because t_o was varied in discrete increments, there is an area of uncertainty where feasible solutions may or may not exist. The maximum allowable value of t_o decreases from 3.0 g/l for 85% purity to 0.3 g/l if 99% purity is required. As t_o increases above 2 g/l, a large area of the solution domain, spreading out in this case from the line AB in Figure 6, becomes non-feasible because a negative m-cresol mole fraction appears in the organic phase. The reason for this is clear from the mass balance considerations applying to each stage: the total quantity of cresols entering equals that leaving and the compositions of the two outgoing streams are linked by

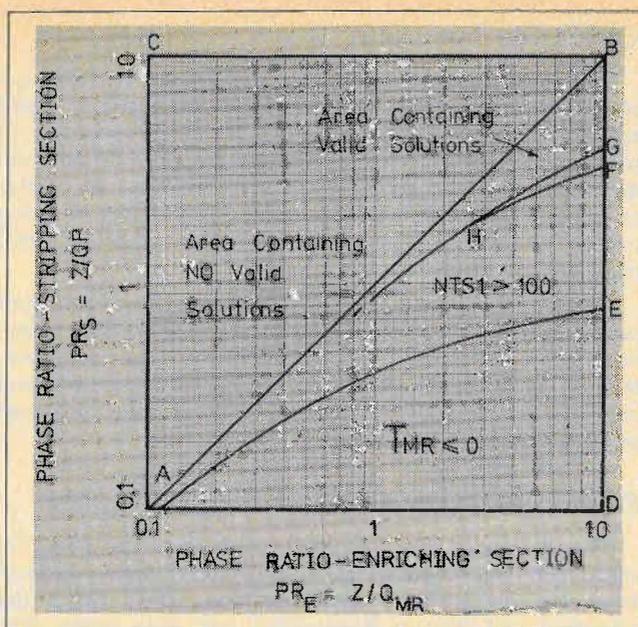


FIGURE 6. Base case for sensitivity analysis of cresol separator.

the equilibrium relation. If too large a quantity of cresols enter in the aqueous stream, then the amount of one or both cresols entering the stage in the organic stream may be required to be impracticably small or even negative.

Experimental Assessment

To assess the validity of the computer model of the cresol separator, an experimental test was made⁽⁵⁾ using a small-scale mixer-settler⁽⁶⁾ suitable for use in a laboratory. Reasonable agreement between the experimental and computed interstage concentrations was obtained.

Sub-optimization of the Distillation and m-cresol Recovery Units

The flow of information for the separation process is shown in Figure 10 to be acyclic. The main flow of information is outwards from the cresols separator, firstly to the p-cresol distillation unit and secondly, via the m-cresol recovery extractor, to the m-cresol distillation stage. This acyclic flow permits the use of dynamic programming for the overall optimization of the separation process. In this, the downstream units are sub-optimized with respect to the information flow from the cresol separator, for according to the principle of optimality, an acyclic system is optimized when its down-stream components are sub-optimized with respect to the feed they receive from upstream. Use of dynamic programming can reduce an otherwise lengthy optimization procedure to one requiring a relatively small number of solution evaluations. However, if the optimization involves a large number of variables which can take any value between certain constraints, the complexity becomes so great that the use of additional optimization techniques, such as gradient or direct search, is desirable. These latter techniques may be alone, but dynamic programming provides valuable information about the various sub-optimized parts of the process, such as their relative sensitivity to the individual variables.

For this reason, the sub-optimizations of the distillation units and the m-cresol recovery section were investigated, although space permits only an outline of the procedure to be given here.

Objective Function

The objective function to be used in the optimization of the economics of the separation process could be based either upon maximization of profit or on minimization of total manufacturing costs. Although the former criterion might have the greater commercial interest, the latter criterion was chosen, as it avoids the difficulties in fixing values for sales prices or transfer prices of the final products and raw materials.

In the sub-optimization two objective functions were considered: firstly, *annual costs* based on variable operating costs for 8,000 hours of production plus a proportion of fixed capital costs, and secondly, *discounted total project costs* at 10, 15 and 20% interest rates and with project lives of 5, 10 and 15 years.

Delivered and Installed Capital Costs

The delivered and installed fixed costs of items of equipment were derived from cost correlations obtained from the literature, updated to June 1972 using the Chemical and Process Engineering cost data index. The installed fixed capital costs were estimated from the delivered costs, using a factorial method of estimation⁽⁷⁾ to

cover costs of erection, piping, instrumentation, electrical work, civil engineering and lagging.

Sub-optimization Strategy

The following summarised steps were used in the sub-optimizations:

(i) The variables in the sub-system were assigned to the categories: externally fixed, design, and state variables and the design relationships between them established, together with their order of evaluation.

(ii) A Fortran computer module of the sub-system was created based on the information flow structure. This contained cost data inputs used to calculate capital and operating costs from various parameters within the module.

(iii) The variables fixed by environmental factors, such as cooling water inlet temperatures for heat exchangers, were assigned appropriate values. The expected range of each design variable was decided, together with the incremental change to be used to scan the range. One or more of these design variables would be chosen to be sub-optimised with respect to the other variables.

(iv) A systematic scan of the design variables was made over the specified range of each variable. For each set

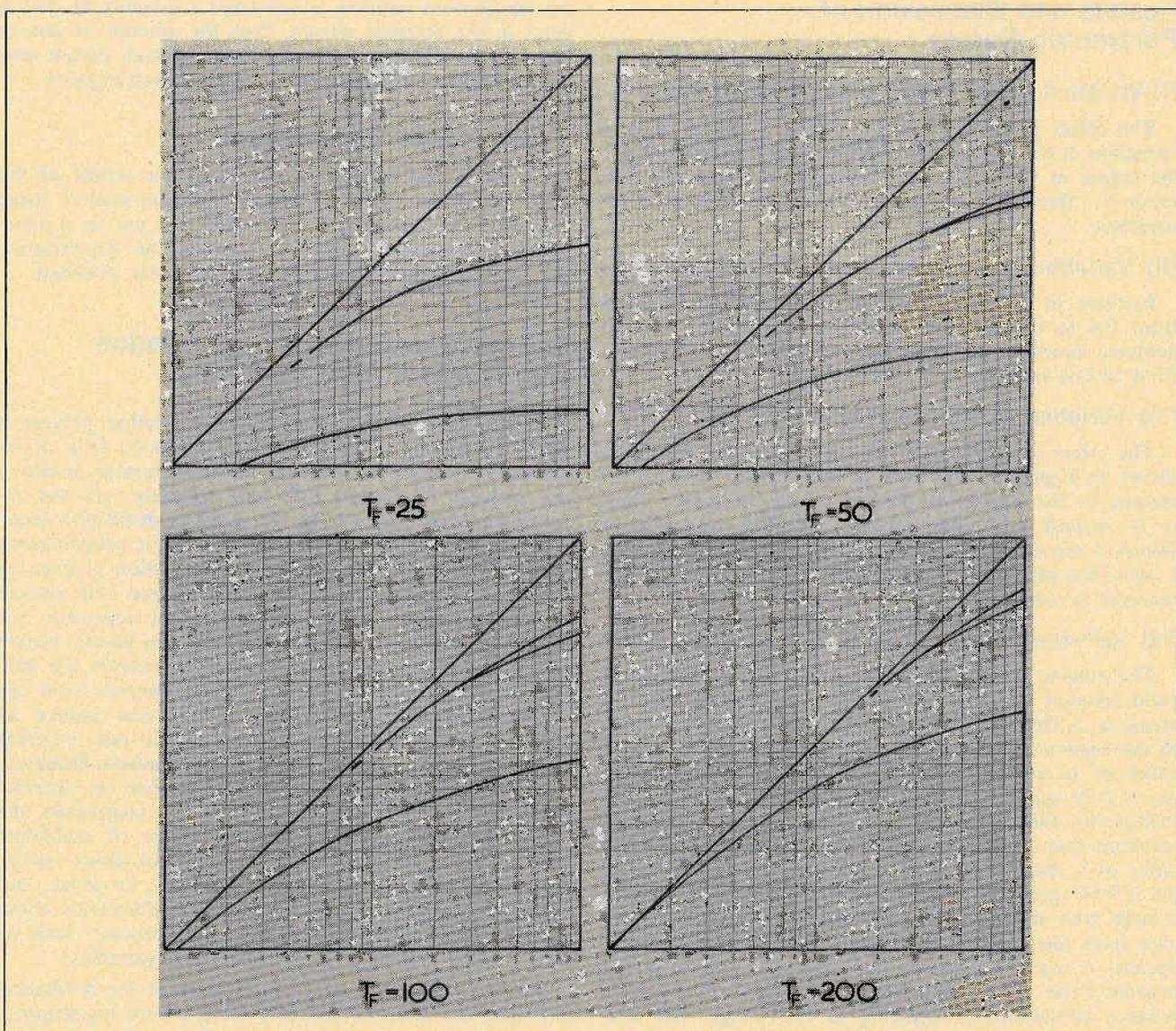


FIGURE 7. The effect of cresol feed concentration in the usable cresol-free phase ratios in the cresol separator.

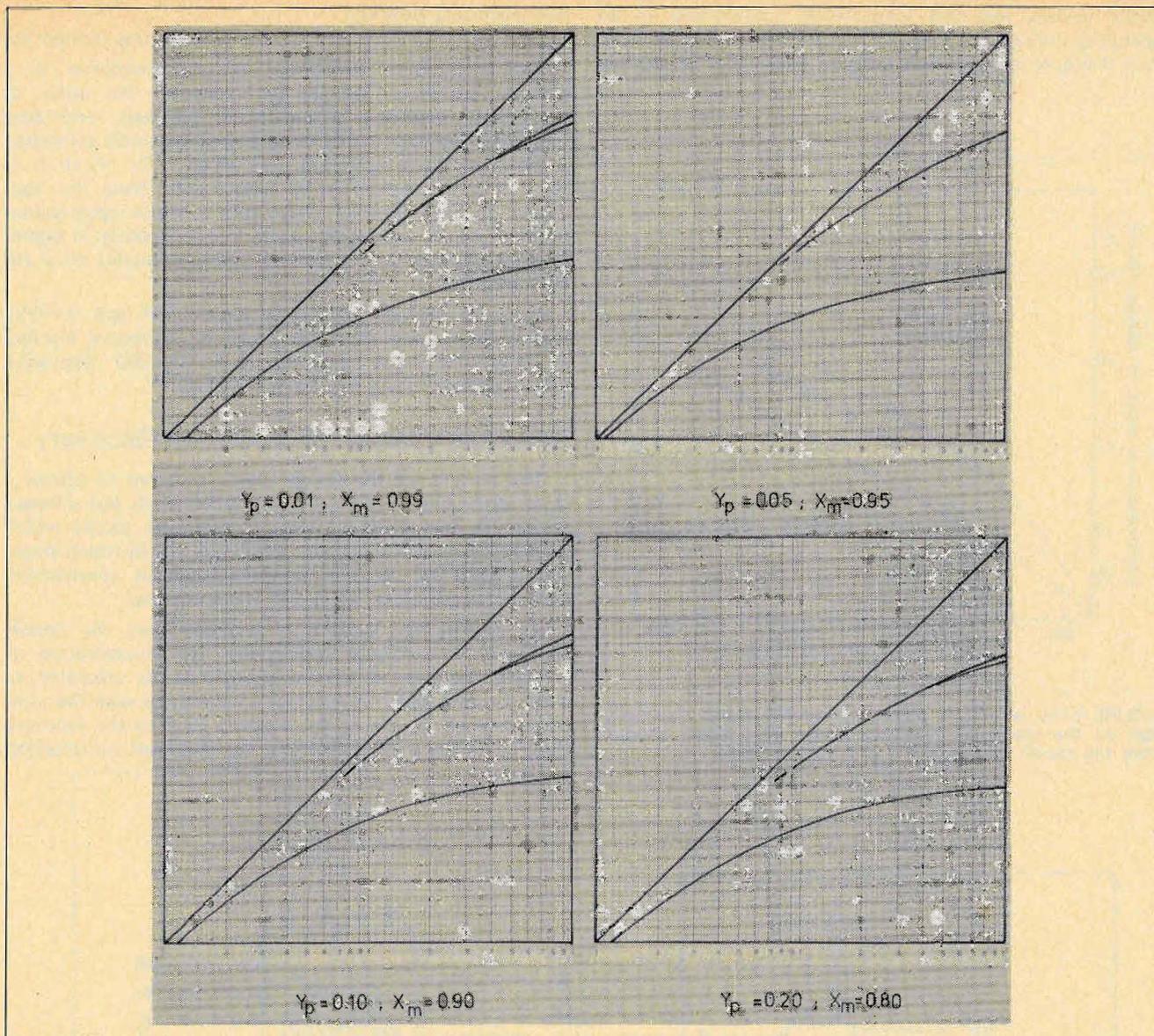


FIGURE 8. The effect of cresol product purity on the usable cresol-free phase ratios in the cresol separator.

of input variables, the important state variables and output cost parameters were recorded and stored on magnetic tape.

Incorporated into the computer module were various warnings which were output when violations occurred of the constraints placed on certain variables. The Filestore facility of the ICL George III Computing Systems was found very convenient, as it allows output of this monitoring information to be recorded on a file separate from that taking the main output.

(v) The raw output data obtained, which was essentially capital and operating cost data relating to a particular set of input variables, was edited to remove any set of data for which a variable constraint violation was recorded and then used to obtain annual and discounted costs for each set of input variables. This new data was also stored.

(vi) The data was stored in blocks in which only the variable to be optimised changed in value, the other design variables being constant. The costs in the block were then searched to find the minimum cost and the associated value of the variable being optimized.

(vii) This sub-optimal data was then modelled using multiple linear regression. In each case, the optimal para-

meter was modelled as a function of the input design variables.

For example, the sub-optimization of the continuous distillation stages used as design variables: (1) flow rate of solvent in feed, S . (2) concentration of cresol in feed, C and (3) the variable to be optimized — the external reflux ratio, RR . In a sub-routine, costs are evaluated for each combination of S , C and RR to produce 'raw' data. For each combination of S and C , a search was made to find the minimum cost and the associated value of RR . Finally, the optimum costs were modelled as a function of S and C .

The raw cost data for the separation of *m*-cresol from benzene and *m*-cresol from chloroform were determined for values of reflux ratio from 1.05 to 8.95 times the minimum reflux ratio (18 separate values) solvent flow, S , from 2,500 to 100,000 l/hr (7 values) and cresol concentrations in the feed, C , of 5, 10, 50, 100 and 500 g/l. Thus, for each chemical system at a particular column operating pressure, $18 \times 7 \times 5 = 630$ sets of output data were obtained.

The operating temperature of the distillation column must not exceed that at which thermal degradation of

cresol occurs, and this temperature corresponds to an operating column pressure of approximately 300 mm Hg. Any decrease in operating pressure below this resulted in

best operating pressure. higher operating costs and so 300 mm Hg represented the

The continuous distillation unit was modelled as a Fortran computer module in which all the items of equipment, including column shell, internals, preheater, condenser, reboiler, stock tanks and pumps with associated drives were sized separately and costed. The selection of the out-going cooling water temperature from the condenser and top product cooler was a minor optimisation problem on its own: large water flows resulting in higher log-mean temperature differences and so smaller areas for heat transfer.

Top and bottom purities of both 0.999 and 0.99999 mole fraction were considered and the minimum number of theoretical stages required for a particular separation was calculated using the Fenske equation⁽⁸⁾.

Sub-optimization of m-cresol Recovery

The number of theoretical stages required to obtain a given extraction of cresol from specified feeds and solvent/feed ratio was obtained from a computer model which operates in an analogous manner to the way in which stages are 'stepped-off' on the standard graphical construction showing equilibrium curve and operating line.

To obtain high purities of p-cresol from the cresols separator, it has been shown that the concentration of cresol in the aqueous stream recycled to the separator, t_o , must be low, and very small in comparison with the concentration of cresols in the aqueous feed to the recovery unit, t_m . In these circumstances, the graphical construction

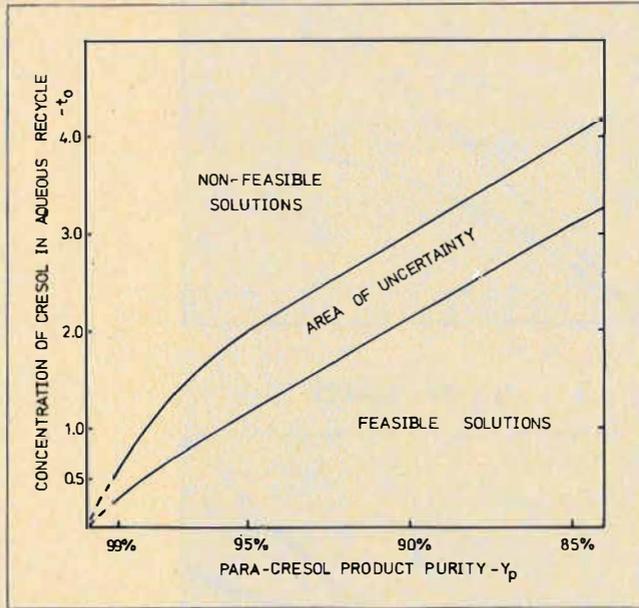


FIGURE 9. The effect of aqueous recycle cresol concentration on the maximum available purity of p-cresol product from the cresol separator [$Y_f = 0.4; X_m = 0.99$].

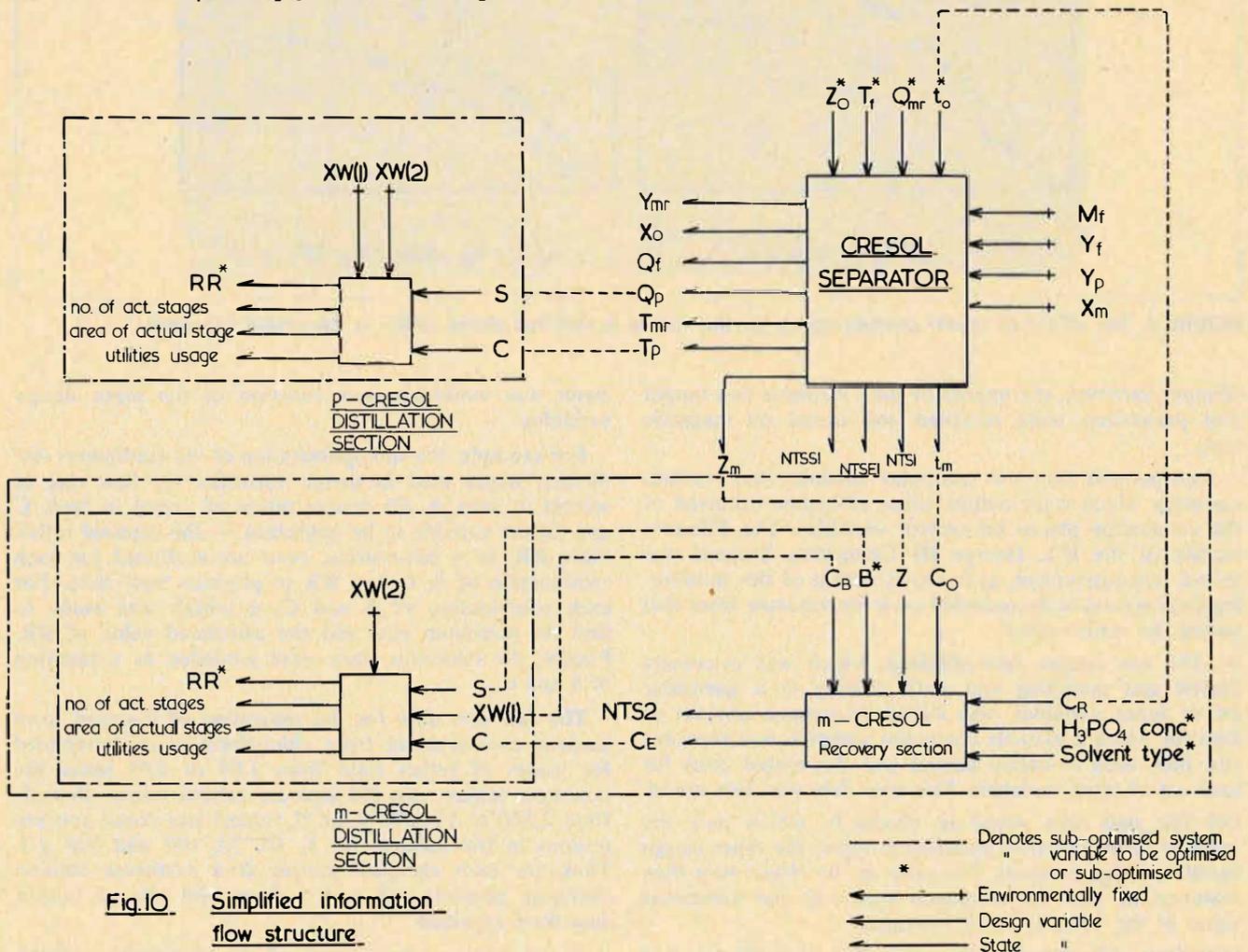


Fig.10. Simplified information flow structure.

FIGURE 10. Simplified information flow structure.

indicates that most of the theoretical stages are used in the lower range of aqueous cresol concentrations and the number of theoretical stages is relatively insensitive to t_m . Also, the concentration of cresol in the extract stream will not be particularly sensitive to change in t_m , because at low values of t_o , it is not possible to change markedly the slope of the operating line. This is constrained in one direction by the equilibrium curve and in the other by the usable phase ratios of the contacting equipment.

The optimization of the cresol recovery unit was therefore simplified by consideration of only one aqueous feed concentration of 45 g/l. This represents an average value of t_m which the parametric survey showed could vary only in the range 37-53 g/l.

Determination of Number of Stages for m-cresol Recovery

Specific values are set for the cresols concentration in the aqueous phase entering and leaving the recovery contactor, t_m and t_o , and also in the organic solvent feed to the unit from the distillation stage. The flow ratio in the recovery contactor of solute-free organic and aqueous solvents, B:Z, was also chosen. The independent variables are then the extract cresol concentration in organic solvent leaving the unit, determined by the overall cresols balance, and the number of theoretical stages. The calculation proceeds stepwise using the modelled equilibrium data and the cresols mass balance over the stage. The calculation is repeated until the concentration of cresols in the aqueous stream leaving a stage is equal to or less than that previously specified as the raffinate concentration.

Costing and Sizing of Contacting Equipment

There is a wide choice of contacting equipment available which could be used for this cresols separation process. A device specifically designed for use in the coal tar industry, where emulsion formation can be a problem, is the Graesser raining bucket contactor. This is a differential contactor, in which the phases flow counter-currently through the horizontal cylindrical shell, and a sectioned rotor disperses each phase in the other by pouring it from bucket-shaped metal cups as large drops which rain downwards or upwards to the interface. This type of contactor is relatively cheap in capital and operating costs and was chosen as the type on which the economic evaluation of this cresols separation process would be based. The modular structure of the costing procedures used permits easy adjustment to allow for the use of other types of equipment.

Design procedures and cost information for Graesser contactors were supplied by the contactor's designer, Mr. J. Coleby. The important parameters used to obtain the capital cost of the equipment were diameter and length of shell, and materials of construction.

Phosphoric Acid Addition and Neutralization

If phosphoric acid is added to aid the m-cresol recovery, the equilibrium curve moves to give greater flexibility in the solvent/aqueous feed ratio. A disadvantage is that the phosphoric acid added must be neutralized after the aqueous raffinate stream has left the recovery extractor so that it does not have a detrimental effect on the operation of the primary cresol separator.

When it is used, the phosphoric acid is presumed to be metered from a rubber-lined storage tank into the aqueous feed before it enters the contacting equipment of the recovery section, and it is neutralized by an aqueous solution of caustic soda, metered into the raffinate stream as it leaves the contacting equipment.

During the neutralization reaction, a quantity of water is produced, together with tri-sodium phosphate. The net effect is to increase the strength of the phosphate solution, and water addition (prior to neutralization, to prevent crystallisation of phosphate) is required to maintain the original solution strength. The excess phosphate solution is bled from the system and, because it will be contaminated with cresols, it must be treated as a toxic effluent and rendered harmless. The costing of this portion of the process, including costs of disposal of phosphate effluent, were calculated by a separate computer sub-routine.

Master Segment for Sub-optimization of m-cresol Recovery Section and Distillation from Organic Solvent

The sub-routines described above are linked together by a master computer segment which sizes and costs the equipment and materials not already costed. The program contains a number of loops covering the various flow rates of aqueous phase and cresol concentrations of aqueous feed and raffinate to be considered. At every traverse through a loop, the cresol recovery section and the associated distillation section are costed. In the sub-optimization of m-cresol recovery and distillation, the total costs of this section should be minimized for a given aqueous feed (to the recovery section) flow rate and cresol concentration, and also for a particular concentration of cresol remaining in the raffinate. The two variables to be sub-optimized are the ratio of solvent and aqueous flows in the contactor, (B:Z), and also the amount of phosphoric acid added to the aqueous feed. Sub-optimization of the cresol raffinate concentration must be left until the final optimization, because its value will also affect the operation and costs of the cresol separator.

As the quantity of organic solvent is increased relative to the aqueous feed in the recovery contactor, a given separation may be achieved in fewer theoretical stages. However, the reduction in costs from this effect is countered by an increase in costs resulting from the distillation of larger quantities of increasingly dilute cresols in organic solvent. Also, the capital cost reduction following decrease in length of the contactor, if the number of stages is reduced, will tend to be offset by increased costs of providing the larger cross-sectional area necessary to handle the increased quantities of solvent.

The minimum value of solvent: aqueous flow ratio, $(B:Z)_{min}$, for a particular solvent and aqueous phase concentration of phosphoric acid (if used) is largely independent of cresols concentration in aqueous feed and organic extract streams and depends primarily on the cresol concentration in the aqueous raffinate and organic solvent feed. For aqueous raffinate cresols concentrations of 4.0 g/l and below, the $(B:Z)_{min}$ ratios were determined by direct measurements from large-scale drawings of the low concentration region (less than 8 g/l) of the equilibrium curves for various solvents and phosphoric acid concentrations. Values of $(B:Z)_{min}$ ranged from the level of 0.1, taken as the minimum allowable in Graesser contactors, up to 8.2. Increasing amounts of solvent had to be used as the raffinate cresol concentration decreased. Phosphoric acid addition resulted in a considerable reduction in the proportion of solvent required, showing that it is important to consider the economic consequences of phosphoric acid addition, the costs of which could be counter-balanced by the saving in distillation costs.

To determine the optimum (B:Z) ratio for a total range of this variable from the minimum to 10:1, the range was divided into 10 equal parts and scanned; the total capital and variable operating costs being calculated for each set of input variables. Chemical systems considered were:

1. benzene; m-cresol; 0.5M Na₃PO₄
2. chloroform; m-cresol; 0.5M Na₃PO₄
- 3 - 5. chloroform; m-cresol; 0.5M Na₃PO₄ with 3 different levels of H₃PO₄ added: 5, 10 and 20 g/l.

The raw cost data for variable operating costs and capital costs were processed to produce annual costs at 15% depreciation of capital and discounted costs. In Figures 11, 12 are shown some examples of the variation of annual costs as a function of (B:Z) ratio for various addition concentrations of phosphoric acid to the system and values of cresol concentration in aqueous raffinate, t_o of 1.0 and 0.25 g/l. The flow of aqueous feed, Z, is taken as 2500 l/h in these figures.

General conclusions from the whole data set (125 curves for each method of costing) were:

- (i) costs increase as raffinate cresol concentrations, t_o , are lowered;
- (ii) all the optimum values of solvent/aqueous flow ratio were close to the minimum, (B:Z)_{min}, values;
- (iii) the optimum solvent/aqueous flow ratio is independent of the flow rate of aqueous feed and approximately the same for both the annual and discounted cost methods;
- (iv) in all cases, the minimum cost of recovering m-cresol to a given raffinate concentration is achieved with 5 g/l of added phosphoric acid;
- (v) confirmation that the feed aqueous concentration of cresols has no significant effect is that differences in costs for feeds containing 35 and 45 g/l were less than 0.1%.

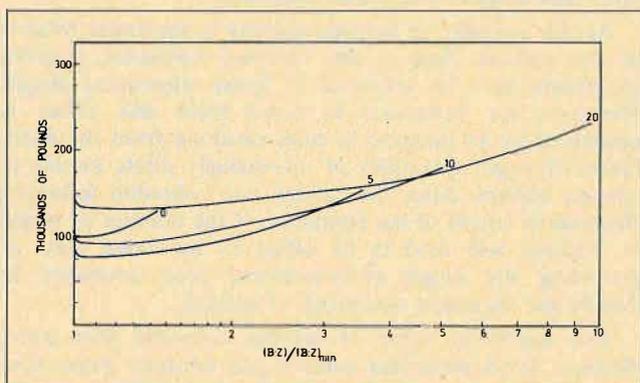


FIGURE 11. Annual costs of recovering m-cresol from 0.5M Na₃PO₄ (containing various quantities of H₃PO₄) using chloroform as the extracting solvent Z = 2500 l/hr, t_o = 1.0 g/l.

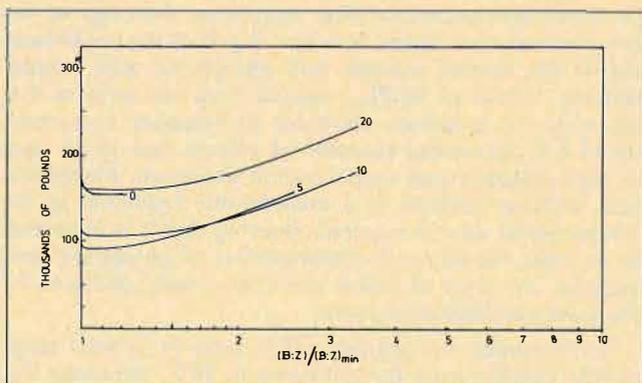


FIGURE 12. Annual costs of recovering m-cresol from 0.5M Na₃PO₄ (containing various quantities of H₃PO₄) using chloroform as the extracting solvent Z = 2500 l/h, t_o = 0.25 g/l.

Finally, having evaluated the optimum B:Z ratios for the various aqueous reflux cresol concentrations, the corresponding fixed capital and operating costs were modelled by multi-variable regression analysis and the regression models incorporated in a computer sub-routine used in the final optimization.

Overall Optimization

A direct search technique was used to find the overall optimum. The advantages claimed for these techniques, which do not require the explicit evaluation of the objective function being:

- (i) they may provide solutions to problems which cannot be solved, or are not easily solved, by other methods;
- (ii) they are well adapted for use with high-speed computers;
- (iii) they provide approximate solutions which become increasingly better as computation proceeds, thus providing tentative results early, before the final solution is realized.

These techniques are particularly suitable for problems involving a large number of variables and/or where lengthy calculations are required to calculate one function value within the solution domain of the objective function. The procedure used was closely similar to the Hooke and Jeeves method, which has previously been used by Jeffreys, Mumford and Herridge⁽⁹⁾ in the optimization of a solvent extraction process.

The search to discover the minimum value of an objective function is begun following the selection of initial values for the independent variables and the calculation of the corresponding value of the objective function. This forms the initial 'best' point so far discovered, the initial base point of the search. The local geography of the objective function surface is then tested by a series of exploratory moves. Each independent variable is sequentially perturbed by a specified amount, the 'step size', and the objective function re-evaluated. If the function value after the first perturbation for a particular variable is less than at the current point, then the latest point becomes the current point. The second variable is then perturbed. If, however, the first perturbation does not lead to a new current point, a second perturbation is made of equal magnitude, but in the opposite direction. If this second perturbation does not result in a new current point, the variable is restored to its original position.

After the whole series of exploratory moves for all the variables, if the current point is less than the base point, then the current point becomes the new base point. A 'pattern move' is then made which repeats the overall vector change of the previous exploratory moves, for this is likely to result in a closer approach to the minimum. The objective function following the pattern move is not evaluated, but another series of exploratory moves is completed and a second pattern move made if the exploratory moves are successful. In this way, an alternating series of exploratory and pattern moves are made which give direction to the search. When a pattern move-exploratory move set is a failure, the current point returns to the base point, the step size is reduced and a new set of exploratory moves made. The search is terminated when the step size for each variable perturbation has been reduced to, or is below, some previously specified value, which may be different for each variable.

A problem with this type of search is to distinguish between a local minimum or a saddle point and the overall 'global' minimum, but confidence grows if the same minimum is found with searches starting from widely different initial positions within the solution domain.

The criterion of minimum step size as the means of terminating the search may have disadvantages in comparison to a test based upon the degree of convergence of the objective function values, and a mixture of step size and absolute convergence criteria was used in practice in the search, which was carried out in a number of stages. Firstly, a relatively large initial step size was taken for each variable together with a relatively large minimum step-size. The search was commenced, and after a pre-determined number of function evaluations, the value of the objective function at the current base point was reported. The search would be continued and if the next value of the function reported was not considered to be significantly different from the previous value, the search would be stopped. On the other hand, if the search proceeds to termination and function convergence was not considered to have been obtained, a new search would be initiated using as initial values and step-sizes those reported at termination but with a smaller minimum step-size being specified. In this way, the search was monitored both from the aspect of changing function value and also changes in the independent variables.

Trials were carried out with two test mathematical functions to evaluate the search procedure and gain practice in the selection of step-sizes.

For the final optimization, a function was developed covering the overall process fixed capital, working capital and operating costs. This function included those parts of the process not covered in the sub-optimizations described previously, for example, the Graesser contactors presumed to be used in the cresol separation unit, storage of solvents and aqueous reagent for this part of the process, estimates of solvent and reagent losses and various mixing and accumulator vessels for processing feeds and reflux to the contactors.

The objective function for the final minimization, the overall capital and operating costs of the process, was expressed in the same two ways as for the sub-optimizations:

Total Annual Costs

These were evaluated on the following basis:

- (i) The plant operates for 8,000 hours per year.
- (ii) Direct labour cost was estimated at £2.50 per hour of plant operation (1972 valuation). This sum was added to the variable operating cost per hour for steam, power etc.
- (iii) The total capital investment was taken as 1.3 times the physical plant cost for major plant items including erection, piping, instrumentation etc. This factor covers design, commissioning, working capital, buildings etc.⁽¹⁰⁾.
- (iv) Annual depreciation charges were taken as 10% of capital (straight line basis).
- (v) Annual opportunity cost of capital was taken as 10% of total investment.
- (vi) Annual capital related charges of 10% of total capital were envisaged to cover maintenance and central services overheads.

$$\text{Annual Costs} = \left[\begin{array}{c} 1.3 \text{ times} \\ \text{physical} \\ \text{plant cost} \end{array} \right] \left[\begin{array}{c} 30\% \text{ factor for} \\ \text{depreciation} \\ \text{capital charges} \\ \text{and related costs} \end{array} \right] \\ + 8000 \left[\begin{array}{c} \text{hourly} \\ \text{variable} \\ \text{cost} \end{array} + \begin{array}{c} \text{hourly} \\ \text{labour} \\ \text{cost} \end{array} \right]$$

Discounted Costs of Overall Project

This was more fundamentally based upon estimates of the total costs for each year of the project life, discounted to give a net present value. Assumptions made were:

- (1) Useful project life was taken as 10 years.
- (2) Fixed capital expenditure was equally divided between years 1 and 2 of project life.
- (3) Working capital (10% of fixed capital) was charged in year 2 and recovered in the final year, together with scrap value of 10% of fixed capital.
- (4) Capital related costs for years 3 - 10 were 10% of fixed capital.
- (5) The discount rate was taken as 15% per annum.
- (6) Again, the plant availability was 8,000 hours per year; direct labour cost £2.50/h.

The independent variables chosen to be optimised were: Z , T_r , Q_m and t_o . Constraints exist on these variables; those on t_o have already been discussed and others are: all independent variables have positive non-zero values; flow ratio of organic/aqueous solvents must be in the range 1/10:10; $t_o \geq 0.2$ g/l; $T_r \leq 300$ g/l; $Z \leq 12.5$ m³/h.

The final optimization was performed on an interactive, time-sharing computer system. This enabled a search to be initiated, the results quickly analysed, and further modified searches performed without the delays inherent in 'batch-wise' computer operation. To reduce computing costs, initial values of the independent variables were chosen from the feasible solutions for the operating conditions of the cresols separator, determined during the parametric survey, but searches were started using a number of widely different sets of variable values and the reproducibility of minima from the different starting positions was quite good.

Purities of each product chosen for separate consideration in the final cost minimization were 99%, 95%, 90% and 85%; lower purities were not considered to have any commercial significance. The feed composition to the process was fixed at 40 mole% m-cresol, which is a typical feed from a crystallization process. The feed mass flow rate was also kept constant at 50 kg/h.

Results and Discussion

The results of the direct searches for optimum costs carried out for the four separate product purities are shown in Table 3, which lists the optimal values of the four independent design variables together with the values of important state variables at the optimum process configuration. The annual costs are given at the foot of the Table and, as for the sub-optimizations, cost evaluation on an annual basis or as net present value had only a negligible effect on the position of the optimum.

The annual costs are plotted in Figure 13 and net present value in Figure 14, both being shown as a function of product purity. Costs clearly rise steeply as the degree of product purity required increases.

For 99% product purity, the optimum cresol concentration in the feed, T_r , rises sharply from about 175 g/l to 300 g/l. Without this increase, the feed flow rate of organic solvent, Q_o , would rise to values which would produce flow ratios in the enriching and stripping sections of the cresol separator that do not lie in the feasible region. The recycle cresols concentrations, t_o , also reaches its constrained limit for 99% purity. The cost of recovering m-cresol product from the aqueous phase represents approximately half the capital cost of the plant and, on average, 93% of the total variable cost. The recovery costs increase considerably as the raffinate concentration of

cresols decreases and so the optimum value of t_0 is close to its maximum allowable value. A contributory factor towards high cresol recovery costs is the low concentrations of cresols in certain process streams which imply large quantities of organic solvent or aqueous reagent which require large plant items to be physically contained. In the case of the aqueous reagent, cresol concentrations are severely constrained by the type of reagent used, the choice for which is limited.

A possible way of eliminating the need to return exceptionally low aqueous recycle cresol concentrations might be to use an external reflux of p-cresol in the stripping section of the cresol separator, but the full economic effects of this have not been evaluated.

The total process costs, as shown in Table 3, are quite high in comparison with the market price of the cresols isomers at corresponding 1972 valuation: these are estimated as £380/ton for m-cresol and £300/ton for p-cresol for isomers of 99% purity, so that the sales revenue from a plant fed with 400 tons/ year of 40% m-cresol, 60% p-cresol would be £133,000. At these 1972 values, this indicates that this cresols separation process would be unlikely to be profitable, although prevailing prices at different dates and places may differ considerably from those used here and it is possible that a better reagent than sodium phosphate may be found, resulting in lower separation costs.

Comparison with a 'Classical' Dissociation Extraction Process

A comparison would be valuable between the economics of the process described here and a 'classical' process, in which the cresols feed would be contacted with a deficiency of aqueous strong base, such as caustic soda. Accurate comparison is impossible without a corresponding economic optimization of the classical process, but some relevant observations may be made. The major cost difference will be related to the method of recovery of the

m-cresol product after separation, which takes a considerable proportion of total cost. In the process described here, these costs are large because a high recovery of m-cresol is required, not chiefly because of its own intrinsic value, but because a high-purity p-cresol product can not be obtained if much cresol is recycled to the primary cresols separator. This high recovery is obtained by phosphoric acid addition, the use of a large solvent/ aqueous flow ratio and a large number of theoretical stages in the recovery section. In a classical process, there is no aqueous phase recycle, so there is no absolute requirement for a very high m-cresol recovery. In this case, following acidification, the displaced m-cresol product would be only sparingly soluble in the aqueous salt solution and so could be easily separated. This eliminates the need for distillation in the recovery section, together with the need for phosphoric acid addition and expensive counter-current contacting equipment. On the other hand, the classical process involves extra operating costs for caustic soda and mineral acid, which are continuously consumed and result in the formation of a probably worthless salt which must be disposed of, together with the aqueous effluent, contaminated with traces of dissolved cresols.

Conclusions

A cresols separation process using tri-sodium phosphate as reagent has been mathematically modelled and the influence upon process design of the important variables has been demonstrated. The process has been optimized to minimize manufacturing costs by a combination of dynamic programming and direct search techniques.

The economics of the classical process clearly deserve further examination as it could be the cheapest method for 'difficult' dissociation extraction processes like the cresols separation, especially where high product purities are required.

The modelling techniques which have been described in this paper could well be capable of easy adaptation to

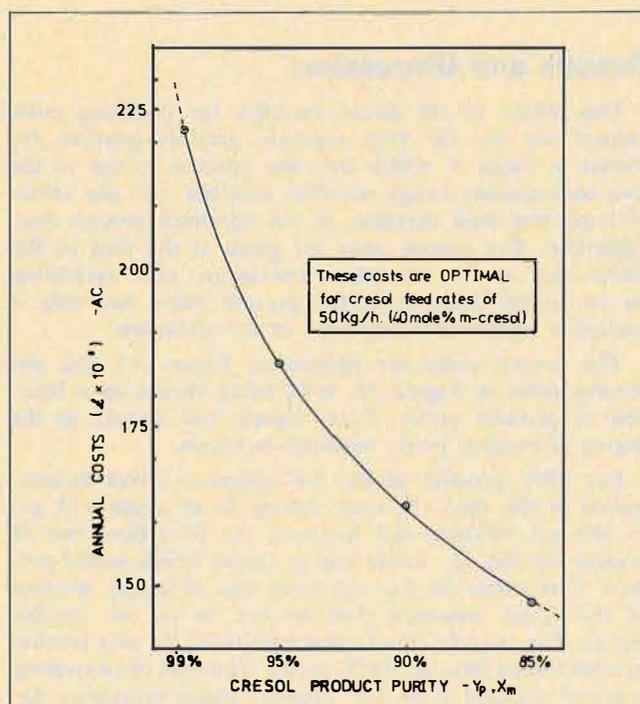


FIGURE 13. Minimum annual costs for processing 50 Kg/h of 40 mole% m-cresol: 60 mole% p-cresol to cresol products of 85 to 99% purity.

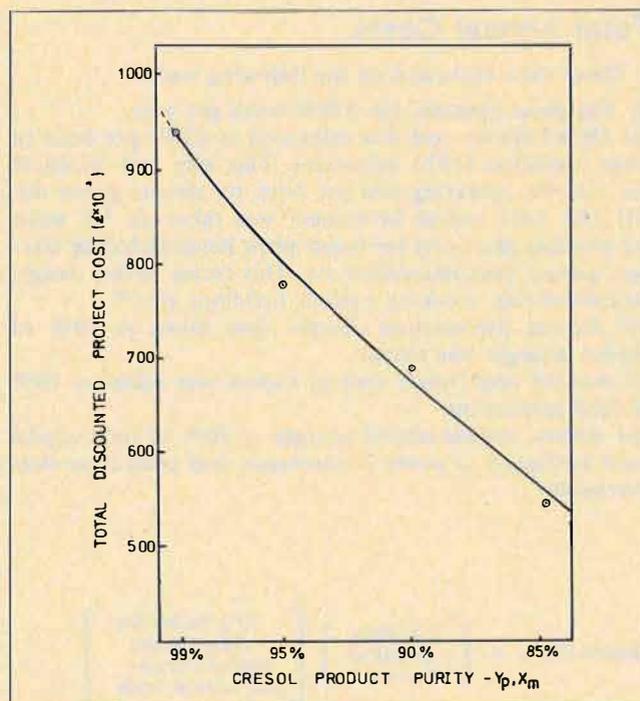


FIGURE 14. Minimum present worth of project costs (Discounted at 15%/annum) for processing 50 Kg/h of 40 mole% m-cresol:60 mole% p-cresol to cresol products of 85 to 99% purity.

TABLE 3. Optimum Values of Design and State Variables for Various Product Purities of Meta and Para-cresol

Feed mass flow rate (M_f) = 50 Kg/hr; Feed purity (Y_f) = 0.4

Variable	Symbol	Product Purities			
		85%	90%	95%	99%
Concentration of cresol in the feed	T_f	178	170	172	300
Flow rate of organic carrier solvent in feed	Q_f	282	294	291	167
Concentration of cresol in m-cresol reflux	T_{mr}	130	135	130	142
Flow rate of organic carrier solvent in m-cresol reflux	Q_{mr}	724	765	830	855
Concentration of cresol in p-cresol product stream	T_p	32.0	29.5	27.3	29.5
Flow rate of organic carrier solvent in p-cresol product stream	Q_p	1006	1059	1121	1022
Flow rate of aqueous carrier liquid	Z	2377	2514	2560	2800
Concentration of cresol in aqueous recycle stream	t_o	3.0	2.0	1.0	0.2
Concentration of cresol in m-cresol product stream	t_m	50.2	50.5	50.9	50.7
Number of theoretical stages in cresol separator	NTSI	44	56	65	69
Number of theoretical stages in stripping section	NTSSI	26	32	35	33
Number of theoretical stages in enriching section	NTSEI	18	24	30	36
Total number of Graesser Contactors in separator		3	4	4	5
Total number of Graesser Contactors in stripping section		2	2	2	2
Length of Graesser contactors in stripping section (ft)		21.4	26.8	29.5	28.7
Diameter of Graesser contactors in stripping section (ft)		3	3	3	3
Length of Graesser contactors in enriching section (ft)		29.6	20.1	25.3	20.3
Diameter of Graesser contactors in enriching section (ft)		3	3	3	3
Installed fixed cost contactors in stripping section (£)		25300	28930	30680	30140
Installed fixed cost contactors in enriching section (£)		15370	29460	27930	37440
Cost of aqueous Na_3PO_4 in contactors			NEGLIGIBLE		
Hold-up of solvent in Graesser contactors (m^3)		7	9	11	12
Hold-up of solvent in Graesser in p-cresol still (m^3)		6.2	6.2	6.2	6.2
Cost of organic carrier solvent (£)		1077	1235	1352	1425
Cost of solvent losses (£/hr)		0.03	0.03	0.03	0.03
Installed fixed cost of p-cresol still (£)		55790	56023	56230	55810
Cost of utilities in p-cresol still (£/hr)		0.39	0.41	0.43	0.39
Total installed cost m-cresol recovery section (£k)		108	113	146	201
Cost of utilities in m-cresol recovery section (£/hr)		5.25	6.29	7.18	8.49
Total installed cost of various storage and mixing vessels including mixed cresol feed storage, solvent.		—	—	—	—
Feed mixing tank, m-cresol reflux intermediate store, m-cresol reflux and solvent mixing tank hexane-benzene storage		4420	4600	4320	4760
Total installed fixed cost of plant items (£k)		210	233	266	330
Total variable cost of operating plant (£/hr)		5.67	6.73	7.64	8.91
Annual Cost (£k/yr)		147	165	185	220

similar dissociation extraction or solvent extraction processes, so that these may be optimized and information obtained concerning the relative sensitivity of the process performance and economics to changes in the design variables.

Acknowledgments

For helpful discussions we are very grateful to Mr. J. H. Young and Mr. J. Stokes of Croda Synthetic Chemicals Ltd., Mr. J. Coleby of Graesser Contactors Ltd., and to Professor W. L. Wilkinson and Mr. D. Houtby of the University of Bradford.

NOTATION

Q	= flow rate of organic solvent, exclusive of cresols, in cresols separator, 1/h
B	= flow rate of organic solvent, exclusive of cresols, in m-cresol recovery stage, 1/h
Z	= flow rate of aqueous phase, exclusive of cresols, 1/h
T	= total concentration of cresols in organic phase, g/l of carrier solvent
t	= total concentration of cresols in aqueous phase, g/l of (cresol free) aqueous phase
M	= feed rate of cresols, g/hour
X	= mole fraction of m-cresol in total cresols in aqueous phase
Y	= mole fraction of m-cresol in total cresols in organic phase
NTSSI	= number of theoretical stages in stripping section of separator
NTSEI	= number of theoretical stages in enriching section of separator
NTSI	= number of theoretical stages in both sections of separator

RRS	= internal reflux ratio in stripping section
RRE	= external reflux ratio in enriching section
PR	= phase flow ratio
S	= flow rate of solvent (cresol free) fed to distillation stage, 1/h
C	= concentration of cresols in feed to distillation stage, g/l
D'	= overall distribution coefficient of cresols: T/t
RR	= external reflux ratio of distillation
C_B, C_E, C_O, C_R	= concentration of cresol in, respectively, organic solvent feed, organic extract, aqueous feed and aqueous recycle streams in m-cresol recovery section; g/l of solvent
XW(1), XW(2)	= mole fractions of solvent and cresol respectively, in recovered solvent stream from distillation unit

Subscripts — used to identify process streams

f	= feed	mr	= m-cresol reflux
o	= aqueous recycle to cresols separator	E	= enriching section
p	= p-cresol product	S	= stripping section
m	= m-cresol product	F	= feed plate

numbered subscripts refer to the stage number within the contactor.

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DISCUSSION

A.S. Kertes: Concerning the chemistry underlying the process, I would like to know whether using a solvent which has a higher affinity toward (undissociated) m-cresol will increase the separation factor? What I have in mind is a polar long-chain alcohol, or a mixture of benzene and such an alcohol. Can the temperature effect upon partition of the two isomers be utilized for increasing the separation factor?

M.W.T. Pratt: In general, the separation factor will be greater if the organic solvent phase has a higher affinity for the undissociated isomer which is the weaker acid (p-cresol). This will support the separation effect caused by the difference in dissociation constants of

the components, which leads to a concentration in the aqueous base phase of the more acidic component (m-cresol). For more organic solvents, the difference in affinity for the individual undissociated isomers may be small but, if there is a difference, it should be in the direction indicated. This was the case for the solvents we have used (hexane/benzene and chloroform) although other solvents may be better.

We have studied the effect of temperature upon the distribution of m- and p-cresols between aqueous sodium phosphate and benzene/hexane over the range 10° to 30°C and found no significant variation in separation factor. If other similar systems do show an affect of temperature upon separation factor, this could indeed be useful: in the paper presented at ISEC 1974 (Vol. 1 p. 895) we included this principle in a suggested process for the separation of the bases 2-6 luridine, 3- and 4- picoline.

T.C. Lo: What would be the economical comparison between a dissociation extraction process and a liquid chromatogram process assuming the separation can be done by both processes?

M.W.T. Pratt: It would be interesting to know this, but unfortunately we do not have any information on large-scale chromatographic processes for separation of cresols.

Chapter 15

Analytical Topics

Sessions 17 and 32



Dr. A.W. Ashbrook



Dr. H. Steiger

Session Co-Chairmen

Chapter 15

Statistical Inference

Section 15.1



Figure 15.1



Figure 15.2

Section 15.2

Applications of Chromatography in the Investigation of Organic Losses in Solvent Extraction Processes for Copper and Uranium*

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ABSTRACT

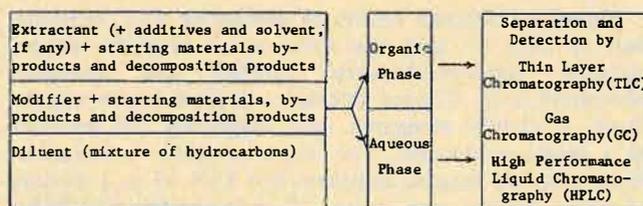
Thin layer chromatography (TLC), gas chromatography (GC) and high pressure liquid chromatography (HPLC) were evaluated and applied for the investigation of organic losses in the LIX 64N system for copper and in the Alamine 336 system for uranium. Chromatographic conditions for analysis are reported and discussed. The compositions of commercial extractants and of organic and aqueous phases were examined. Samples included synthetic mixtures and industrial samples. The organic composition of aqueous raffinate was found to be complex. There is evidence that in commercial operations with LIX 64N the concentration of hydrocarbons and reducing compounds in raffinate can exceed that of the parent oxime. The organic components in the Alamine 336 system are difficult to resolve and consist of a homologous series of tertiary amines, kerosene, alcohol and modifier. Sample handling is discussed briefly.

Introduction

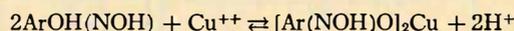
THERE IS A NEED TO DEVELOP GREATER UNDERSTANDING about organic losses associated with commercial solvent extraction processes for reasons which include improvement of the efficiency of metal recovery, protection of occupational health, and preservation of water resources for humans and wildlife. In order that organic losses be kept to a minimum for economic reasons, much attention in commercial operations is given to estimation of active reagent and to process control. Analytical procedures in the past have generally relied on titrimetric or spectrophotometric techniques. This paper briefly describes the development and application of some chromatographic techniques for the investigation of organic losses in solvent extraction systems for copper and for uranium.

Losses can occur by a number of ways such as solubility in the aqueous phase, chemical or photochemical reactions, thermal degradation, entrainment, adsorption and evaporation. A detailed examination of losses which can occur through the aqueous raffinate requires attention to not only the major components but to minor water-soluble products which may arise as by-products and decomposition products of manufacture or as decomposition products from the solvent extraction process. The starting diluents,

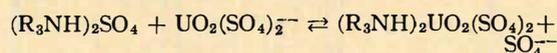
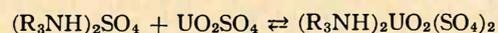
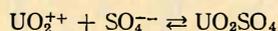
extractants and modifiers themselves are not single, pure compounds but commercial mixtures made to meet certain specifications. Another complication in analysis for minor components is that batch-to-batch variation can occur even though specifications are met. Some compounds may not be lost to the system as a whole but may accumulate in the organic phase. Because of the variety of known and unknown compounds likely to be encountered over a wide range of concentrations in both aqueous and organic phases, the experimental approach having the most general applicability at this stage of investigation was one based on chromatographic techniques. Expressed in simplified form diagrammatically, the major elements of the analytical problem are as follows:



For this study the solvent extraction systems selected were those employing LIX 64N for copper and Alamine 336 for uranium. Both extractants are products of General Mills Inc. and are well established commercially. The major active ingredient in LIX 64N is an aromatic hydroxyoxime. The general reaction during extraction involves chelation as follows:



Alamine 336 is a symmetrical, straight chain saturated amine containing mainly C₈ alkyl groups. Tertiary amines extract uranium from sulfate solution by reaction with uranyl sulfate or anionic uranyl sulfate^(1,2).



Copper — LIX 64N System

LIX 64N is a mixture of 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N) and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) in an aliphatic kerosene-type diluent reported to be Napoleum 470⁽³⁾. The current designation of Napoleum 470 is Kermac 470B. The concentration of *anti* isomer of the aromatic oxime is 40.1

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TABLE 2. Input Data

To be given when asked for by the computer or to be inserted in the program prior to the start in an AKUFVE run. [- - -] refers to the line number in the program. (See* Figure 4.)
The different symbols represent the variables used in the program.

Input data description

(1) Aφ = YES or NO. The answer should be given following the question asked by the computer: "HAVE YOU TRANSFERRED PREVIOUS DATA IN FILES DLCD1. DAT, DLCD2. DAT, DLCD3. DAT TO OTHER FILES?" The program continues only when a YES answer is given confirming that the reserved files in the disc for storing the data have been cleared from the previous data. The number of files reserved must correspond to the number of temperature levels to be used in the experiment. If a NO answer is given the program is discontinued. [3100]
(2) D1\$, B5 = Month Date. Month given in 3-letters abbreviation and date in number. A calendar is implied in the program and an automatic change of year, month and date will take place when such a change is required during the experiment. [3164]
(3) T1\$, T2\$, T3\$, T4\$, T5\$ = Specification of title to be given in 5 lines of which the last three need not be changed. [3200, 3220, 3235, 3240, 3242]
(4) C\$ = YES or NO: Specification whether coulometric titration will be required; if it is the case the following additional parameters must be given:;
I = preset current in mA [3246]
S(1) = time interval in seconds between two coulometric titration runs during which no current is passed.
S(11) = time interval in seconds during which current is passed.
R6 = Relay No. used to short circuit the coulometer
(5) X\$ = YES or NO: Specification whether glaselectrode is in function for pH measurement; if the answer is yes the following additional input data must be given: [3280, 3320]
Eφ = constant in mV which is specific for the electrode used in the Nernst expression for the EMF of the glaselectrode $E = E_{\phi} + (RT/10/F) \log (H^+) + j (H^+)$
j = correction for liquid junction potential in mV/M
F9 = criterion for the value of (H⁺) calculated from a given value of E [3280, 3320]
(6) C1\$ = Specification of mode of burette operation, i.e. constant volume additions from specified burettes or automatic adjustable volume additions from the burettes available. For the first mode of operation C1\$ = "MANUAL" and for the second C1\$ = "AUT". [3335]
(7) N1 = number of experimental points required. [3380]
S1 = time between readings in seconds, i.e. waiting time before a new reading is made.
S2 = preset time in seconds for the scalars.
(8) Aφ = minimum number of counts required. [3460]
S(15) = maximum time in seconds for scalars reading.
Scaler reading is stopped if the conditions required by either Aφ or (S15) are met.
Q(1) = waiting time in seconds after burettes addition before a new reading is made.
(9) Fφ = deadtime in second/count of the detector system to correct counts reading (3540)
(10) F1, F2 = background effect in cps for detector 1 (org) and detector 2 (aq) F7 = correction factor for different efficiency between the two detectors, $D_{cor} = D_{exp} \times F7$ where D represents the distribution ratio. F7 may be determined by either comparing the value of the distribution ratio D for a given extraction conditions found from Akufve measurement with the value found from off-line measurement using an external detector, or by passing the same active solution through the two detectors. [3600]
(11) F6 = criterion for phase equilibrium, e.g. we define the two-phase system to be in equilibrium when $\Delta \log D \leq Fe$. [3680]
(12) N2 = number of EMF readings to be made from the digital voltmeter for each cycle which is integrated and a mean value calculated. [3780]
S5 = waiting time in seconds between two consecutive reading cycles.
F3 = resolution of digital voltmeter in mV
F4 = criterion for EMF stability in mV
(13) R1 = position in relay-box used for on and off triggering control of the heater in the thermostat bath. [3860]
S(16) = duration of heating process in the thermostat in seconds
(14) F8 = criterion for temperature constancy in °C. [3940]
(15) N6 = number of temperature levels required. [3990]
X = temperature vector specifying the required direction of temperature change, i.e. X = 1 implies to start experiment at the highest temperature level required and successively step down to lower temperature levels; X = -1 operation of opposite order.
T(X6) = specification of the required temperature levels T(1), T(2), . . . T(N6). [4120]
(16) Y\$ = specification whether (H⁺) is the main parameter to be varied stepwise (= C(2)), if so the order "STEP" is given. [4160]
W\$, Wφ, W7, W8, W9 = month, date, hour, minute, second, rendezvous time at which time the process control is discontinued and new input data may be given. Thermostating of the system at a given temperature level is continued during the waiting time. The month given in 3-letters abbreviation, e.g. JAN for January, hour, min, sec. in numbers.
(17) Q(5); X\$(Q(5)): No. burette used for automatic adjustment of volume ratio VF(O/A) to a given constant value fixed at the start of the experi-

ment; the symbol "VF" specifies that the burette is reserved for the above mentioned purpose, otherwise "NO" may be written. [4186]
T(5); X\$(K5): the same specifications as the first mentioned burette. Two burettes are required for volume ratio adjustments, i.e. containing organic and the other aqueous solution. In an experiment the volume ratio will thus be adjusted to the required value whether the volume ratio change is due to a change of the organic phase or the aqueous phase.
(18) N3 = number of burettes to be used
N7 = number of concentration variables to be considered in the calculations. [4240]
(19) C\$(X3) = alphanumeric name of component, e.g. TBP, ZN(11), in burette No. X3
A\$(X3) = specification whether the burette No. X3 contains ORG solution or AQ solution
B\$(X3) = specification of maximum capacity of burette No. X3 10, 20 or 50 ml, and indicated by the symbol V10, V20 or V50. The use of a combination of all three types of burette are allowed. [4500, 4520, 4540, 4580, 4600, 4640]
The specifications of the burettes must be given for X3= 1, 2, . . . N3.
Y1(X3) = Component No. in burette No. X3
V(X3, 3) = volume added from burette No. X3 at the start of the experiment in ml
V(X3, 4) = maximum allowable volume in ml to be added from burette No. X3
C(X3, X7) = concentration in moles/l of component No. X7 in burette No. X3
M\$(X7) = chemical symbol of component No. X7, e.g. Fe(3+), HTTA
Specifications must be given for all burettes X3 = 1, 2, . . . N3, and all components X7 = 1, 2, . . . N7. Component No. 1 is reserved for the component of which the distribution is studied, e.g. Zn(11), and component No. 2 for the main parameter to be varied stepwise, e.g. HDEHP. Component No. 3 is reserved for H⁺. If the concentration of H⁺ is to be varied stepwise then it should be placed as component No. 2, since it is then considered as the main parameter.
(20) M\$(X7) = alphanumeric name of component No. X7 added in the mixer at the start of the experiment
M(X7) = number of millimoles of component No. X7 added in the mixer at the start of the experiment.
These specifications are to be given for all components No. X7 = 1, 2, . . . N7. [4860]
(21) V(φ, 2) = start volume of aqueous phase in the mixer in ml [5105]
V(φ, 1) = start volume of organic phase in the mixer in ml
The volume ratio $VF = V(\phi, 1)/V(\phi, 2)$ will be kept constant during the experiment if burettes are reserved for the adjustments as specified in point No. 17.
(22) V1(X3) = volume in ml to be added from burette No. X3 if mode of operation C1\$ = "MANUAL", i.e. constant volume additions from specified number of burettes (cf. point No. 6). The specification is to be given for all burettes No. X3 = 1, 2, . . . N3. [5218]
(23) X1\$ = mode of operation requiring pH-stat control of the system, by specifying with the symbol "PHSTAT", in which case the following additional input data must be given:
L1 = required pH level to be kept constant
F5 = criterion for pH constancy in pH-unit, e.g. ± 0.05
Y2; V2 = Burette No. to be used for acid solution; volume in ml to be added each time a correction to a lower pH value is required
Y3; V3 = Burette No. to be used for addition of alkaline solution; volume in ml to be added each time a pH correction to a higher value is required. [5135]
(24) D2 = step variation of the main ligand in pC = - log C units in case the experiment is to run with mode of operation C1\$ = "AUT", i.e. automatic adjustable volume additions from the burettes available (cf. point No. 6). If the calculated concentration change pC is smaller than can be made by addition of any solution from the available burettes, the minimum volume possible will be added from the appropriate burette. If the volume to be added can not be met by any available burette the process control will be discontinued for both modes of operations "MANUAL" and "AUT" and a refilling of the burettes required. The system will automatically be thermostated by the computer at the required temperature level. After refilling of the burettes the experiment can be restarted from the point of discontinuation. [5143]
(25) Z\$ = YES or NO, if the answer is YES the process control by the program will start; if NO a respecification of input data will be required. The answer YES or NO should be given after the start of the program when the following question is asked: ARE INPUT DATA OK? ANSWER: YES OR NO. [5200]
(26) Since the core memory of the computer (28 K) is found not big enough to contain the complete program, and also to make more efficient use of it during the process control, we make at this stage an "OVERLAY" operation of the program, i.e. part of the program which has been used and will not be used further in the experiment is deleted and the space in the core memory which was previously occupied is now available for use. By making use of this type of "OVERLAY" operation one can, by appropriate organization of his program, run an extensive program even in a computer with very limited core memory capacity (e.g. 16 K). For more detailed information the reader is referred to the PDP manuals. — The "OVERLAY" instruction to part of the program named "Z9. BAS" is implied to the main program "DLCTZ9. BAS" and no any action from the user is required to overlay these two programs.

make changes in the main part of extraction parameters given previously as input data, e.g. change of mode of operation from "MANUAL" to "AUT", change of temperature level, change of criterion for phase equilibrium, etc. The interrupt system is based on an instrumental "flag" indication system, e.g. as soon as the computer reading from a given instrument exceeds a given value the process control is interrupted and bypassed to a subroutine through which the parameter changes can be made. In this program the interrupt flagging system is an EMF reading which is greater than 1000 mV. In the current digital voltmeter used in the system (Dynamo DM 2022S) this can be realized by manually setting the reading to "Cal" position, which gives a reading of $E = 1019$ mV. In principle, one can use any instrumental "flagging" system by bringing a small change in the BASIC program. The current version of program may be interrupted during an AKUFVE experiment and changes in experimental conditions made as given in Table 3. An illustration of

such program interrupt is given in Figure 5 in the following conditions:

(a) If during an AKUFVE run any of the burettes to be used does not contain enough solution as required by the input data specified or, in case "AUT" mode of burette addition is used (this is the case with the burette which contains the most concentrated solution). In such a case the following message will be printed: REFILL BUR X, where X represents the number of the burette which has to be refilled. During the waiting time for burette refilling, the system is automatically thermostated at the current temperature level specified. After the burette has been refilled the process control can be restarted again from the point of interrupt using the instrumental "flagging" system described previously.

(b) Automatic program interrupt also takes place if for some reason the temperature of the system is coming out of control, e.g. $T > 80^{\circ}\text{C}$ or $T < 1^{\circ}\text{C}$. The program will

Table 2 continued

Input data description

- (27) B ϕ , B1, B2, B3 = Specification of the required starting time: date, hour, minute and second. The input data are to be given following the question asked by the computer: REQ START: DATE, H, M, S. [13300]
- (28) W2\$ = YES or NO. The answer should be given following the question asked by the computer: NEW RENDEZ VOUS DATE, YES OR NO? If the answer given is YES, i.e. the previous given rendez-vous data as input data (cf. point No. 16, line number 4160) is to be changed, the following question will be printed and a new specification of the rendez vous date should be given: MONTH, DATE, H,M,S ? (W\$, W ϕ , WM, W8, W9) if the answer is NO input data specified in point No. 29 is required.
- (29) W2\$ = YES or NO. The answer should be given following the question asked by the computer: NEW DATE, YES OR NO? If the answer is YES, i.e. the previous given input data of date (cf. point No. 2, Line number 3164) is to be changed, the following question will be printed and the current date should be given: MONTH, DATE (D\$, B5) [13315] If the answer is NO input data specified in point No. 30 is required [13317]
- (30) S(20), S(21), S(22) = Specification of the current time in hours, minutes, seconds. The input data should be given following the question: TIME, H,M,S? [13320]
- (31) W2\$ = YES or NO. The answer should be given following the question asked by the computer: "OK? YES OR NO" If the answer is "YES" the computer will start to take control of the experiment under the conditions specified by the given input data. If the answer is "NO" a respecification of input data beginning from point No. 27 to No. 30 will be required. [13335]

TABLE 3. Program Interrupt Output and Input Data

Output and input data to be given when the process control during an AKUFVE run is interrupted using an instrumental "flagging" system to make changes in the experimental parameters. The different symbols represent the variables used in the program. The point numbers given in the text refer to those in Table 2. [- -] refers to the line number in the program in which the input data is given.

Input data description

- DATE: The date and time of interrupt will be output by the computer, e.g. 12-FEB-1977 10H:24MIN:5SEC
- NEW RENDEZVOUS: MONTH, DATE, H, M, S: (W\$, W ϕ , W7, W-, W9) Specify new time for rendez-vous. [15012]
- NEW INPUT? YES OR NO: If the user gives a YES answer then the following input data are required otherwise the process control is restarted from the point of interrupt. [15020]
- YES OR NO?: Give one of the alternatives for the following questions on whether a given input data is to be changed from the values previously given.
- C1\$?: Change of operation mode (cf. point 6). Table 2. [15050] If the answer given is YES then the following two alternatives can take place: a) a change from operation mode "MANUAL" to "AUT", in which case the following additional input data is required: D2: step variation of main ligand (cf. point 24, Table 2) b) a change of operation mode from "AUT" to "MANUAL", in which case the following additional input data are required: V1(X3): volume addition in ml from burette No. X3 (cf. point 22) Table 2 and specification will be required for all burettes in use No. X3 = 1, 2, ... N3
- N1, S1, S2: If YES answer then new specification of input data as given in point 7 is required [15080]
- A ϕ , S(15), Q(1): If YES answer then new input data as specified in point 8 are required. [15110]
- N2, S5, F3, F4: If YES answer then new input data as specified in point 12 must be given. [15160]
- S(16), F8: If the answer is YES then new input data are required as described at points 13 and 14. [15180]
- BUR ADD AND MAX V: Input data for volume addition to be made by each burette and the maximum allowable volume addition. If a YES answer is given requiring a change from previous given values the following additional input data are asked by the computer: V(X3, 0), V(X3, 4): the pair of values to be given for each burette from burette No. X3 = 1, 2, ... N3. [15230]
- PHSTAT: Whether PHSTAT operation mode is to be used (cf. point 23). If the answer is YES then the following change in input data is to be given: X1\$, L1, F5, Y2, V2, Y3, V3: Specifications for conditions of pHstat control as given in point 23) [15270]
- D2: If operation mode "AUT" (cf. point 6) and change of step variation of main ligand is required then a YES answer is to be given and the new input data printed following the next question: [15280]
- D2: cf. point 24 [15280]
- COUL: Is coulometric titration to be used in the experiment that follows? If YES then the following additional input data specifying the conditions of coulometric titration are required: [15290]
- C\$, I, S(1), S(11): Cf. point 4. [15295]
- OK: Give a YES answer if everything is alright and the process control will be restarted from the point of interrupt and the new input data given will now be valid. If a NO answer is given a respecification of input data from the beginning will be required. [15310]

```

DATE: 23 -MAR- 1977 13 H: 57 MIN: 9 SEC
NEW RENDEZVOUS:
MONTH, DATE, H, M, S:
?23          BUR ADD AND MAX V: ?YES
?18          BUR 1
?0           ?71
?0           ?150
NEW INPUT?YES OR NO
?YES         BUR 2
YES OR NO?  ?71
C1$: ?YES   ?150
?AUT        PHSTAT: ?YES
?2:         X1$, L1, F5, Y2, V2, Y3, V3:
? - 0.02    ?PHSTAT
N1, S1, S2: ?YES  ?3. 5
?50         ?0. 1
?120       ?3
?1          ? 1
A0, S(15), Q(1): ?NO  ?4
F6: ?YES    ? 1
?0. 03     D2: ?NO
N2, S5, F3, F4: ?NO  COUL: ?NO
S(16), F8: ?YES     OK: ?YES
? 5
? 2

```

FIGURE 5. An example of a program interrupt during an AKUFVE run by means of an instrumental "flagging" system (cf. Table 3). The new input data replace these given previously.

```

INPUT DATA FROM FILE DLCD1.DAT
*****
EXTRACTION OF ZN(II) BY HDEHP-ISOPAR H FROM 2.5 M(N.A.H.ZN)
504 AT 25 C, C*(ZN)=150 G/L HAY LIEN 16/3 1977
DATA SAVED IN DLCDX.DAT A5: X1.E1 MV.T C.53 S.A1 COUNTS
A2 COUNTS.57 H.58 M.59 S. C(1) M. C(2) M. C(3) M
C(4) M. C(5) M. 11 CFS, 12 CFS

NO.      C(ZN)AQ      C(HDEHP)ORG      C(HDEHP)ORG      C(H+)AQ
MOL/L    MOL/L          G/L              G/L
1        2.29747    .287359          92.6523          .0381729
2        2.29747    .300091          96.7574          .0439147
3        2.29747    .312635          100.802          .0484027
4        2.29747    .324997          104.788          .0521179
5        2.29747    .33718           108.716          .0523212

NO.      C(S04)AQ      C(NONE)AQ      LOGC(ZN)AQ      LOGC(HDEHP)ORG
MOL/L    MOL/L          (MOL/L)        (MOL/L)
1        2.5          2.98063E-28    .36125          -.541575
2        2.5          2.95858E-28    .36125          -.522747
3        2.5          2.93686E-28    .36125          -.504962
4        2.5          2.91545E-28    .36125          -.488121
5        2.5          2.89436E-28    .36125          -.472138

NO.      LOGC(HDEHP)ORG      LOG(H+)      LOGC(S04)AQ      LOGC(NONE)AQ
(G/L)        (MOL/L)      (MOL/L)          (MOL/L)
1        1.96686          -1.41824      .39794          -27.5257
2        1.98568          -1.35739      .39794          -27.5289
3        2.00247          -1.31513      .39794          -27.5321
4        2.02031          -1.28301      .39794          -27.5353
5        2.03629          -1.28132      .39794          -27.5384

NO.      VF(ORG/AQ)      D=      ZN(AQ)      ZN(ORG)
I(ORG)/I(AQ)      I(ORG)/I(AQ)      MOL/L      MOL/L
1        1            .036505      2.21655      .0809152
2        1            .0383556     2.2126       .0848657
3        1            .0378816     2.21361     .0838552
4        1            .0421655     2.20452     .0929545
5        1            .0375477     2.21433     .0831429

NO.      LOGD      XEXTR(ZN)      I(AQ)      I(ORG)
CPS      CPS
1        -1.43765    3.52193      97.3065      3.55217
2        -1.41617    3.69388      97.8757      3.75408
3        -1.42157    3.6499       95.8059      3.62928
4        -1.37504    4.04595      95.6424      4.05291
5        -1.42542    3.61889      95.6809      3.5926

TEMPERATURE LEVEL= .25 C
THE FOLLOWING DATA HAVE BEEN USED FOR THE CALCULATIONS.
CORRECTION FACTOR FOR DEADTIME T0= 0 MIN/COUNT
BACKGROUND= 0 CPM; MOL. WEIGHT= 322.427

NO.      LOG(H+)      C(ZN)AQ      C(HDEHP)AQ      C(S04)AQ
MOL/L    MOL/L          MOL/L          MOL/L
1        -1.41824     2.29747      .287359         2.5
2        -1.35739     2.29747      .300091         2.5
3        -1.31513     2.29747      .312635         2.5
4        -1.28301     2.29747      .324997         2.5
5        -1.28132     2.29747      .33718          2.5

NO.      C(NONE)AQ      VF(ORG/AQ)      I(AQ)      I(ORG)
MOL/L    CPS            CPS
1        2.98063E-28    1            97.3065      3.55217
2        2.95858E-28    1            97.8757      3.75408
3        2.93686E-28    1            95.8059      3.62928
4        2.91545E-28    1            95.6424      4.05291
5        2.89436E-28    1            95.6809      3.5926

PROGRAM FOR T-STAT AKUFVE
REQUIRED T= 25 +- .05
THE LIST GIVE READ T WITH ABS(T- 25 >> 5

```

FIGURE 6. Output of a computer controlled AKUFVE run using the data which have been stored in the Disc and the program HLDACO. The input data listed in Figure 4 have been used for the experiment. After the program is executed the AKUFVE system is automatically thermostated using the program "TSTAT.BAS" at 25°C.

be discontinued waiting for the attention of the user. The data already collected will be output and the system thermostated using another subroutine.

Prognosis of Extraction Process

In the program a subroutine is included which will output an approximate prognosis of the extraction process using a least-squares method. After each equilibrium data

```

1080 REM GIVE CHEMICAL SYMBOL OF METAL EXTRACTED, AND IN WHICH PHASE
1090 DATA "ZN","AQ"
1100 REM GIVE CHEMICAL SYMBOL OF LIGAND WITH VARIABLE CONC
1110 REM AND IN WHICH PHASE
1120 DATA "HDEHP","ORG"
1130 REM GIVE CHEMICAL SYMBOL OF LIGAND NO. 2, AND IN WHICH PHASE
1140 DATA "H+", "AQ"
1150 REM GIVE CHEMICAL SYMBOL OF LIGAND NO. 3, AND IN WHICH PHASE
1160 DATA "S04", "AQ"
1170 REM GIVE CHEMICAL SYMBOL OF LIGAND NO. 4, AND IN WHICH PHASE
1180 DATA "NONE", "AQ"
1190 REM GIVE EXPECTED MAXIMUM NUMBER OF POINTS
1200 DATA 50
1210 REM GIVE BACKGROUND IN COUNTS/SEC
1220 REM IF AKUFVE DATA ARE USED AS INPUT GIVE X0=0
1225 DATA 0
1230 REM GIVE MOLECULAR WEIGHT OF THE ACTIVE LIGAND
1240 DATA 322.427
1245 REM GIVE MOLECULAR WEIGHT OF ACID USED
1247 DATA 98
1250 REM GIVE DEAD TIME IN COUNTS/SEC
1260 REM GIVE DEADTIME T0=0 IF AKUFVE DATA ARE INPUT
1270 DATA 0
1360 REM PRINT: "STEP" IF [H+] IS VARIED IN STEPS ([H+]=C(2))
1370 REM PRINT: "NO STEP" IF NOT ([H+]=C(2))
1380 DATA "NO STEP"
1381 DATA 0 REM CHARGE OF METAL EXTRACTED FOR [H+] CORR
1382 REM PRINT: NO. OF FILES TO BE ASSESSED
1383 DATA 1
1384 REM PRINT: FILE NAMES
1385 DATA "DLCD1.DAT", "DLCD2.DAT", "DLCD3.DAT"

```

FIGURE 7. Part of the program HLDACO to treat the data of a computer controlled AKUFVE run which were stored in file "DLCD1.DAT" in the Disc. The given input data are to be given prior to start of experiment. The input data listed in Figure 4 have used for the experiment and the final output in Figure 6.

output, the equation of the distribution of the metal ions between the two phases is calculated in the form of $\log D = A \log C + B$, where D is the distribution ratio, C the total concentration of the reagent varied and A, B constants calculated using a least squares technique. The prognosis is made using all points available and another using only the last two points. The first calculated line indicates the main extraction process and the second one the tendency of the change of slope. An illustration of a prognosis of a metal extraction during an AKUFVE run is given in Figure 6.

Data Transformation

After the end of the experiment, i.e. the number of experimental points required is met, the data which are stored in files in the disc are automatically used as input data for another program (HLDACO) which transform the data into a more readable form, and also in a form suitable for use in off-line LETAGROP-DISTR⁽⁵⁾ analysis. An illustration of such an output is given in Figure 6. The HLDACO program automatically replaces the process control program by means of a "CHAIN" instruction in BASIC (cf. Ref. 9). Prior to the start of an AKUFVE run the input data given in Figure 7 must be inserted in the HLDACO program.

Illustration of the Application of the Program

1. Distribution Studies of Methylmercury(II) using 203-Hg Labelled MeHg(II) in the Two-Phase System 1.0 M (Na,H)(Cl,NO₃)/o-xylene⁽¹⁰⁾

Figure 8 shows the distribution of MeHg(II) at pH = 2.00 as a function of C_{Cl} at different constant temperature levels, 22, 25, 30 and 35°C. Computer analysis of the distribution data using the LETAGROP-DISTR program⁽⁵⁾ indicates the formation of the methylmercury species MeHgCl(aq), MeHg₃(org) and MeHgCl(org) and increase of extraction of MeHg(II) with decreasing temperature.

2. Distribution Studies of MeHg(II) in the Two-phase system 1.0 M (Na,H)(Br,Cl,NO₃)/o-xylene (cf. Ref. 11,12)

The complex formation between MeHg(II) and Br⁻ in the two-phase system MeHg(II)-1.0 M (Na,H)(Br,Cl,NO₃)/o-xylene has been studied using the conventional manual method and an AKUFVE computer-controlled technique. Figure 9 shows part of the distribution data obtained by AKUFVE. Computer analysis of the data using LETAGROP-DISTR program⁽⁵⁾ indicates the formation of MeHgBr(aq) and MeHgBr(org) with the following equilibrium constants:



Distribution Studies of Zn(II) in the Two-phase System 1.0 M (H,Na)SO₄/HDEHP-IsobarH⁽¹³⁾

Figure 10 shows part of the data obtained for the extraction of Zn(II) at 25°C from a computer-controlled

AKUFVE run given as % Zn(II) extracted as a function of pH for C_{HDEHP} = 0.5893 M.

Figure 11 shows a perturbation test of extraction equilibrium by alternately varying the temperature level in one single experimental run. The result clearly indicates that the system has reached chemical equilibrium within the time intervals studied. It also shows that the system studied was stable up to at least 40 hours.

Distribution Studies of Yb(III) in the Two-phase System 0.10 M (Na,H)ClO₄/HDEHP-Toluene at Several Temperature Levels⁽¹⁴⁾

The distribution of Yb(III) between 0.10 M (Na,H)ClO₄ and HDEHP-toluene has been studied as a function of C_{HDEHP} at a constant pH for different temperature levels, 15, 20, 25, and 30 C. Figure 12 shows part of the data obtained by a computer controlled AKUFVE run.

Discussion

The computer-controlled AKUFVE operating system has shown to be a powerful and effective method for collecting accurate distribution data. The program gives the user a wide flexibility of alternatives in choosing the experimental parameters as required by the type of experiment and the degree of precision. The computer enables us to design experiments which manually will be too laborious if not impossible to perform. The current program has primarily been developed to process control distribution studies using AKUFVE apparatus. However, by minor changes in the program it can also be used for other applications, such as computer-controlled potentiometric titration in equilibrium studies, kinetic studies of metal extraction etc., which can make use of the subroutines which are callable via BASIC (cf. Table 1). The current version of the program is run using a 28 K core memory. However, by slight rearrangements of the

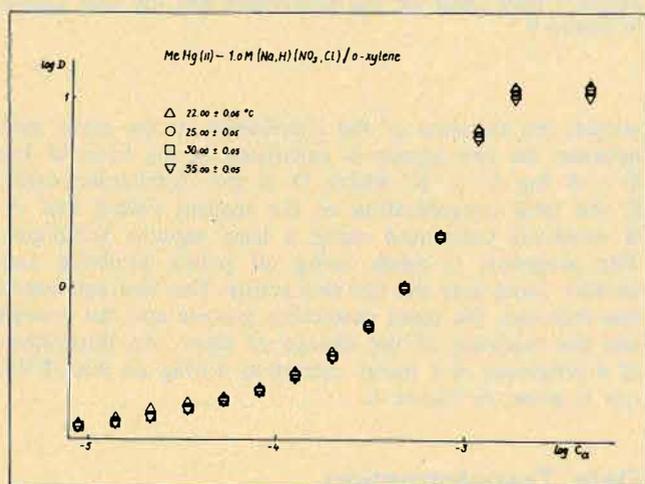


FIGURE 8. The distribution of MeHg(II) between 1.0 M (Na,H) (Cl,NO₃)/o-xylene at pH=2.00 as a function of C_{C1} at different constant temperature levels: 22 (Δ), 25 (○), 30 (□) and 35 C (▽), as obtained by a computer controlled AKUFVE run. The burette additions have been effected using the operation mode "AUT" corresponding to an increase of a specified ΔpC_{C1} for C_{C1}. (cf. Table 2, point 24).

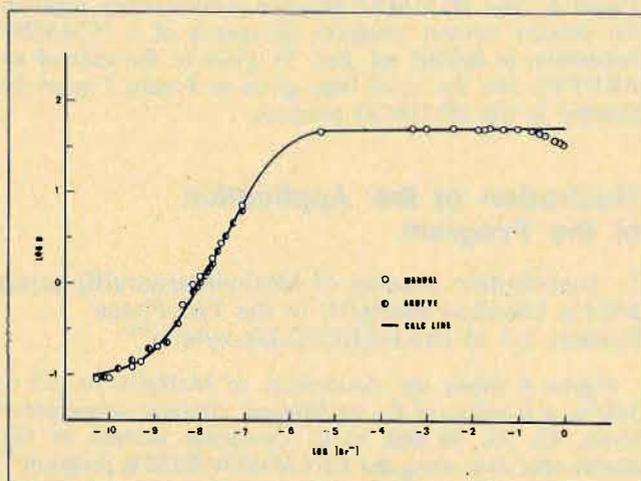


FIGURE 9 The distribution of MeHg(II) between the two phases 1.0 M (Na,H) (Br,Cl,NO₃)/o-xylene as a function of C_{Br}, studied by a computer controlled AKUFVE. The C_{Br} was varied using the operation mode "AUT". (cf. Table 2, point 24)

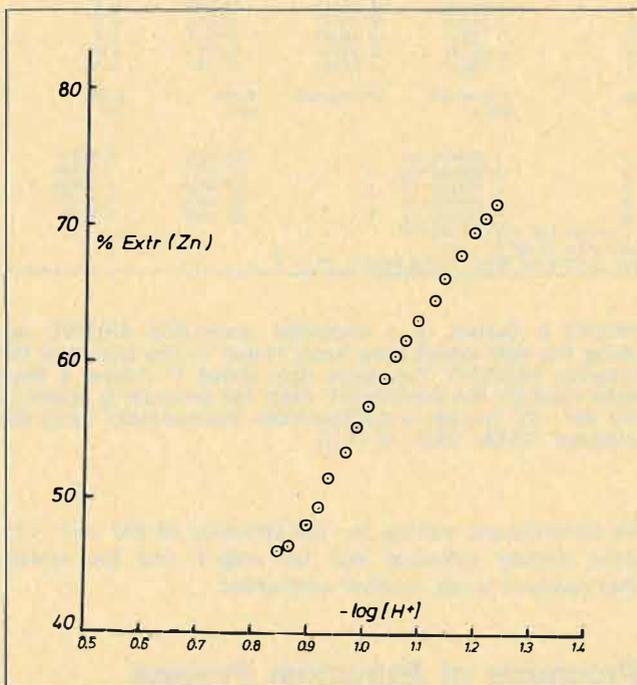


FIGURE 10. Distribution studies of Zn(II) in the two-phase system 1.0 M (H,Na)SO₄/HDEHP-isobar H at 25°C from a computer controlled AKUFVE run using operation mode "AUT". (cf. Table 2, point 24)

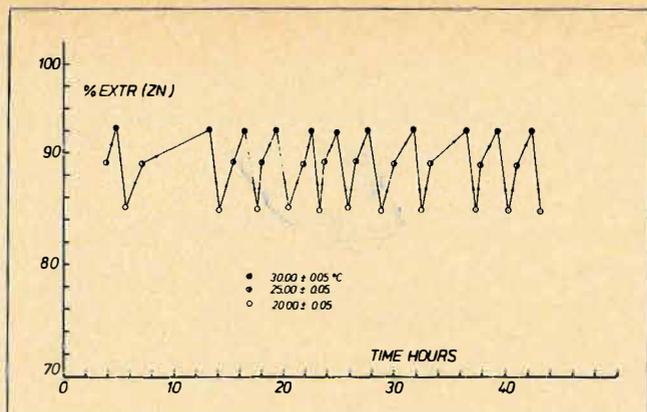


FIGURE 11. Perturbation test using a computer controlled AKUFVE for the extraction equilibrium of the system Zn(II)-1.0 M (H,Na)SO₄/0.5893 M HDEHT-isobar H at pH=2.00, $VF = \frac{V_{org}}{V_{aq}} = 0.96$ at three different temperature levels (20(○), 25(○) and 30°C(●).

program and making use of "OVERLAY" procedure in BASIC, less core memory may in principle be used. The RT-11 software package requires, however, a minimum of 16 K core memory. A less extensive program than that which is described in the present paper, but which contains the main parts of the process control functions and can be run with only 16 K core memory, has also been developed and tested.⁽¹⁵⁾

The current version of program can be used for distribution studies at several temperature levels in a single AKUFVE run, which is valuable for the determination of other thermodynamic quantities such as ΔH and ΔS . As shown in Figure 11 this may even be used as an equilibrium test of the metal extraction studied. The adjustment of temperature in the specified range is usually the determining factor for the speed of the data collection. The thermostat used in this system has a constant cooling effect and the temperature is adjusted to the specified level by using heat pulses controlled by the computer. A better temperature control may be achieved if the cooling system is also under program control. Work to improve the temperature control by this method is in progress. A limitation of the AKUFVE technique is the amount of reagents required, which in our system correspond to approximately 600 ml of each phase. With such a volume of liquid the current AKUFVE is more expensive in reagents expenditure compared with conventional batch technique. On the other hand, the advantages of the technique to collect accurate distribution data in a most efficient way seem to be self-evident.

Acknowledgments

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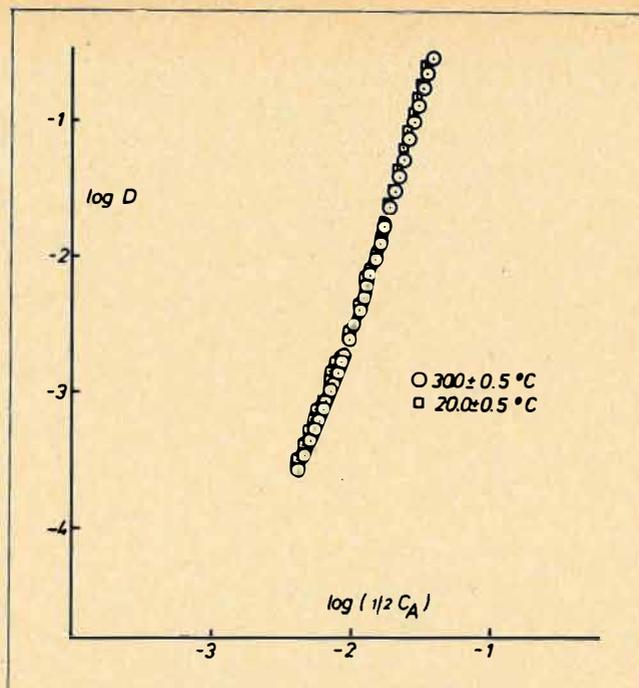


FIGURE 12. The distribution of Yb(III) in the two-phase system Yb(III)-0.10 M (Na,H) ClO₄/toluene at several constant temperature levels (20 and 30°C) as obtained from a computer controlled AKUFVE run. The C_{HDEHP} was varied using the operation mode "MANUAL" and the volume ratio kept constant at 1.0 by assigning one burette with an aqueous solution as volume ratio corrector.

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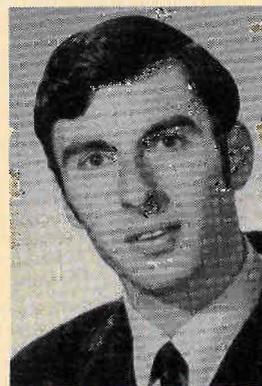
Chapter 16

Environment

Session 2



Dr. Ruth Blumberg



J.R. Hawley

Session Co-Chairmen

Chapter 16

Environment

Section 1



John F. Kennedy



Lyndon B. Johnson

Section 2

Losses of Organic Compounds in Solvent Extraction Processes

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Introduction

SOLVENT EXTRACTION PROCESSES for the separation and recovery of metals on an industrial scale have been intensively applied in the uranium and nuclear fuel reprocessing industries (Jenkins, 1972). In recent years there has been steady progress in the adoption of solvent extraction in hydrometallurgical systems for recovery of non-ferrous metals such as copper (Flett, 1972). There are also examples of solvent extraction processes for the production of inorganic compounds such as phosphoric acid (Blumberg, 1971) and sodium bicarbonate (Blumberg, 1974). The recovery of nitric and hydrofluoric acid from waste stainless steel pickling solutions can be achieved by solvent extraction (Kaylenstierna, 1974).

The size and variety of the mining and metals industry in Canada indicate that there will be scope for utilization of solvent extraction processes. However, advances made in other countries are not directly transferable to Canadian conditions. Apart from differences in the nature of metal-bearing ores and materials, there are special constraints with respect to safeguarding the working environment and freshwater resources. Processes suitable in mild climates or arid regions are inappropriate where the work place must be enclosed and heated, and where water resources have value for fisheries, tourism and vacationing, in addition to other industrial and domestic uses.

Organic losses, whether due to solubility, degradation, evaporation or adsorption, are of considerable economic concern as well as having significance in process control. As processing of metals by solvent extraction becomes more widely adopted because of its advantages for certain applications, the subject of organic losses will continue to be important from an economic and production viewpoint. Organic losses will also be viewed more from the perspective of environmental impact than they have been in the past (Ritcey, 1974).

The stability of extractants and other components of the organic has received much attention in the atomic energy field because radiolysis of organic compounds during processing of nuclear fuels is an inherent problem. In the case of ordinary metals such as copper, the cost of reagents, modifiers and diluents is an important factor. Organic losses in the latter case have usually been estimated by measurement of quantities required for inventory make-up in actual plants.

Average loss of mixed reagents at Bagdad Copper Corporation, Bagdad, Arizona is reported to be 0.06 USg per 1000 gallons of treated aqueous feed (Swinson, 1976), whereas at Ranchers Exploration and Development Corporation, Miami, Arizona the loss is reported to average 0.2 USg per 1000 gallons aqueous feed (Power, 1976). This variation from plant to plant makes it important to establish base line expected organic loss irrespective of plant design or operation. These data are of use in

assessing both adequacy of plant design and environmental consequences of solvent extraction processing.

This paper presents data on organic losses during the processing of copper leach liquors by solvent extraction with LIX 64N. Of concern were losses due to solubility, decomposition and evaporation. A summary of available data on reagent toxicity is presented. Losses of organic due to spills, crud formation, adsorption, etc., although very important in terms of total organic lost from a solvent extraction circuit, may vary from plant to plant and were therefore not included in this study.

A number of analytical techniques were employed in the work described. These included:

1. thin layer chromatography
2. total organic carbon analysis
3. high pressure liquid chromatography
4. gas chromatography
5. mass spectrometry
6. thermal analysis.

The development and application of these methods for determining losses of solvent in solvent extraction processes is given elsewhere in these proceedings (Ashbrook, 1977).

LIX 64N-Copper System

LIX 64N is a mixture of 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N) and 5, 8-diethyl-7-hydroxy-6 dodecanone oxime (LIX 63) in an aliphatic kerosene-type diluent. The structures of the organics making up the extractant are given in Figure 1. The diluent used in this study was Escaid 100, a kerosene with a boiling range of 195 to 260°C and a composition of 85% naphthenic paraffinic and 15% aromatic hydrocarbons.

Analysis of a number of batches of reagent received from General Mills Chemicals Inc. show considerable batch to batch variation in active reagent. LIX 65N content varied from 44.33% to 48.85%. LIX 63 content varied from 1.1 to 1.5 wt.%. In addition to these two major active components, purchased reagent contains diluent and a considerable quantity of unidentified components as detected by gas chromatography (Figure 2). The unidentified components are probably unreacted starting materials used in the reagent synthesis.

Soluble Organic Losses

The loss of organic by solubility was evaluated in the laboratory. Results obtained were compared with analyses carried out on Ranchers Exploration and Development and Cyprus Bagdad plant raffinates sampled over a number of months. The comparison was complicated by the fact that different diluents were used by the two plants, neither of which was Escaid 100. Ranchers Exploration and Development Corporation used KERMAC 470B and Cyprus Bagdad used Chevron IX Solvent.

Initial studies were carried out to verify that raffinate samples would truly be representative; i.e., that soluble

organic would not be adsorbed on the sample container. Raffinate simulating solvent extraction of copper from dump leach operations was saturated with organic by contacts with 12% v/v LIX 64N in Escaid 100. After coalescence the sample containers were rinsed with the raffinate and a sample taken. Figure 3 shows that within experimental error no organic loss to the glass or polyethylene sample container occurred over 29 days.

Base line data on soluble organic losses were obtained by generating test raffinate in the laboratory. A copper-LIX 64N circuit was run under simulated Ranchers

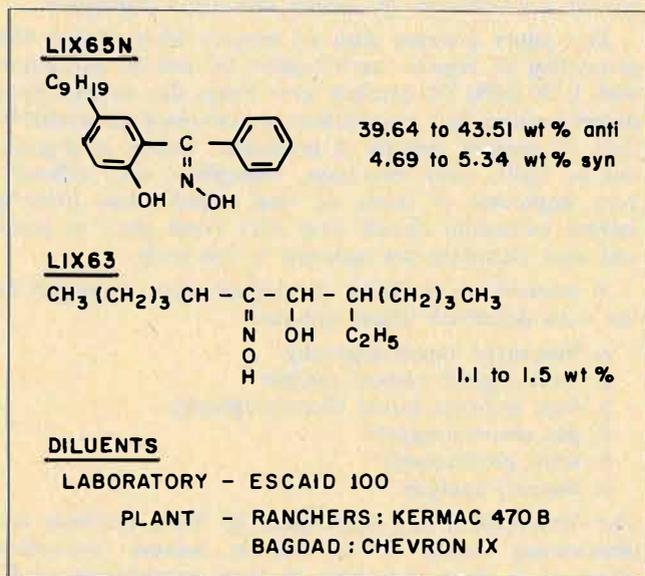


FIGURE 1. LIX 64N — Copper system.

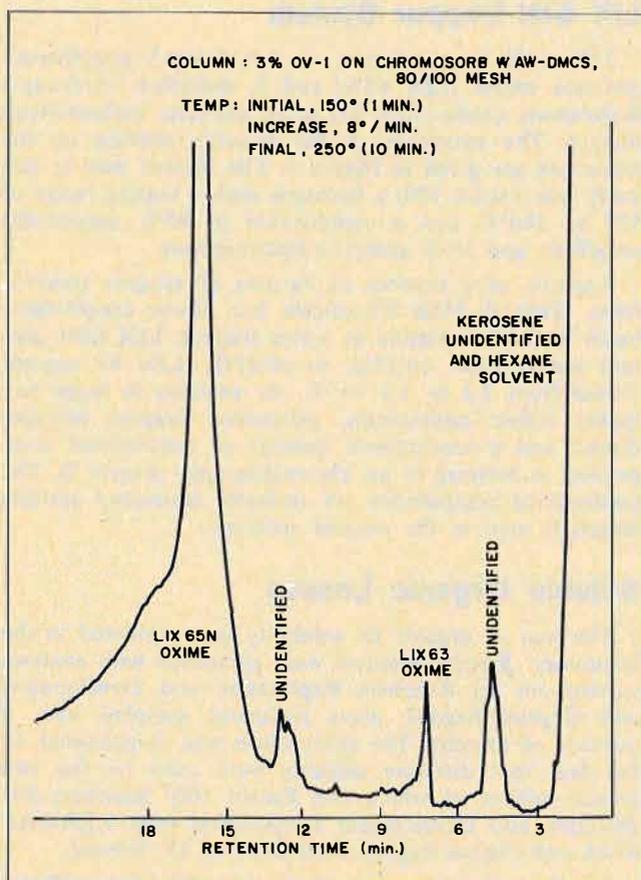


FIGURE 2. GC of commercial LIX 64N.

Exploration and Development Corporation plant conditions using a laboratory-scale multi-stage mixer settler unit and electrowinning cell as shown in Figure 4. The mixer settler compartments were constructed of polypropylene. Teflon tubing was used throughout the circuit to prevent organic contamination of the aqueous. The circuit was operated continuously for 68.5 hours (120 organic passes) producing about 100 gallons of raffinate. Entrained organic in the raffinate was removed by coalescence.

The results, with respect to organic soluble losses, are given in Table 1 and are summarized below:

1. Total organic carbon levels in the raffinate during the initial part of the run were as high as 165 ppm and decreased to about 20 ppm at the end of the run.

The high initial levels are attributed to the presence of

TABLE 1. Total Organic Carbon Analysis of Aqueous Streams Produced in LIX 64N-Copper Run*

Aqueous Stream Description	No. of Operating Hours	No. of Organic Passes	TOC (ppm)
Raffinate - Circuit	25	42	22.1
"	37	63	20.9
"	49	84	19.3
"	68	105	18.1
Raffinate - Composite	0 - 1	0 - 2	165.
"	1 - 13	2 - 23	25.8
"	13 - 63.5	23 - 111	16.3
"	63.5 - 68.5	111 - 120	19.7
Pregnant Electrolyte - Circuit	13	21	65.2
"	25	42	54.8
"	37	63	65.5
"	49	84	63.2
"	68	105	56.5

*Aqueous Feed: 2.0 gpl copper, 4.0 gpl sulfuric acid,

0.05 gpl iron

Organic Feed: 12% V/V LIX 64N in ESCAID 100 containing

0.25 gpl copper

Temperature: 25°C

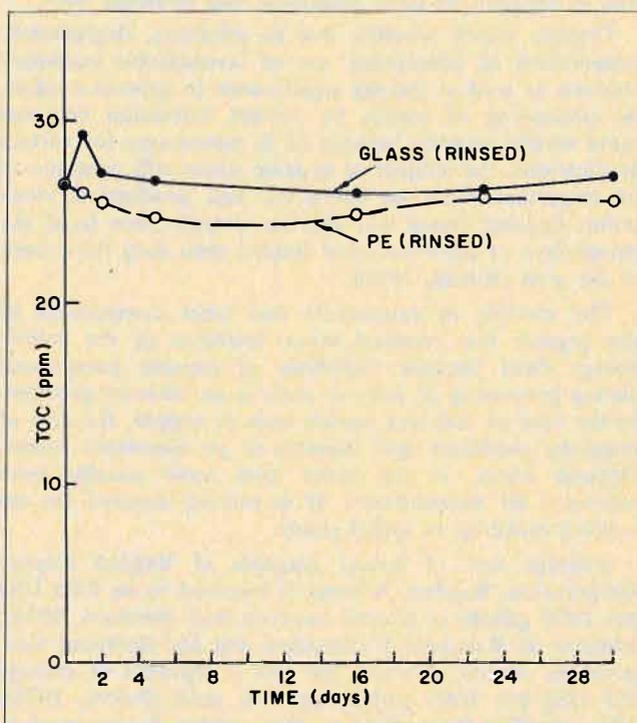


FIGURE 3. Adsorption of LIX 64N Simulated raffinate on glass and polyethylene containers.

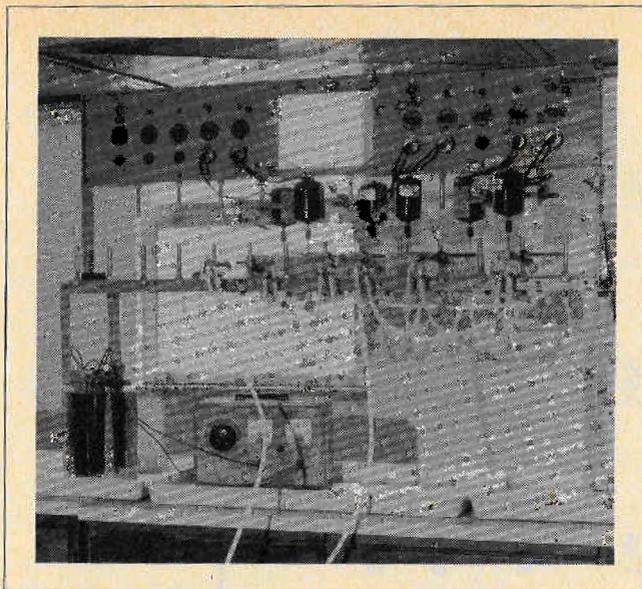


FIGURE 4. LIX 64N-Copper circuit.

aqueous-soluble organic components present in fresh organic which are rapidly removed by wash-out. Raffinate soluble organic loss at the end of the run represents only 13 to 17% of the total organic loss reported by Ranchers Exploration and Development Corporation for their Bluebird operation.

2. Organic levels in the electrowinning electrolyte were constant throughout the run at between 55 and 66 ppm total organic carbon. These higher levels of organic in the electrolyte compared to the raffinate (a factor of three) are probably related to both the high ionic strength and copper tenor in the pregnant electrolyte.

Towards the end of the study raffinate samples were received from Cyprus Bagdad Copper Company, Bagdad, Arizona and Ranchers Exploration and Development Corporation, Miami, Arizona. Tables 2 and 3 give the total organic carbon analyses of the received samples.

Soluble organic in the Ranchers samples are about twice that observed in both the laboratory and Bagdad raffinates. This higher level of organic may be due to partial solubilization of flotation agents used at Miami to remove entrained organic from raffinate. The complications posed by the presence of foreign organics in the Ranchers sample necessitated termination of our study of these samples.

Organic in the Bagdad raffinate compared favourably with those produced in the laboratory mixer-settler circuit. Total organic carbon in these samples varied between 16 and 24 ppm. The raffinates were examined by thin layer chromatography (TLC) and gas chromatography (GC) in an attempt to characterize the organic components contributing to soluble loss.

By TLC neither LIX 65N nor LIX 63 were detected with the copper chloride spray usually used for oximes. Figures 5-1 and 5-2 show results with molybdophosphoric acid and dinitrophenylhydrazine sprays. Only a trace of LIX 65N was detected in the raffinate. There were considerable quantities of unidentified materials, obviously strongly reducing compounds. These reducing compounds are unlikely to arise from the diluent, although it also contains some reducing material. The zone near the solvent front contains a mixture of several compounds, one of which is trace amount of ketone as well as other polar carbonyl compounds. This observation does not imply that ketone is a minor product of LIX 65N de-

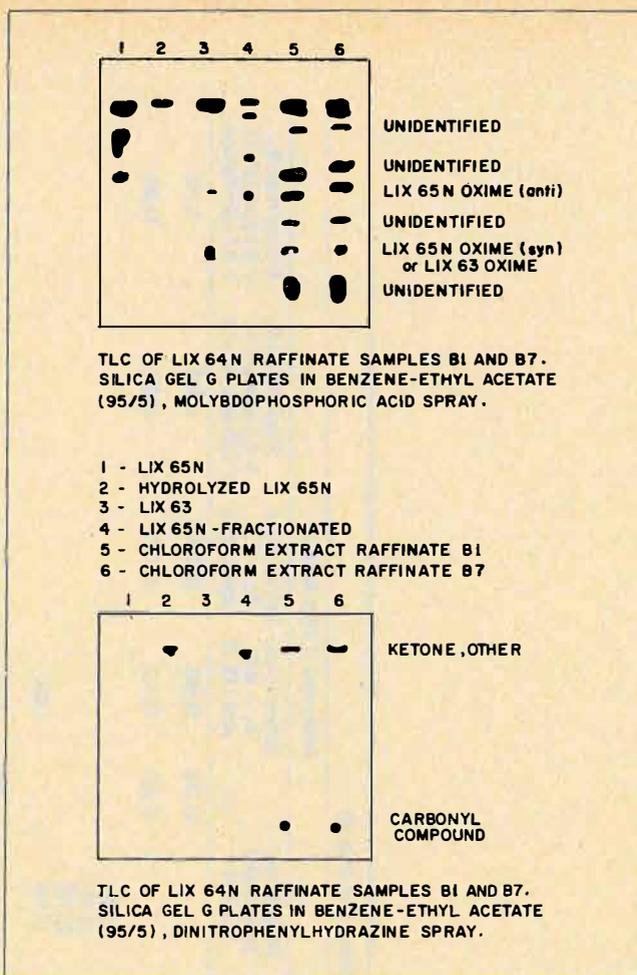


FIGURE 5. Thin layer chromatograms of Bagdad raffinates.

TABLE 2. TOC of Bagdad Raffinate Samples in Polyethylene Containers

Bagdad Sample No.	Date Sampled	TOC (ppm)	Circuit Changes
B1	12/12/75	16.0	None
B2	12/19/75	17.7	none
B3	12/26/75	14.0	None
B4	1/2/76	12.4	none
B5	1/9/76	19.9	none
B6	1/20/76	18.7	100 gpm drop in flow
B7	1/23/76	18.2	none
B8	1/30/76	18.4	none
B9	2/6/76	20.2	raining
B10	2/17/76	24.3	none
B11	2/23/76	18.0	none
B12	2/27/76	24.2	none

TABLE 3. TOC of Ranchers Raffinate Samples

Ranchers Sample No.	Date Sampled	Container	TOC (ppm)*	TOC (ppm)**	Circuit changes
R8	1/15/76	Polyethylene	38.2	36.7	none
R9	1/21/76	Polyethylene	32.7	33.8	yes
R10	1/29/76	Polyethylene	40.0	37.0	yes
		Glass	38.7	34.2	yes
R11	2/4/76	Polyethylene	35.5	42.2	yes
		Glass	35.3	43.6	yes

*Filtered on Whatman no. 42 paper **Not filtered

TABLE 4. GC of Chloroform Extracts of Bagdad Raffinate

Retention Time (sec)	Peak Area (Integrator Output)										
	Raffinates (1 litre Basis)										
	LIX 65N Anti Oxine 5.35 mg/5.0 ml	Commercial LIX 65N (40 UG Injection)	LIX 65N Ketone Product 6.65 mg/25ml	B ₁₀	B5 + 1 mg Commercial LIX 65N	B4 + 10 mg Commercial LIX 65N	B ₃	Extract from B ₃ + 0.03 ppm LIX 63	Extract from B ₃ + 0.1 ppm LIX 63	Extract from B ₃ + 0.1 ppm LIX 63 + 0.05 ppm Ketone	Extract from B ₃ + 0.1 ppm LIX 63 + 0.1 ppm Ketone
40		55,894		16,702			11,204	10,563	10,739	8,644	8,744
45		113,061									
52		241,952		157,621	15,579		47,425	48,727	42,203	40,577	41,365
kerosene)											
59		146,215			5,244						
69		138,053			7,724						
82		43,497									
100		29,971									
129											
194											
279	5,102	4,537			1,530	2,627	1,344	1,261			
428 (LIX 63)									2,364	2,039	2,026
469					1,077						
516				5,982							
645											
722 (unidentified)				32,583							
750			22,577								2,483
770			22,465								
789			14,720								
840	5,174	27,378			2,668	27,070	2,476		2,002		1,795
856	5,098	10,105				20,245					
800-946 (LIX 65N)	112,929	171,001		11,610	21,177	62,017	2,779	2,265	2,236	1,931	1,845
998								1,099			
1068				7,401	1,065						
1314											
TOC (ppm) in straight raffinate				24.3	19.9	12.4	14.0	14.0	14.0	14.0	14.0

composition. It may accumulate in the organic phase or it may be further decomposed. Some of the major unidentified by-products in the raffinate appear similar to unidentified by-products in commercial LIX 63 (Figure 6). Therefore LIX 63 decomposition may contribute significantly to the mixture of organic compounds in the raffinate.

Gas chromatography was used in an attempt to quantify identified organic constituents in Bagdad raffinate. Some success was achieved with analysis of chloroform extracts of the raffinate. GC was on 3% OV-1 on Chromosorb WAW-DMCS, 80/100 mesh. Temperature conditions were initial 150°C (1 min), increase 8°/min, final 250°C (10 min). Table 4 shows retention times and peak areas for treated B₃, B₄, B₅ and B₁₀ raffinates. Also in this table are data for some of the reference materials.

Analysis of these data indicates that raffinates from the Bagdad plant contain up to 5 ppm diluent, less than 0.1 ppm LIX 63, less than 0.1 ppm ketone and between 0.1 to 0.5 LIX 65N. Unidentified organic constituents in the raffinate, presumably decomposition products of either the reagent and/or diluent, account for the remaining 8 to 10 ppm organic.

In summary,

1. Soluble organic in pregnant electrolyte is about three times the level found in raffinate.
2. Soluble organic losses in plant operations are only a small percentage of total organic losses.
3. Commercial raffinates from Bagdad contain less than 0.1 ppm LIX 63, between 0.1 and 0.5 ppm LIX 65N, less than 0.1 ppm ketone and up to 5 ppm diluent. These values account for 9% of the average loss experienced in the plant.
4. Bagdad raffinates contain decomposition products of LIX 65N. These decomposition products include ketone along with small amounts of several other phenolic, reducing and carbonyl compounds.

LIX 64N Decomposition

Statistically designed experiments were carried out to evaluate the effects of temperature, acid concentration, phase ratio, aqueous copper concentration and contact time on the decomposition of syn and anti isomers of LIX 65N and LIX 63 in 12% v/v LIX 64N in Escaid 100. Statistical techniques of data analysis with various experimental strategies are useful in process investigation. In order to gain an insight into the decomposition of LIX 64N, the simplest model form was chosen. The linear model describing decomposition in terms of the variables or factors, such as A/O or temperature, is given below:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_4x_4 + \beta_5x_5 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{14}x_1x_4 + \beta_{15}x_1x_5 + \beta_{23}x_2x_3 + \beta_{24}x_2x_4 + \beta_{25}x_2x_5 + \beta_{34}x_3x_4 + \beta_{35}x_3x_5 + \beta_{45}x_4x_5 + e$$

$$y = \% \text{ decomposition of LIX 65N or LIX 63}$$

β 's = parameters to be determined

x_1 = acidity

x_2 = temperature

x_3 = aqueous copper concentration

x_4 = phase ratio (A/O)

x_5 = time

e = residual term representing the difference between the measured response value y and the response value predicted by the fitted model (adequacy of fit).

$\beta_{12}x_1x_2$ = interaction term describing effect of acidity plus temperature on decomposition

In this model, interactions involving more than two factors are neglected as they are rarely found in practical examples (Davies, 1954).

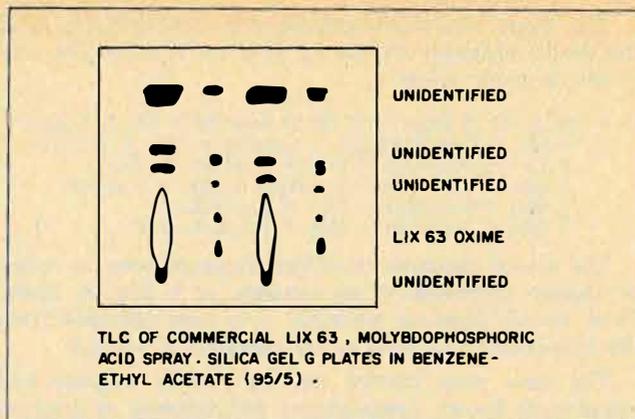


FIGURE 6. Thin layer chromatogram of commercial LIX 63.

To evaluate both the effect of the individual variables and their combined influence on decomposition, a factorial experimental design was chosen. An economic and effective type of complete factorial design is one in which every variable has only two levels or values. The two levels (high and low) effectively define the operating range of interest for each variable.

For LIX 64N decomposition the following variable levels were chosen:

	Low level	High level
Acidity	4 gpl	60 gpl
Temperature	28°C	60°C
Aqueous Copper	2 gpl	60 gpl
A/O	0.3	3
Time	5 days	15 days

The levels for acidity, aqueous copper and phase ratio were chosen as typical of loading and stripping operations in an "LIX" circuit. The levels of temperature were chosen as typical of dump leach and pressure leach liquor applications.

To facilitate interpretation of the results the variables were coded in the following manner:

$$\text{Low temperature (coded)} = \frac{28 - 1/2(60 + 28)}{1/2(60 - 28)} = -1$$

$$\text{High temperature (coded)} = \frac{60 - 1/2(60 + 28)}{1/2(60 - 28)} = +1$$

The coded variables (high and low levels) are shown below:

	Low level	High Level
Acidity	-1	+1
Temperature	-1	+1
Aqueous Copper	-1	+1
A/O	-1	+1
Time	-1	+1

The complete 2⁵ design would involve 32 tests to completely describe decomposition in terms of the five variables chosen. To economize on time and since interactions of order higher than two may (if warranted) be neglected, a half-factorial design was chosen. The runs chosen were those runs for which the interaction $x_1 x_2 x_3 x_4 x_5$ has a value of +1. The complementary 1/2 fraction would be where $x_1 x_2 x_3 x_4 x_5$ had a value of -1.

Cutting down on the number of tests results in a loss of information inasmuch as now all single factor effects include the four factor interaction, all two factor interactions include three factor coefficients, and no information can be obtained on the interaction of all five factors.

The model described previously is a simplification of the model obtained for the 1/2 fraction chosen. The true model is given below:

$$y = \beta_0 + (\beta_1 + \beta_{2345})x_1 + (\beta_2 + \beta_{1345})x_2 + (\beta_3 + \beta_{1245})x_3 + (\beta_4 + \beta_{1235})x_4 + (\beta_5 + \beta_{1234})x_5 + (\beta_{12} + \beta_{345})x_1x_2 + (\beta_{13} + \beta_{245})x_1x_3 + (\beta_{14} + \beta_{235})x_1x_4 + (\beta_{15} + \beta_{234})x_1x_5 + (\beta_{23} + \beta_{145})x_2x_3 + (\beta_{24} + \beta_{135})x_2x_4 + (\beta_{25} + \beta_{134})x_2x_5 + (\beta_{34} + \beta_{125})x_3x_4 + (\beta_{35} + \beta_{124})x_3x_5 + (\beta_{45} + \beta_{123})x_4x_5 + e$$

The above equation describes decomposition in terms of sixteen unknowns if an estimate of e can be made. Since sixteen separate estimates of y were obtained from the experiments, solution of the equation is possible.

The tests were carried out by placing organic and aqueous of known compositions and volumes in pressure bottles. The sealed bottles then were placed in an Eberbach shaking bath at controlled temperature. After agitation at temperature for the selected time the samples were removed, quenched in cold water and the phases separated.

To remove entrainment the aqueous was filtered through Whatman #42 filter paper and the organic filtered through IPS phase separating paper.

TABLE 5. Variables for Samples in Statistical Test with LIX 64N

Test No.	X ₁ Acidity H ₂ SO ₄ g/l	X ₂ Temp. °C	X ₃ Aqueous Cu g/l	X ₄ Phase Ratio A/O	X ₅ Time days
1	4	28°	2	0.3	15
2	160	28°	2	0.3	5
3	4	60°	2	0.3	5
4	160	60°	2	0.3	15
5	4	28°	60	0.3	5
6	160	28°	60	0.3	15
7	4	60°	60	0.3	15
8	160	60°	60	0.3	5
9	4	28°	2	3.0	5
10	160	28°	2	3.0	15
11	4	60°	2	3.0	15
12	160	60°	2	3.0	5
13	4	28°	60	3.0	15
14	160	28°	60	3.0	5
15	4	60°	60	3.0	5
16	160	60°	60	3.0	15

TABLE 6. HPLC Analysis of LIX 65N in LIX 64N Statistical Test

Test No.	Concentration of Organic Compounds Relative to Starting Organic*	
	Anti	Syn
Starting Organic	100.00	100.00
12% LIX 64N in Escaid 100		
1	94.85	96.86
2	100.22	102.64
3	98.65	70.10
4	90.50	113.0
5	99.69	114.79
6	96.38	130.87
7	103.63	0
8	97.81	76.46
9	96.49	100.78
10	91.23	108.37
11	103.48	26.02
12	89.03	87.53
13	104.50	0
14	95.44	112.61
15	97.04	64.50
16	91.18	80.32

*All organics were stripped with sulfuric acid before analysis.

The tests conditions are given in Table 5, and the raw analytical data in Tables 6 and 7. Only analyses on acid washed organics were used as the presence of copper in the organic gave inconsistent analyses.

Analysis of the data for both the syn and anti isomers of LIX 65N, LIX 63 and in-batch variance (Davies, 1954) gave the following reduced uncoded equations which can be used to predict the experimental variable levels studied.

LIX 65N - Anti Isomer

$$(1) \text{ Final Anti Isomer (\% of original)} = 88.31 + 3.26 \text{ A/O} + 0.73 \text{ Time} + 0.091 \text{ Temp.} + 0.079 \text{ Acid} - 0.22 \text{ A/O} \cdot \text{Time} - 0.046 \text{ Cu} - 0.014 \text{ Acid} \cdot \text{A/O} - 0.0045 \text{ Acid} \cdot \text{Time} - 0.0011 \text{ Acid} \cdot \text{Temp.}$$

The coefficients associated with acidity and the interaction term acidity * time are significant at less than the 0.01 level. Those associated with aqueous copper concentration and the interaction terms acidity * temperature, acidity * phase ratio and phase ratio * time are significant between the 0.01 and 0.05 levels.

The reduced equation accounts for 93% of the total variation in the model. The eliminated terms account for the remaining 7% of the variation.

LIX 65N - Syn Isomer

$$(2) \text{ Final Syn Isomer (\% of original)} = 104.68 + 9.61 \text{ Cu} + 0.045 \text{ Acid} \cdot \text{Time} - 3.98 \text{ Time} - 0.91 \text{ Temp.} - 0.18 \text{ Acid} - 0.061 \text{ Cu} \cdot \text{Time}$$

The significance levels for the terms in the reduced equation are given below:

Coefficient	Significance Levels
Acidity	<0.01
Temperature	<0.01
Acidity · Time	<0.01
Time	0.01 — 0.05
Copper · Time	0.01 — 0.05

The above equation does not adequately describe the final syn isomer concentration under the conditions studied. Of the total variation only 84% is accounted for by the terms in the reduced equation.

LIX 63

$$(3) \text{ Final LIX 63 (\% of original)} = 13.11 + 28.49 \text{ A/O} + 2.52 \text{ Time} + 1.28 \text{ Temp.} + 0.30 \text{ Acid} + 0.18 \text{ Cu} + 0.012 \text{ Acid} \cdot \text{Time} - 0.64 \text{ A/O} \cdot \text{Time} - 0.43 \text{ Temp.} \cdot \text{A/O} - 0.055 \text{ Temp.} \cdot \text{Time} - 0.041 \text{ Acid} \cdot \text{A/O} - 0.0049 \text{ Acid} \cdot \text{Temp.} - 0.0021 \text{ Acid} \cdot \text{Cu}$$

Again the significance levels of the terms in the equation are given below:

Coefficients	Significance Levels
Temperature	<0.01
Temperature · A/O	<0.01
Acidity · Temperature	<0.01
Acidity	0.01 — 0.05
Acidity · Aqueous Copper	0.01 — 0.05
Acidity · A/O	0.01 — 0.05
Acidity · Time	0.01 — 0.05
Temperature · Time	0.01 — 0.05
A/O · Time	0.01 — 0.05

The above equation is quite complicated but further elimination of terms was not statistically possible. Of the total variation in the unreduced model the reduced equation above accounted for 97%.

To test the adequacy of fit, two of the original experiments were repeated months after the initial design was completed. The organic was analyzed as before and the data compared with the concentrations of the three components as predicted by equations (1), (2) and (3). The

TABLE 7. GC Analysis of LIX 63 in LIX 64N

— Statistical Test —

Test No.	LIX 63 Concentration Relative to Starting Organic LIX 63*
Starting Organic 12% LIX 64N in Escaid 100	100.0
1	70.1
2	95.3
3	89.2
4	104.2
5	69.7
6	101.7
7	81.1
8	86.1
9	98.5
10	121.2
11	61.1
12	79.1
13	89.8
14	101.5
15	97.5
16	52.4

*All organics were stripped with sulfuric acid before analysis.

results presented in Table 8 show inherent variation in measured responses. Whether this is due to experimental error or analytical difficulties is uncertain at this time. Even accounting for this uncertainty the data show that the reduced equations developed adequately predict concentrations of anti LIX 65N and LIX 63. An adequate prediction of syn LIX 65N was not obtained.

Losses of reagent under typical dump leach operations were inferred from experimental data generated in runs 8 and 9 of the statistical design. Using the equations generated, predictions were made for total LIX 65N and LIX 63 concentrations under loading and stripping conditions. The results, given in Figure 7, indicate that substantially more of the active reagent is lost from the circuit during stripping than in loading. On a percentage basis this increased loss (presumably due to decomposition) is greater for the LIX 63 component than for LIX 65N. These results are in agreement with reported decomposition under conditions of high temperature and acid concentration as typified by stripping (Sudderth, 1975).

In review,

1. Complex equations have been developed to predict loss of anti and syn LIX 65N and LIX 63
2. The equation for syn LIX 65N loss is inadequate
3. LIX 65N and LIX 63 decomposition is substantially greater under stripping conditions than under loading conditions.

Evaporation Studies

The loss of organic through evaporation represents not only an economic debit for a solvent extraction plant but it may also constitute a safety hazard in terms of potential ignition of fumes. More important, evaporative losses represent a potential health hazard for operating personnel who are breathing organic fumes daily. In addition, the organics being petroleum-based represent an energy debit to the system when lost.

What little information is available on losses due to evaporation has been qualitative in nature. Holmes reporting on the Nchanga solvent extraction plant stated that "diluent losses by evaporation have been larger than expected" (Holmes, 1976).

In this section, quantitative evaporation data are presented for 12% v/v LIX 64N in Escaid 100 over the

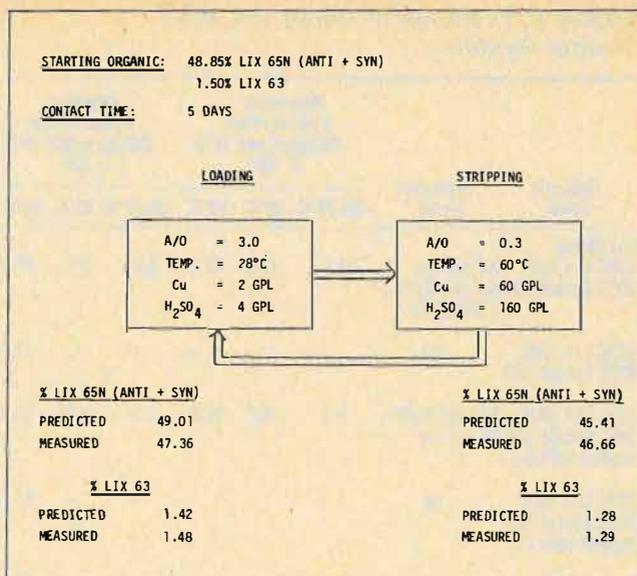


FIGURE 7. Predicted losses of reagents under process conditions.

Table 8. Test of Statistical Models

Conditions	Run Number			
	3	3 Repeat	16	16 Repeat
Organic Phase initial: 12% LIX 64N in Escaid 100 (Acid Washed)				
Acid (H ₂ SO ₄) (gpl)	4	4	160	160
Aqueous Copper (gpl)	2	2	60	60
Phase Ratio (A/O)	0.3	0.3	3.0	3.0
Temperature (°C)	60	60	60	60
Time (Days)	5	15	15	15
Results	% of Original Component			
Anti LIX 65N				
Measured	98.65	100.15	91.18	85.08
Predicted		98.89		86.43
Syn LIX 65N				
Measured	70.10	85.71	80.32	75.40
Predicted		66.97		87.28
LIX 63				
Measured	89.20	97.20	52.40	65.70
Predicted		86.40		58.20

temperature range 20 to 55°C. Tests were carried out simulating loading and stripping conditions for both the mixer and settler components of a solvent extraction stage. For comparative purposes data were obtained on organic evaporation in the absence of aqueous phase and also for Escaid 100 alone. Stagnant air flow conditions were assumed throughout the test. The results are given in Table 9 and trends and observations for the data are given below:

1. Evaporation of organic increases with increasing temperature.
2. The organic evaporation rate is greater in the loading stages than in stripping and in the mixer when compared to the settler.
3. Aqueous/organic dispersion substantially retards organic evaporation rate.

The practical consequences of organic evaporation have been calculated in terms of economic and energy considerations for a Bagdad-sized solvent extraction plant as given in Table 10. Assuming 24 hours per day operation,

**TABLE 9. Evaporation Rates LIX 64N/
Copper System**

Organic Feed	Aqueous Feed	Aqueous Evaporation (USgpm per ft ²) × 10 ⁵			Organic Evaporation (USgpm per ft ²) × 10 ⁶		
		20-22°C	35°C	55°C	20-22°C	35°C	55°C
(A) Mixer							
12% LIX 64N 88% Escaid 100	2.0 gpl Cu 4.0 gpl H ₂ SO ₄ 0.05 gpl Fe	11.7	21.5	42.0	1.8	2.6	22.4
12% LIX 64N 88% Escaid 100	nil	—	—	—	—	—	31.2
12% LIX 64N 88% Escaid 100	150 gpl H ₂ SO ₄ 28 gpl Cu loaded with Cu	9.6	18.6	26.8	1.5	3.9	18.8
12% LIX 64N 88% Escaid 100 loaded with Cu	nil	—	—	—	—	—	27.1
Escaid 100	nil	—	—	—	—	—	19.7
(B) Settler							
12% LIX 64N 88% Escaid 100	2.0 gpl Cu 4.0 gpl H ₂ SO ₄ 0.05 gpl Fe	0.04	0.1	0.62	0.07	1.0	3.5
12% LIX 64N 88% Escaid 100	150 gpl H ₂ SO ₄ 28 gpl Cu loaded with Cu	0.05	0.1	0.25	0.06	0.9	4.1
Escaid 100	nil	—	—	—	0.1	—	8.0
LIX 64N	nil	—	—	—	0.1	—	—

300 days per year, open mixer-settlers and stagnant air flow total organic lost through evaporation varied from a low of 4696 US gallons per year at 22°C to a high of 166,172 US gallons per year at 55°C (Table 11). These losses represent a net cost in terms of cents per lb copper produced of between 0.15 and 5.10 and in terms of energy loss of 699 and 24,568 million Btu per year at the two respective temperatures (Table 12).

These losses may appear to be insignificant. If expressed in terms of soluble loss to the raffinate they represent 18 ppm at 22°C or almost 4 times the diluent found in Bagdad raffinate.

Summarizing,

1. Organic evaporation rate increases with increasing temperature.
2. The presence of aqueous/organic dispersion in the mixer substantially reduces organic evaporation rates in comparison with rates obtained with no aqueous present.
3. Settler evaporation rates are substantially lower than organic evaporation rates in the mixer.

Toxicity

Very little information is available on the toxicity of solvent extraction reagents. Much of what has been experimentally determined was commissioned by General Mills Chemicals, Inc. when needed for verifying safe transport and handling. The data presented in this part of the study was kindly supplied by General Mills. The experimental work was carried out by either the Chemicals Inspection and Testing Institute, Japan or B.C. Research. The reports were reviewed by Ontario Research Foundation and competent toxicologists. Below is a review of the data.

The reagents, LIX 65N and LIX 63, are non-biodegradable, with BOD's of 1.08% and -2.72%, respectively. The oximes have been shown to inhibit normal bacterial growth in agreement with other reported work on the inhibition of bacterial leaching activity of Thiobacillus ferrooxidans (Torma, 1976). These tests were carried out by Chemicals Inspection and Testing Institute, Japan, using biologically active sludge inoculated with pure reagents, then incubated.

TABLE 10. Circuit

Extraction:	
SX Feed	— 1.5 gpl Cu 600 USgpm
No. of Stages	— 4
Organic Feed	— 12% LIX 64N 88% Escaid 100 650 USgpm
Organic recycle	— Nil
Mixer retention time	— 2.5 minutes
Settler Area	— 10 ft ² per USgpm of total flow into the settler
Mixer	— 8 ft diameter × 10 ft high
Settler	— 20 ft × 60 ft × 4 ft deep
Stripping:	
No. of Stages	— 3
Strip Liquor	— 28 gpl Cu 128 USgpm
Aqueous Recycle	— 522 USgpm
Mixer Retention Time	— 2.5 minutes
Settler area	— 0.92 ft ² per USgpm of total Flow into the Settler
Mixer	— 7 ft diameter x 10 ft high
Settler	— 20 ft × 60 ft × 4 ft deep

TABLE 11. Total Organic Evaporation

	(US gallons per year)*		
	22°C	35°C	55°C
Mixers			
Loading	1,564	2,258	19,456
Stripping	748	1,945	9,377
Settlers			
Loading	1,451	20,736	72,576
Stripping	933	13,997	63,763

*24 hours per day, 300 days per year open System, Stagnant Air Flow

**TABLE 12. Economic and Energy Considerations
of Escaid 100 Evaporation**

Temperature	\$/year	c/lb Cu	Million Btu/year
22°C	4,696	0.15	699
35°C	38,936	1.20	5,794
55°C	165,172	5.10	24,578

ESCAID 100; \$1.00 per US gallon; 18,600 Btu per lb

Median tolerance limits for the pure reagents, given in Table 13, show that LIX 63 is more toxic than LIX 65N. TLM₄₈ for Red Medaka was 2.7 ppm (LIX 65N) and 1.7 ppm (LIX 63). Median tolerance limits for the diluted reagent using juvenile Coho salmon as the test species (Table 14) compare favourably with the results reported above. The concentrations of the reagents used in these studies are up to an order of magnitude larger than the soluble losses observed in our study. Therefore one may question the true meaning of the results.

Bioaccumulation data given in Table 15 is interpreted to indicate that the reagents do not accumulate in carp to any large extent.

From the data presented above the following conclusions can be drawn:

1. LIX 64N is toxic to moderately toxic.
2. Bioaccumulation is not strikingly high.
3. Cumulative toxicity is a possible question as slow biodegradation rates are observed.
4. Data of use only in providing criteria for safe transport and handling measures.

Summary and Conclusions

1. The LIX 64N reagent system is complex.
2. Very little of the reagent, be it the LIX 65N component or LIX 63 component, is lost through solubility during the processing of copper dump leach liquors.
3. Of the total soluble organic found in plant raffinate, in excess of 50% is unidentified and is considered to be decomposition product of the reagent and/or diluent.
4. Decomposition of reagent can be expected to be more pronounced in stripping compared to loading.
5. LIX 63 decomposition occurs at a substantially faster rate than LIX 65N.
6. Evaporation is to be designed for, especially in the Canadian environment where the work place is enclosed and solvent extraction for copper will be used to treat hot pressure leach liquors.
7. The toxicity data apparently generated to date, should not be used by Government regulatory agencies except where criteria are needed for transport and handling.
8. From an environmental control point of view the decomposition products observed in plant raffinates have to be identified if any useful toxicity data are to be generated.

Acknowledgments

The authors wish to acknowledge the support of the Canadian Federal Government who funded the majority of this study; the Ontario Provincial Government whose initial funding started the project; Ranchers Exploration and Development Corporation and Cyprus Bagdad Copper Corporation who both kindly provided useful data on plant operation and organic losses as well as engaging with us in a sampling program stretching over several months; General Mills Chemicals Incorporated who kindly provided all the toxicity data; and finally Mrs. Bridget Licht and Mr. Warren Reishus who carried out the testwork at Ontario Research Foundation.

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TABLE 13. Median Tolerance Limits. 100% LIX 65N (A); 100% LIX 63 (B)

Test Conditions:				
Fish	: Red Medaka, 10 fish/treatment (0.3 g/fish)			
Volume	: 4 litres			
Temperature	: 25 ± 2°C			
Reagent	Test Concentration (ppm)	% Survival 48 hr	TLM ₄₈ ppm	
LIX 65N	4.2	20	2.7	
	2.4	60		
	1.4	100		
LIX 63	4.2	20	1.7	
	2.4	60		
	1.4	100		

Tests carried out by Chemicals Inspection and Testing Institute, Japan

TABLE 14. Median Tolerance Limits 10% v/v LIX 64N in Napoleum 470

Test Conditions:						
Fish	: Juvenile Coho Salmon, 10 fish/treatment (0.3 g/fish)					
Volume	: 3 litres					
Temperature	: 11 ± 1°C					
Dissolved Oxygen	: > 8 mg/l					
Test Concentration* (% V/V LIX 64N)	% Survival			Remarks	TLM ₉₆	
	24 hr	48 hr	96 hr		% (V/V)	ppm (UL/L)
1.0	0	0	0	<12 hr		
0.1	0	0	0	<12 hr		
0.035	40	0	0		0.024	240
0.030	80	50	0			
0.025	90	70	40			
0.020	90	90	90			
0.010	100	100	100			
Control	100	100	100			

*All solutions were stirred vigorously for 1 min prior to addition of test fish. Tests carried out by BC Research

TABLE 15. Bioaccumulation Studies

Test Conditions:					
Fish	: Carp, about 30 g weight, 11 cm length				
Volume	: 100 litres, water flow 576 l/day				
Temperature	: 25 ± 2°C				
Concentration	Magnification Factor (Relative to Oxime in Water)				
	2 wk	4 wk	6 wk	8 wk	
2 ppb LIX 65N-100	<400	<425	<425	<500	
20 ppb LIX 65N-100	<40	130	110	160	
1.5 ppb LIX 63-100	0.7	3.7	3.2	5.5	
15 ppb LIX 63-100	1.8	4.1	4.6	5.4	

Tests carried out by Chemicals Inspection and Testing Institute, Japan

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DISCUSSION

T.K. Mattila: Can you give any general distribution percentage between solubility, entrainment, evaporation and degradation solvent losses, which would be valid for all solvent extraction processes of similar type?

I.J. Itzkovitch: What you ask is impossible. The data we reported on solubility for 12% LIX 64N in Chevron IX solvent could possibly be extrapolated for all similar dump leach operations if all operating conditions are identical. The other factors you mentioned that contribute to solvent loss would be dependent on plant design and operation. As we have indicated, Ranchers Exploration and Development Corporation has quoted loss of reagent of 0.2 USg per 1000 gallons of aqueous feed treated, whereas at Bagdad, losses are only 0.06 USg per 1000. A perfectly designed and operated plant would give reagent loss significantly less than the Bagdad figure — probably 0.02 to 0.03 USg per 1000.

G.A. Kordosky: Were measurements for total carbon made on the SX feed solution, i.e. did you do any organic extraction experiments on the feed with chloroform? Can some of the decomposition products, which are at present unidentified, be derived from the kerosene?

I.J. Itzkovitch: The SX feed solution at Bagdad is recycled raffinate through the dumps therefore chloroform extraction on the feed may only indicate if organic is being absorbed on the clay materials in the dump.

We are not in a position to say if the unidentified products in raffinate come from the kerosene or reagent. We do know from our statistical study that the components of LIX 64N do decompose. Presumably decomposition of the diluent is also occurring.

R.J. Whewell: Our work in Bradford, presented as paper 4a of ISEC '77, shows that the aqueous solubility of LIX 63 is greater than that of LIX 65N. Other work which we hope to publish shortly demonstrates, among other things, a high rate of degradation of LIX 63 in the presence of sulphonic acid by comparison with that of LIX 65N.

I.J. Itzkovitch: With regards to your first comment on solubility of LIX 63 compared to LIX 65N, we would agree with you. The aliphatic nature of LIX 63 compared to the aromaticity of LIX 65N would in general give increased solubility in aqueous solutions. The reason for the much lower concentration of LIX 63 compared to LIX 65N in Bagdad raffinates is related to their relative concentrations in the feed organic. Analysis of

feed organic showed the ratio LIX 65N to LIX 63 in LIX 64N to be about 36 to 1.

Your second comment on the rate of degradation of LIX 63 in sulphuric acid is in partial agreement with the data we presented on decomposition studies and previously reported data by General Mills (Sudderth, 1975). Under conditions of high acidity and high temperature a loss of 15% of the LIX 63 component of LIX 64N was measured compared to 1% under loading conditions. This compares to only a 4% loss in the LIX 65N component under the conditions of high acidity and temperature. Whether this increased degradation of LIX 63 compared to LIX 65N is due solely to acidity or to acidity and temperature is not known at this time.

G.T. Mejdell: Relating to the factorial experiment on solvent degradation: would you not expect the rate of degradation to be more proportional to the interfacial areas rather than to the organic/aqueous ratios? The reported limits of O/A-3.0 and 0.3 should thus be expected to give rather similar interface areas.

I.J. Itzkovitch: You are absolutely correct. Rate of degradation should be more proportional to the interfacial areas than phase ratio. What we have attempted to do is assess typical plant loading and stripping conditions and determine what parameters can be used to predict decomposition. For the anti isomers of both LIX 65N and LIX 63, the term phase ratio must be retained in the equation developed to calculate final concentrations. This is not to be interpreted that phase ratio has a significant role in decomposition. A simpler model should be developed to gain a true insight into the chemistry of decomposition.

R.H. Edwards: What methods were used for measuring evaporation losses?

Were measurements made of losses from pipe joints and from pump glands?

I.J. Itzkovitch: Evaporation losses were measured by volume changes over the length of time required to complete the experiment. Final volumes were corrected for changes due to loading of copper into the organic; i.e., all evaporation rates are referred back to original (untreated) organic.

No, we did not measure these losses. In a plant situation the losses you refer to are probably the major contributing factor to solvent loss. To simulate these factors on a laboratory scale is an impossible task. Results obtained in the laboratory would be meaningless as they would vary from plant to plant depending on general housekeeping, design and age of the plant, etc.

G.M. Ritcey: What was the mixer design and would you consider the design a factor in evaporation rate? Does rpm have an effect?

What was the effect of the dispersed phase on the evaporation rate?

I.J. Itzkovitch: The mixer design chosen was common to that used in copper solvent extraction plants. The mixer was a cylinder having a height to diameter ratio of 1.25. A pump-mix impeller was used. Agitation was sufficient to create good dispersion. Agitation rate (rpm) was not observed to have an effect on evaporation rate.

We did not investigate the effect of dispersed phase on evaporation. In all our tests the dispersed phase was aqueous.

The Applicability of Solvent Extraction to Waste Water Treatment

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ABSTRACT

Solvent extraction has not found general acceptance as a treatment process for removing and recovering contaminants from waste waters. The few installations are in the coal/coke processing industries for phenol removal. The main impediments to implementation are believed to be the economic and contamination problems due to solvent loss, and the failure to remove a substantial fraction of the compounds present in waste water (the most attractive feature of biological oxidation processes). The thermodynamic basis of solvent selection and the correlation of solvent-solute system properties are discussed. Recent developments in process configurations are described, particularly the use of a dual solvent system in which a polar solvent extracts the solute and the dissolved polar solvent is extracted by a volatile hydrocarbon solvent which can be recovered from the water effluent by stripping. Some current investigations and applications of solvent extraction and its economic feasibility are briefly reviewed. It is concluded that the principal applications may lie in processing streams containing 1% or more of saleable organic materials and in treatment of toxic effluents from the coal, hydrocarbon, and chlorinated hydrocarbon processing industries.

Introduction

DESPITE A NUMBER OF FAVOURABLE FEATURES, solvent extraction has not gained general acceptance as a process for removing and recovering contaminants from waste waters. The few installations are in the coal and coke processing industries for phenol removal. The purposes of this paper are to examine the current state of knowledge regarding the application of solvent extraction to waste water treatment, to identify the impediments to more widespread adoption and to speculate on future likely areas of application in the hope that the process may be evaluated for specific applications. Previous reviews have been presented by Kiezyk and Mackay⁽¹⁾, A.D. Little, Inc.⁽²⁾, Bailes et al⁽³⁾ and in a series of papers from a group at the University of California (Berkeley) directed by King and Prausnitz^(4,5,6,7).

An inherent advantage of solvent extraction is that it is a recovery rather than a destruction process, thus raising the possibility that the recovered solute may be saleable. Thus solvent extraction may be most applicable when the solute is present in high concentration, since there is a greater credit per unit volume of water treated. Interestingly, these are often the conditions under which biological degradation processes (the principal method of waste water treatment) may be inapplicable due to the toxic effect of the solute. As the concentration of the solute drops, solvent extraction is likely to become less suitable and biological treatment more attractive. The other "competitors" with solvent extraction are gas-liquid

separation processes such as stripping (which is usually favoured for volatile or gaseous solutes such as hydrogen sulphide) or solid-liquid separation processes such as adsorption or ion exchange.

Another advantage of solvent extraction is that being a physical process, it is not subject to the instabilities which occur when biological treatment systems are subjected to accidentally high concentrations of toxic solutes. It can thus play a useful role as a pre-treatment step to safeguard biological treatment systems from shock exposure to toxic solutes.

An inherent advantage of solvent extraction is that it is effective for those compounds which display a high partition coefficient into a non-aqueous phase, usually as the result of high activity coefficients (on a Raoult's Law basis) or low solubilities in the aqueous phase. Such hydrophobic compounds also tend to have high partition coefficients into the lipid phase of cell membranes where they can play a disruptive role by modifying ion transport or enzymatic processes, leading to toxic effects. These compounds may also undergo chemical conversion in the cell to compounds which have mutagenic or carcinogenic properties. Recently environmental regulatory agencies in both the United States and Canada have devoted much effort to identifying environmental contaminants which are hazardous to human health. Many of these are hydrophobic substances which are readily extracted from water, for example, hydrocarbons and chlorinated hydrocarbons. The environmental concern about compounds such as chlorinated hydrocarbons, particularly polychlorinated biphenyls (PCBs) arises from their very slow degradation rate in the environment by natural microbial and chemical processes. These compounds can thus be expected to be refractory during biological treatment and although removed from water into the biomass, they may remain unconverted and can be released after sludge disposal. Solvent extraction may thus have a role to play in the treatment of waste waters from facilities handling compounds which are highly lipophilic or hydrophobic and hazardous both as a routine treatment process and as a means of safeguarding the environment from accidental releases in waste water streams.

As world oil supplies become depleted and costs rise, increasing attention is again being paid to coal as an energy source. It is generally accepted that environmental problems place a major constraint on coal development. In addition to land disruption during strip mining, reclamation of abandoned mines, sulphur removal and treatment of airborne contaminants, there is a difficult problem associated with treatment of aqueous effluents. Many of the technologies of coal processing and even storage will result in the production of aqueous streams which contain dissolved organic materials, some of which are highly toxic and odorous and whose disposal could present major problems. The obvious examples are phenols but organic nitrogen and sulphur compounds are also present. The present technologies for handling such waste waters derive from the steel industry where relatively small quantities of effluents are produced. How-

ever, if coal again becomes a major energy source, the quantities and concentrations of toxic waste waters may increase substantially, and biotreatment processes may prove inadequate.

Finally, there is increasing environmental concern about the dispersal of toxic metals into the environment, notably mercury, lead, cadmium and chromium. It is possible that the liquid ion exchange agents may be attractive in some cases. Of particular interest are organo-metallic compounds which may not be removed during ionic metal removal processes such as ion exchange but which could be removed by partition into an organic phase.

In summary, it is suggested that two factors may make solvent extraction more attractive as a treatment and recovery process. These are the increasing environmental concern associated with hydrocarbons and chlorinated hydrocarbons and the possibility of a significant increase in coal processing leading to the production of aqueous effluents containing toxic organic compounds.

In reviewing this topic, we first examine the thermodynamic factors influencing solvent selection, since it is the availability of a suitable solvent which determines the applicability of solvent extraction to water treatment. This is followed by a discussion of possible process configurations, some specific applications and finally a brief statement of the process economics.

Thermodynamics of Solute Partition

The most convenient method of characterizing equilibrium concentrations of a solute between aqueous and solvent phases is to equate the solute fugacity f , which can be expressed in terms of the solute mole fraction x , activity coefficient γ and a reference fugacity f^R as shown below

$$f = x\gamma f^R$$

Equating the fugacities in the water (w) and solvent (s) phases, leads to a definition of the partition coefficient K

$$f_w = x_w\gamma_w f^R = f_s = x_s\gamma_s f^R$$

$$K = x_s/x_w = \gamma_w/\gamma_s$$

K is thus the ratio of the water and solvent phase activity coefficients. The water phase activity coefficient is determined by the solute, e.g. for phenol in water, γ_w is 50.4 at 25°C⁽⁶⁾. Clearly the aim must be to select a solvent in which the solute activity coefficient γ_s is as low as possible.

In the following discussion, phenol is used as an example, since considerable data exist on its partition properties⁽⁶⁾. The principles, however, apply also to other solutes. In benzene, phenol has an activity coefficient of about 4.4, giving a mole fraction partition coefficient of 11.5; in the less polar hexane, the phenol activity coefficient is 52 and K is about 1.0. Increasing the polarity of the solvent reduces the activity coefficient and in some cases such as butyl acetate this leads to association between the phenol and the solvent, giving a phenol activity coefficient of about 0.1 and a K of about 500. Unfortunately, increasing the polarity of the solvent (especially introducing hydrogen bonding groups) has the effect of increasing the solubility of the solvent in water. For example, the three solvents considered above have the appropriate solubilities: hexane 0.001 weight percent, benzene 0.18 weight percent and butyl acetate 1.2 weight percent. Clearly there is a compromise necessary between high solubility and partition coefficient and low aqueous solubility and low partition coefficient.

It should be noted that the partition coefficient expressed

here is in the form of the mole fraction ratio. Other definitions are possible, particularly the concentration ratio (g/l per g/l) or most important for industrial calculations using the mass fraction or ratio.

It is interesting and useful to correlate K or γ_s as a function of the nature of the solvent since successful correlation can be used to suggest new solvents on the basis of advantageous chemical structures, screen suggested solvents and elucidate the likely effects of variables such as temperature and the presence of other solutes on the partition coefficient. A number of theories of solution are available which provide bases for such predictions. A comprehensive review of this topic is beyond our scope here. However, a few comments are appropriate.

The activity coefficients γ_w of aromatic solutes in dilute aqueous solutions have been correlated empirically by Tsonopoulos and Prausnitz⁽⁹⁾. Such approaches are most useful when there is a number of solutes present and it is time consuming to obtain data for all solutes. There is, however, no substitute for actual experimental measurement.

The Regular Solution theory developed by Scatchard and Hildebrand has been successfully used to correlate the enthalpy of mixing and thus the excess free energy in the systems where the excess entropy is small. The key assumption is the use of a geometric mean rule for calculating the cohesive energy density of the interaction between unlike molecules. This simple assumption fails to describe the interaction between polar and nonpolar compounds. In an attempt to overcome this difficulty, Weimer and Prausnitz⁽¹⁰⁾ separated the cohesive energy density of the polar species into a nonpolar part which can be calculated from the cohesive energy density of a similar sized (homomorph) but nonpolar molecule and a polar part. Helpinstill and Van Winkle⁽¹¹⁾ extended this to include polar-polar interactions. In both cases, a term was added corresponding to the Flory-Huggins entropy of mixing to account for different molecular size. This approach has been successfully used to correlate the activity coefficients of alkane, alkene and aromatic hydrocarbons in various solvents which are potentially useful for extractive or azeotropic distillation or solvent extraction. Kezyk and Mackay⁽⁸⁾ used the same model in an attempt to correlate the activity coefficients of phenol in nonpolar and polar solvents. This approach is probably satisfactory for hydrocarbon solvents but is now regarded as misguided for application to polar solvents because it ignores the fundamental nature of such systems, which is the strong chemical interaction between phenol and the hydrogen bonding solvent which gives rise to activity coefficients of about 0.1. It seems unlikely that any solution theory based on cohesive energy-density concepts will be capable of describing adequately the properties of highly associated solutions.

A number of other solution theories have been developed in recent years which are promising as a means of correlating partition coefficient data. Notable are those of Tiepel and Gubbins⁽¹²⁾ who developed a molecular solution theory which predicts infinite dilution activity coefficients of nonpolar solutes in polar solvents quite accurately, Abrams and Prausnitz⁽¹³⁾, who developed a universal quasi-chemical equation which permits the calculation of activity coefficients in polar non-electrolyte multicomponent liquid mixtures with only two binary adjustable parameters, and the group contribution theory of Derr and Deal⁽¹⁴⁾ which has been later extended by Fredenslund et al⁽¹⁵⁾.

In solutions where there is strong interaction between the molecules, for example, phenol ester mixtures, it is probably best to use a theory of associated solutions and

postulate the formation of aggregates of polymers of similar and dissimilar molecules. This approach has been used by Abrams and Prausnitz⁽¹⁶⁾ in predicting distribution coefficients of phenols in polar and nonpolar organic solvents. These approaches are capable of explaining the variation in distribution coefficient with concentration which was observed at low solute concentrations, (Won and Prausnitz)⁽¹⁷⁾. This variation is not explainable by regular solution based theories.

Medir and Mackay⁽¹⁸⁾ investigated the partition coefficient characteristics of phenol between various solvent mixtures. They observed that most mixtures exhibited a positive deviation from linearity, although the deviations were generally small when one of the solvents was an alkane. Alcohol, aromatic hydrocarbon and alcohol, ester mixtures gave mixtures which had higher partition coefficients than either pure solvent. In qualitative terms, the picture which emerges is that phenol probably associates with alcohols in their monomer, dimer and polymer forms, and as the alcohol is diluted, the chemical association equilibrium moves towards creating enhanced concentrations of the alcohol species (probably monomers) which associate most readily with the phenol. Clearly there is a complex series of interactions which can only be described by a chemical association model.

The issue is complicated by the presence in the solution of variable amounts of water which can play a significant effect in the equilibrium. If chemical equilibrium theories can be successfully developed to describe such systems, it raises the interesting possibility that mixtures of polar solvents including alcohols, esters, ethers and aromatic and alkane hydrocarbons can be tailored to give the required distribution coefficient properties while minimizing aqueous solubility.

A considerable amount of work has been done on the extraction of phenol with various solvents in the presence of electrolytes and other organic substances such as ethylene glycol, acetone, diethylene glycol, urea and glycerol, benzophenone, camphor, borneol, dimethyl phthalate. An extensive amount of work has been reported by a series of papers by Korenman⁽¹⁹⁾ who has also interpreted the findings in terms of the formation of the molecular complexes between phenol and the various solvents. Similar approaches could be used for other compounds.

Process Configurations

A typical schematic flow sheet for a solvent extraction process is shown in Figure 1.

Solvent Extraction Stage

The solvent extraction phase is most likely to be a multistage countercurrent column with some form of internal agitation or baffling to promote greater efficiency. Since it is desirable and usually possible to obtain a solvent in which there is a high solute partition coefficient from water (for example, esters or alcohols can give partition coefficients in excess of 30 for phenol), it is common practice to operate the column under conditions such that the equilibrium line slope exceeds that of the operating line by a factor of 1.5 to 3.0⁽⁴⁾. This will result in very low solvent to water flowrate ratios. Earhart et al⁽⁴⁾ have argued that since it is difficult to operate with solvent rates less than about one-tenth that of the water rate without sacrificing good contact, it can be concluded that the most likely contacting condition is a solvent to water rate of about 0.1 and a partition coefficient of about 20. Higher coefficients produce little further gain unless the solvent rate can be reduced accordingly. It seems likely,

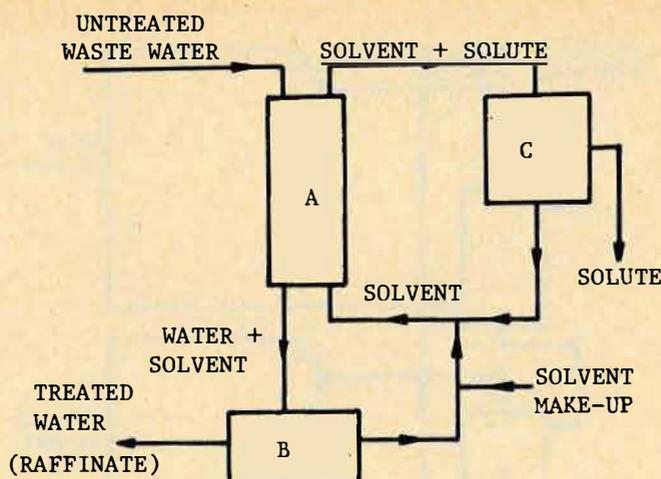


FIGURE 1. Typical solvent extraction flowsheet showing solvent extraction (A), solvent recovery (B), and solute removal (C)

however, that extractors could be designed to accommodate very low solvent to water flow rates and thus take advantage of the existence of higher partition coefficients. Under such conditions, there may be advantages to dispersing the water through a continuous solvent phase for mass transfer area reasons. The hydrodynamic design obviously requires careful consideration. It is worth noting that the mass transfer characteristics of the column are such that the major resistance to mass transfer will lie in the water phase where the solute is most dilute. Thus the contacting system should be designed to maximise turbulence in that phase.

Solvent Recovery Stage

The major disadvantage of solvent extraction is that it is usually necessary to recover the dissolved solvent from the waste water because of contamination or economic considerations. The most attractive methods of solvent recovery are a second solvent extraction or gas stripping. Gas stripping is likely to be applicable only under conditions where the solvent is highly volatile, for example, hydrocarbons in the C₄-C₆ range. The major disadvantage of gas stripping is that it can have a high energy consumption.

Unfortunately when hydrocarbons are used as solvents for oxygenated organic solutes, the partition coefficients often lie in the range 1 to 5, for example, phenol partition between benzene and water is 2.9 on a mass fraction basis⁽⁴⁾. It is thus often advantageous to use a more polar solvent in which the solute has a lower activity coefficient. Unfortunately this tends to result in a solvent with a higher aqueous solubility. An attractive and ingenious approach to solvent recovery under these conditions has been proposed by Earhart et al⁽⁴⁾ who have suggested a dual solvent system in which a second solvent is used to remove the first solvent from the water.

It is clear for example, when considering the removal of phenol from water with isobutane, benzene or n-butylacetate as solvents that isobutane is not suitable alone because it would require a solvent to water ratio of at least 0.5. Butyl acetate, with a high partition coefficient of 65, could be used in much smaller quantities. The approach is to contact the water first with butyl acetate to extract phenol and then extract the dissolved butyl acetate using isobutane. The partition coefficient of butyl acetate into isobutane is 107, thus low solvent to water

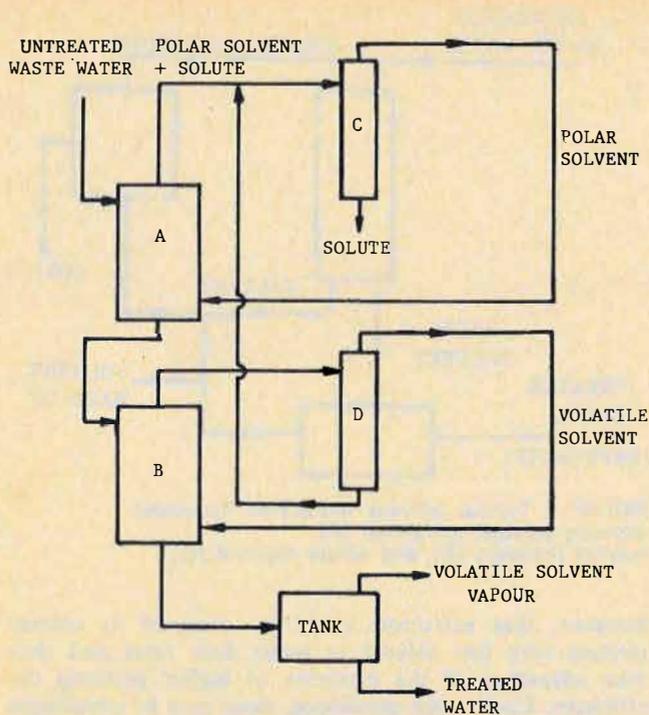


FIGURE 2. Dual solvent extraction process with separate solvent cycles (4) showing polar solvent extractor (A), volatile solvent extractor (B), polar solvent — solute splitter (C), volatile solvent — polar solvent splitter (D)

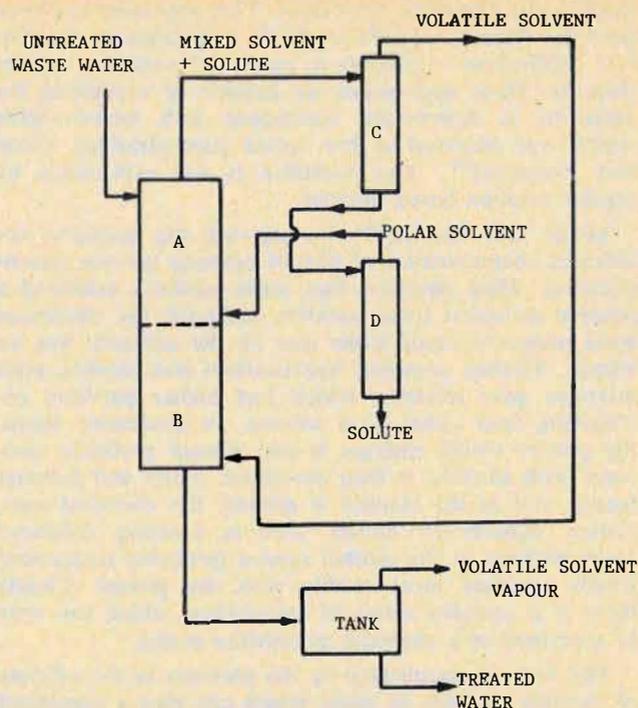


FIGURE 3. Dual solvent extraction process with separate solvent cycles (4) showing mixed solvent extractor (A), volatile solvent extractor (B), volatile solvent — polar solvent splitter (C), polar solvent — solute splitter (D)

ratios can be used for both extractions. Earhart has suggested two configurations, illustrated in Figure 2 and 3. In the first, the waste water is contacted first with the polar solvent then separately with the volatile solvent. The extract streams are then sent to separate distillation columns for solute removal and the solvents separately recycled. The second approach is to undertake both extractions in the same column, feeding the isobutane to the bottom of the column and the polar solvent to the middle. The system described in Figure 3 has the advantage that only one extraction column is required. However, the presence of the volatile solvent has the effect of diluting the polar solvent and reducing the partition coefficient in the upper part of the column. If the partition coefficient is very high, the reduction may be of little consequence. A third possibility is to use a mixture of a volatile solvent such as a butane and a polar solvent and use this "tailored" mixture to give sufficient solute removal yet depress polar solvent solubility to an acceptably low value. The use of solvent mixtures has been investigated by Medir and Mackay⁽¹⁸⁾.

Solute Recovery Stage

Normally this can be accomplished by distillation, but in the case of organic acids such as phenol, a solvent extraction into an aqueous alkaline solution such as sodium hydroxide is effective.

Specific Applications

Solvent extraction has been used to remove phenolic compounds from water effluents of the petroleum refining, petrochemical, coal-processing, steel and plastic industry, coal tar industry and phenol resin plants^(1,2,4,20).

Several hundred pounds of phenols per day may be discharged with the effluent waters from the catalytic

cracking of petroleum fractions. In the Phenex process, 75 to 90% of these phenols are extracted with a light catalytic oil by single-stage contacting. Oil, entrained in the aqueous phase, is also removed⁽²¹⁾.

The most common solvents used to extract phenols from waste waters have been found to be: benzene, toluene, "benzol", aromatic light oil, isobutane, isobutylene, methylene chloride, light or medium naphthas, isopropyl ether, n-butyl acetate, methyl isobutyl ketone, and tricresyl phosphate^(4,20,22,23). Since phenols are weak acids, a basic organic compound gives a higher distribution coefficient. Pollio et al⁽²⁴⁾ proposed the extraction of phenolics from waste waters with water-immiscible amines, or mixtures of amines. They also investigate the use of mixture of amines with high boiling petroleum distillates or with light aromatics (benzene, toluene or xylene).

Earhart et al⁽⁴⁾ studied the potential for removal of phenols, aromatic hydrocarbons, oxychlorinated hydrocarbons, ketones, esters and aldehydes from waste waters produced in styrene manufacture, lube-oil refining, hydrofiner condensate of a refinery, oxychlorination plants, naphtha-pyrolysis olefin plants, phenol-formaldehyde resin manufacture plants, and the evaporator condensate of a manufacturing cresylic acid plant. They studied simple volatile solvent extraction and dual-solvent extraction. The dual-solvent process consists of extraction with a polar solvent with high distribution coefficient, i.e. n-butyl acetate or methyl isobutyl ketone followed by extraction with a volatile solvent of lower distribution coefficient and lower solubility in water, i.e. isobutylene or isobutane. The dual-solvent process gave very good results where phenolic substances were major contaminants, allowing the use of low solvent/water ratios which is desirable since it reduces the equipment size and the utility cost for solvent regeneration. A major

reduction in the COD (chemical oxygen demand) was also obtained with this process. Experiments were carried out in a rotating disc contactor. The extraction with mixtures of a volatile (i.e. isobutylene) and a polar solvent (i.e. n-butyl acetate or methyl isobutyl ketone) gave comparable results to the ones of the dual-solvent process. Dual-solvent extraction is usually favoured over simple volatile solvent extraction when the distribution coefficient for both dual-solvent steps is 20 or greater, and the one for direct volatile solvent extraction is less than about 5. Laboratory experiments on extraction of waste water from a lemon-juice processing plant with n-pentane, showed promise for the removal of emulsified lemon oil and suspended matter.

Prausnitz and King⁽²⁵⁾ have also investigated the extraction from water of phenol with pentylaldehyde, nitroethane or pentanol, followed by extraction with isobutylene, as well as the extraction of chloral and acetic acid with tributyl phosphate followed by isobutylene extraction.

A new application of solvent extraction has been developed by Hydrosience Environmental Systems (Knoxville, Tenn.) to remove acetic acid present in water effluents at concentrations from 5% to as low as 0.5%. Acetic acid is present in many water effluents from processes such as acetylation and esterification, high-pressure petroleum-refining operations (e.g. cracking, reforming), wood pulping, pharmaceutical plants, brewing processes, and coal processing. The solvent used is trioctylphosphine oxide (TOPO) mixed with a kerosene-like aliphatic hydrocarbon, which acts as carrier for TOPO and avoids problems of solidification, since TOPO has a high melting point. Previously developed systems used ether as an extractant and could only handle effluents containing at least 10% acetic acid⁽²⁶⁾.

Solvent extraction is also used commercially for the recovery of valuable products like fatty acids from the effluent waters produced in wool scouring. These effluent waters contain a wool grease which is separated by addition of acid and then the grease is extracted with an alcohol, to obtain the free fatty acids⁽²⁸⁾.

A process for de-oiling quench water, containing about 6000 ppm of dissolved and emulsified oil, was developed by Gulf Oil Corporation. The quench water is extracted with a light aromatic oil solvent, the extract is recycled for refinery processing, and the extracted water contains about 20 ppm of oil. The coalesced oil is reused in the plant⁽¹⁾.

Resources Conservation Co. (Renton, Wash.) is developing the Basic Extractive Sludge Treatment (B.E.S.T.) to remove water and oil from inorganic and organic sludges and so obtain very dry solids (4-5% moisture)⁽²⁾.

Union Carbide has been investigating the potential for the extraction of caprolactam and acrylonitrile/acetonitrile from manufacturing waste waters. As reported by A.D. Little⁽²⁾, the company claims that this process has potential applicability.

Solvent extraction has been found to be feasible and economical for reducing the organic material (chemical oxygen demand) of sewage waters. Sandall et al⁽²⁷⁾ studies the treatment of a secondary municipal effluent (containing humic substance, carbohydrates, proteins, tannins, lignin, detergents, etc.) and an aqueous solution of benzaldehyde (as a representative pollutant) by solvent extraction. Several commercial solvents, toluene and carbon tetrachloride were used for extraction in a packed column. The Isoparaffin-150 (Standard Oil Company of California) was found to be a promising solvent. Water treatment cost estimated for this solvent, from the overall mass-transfer

coefficient, was found to be comparable to costs for current tertiary treatment processes.

Hewes et al⁽²⁸⁾ undertook an economical analysis comparing the treatment of waste waters from chlorination processes by solvent extraction with an oil as solvent, and by stripping. Stripping is preferable for volatile solutes. However, when the waste is concentrated and the solute is non-volatile and valuable, extraction may be preferable. The energy requirements for the extraction operation are also lower.

A new and potentially significant field for the application of solvent extraction is present in the removal of noxious and hazardous materials from the waste of coal processing operations (mining, storage, refining, liquefaction, gasification and slurry transportation). An analysis of the waste products and effluents of the synthene process for coal gasification was carried out by Forney et al, showing the following compounds: mono- and poly-substituted phenols, cresols, naphthols, indenols, pyridines, aromatic, polyaromatic and heterocyclic hydrocarbons, sulfur compounds, nitrogen heterocycles, and arylamines. The concentration of the main compounds ranged from about 0.1 ppm up to a few g/l for phenols. Compounds present in the tars could also be present in the water effluents. The Synthene process uses about $\frac{3}{4}$ ton of water for each ton of coal processed⁽²⁹⁾. A full-scale commercial plant of coal gasification may produce a water effluent flow of 0.4 up to 1.2 million gallons/day⁽³⁰⁾ causing, therefore, an important environmental problem. The oxidative pretreatment of bituminous coals to prevent caking in the gasification process may also result in the presence of phenols and other organic compounds in the waters⁽³¹⁾.

Solvent extraction will be used for extraction of phenols and other organic compounds from waste waters of a coal gasification plant being built in Northwestern New Mexico by El Paso Natural Gas Company, based on Lurgi technology. The Phenosolvan Process with isopropyl ether as extract solvent will be used and the effluent water will contain less than 20 ppm of steam volatile phenols⁽³²⁾.

Although biological oxidation is used in the treatment of waste waters from some coal conversion processes, it only removes 90% of the Biological Oxygen Demand (B.O.D.). Magee and Shaw⁽³³⁾, suggested that the remaining B.O.D. may contain carcinogenic compounds. If the compounds are refractory to biological oxidation, with the water being recycled in the process, they will tend to build up and possibly be discharged into the environment from evaporation or with the spray from cooling towers. In that case other methods capable of removing those compounds may be necessary, making solvent extraction a potential method.

Some possible future applications of solvent extraction outlined by A.D. Little⁽²⁾ are the recovery of tetrahydrofuran from tetrahydrofuran/water waste mixture by extraction with toluene, and the recovery of dimethyl formamide from a dimethylformamide/water waste mixture by extraction with methylene chloride.

There are many industrial processes where the waste waters are contaminated with organicoxious compounds (phenols, hydrocarbons, carboxylic acids, N-derivatives, etc.). However, the possibility of application of solvent extraction will depend on the process configuration, the organic compounds concentrations in the waste waters, the economic value of the recovered compounds, and the economics of solvent extraction versus other waste water treatment processes.

There may be a potential for application of solvent

extraction in processes like bleaching and dyeing of textiles, manufacturing of dyestuffs, paints, pharmaceutical products, pesticides, fertilizers and organic chemicals, in the food industry, pulp and paper and plastics industry.

The following list includes the compounds which may be removed from waste waters by solvent extraction:

Phenol, o-, m-, p-cresol, xylenols, ethylphenols, mesitol, naphthols, polyhydric phenols (catechol, resorcinol), pyridines, indenols, mono- and polyaromatic hydrocarbons, chlorinated hydrocarbons, acetone, methyl ethyl ketone, n-butyl acetate, acetic acid, acrylic acid, glycol, crotonaldehyde, caprolactam, acrylonitrile, acetonitrile, benzaldehyde, benzene acid, salicylic acid, amyl alcohol, aromatic ketones, sulfur compounds, arylamines, humic and fulvic acids, carbohydrates, proteins, tannins, lignin, detergents, sugar, essences, essential oils, flavour components, glycine and wool grease.

Economic Aspects

There are few data on the cost of waste water treatment by solvent extraction and it is difficult to generalize about likely costs^(1,2,4,26). It seems likely that extraction costs will lie in the range of \$3-\$10/1,000 USgal. Since this cost is high in comparison to normal waste water treatment costs, solvent extraction is only likely to be feasible when credit accrues to the operation as a result of the sale of the solute or where other treatment methods prove ineffective. An approximate indication of economic viability can be obtained by calculating the value of the solute per 1,000 gallons. For example, a solute present at a concentration of 1% (wt) and saleable at 10¢/lb will result in a credit of \$8.3 per 1,000 gallons of water treated. This lies in the range where the process may prove feasible. It seems unlikely that concentrations lower than 0.1% are likely to be processed economically by solvent extraction unless the overriding consideration is the necessity to remove the solute for environmental or other reasons. An example is chlorinated hydrocarbons. Clearly in a complex petrochemical plant where there are many waste water streams, it is advantageous to process segregated streams for extraction of specific solutes prior to combining the waste waters for total treatment. It then becomes a matter of debate whether the extraction process is regarded as a waste water treatment process or as an inplant process.

Conclusions

The present limited use of solvent extraction for treatment of waste waters is due to the relatively high costs which lie in the range of \$3 to \$10 per 1,000 USgal. When credit can be obtained by selling the recovered solute, the process may be attractive, particularly when the solute concentration exceeds 1%. An advantage of solvent extraction is that it may be capable of removing toxic and persistent compounds from waste waters more effectively than biological treatments. Application is most likely in the coal, and hydrocarbon and chlorinated hydrocarbon processing industries. A review has been presented of other possible applications.

Ultimately the successful applications of solvent extraction to waste water treatment depends on (i) the availability of a solvent with a suitably high partition coefficient and low aqueous solubility, the thermodynamic aspects of which have been reviewed, (ii) the ability to devise a suitable process configuration for solvent extraction and recovery and solute-solute separation, the most

promising approach being the use of a dual volatile-polar solvent system and (iii) the overall economics.

NOTATION

f	= fugacity (atm)
f^R	= reference fugacity (atm)
z	= mole fraction of solute
κ	= partition coefficient (mol. gm/mol. gm)
γ	= activity coefficient

Subscripts

s	= water phase
w	= solvent phase

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DISCUSSION

Y. Marcus: The process described essentially replaces the toxic pollutant in the aqueous waste with the less toxic solvent (say polar solvent plus hydrocarbon mixture), but at its equilibrium solubility level, or at the even higher mechanical entrainment level, leads to poor economics. I suggest that the solvent should be absorbed or adsorbed on some suitable solid support, to minimize its loss by solubility or entrainment, still permitting effective removal of the organic pollutant from the aqueous waste.

D. Mackay: I fully accept Dr. Marcus's comment. Any process change which will reduce the amount of solvent loss is beneficial but I have the intuitive feeling that this benefit will probably be associated with less favourable equilibrium or kinetic performance. It is an approach worth pursuing.

H.M. Stoenner: You mentioned that you are looking for an economical, volatile and easily recoverable solvent. Do you know that this was published 20 years ago in Germany (Author: Jauernik, Paper: Erdöl und kohle)?

Use of Di-isopropylether in many phenol extraction plants* has made the extraction economical. (*Known as Phenosolvan® - Process).

The peroxide problem, mentioned by you in private discussion, has been solved. (Phenol mixtures contain peroxide inhibitors).

D. Mackay: In this review, we have emphasized future applications rather than existing processes such as Phenosolvan which we discussed in our earlier review. I was surprised to learn of the extent to which the Phenosolvan process is used in Germany (over 20 plants). It now appears to be the "standard" process in Germany, but I do not know if it will become the standard process in North America. Perhaps the peroxide problem has been exaggerated, but it would, I believe, be preferable to use a less hazardous solvent of comparable partition properties.

A.E. Karr: There appears to be a fairly widespread "belief" that an extraction column should not be operated at feed phase ratios greater than 10. This may be true in some type of column but is definitely not true in the case of the reciprocating plate extraction column, which operates successfully at ratios as high as 50 to 1. When operating at very high ratios the phase having the lowest flow rate should normally be dispersed.

D. Mackay: Dr. Karr is correct in his statement that this belief is widespread, but I have not seen published data to disprove it. I am delighted to hear that this column will operate well under these conditions because it enables us to exploit fully the high partition coefficients which are available for some systems.

R.R. Grinstead: Could you break down major components of \$3-10/M gal. cost of solvent extraction processes?

D. Mackay: There are few published data, but perhaps the most useful and reliable are those kindly provided to me by Mr. Stoenner of Lurgi for the Phenosolvan Process in 1969 U.S.A. dollars.

The capital cost ranges for \$0.3 to 1.0 million for feed capacities of 40 to 50 U.S. gallons per minute. Utilities per 1000 gallons of feed are: steam 80 to 270 lb, solvent 0.6 to 1.2 lb (costing 5 to 8¢ per lb), Cooling water 1500 gallons and electricity 4 to 6 kWh.

For a large plant, this implies a capital charge of about \$1 per million gallons and a similar amount for operating cost. Since 1969, these costs have increased by an amount dependent on the location and energy costs.

L. Robbins: Indeed, there are commercial waste water extraction columns that operate with a water to solvent ratio of about 20. Also I would like to point out that it can be a distinct advantage to run with an extraction factor greater than 1.5 to 3.0. A higher extraction factor can allow a solution to be extracted down to parts per billion with very few theoretical stages.

Concerning the use of a volatile solvent to remove a polar solvent from water, this appears to be an unnecessary complexity by adding another solvent to the process when the polar solvent already has a high relative volatility to water. For example, in the EPA report you referred to, the relative volatility of butyl-acetate to water, is about 200. This, of course, means that it can be easily steam stripped from water. The energy consumption can be kept low by cross exchanging the bottoms with the steam stripper feed for energy recovery.

D. Mackay: I fully accept your comments and am delighted both that high ratios are possible and that the solvent can be steam stripped directly. These factors enhance the feasibility of solvent extraction for waste water treatment.

T.K. Mattila: You only mentioned the recovery of organic components from waste waters. What about the recovery of valuable inorganic components from waste solutions, processes which normally use kerosene-based water-insoluble solvents? Do you think these kind of processes can be accepted without any extra treatment to remove trace quantities of solvent from treated waste water?

Kemira Oy, Finland has developed a process to recover nitrates (as commercial solid KNO_3) from waste waters using an amine-kerosene solvent. We have made fish tests which have shown that there is no harm for aquatic life with respect to those trace quantities of solvent left in the treated water after normal settling.

D. Mackay: I was not aware of the nitrate removal process and I am grateful to you for bringing it to my attention. There are phosphate extraction processes but they are not waste water treatment processes. The aqueous solubility and toxicity of kerosene is dominated by the amount and nature of the aromatics present. I share your opinion that waters which have been in contact with kerosene are relatively non-toxic (unless substantial quantities of kerosene are emulsified) and can probably be disposed of with minimal treatment into receiving waters, which are not used for drinking purposes. Although kerosene is fairly non-toxic, it may have a significant effect on some aquatic species at certain growth stages and seasons, and of course, it has an odor problem.

MAR - Hydrometallurgical Recovery Processes

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ABSTRACT

The MAR-project (Metals and Acids Recovery) was aimed to evaluate hydrometallurgical processes mainly for the recovery of copper, zinc and nickel from waste materials. Two main process routes have been developed and tested: H-MAR, based on sulfuric acid leaching and Am-MAR, based on ammoniacal carbonate leaching. The processes have been evaluated in laboratory and small-scale pilot plant operation and adopted to different kinds of feed materials. Based on the results, preliminary economic analyses of different process alternatives have been made for industrial operations.

Introduction

THE GROWING CONCERN ABOUT ENVIRONMENTAL PROBLEMS and the need for expanding resources by recovery of metal values from waste products have initiated research in this direction in many countries. Due to the diverse nature and complexity of waste materials, a variety of techniques for collection, sorting and separation have been and are under development. When relatively pure metal fractions can be obtained, much of the material can be recycled to the conventional metal production processes without major specific treatment. Other and more complex materials are treated in different hydro- and pyrometallurgical operations to produce usable products or raw materials for conventional processes.

Many industrial metal containing wastes, such as flue dusts, pickling liquors, neutralization residues and metal-bearing effluents, require more complicated or selective chemical methods for metal recovery. Often the incentive is then based not only on the economical value of contained metals but also on the potential reduction of disposal costs and on the need for environmental protection. In this area of metal recovery hydrometallurgical processes will play an increasingly important role as new techniques and applications are developed.

A development project with the aim of applying hydrometallurgical techniques, including solvent extraction, to the recovery of metals and acids, named the MAR-project (Metals and Acids Recovery), was started in Sweden in 1970 at the Chalmers University of Technology with economic support from the Swedish Board of Technical Development. The project was transferred to MX-Processer when this company incorporated in 1973. To date, the economic support from external sources amounts to more than \$1,000,000 with about equal shares from the Swedish Board of Technical Development and from different Swedish industries. In addition to this, some cooperative industries have contributed within their own research facilities and with the building of pilot-plants for the commercial development or testing of specific processes.

The main incentive of the MAR-project has been to evaluate hydrometallurgical processes for the recovery of copper, zinc and nickel from waste materials containing

one or more of these metals. To date, processes for treatment of the following materials have been investigated: a. zinc-rich steel mill flue dust, b. zinc and copper-rich brass mill flue dust, c. galvanic neutralization sludge, d. nickel-cadmium battery scrap.

For this purpose two main process routes, largely based on existing technology, modified for the specific requirements of the "raw material", have been developed:

- a. H-MAR: Sulfuric acid leaching
- b. Am-MAR: Ammoniacal carbonate leaching.

Both these process routes can be adopted for the above-mentioned materials. The optimal choice however, mainly depends on the origin of the material, on which metals shall be recovered, on what products shall be produced and of course, on the process economy.

Based on such considerations, the H-MAR flow sheet was tested for treatment of zinc-rich steel mill flue dust and for zinc and copper-rich brass mill flue dust. The Am-MAR flowsheet was tested for galvanic neutralization sludge and for nickel-cadmium battery scrap. These tests were performed in continuous operation in laboratory and small pilot plant scale. In addition to this a comparative economic evaluation of both flowsheets was undertaken for brass mill flue dust.

This paper will briefly report on the results of the development of the basic flowsheets and the experiences from processing of the different materials. The considerations governing the choice of processing method will be discussed and some economic data will be given.

H-MAR: Sulfuric Acid Leaching

The flue dust from scrap-based steel mills and brass mills are fine powders containing zinc and copper, mainly in oxidic form.

TABLE 1. Typical Analysis for Swedish Steel and Brass Mill Flue Dusts

	Steel mill flue dust	Percent in dry material.	
		Brass mill dust (cyclone)	Brass mill dust (bag filter)
Cu	0.23	16	1.2
Zn	26	30	53
Fe	19	3.1	0.2
Ni	0.1	0.2	0.1
Mn	2.2	0.1	0.1
Pb	5.8	4.3	12

The direct and simple approach is to leach with sulfuric acid at moderate pH, which brings most of the zinc and copper into solution. By adjusting the final pH when leaching, the iron content in the leach solution can be kept below 10 ppm.

Process Flowsheet

The basic flowsheet is given in Figure 1 and can be regarded as two separate interconnected processes, one for copper recovery and one for zinc recovery.

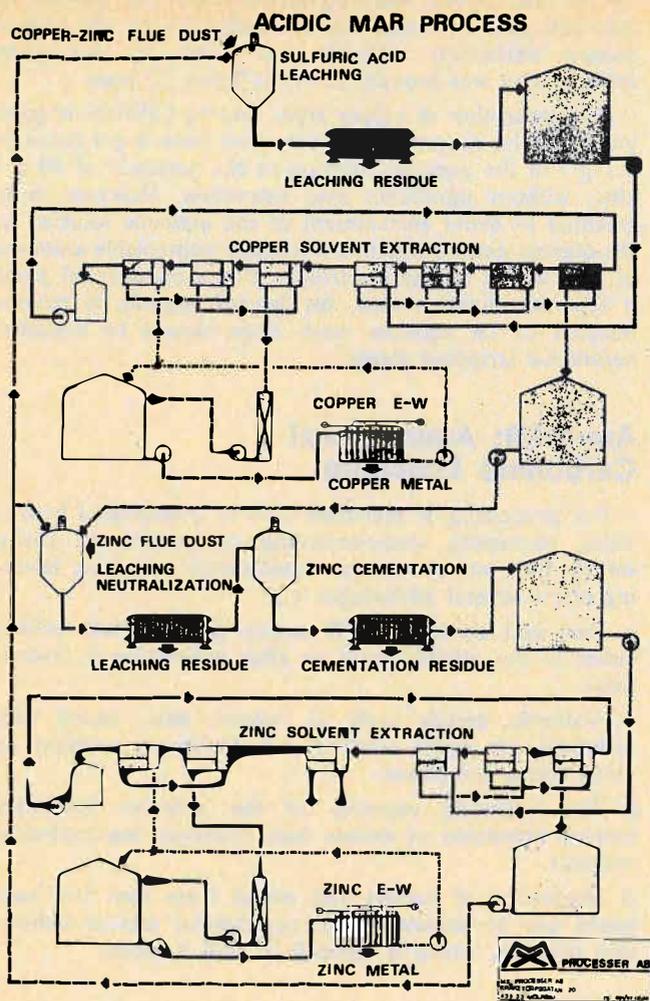


FIGURE 1. Basic flowsheet of acidic MAR process (H-MAR).

In the copper circuit, copper-rich material is leached in a pH-controlled leaching at 60°C with a final pH of 2 - 2.5. Oxidizing conditions should be maintained (e.g. by addition of MnO_2) to promote copper dissolution and prevent cementation of metallic copper if the feed material contains metallic zinc (brass) or iron. An example of the influence of the oxidation potential on the leaching rate for this type of material is given in Figure 2. The leaching residue is filtered off and the leach solution is fed to the copper recovery step. Copper recovery is performed by standard solvent extraction of copper with LIX-64N, stripping with spent sulfuric acid electrolyte and electro-winning of copper.

The zinc circuit consists of a similar pH-controlled leaching at about 60°C under mildly oxidizing conditions. The copper-barren raffinate containing about 0.1 g/l of copper is fed to the zinc flue dust leaching section. Additional leach solution is obtained from the zinc extraction raffinate, which contains sulfuric acid equivalent to the amount of zinc extracted. pH in the leaching is maintained at about 2 for most of the leaching time and slowly raised to about pH 4.5 at the end, bringing down iron levels to below 10 ppm. Zinc flue dusts with low copper content are leached in this section.

By a stepwise countercurrent leach process it would be possible to reach standard electro-winning concentrations. However, it was decided to test solvent extraction of zinc as an intermediate concentration and purification step. Zinc is extracted from the leach solution by 50% di-

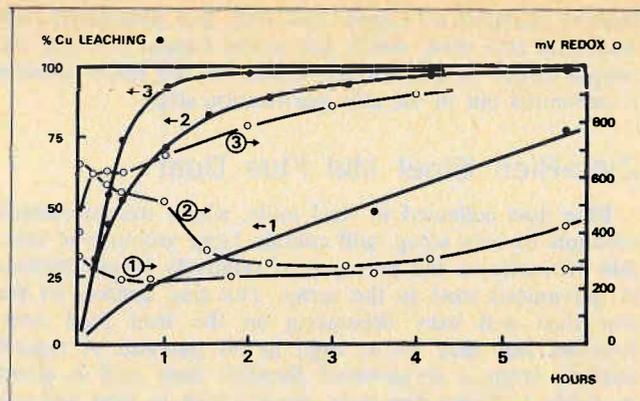


FIGURE 2. Influence of the redox potential on the leaching rate of copper from brass mill flue dust containing reducing components. 1: MnO_2 /dust = 0, 2: MnO_2 /dust = 0.5, 3: MnO_2 /dust = 1.5.

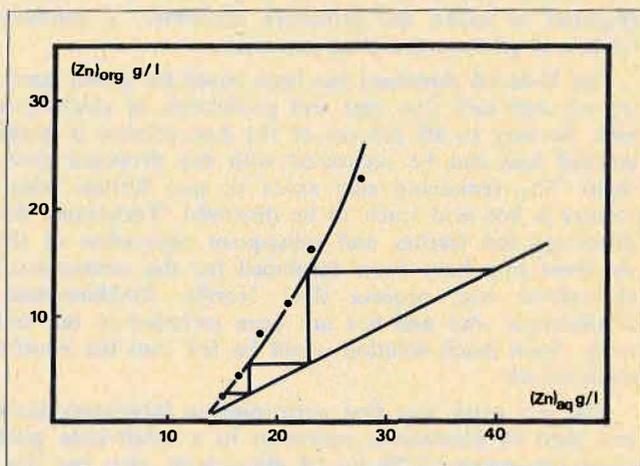


FIGURE 3. Equilibrium curve for extraction of zinc with 50% DEHPA in kerosene at 25°C. Feed compositions 40 g/l Zn, pH 3.2.

(2-ethylhexyl)-phosphoric acid (DEHPA) in kerosene. The equilibrium curve is shown in Figure 3. It has an unusual shape due to the high zinc concentration in the feed solution which results in a high acidity in the aqueous phase, when the zinc is extracted. The net transfer of zinc from the aqueous phase can be maintained at 20-25 g/l. The remaining zinc in the raffinate is recirculated to the leaching.

The zinc extract is stripped with spent electrolyte from the zinc electro-winning and the return electrolyte contains 80-120 g/l of zinc, depending on the acid concentrations. Electro-winning combined with solvent extraction requires higher acidities than are normally used in a conventional electrolytic zinc plant. The spent electrolyte containing about 60 g/l of zinc will contain about 200 g/l of free sulfuric acid. DSA anodes have been tested in the electro-winning and have performed satisfactorily at these high acidities. Traces of the organic phase adversely affects the zinc electro-winning and must be avoided by coalescing aids or active carbon filtration. The acid raffinate from the zinc extraction (pH about 0.7) is returned to the leaching section and distributed between the copper and zinc leaching stages depending on the requirements.

The described flowsheet can be used either for processing of combined copper and zinc-rich flue dusts, adjusting the flows in the copper and zinc circuits to the

relative amounts of copper and zinc. For processing only steel mill flue dust, which has a low copper content, the copper circuit is omitted and copper in the leach solution is cemented out in the zinc purification step.

Zinc-Rich Steel Mill Flue Dust

Flue dust collected in steel mills, which use substantial amounts of iron scrap, will contain large amounts of zinc, due primarily to the presence of relatively large amounts of galvanized steel in the scrap. The zinc content in the flue dust will vary depending on the iron feed composition, but may be as high as 30 percent. A typical analysis from a scrap-based Swedish steel mill is given in Table 1. These flue dusts are too high in iron and too low in zinc to be acceptable as feed material for most commercial electrolytic zinc plants. Several pyrometallurgical processes have been proposed for upgrading the zinc value by fuming off the zinc and lead. Some of these processes involve a reduction process to produce a marketable iron product. Very large units are normally required to make the processes economic, a common feature of pyrometallurgical processes.

The H-MAR flowsheet has been tested for direct leaching of steel mill flue dust and production of electrolytic zinc. Seventy to 80 percent of the zinc content is easily leached and can be recovered with the proposed flowsheet. The remaining zinc exists as zinc ferrites which require a hot acid leach to be dissolved. Techniques for dissolving the ferrites and subsequent separation of the dissolved iron have been developed for the conventional electrolytic zinc process (Det Norske Zinkkompanie, Outokompu, etc) and has not been included in our test work. Such leach solution could be fed into the neutral leach circuit.

The test work was first performed in laboratory scale and then in continuous operation in a small-scale pilot plant producing 10-20 kg of electrolytic zinc per day. The results obtained were satisfactory and economic data for a production of 10,000 tons/y of electrolytic zinc from steel mill flue dust containing 25 percent zinc, has been calculated.

Brass Mill Flue Dust

Dusts from metal refineries producing brass and similar alloys are rich in zinc and copper. The dusts contain the metals mainly in oxidic form but may also contain metallic zinc (brass dust). In addition they may contain lead and tin. The iron content is normally very low. Basically two types of dust are obtained, one high in both copper (10 - 20 percent) and zinc (20 - 40 percent) and one high in zinc (up to 50 percent) and relatively low in copper (1-10 percent).

The metal value of these materials is much higher than in the steel mill dusts due to the copper and the low iron content. The zinc-rich dust should be acceptable as feed to an electrolytic zinc plant, but the amounts available do not normally justify the risk of using an unknown feed material. The copper-rich material can in some cases be processed pyrometallurgically, but some type of agglomeration procedure is required to avoid the dust from blowing off.

The zinc leaches readily with dilute sulfuric acid. The leaching of copper is slower but may be promoted by increasing the oxidation potential. The H-MAR flowsheet has been successfully tested in small pilot plant scale for treatment of typical copper/zinc and zinc-rich dusts in a closed loop system recirculating all the zinc solvent extraction raffinate to the copper circuit leaching section.

In the zinc circuit leaching section only the amount of zinc-rich dust necessary for neutralization of the copper solvent extraction raffinate was used. In this stage residual iron was brought down to below 10 ppm.

The separation of copper from zinc by LIX64N is quite good and the copper can be extracted from 4 g/l down to 0.1 g/l in the aqueous solution in the presence of 40 g/l zinc, without significant zinc extraction. However, it is essential to avoid entrainment of the aqueous solution in the organic extract which can transfer appreciable amounts of zinc to the copper electrolyte. For a commercial plant a separate flotation tank for loaded organic is recommended or an aqueous wash stage should be included before the stripping stages.

Am-MAR: Ammoniacal Carbonate Leaching

For processing of materials such as precipitated hydroxides, containing acid-consuming components or easily soluble iron and chromium, ammoniacal carbonate leaching offers several advantages, e.g.:

- a. Iron and chromium will remain in the leach residue either in the original form or after conversion to hydroxides.
- b. Valuable metals such as copper, zinc, nickel and cadmium are easily leached and remain in solution as metal amine complexes.
- c. The buffering capacity of the solution facilitates solvent extraction of metals with hydrogen ion exchange reagents.
- d. Separation of copper and nickel from zinc and cadmium can be achieved with commercial solvent extraction reagents, which is difficult in acid medium.

Process Flowsheet

The Am-MAR process flowsheet outlined in Figure 4 consists of three main operations:

1. *Leaching* of solid material in a first step with ammoniacal carbonate leach solution dissolving copper, nickel, zinc and cadmium as metal amine complexes and in a second step with sulfuric acid solution dissolving remaining metals as sulfates. In both steps iron and chromium are left in the leach residue.
2. *Solvent extraction* of copper and/or nickel with LIX64N or other suitable reagents from the combined leach solutions leaving zinc and cadmium in the raffinate.
3. *Ammonia recovery and metal precipitation* by thermal stripping of ammonia from the solvent extraction raffinate and precipitation of remaining metals as carbonates by addition of carbon dioxide. After filtration of the precipitated carbonates and absorption of the stripped ammonia in the filtrate, this is returned to the leaching.

When leaching with an ammoniacal carbonate solution, the total concentrations of NH_3 and CO_2 are the dominating variables for the leaching yields. Leaching times longer than 10 hours, or increased leaching temperatures over 20°C have marginal effects. The concentrations of NH_3 and CO_2 are controlled by the addition of their gases. An increase of the NH_3 concentration increases the total "leaching potential" of the system in respect to dissolved metals through a greater tendency towards the formation of metal amine complexes.

The presence of carbonate in the ammoniacal system offers a possibility of controlling the conditions for the formation of metal carbonate. An increase of the CO_2

concentration gives an increased tendency to form insoluble carbonates. This means that the optimum conditions for the precipitation cannot be considered independent of the corresponding conditions for leaching. For a closed process, the balance of NH_3 , CO_2 and metal concentrations is therefore of major importance.

Hydroxide sludge, particularly the sludge obtained from neutralization with $\text{Ca}(\text{OH})_2$, undergoes an ageing process when exposed to air for a long time. This reduces the leaching yields, especially for nickel. The mechanism behind the effect has not been fully explained. It may be a chemical passivation due to the recombination of the grains of metal hydroxide, oxide or carbonate formed. It is therefore necessary to leach the leach residue a second time to achieve a total yield greater than 95%. This second treatment is carried out with sulphuric acid at a pH of 2-3. If the pH is kept at this value, leaching of iron and chromium is negligible as shown in Table 2.

TABLE 2. Electroplating Hydroxide Sludge (Neutralized with $\text{Ca}(\text{OH})_2$)

No. Leaching	Ni g/l	Cu g/l	Zn g/l	Fe g/l	Cr g/l
1. Total leaching ($\text{HNO}_3\text{-HCl}$)	1.35	1.00	1.82	0.74	1.80
2. NH_3 4.0 M NH_4HCO_3 2.5 M 30 °C, 10 hours	0.90	0.81	1.35	0.01	0.02
3. No. 2 residue + H_2SO_4 , pH = 3.0 60 °C, 6 hours	1.31	0.98	1.79	0.01	0.04

The table shows that with only an ammoniacal system, the leaching yields are not sufficient (Cu ca. 80%, Ni and Zn ca. 70%). With a combined leaching (half the volume ammoniacal and half acid in this example), however, leaching yields for Ni, Cu and Zn are greater than 95%, while nearly all Fe and Cr remains in the residue. The sulfuric acid leach solution is combined with the ammoniacal leach solution before solvent extraction.

Copper and/or nickel are extracted from the solution with an organic solution containing a suitable reagent, such as a hydroxyoxime, hydroxyquinoline or β -diketone dissolved in a high flash point kerosene. In the case of hydroxide sludge, copper can be extracted by LIX64N in an initial solvent extraction stage followed by a second extraction of nickel using the same reagent. Copper is preferentially extracted by LIX64N, and by adjusting the flow ratios of organic to aqueous solutions, it is possible to extract essentially all the copper while nickel is rejected. The nickel extracted may be scrubbed with an ammoniacal carbonate solution or with dilute sulfuric acid. The latter procedure also removes extracted ammonia from the organic phase. Zinc extraction can be neglected. Stripping of copper is done with sulfuric acid spent electrolyte and copper is recovered from the strip solution by electrowinning.

Nickel (and remaining copper) can be extracted with LIX64N in a second solvent extraction stage. Significant amounts of ammonia and zinc are extracted with the nickel. Scrubbing of zinc can be achieved with ammoniacal carbonate solution and the remaining zinc and ammonia with dilute sulfuric acid. The pH in the acid scrubbing stage should be kept above pH 2 to minimize stripping of nickel. Nickel is stripped from the extract with dilute sulfuric acid to produce a nickel sulfate

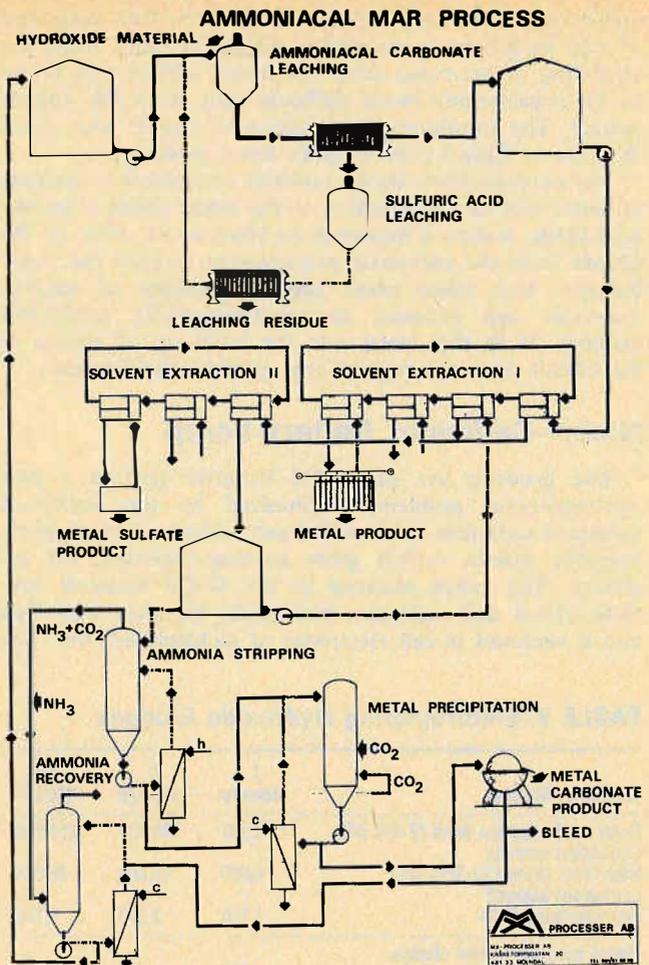


FIGURE 4. Basic flowsheet of ammoniacal MAR process (Am-MAR).

solution containing 90-100 g/l Ni, from which nickel sulfate can be crystallized.

After separation of copper and/or nickel, zinc or cadmium are precipitated as carbonates after the NH_3 concentration is reduced by the thermal stripping of ammonia. Some CO_2 will also be stripped. The precipitation is made complete by cooling the solution and by addition of a CO_2 purge. After filtration of the metal carbonate, the filtrate is used for absorption of the stripped ammonia and the resulting solution is recycled to the leaching step.

Plating Neutralization Waste

Metal-containing effluents from numerous small plating industries and other similar sources are cleaned by neutralization with NaOH or lime, precipitating the metals as hydroxides. The feasibility of metal recovery from such wastes by Am-MAR processing has been tested both in laboratory and pilot plant scale. Typical compositions of the feed material are given in Table 3 below.

Leaching was performed with a solution containing 5.5 moles/l NH_3 and 1 mole/l CO_2 followed by a second leaching of the residue with dilute sulfuric acid at pH 2-3. The final concentrations in the combined leach solution were 4 g/l Cu, 5 g/l Ni and 12 g/l Zn. Recovery of copper as copper cathodes, nickel as nickel sulfate and zinc carbonate followed the basic Am-MAR flowsheet.

In the pilot plant operation special attention had to be given to the balancing of complete copper extraction and

nickel rejection in the copper solvent extraction stage and of zinc scrubbing in the nickel extraction stage. Also, the scrubbing of ammonia from the nickel extract was found to be considerably more difficult than from the copper extract. The simultaneous extraction of copper and nickel (Kennecott Corp.) may simplify these problems.

The neutralization sludge contains considerable amounts of water and this, in addition to the water added from the acid leach, makes it necessary to bleed about 30% of the filtrate from the carbonate precipitation to keep the water balance. This bleed needs special treatment to recover ammonia and produce an environmentally acceptable effluent. With this bleed rate the build up of sulfate in the circuit does not require any special considerations.

Nickel-Cadmium Battery-Scrap

The growing use of Ni-Cd batteries present a new environmental problem, emphasized by the poisonous nature of cadmium. Both nickel and cadmium are relatively valuable metals, which gives another incentive for recovery. The active material in the Ni-Cd batteries contains nickel and cadmium hydroxides together with iron and is enclosed in cell electrodes of nickelplated iron. The

TABLE 3. Electroplating Hydroxide Sludges

Source of Sludge.	I tons/y	II tons/y	III tons/y
From neutralization pond (2-3% DS)	70,000	100,000	250,000
Equivalent amount from filter press (20-30% DS)	6,000	10,000	26,000
Equivalent amount dry substance (DS)	1,700	2,200	5,700
Metal content in the sludge.			
Ni	105	150	180
Cu	135	40	230
Zn	155	300	380
Fe	135	540	130
Cr	120	260	460
Ca (as sulfate)	500	—	2,600
Fe(OH) ₃ + Cr(OH) ₃ + CaSO ₄ (residue)	1,000	1,550	3,700
Potential metal products.			
NiSO ₄ · 6 H ₂ O	470	670	800
Cu-metal	135	40	230
ZnCO ₃	300	575	730

TABLE 4. Cost Factors and Product Values used in the Economic Estimates

	Unit	Sw. Crs.	US \$
Labour			
Blue collar worker (shift)	year	100,000	22,200
Blue collar worker (day)	year	80,000	17,800
Management	year	120,000	26,700
Chemicals			
sulfuric acid	ton	300	67
hydrates lime	"	300	67
ammonia	"	2,000	440
carbon dioxide	"	1,500	330
LIX 64N	"	30,000	6,700
DEHPA	"	14,000	3,100
Kerosene	"	1,500	330
Energy			
Electric power	MWh	150	33
Steam	ton	40	9
Oil	ton	530	120
Product values			
Cu (metal)	ton	6,000	1,330
Zn (metal and oxide)	"	3,500	780
Ni (nickel sulfate)	"	20,000	4,440
Cd (cadmium carbonate)	"	26,000	5,780

Am-MAR process was used for the recovery of both nickel and cadmium.

Before leaching, the electrodes were cut into pieces (1 cm²). The material was then leached with a solution containing 6.5 moles/l NH₃ and 2.5 moles/l CO₂. In the ammoniacal leach about 70% of the nickel and 90% of the cadmium was dissolved. After filtration, the sludge residue was treated in the sulfuric acid leach to bring total recovery of nickel and cadmium to more than 98%. Leaching conditions were adjusted for a concentration of 15 g/l of Ni + Cd in the final solution.

Extraction of nickel with LIX 64N and stripping with sulfuric acid resulted in a pure nickel sulfate solution which was directly used in the battery production process. Separation factors between nickel and cadmium greater than 3000 were achieved.

The precipitated cadmium carbonate was also fed directly back to the production. For precipitation of iron in the sulfuric acid leach, spent potassium hydroxide electrolyte from discarded batteries was used. This necessitates a bleed from the cadmium carbonate filtrate of about 40% to separate potassium sulfate. This large bleed is due to the large portion of metals that were leached in the acid leaching stage compared with the processing of plating wastes. The bleed is treated to recover ammonia and carbon dioxide.

Brass Mill Flue Dust

Leaching of copper and zinc-rich flue dust is quite possible with an ammoniacal carbonate solution. Processing according to the Am-MAR flowsheet has not been tested in detail, but for comparison with the H-MAR processing, material balances and economy have been evaluated.

A main consideration in the choice of a processing route is the metal products obtained. In the H-MAR route, cathode zinc is produced while with the Am-MAR route, zinc carbonate or oxide is obtained. For a large-size operation, a considerably lower product value may have to be accepted because of market limitations, when producing zinc carbonate or oxide.

The economic evaluation was based on a leach solution of 5 g/l Cu and 25 g/l Zn and 95% leaching efficiency without the use of an acid leach stage. These assumptions may be too optimistic, favouring the ammoniacal alternative in the economic comparison.

Economic Evaluation of the MAR Processes

From the results of laboratory and pilot plant studies, material balances and production costs have been calculated. Engineering flowsheets have been used to estimate the investment costs except for Am-MAR processing of Cu-Zn dust, where data from the calculations for Ni-Cd scrap and Cu-Ni-Zn sludge were used.

In the calculation of operating costs, all feed material has been assumed delivered free to the plant except for steel mill flue dust, where a transportation cost has been included. All data have been calculated for 8000 hours operation per year. Cost factors and product values used are given in Table 4.

It must be pointed out that all costs for equipment, labour, chemicals and energy have been calculated for Swedish conditions. However, the discussion and comparison between different alternatives should be valid for other conditions. All costs have been converted to US dollars using a conversion factor of 1 \$ = 4.50 Sw.

TABLE 5. Summary of Process and Economic Data for the MAR-Processes

	H-MAR Zn-dust	H-MAR Cu-Zn- dust	H-MAR Cu-Zn- dust	Am-MAR Cu-Zn- dust	Am-MAR Cu-Zn- dust	Am-MAR Cu-Zn-Ni- sludges	Am-MAR Ni-Cd- scrap
Feed material (tons)	52,500 ¹⁾	6,200 ²⁾	12,400 ²⁾	6,200 ²⁾	12,400 ²⁾	12,000 ³⁾	2,400 ⁴⁾
Product Cu "		480	960	530	1,060	260	—
" Zn "	10,000	2,400	4,800	2,500 ⁵⁾	5,000 ⁵⁾	300 ⁶⁾	—
" Ni "	—	—	—	—	—	180 ⁶⁾	300 ⁶⁾
" Cd "	—	—	—	—	—	—	200 ⁷⁾
Direct investment (USK\$)	12,600	5,100	7,900	3,200	5,300	3,600	3,600
Operating cost "	5,000	1,500	2,600	1,500	2,700	1,100	1,100
Product value "	7,800	2,600	5,100	2,700	5,300	1,400	2,500
Return on assets %	10	8	17	20	32	—	24

1) 25% zinc content (20% in ferrites).

2) 40% copper rich dust and 60% zinc rich dust.

3) dry substance 30%.

4) inclusive of electrode frames, leachable material 60%.

5) as carbonate or oxide.

6) as nickel sulfate.

7) as cadmium carbonate.

crowns. As many recovery facilities will be built in connection with the main production, only nominal costs for laboratory facilities and sales organization have been included. A summary of the evaluation of the different process alternatives is given in Table 5.

In the table, direct investment refers to costs for equipment, construction, commissioning etc. and includes starting chemicals for SX (organic phase). Operating cost includes chemicals, energy, labour, maintenance etc. but not depreciation, capital costs or overhead. Product value has been calculated using the figures in Table 4. "Return on assets" has been calculated as the ratio between total sales minus total cost (operating cost, depreciation and nominal overheads, but not capital cost) and direct investment plus working capital.

A main consideration for judging the economy of a recovery process is the availability of the intended feed material. Processing of steel mill flue dust has been based on dust containing 25% Zn at a production of 10,000 tons of zinc per year. This size is large compared with Swedish scrap-based steel mills. Dust from one mill may contain 2-3,000 tons of zinc. However, a large European steel mill may produce three to four times that amount.

Brass mill flue dust treatment has been evaluated for two different sizes and both with H-MAR and Am-MAR processing. The smaller size, 500 tons Cu and 2,500 ton Zn corresponds to the need for one large European brass mill. A comparison shows that the investment for the sulfuric acid leaching and electrolytic production of zinc is considerably higher than for the ammoniacal leaching and zinc oxide production. The product value for the zinc oxide has been calculated based on the full value of the contained zinc. This may be too optimistic and much depends on the market situation and the quality of zinc oxide that can be produced. Normally zinc oxide quality is judged from the lead content. With a completely different production technique other impurities must be taken into account.

DISCUSSION

C. Bozec: There is a high content of chloride in steel flue dust. Have you considered this point in the H-MAR flowsheet?

Is there any significant build-up of this element in the recycled acid flows?

The process calculation for Am-MAR treatment of hydroxide sludge has been based on 12,000 tons of sludge with 30% dry substance, normally obtained from filter press dewatering. This corresponds roughly to the total amount per year in Sweden. As can be seen in Table 5 the product value covers the operating cost but only partially the depreciation and capital costs. However, it must be taken into account that today, in Sweden, dumping of hydroxide sludge costs \$ 40 per ton regardless of water content. The sludge amounts may also change drastically due to environmental pressures. Presently, discussions about neutralization of mine waters are taking place. Just one of the larger mines would produce some 4000 tons of sludge containing 230 tons of zinc.

For a Ni-Cd battery producer the recovery of Ni and Cd in forms, which can be directly used in the production, can be a profitable operation. Also in this case the size has a dramatic effect on the economy. Estimates for a Swedish company showed that the amount of scrap presently available (800 tons) was too small, to make this type of processing feasible.

It is quite clear that further development in this area will take place and hopefully result in processes which can be made economical for the size of operation needed for single industries. In other cases waste material will have to be collected and transported to a central processing facility where conversion to usable products or raw materials can be made.

Acknowledgment

The MAR-project has been supported by the Swedish Board of Technical Development and by Swedish industries. This support is gratefully acknowledged. The authors also want to express their thanks to all those individuals who have contributed to this project.

S.O.S. Andersson: Yes, we have considered the chloride problem. The rejection of chloride is one aim with the SX step for zinc. Zinc is extracted and transferred to the strip solution, while negative ions remain in the raffinate. Build-up of 10 g/l of chloride in the recycled raffinate can be tolerated. This level is controlled by a bleed stream from the leach circuit. Some build-up of impurities, including chloride, in the strip

solution (electrolyte) will always occur. This is controlled by a small bleed stream, which is recycled to the leaching section, thereby recovering the contained zinc and sulphuric acid.

D.P. Ziegler: $ZnCO_3$ is an intermediate in the production of high surface area ZnO. Have you considered the suitability of the $ZnCO_3$ precipitates produced by your process for production of this sort of ZnO product?

S.O.S. Andersson: We have not tested our $ZnCO_3$ product from the Am-MAR process for this purpose. In normal ZnO production the purity is determined mainly by the lead content. In our case, lead contamination is nil and our main impurity is nickel. Product quality must therefore be determined by the end user and chemical analysis is not sufficient.

J.F. Urstad: With reference to the indicated bleed stream in the sulphate process: is the size of the bleed stream determined by the water balance, if also an anion process, accumulation effects of undesirable elements, e.g., chloride or other factors?

(2) For both processes: In the economic tables, were the operating costs of treating the bleed streams included? How does one propose to treat the bleed streams and deposit the end products?

S.O.S. Andersson: (1) The bleed stream from the leaching circuit of the H-MAR process is determined mainly by the accumulation of undesired elements e.g., chloride, fluoride and magnesium. However, the need for washing of residues put some strain on the water balance and in some cases this may be the critical factor. It depends on the raw material and regulations for the disposal of leach residues.

For the AmMAR process, the raw material normally contains 70% water and this together with wash waters and water introduced from the acid leach, determines the bleed. This bleed is normally more than sufficient to control impurity levels and sulphate build-up.

(2) Yes, the cost for bleed treatment was included in the operating costs. The bleed from the H-MAR process

can be treated with preneutralization and solvent extraction of the remaining zinc and final lime treatment before discharge. Another possibility is to precipitate the zinc with sodium hydroxide and feed the precipitate to the leaching. The filtrate is discharged. The details of the treatment depends on local regulations.

The bleed from the AmMAR process is treated by thermal stripping of ammonia and carbon dioxide to recover the chemicals and produce an acceptable effluent. As the bleed is taken from the filtrate after carbonate precipitation the metal content is very low.

J. Shorr: Does organic matter, e.g., complexing materials, sequestrines, etc. affect the system of the sludge treatment? Since these organics are different from one system to another, does it require a special study for each individual sludge?

S.O.S. Andersson: Organic matter that accumulates in the SX circuits may affect the performance. However, for the typical plating sludges we have tested, this has not been observed. I expect that most of the organic matter remains in the leach residue. Organic material transferred with the solution to the ammonia stripping unit may cause excessive foaming and must then be removed, e.g., with active carbon filtration. If the presence of organic complexing agents, etc. is known, laboratory tests to determine their effect is advisable.

A. Van Peteghem: Did you notice in the H-MAR flow-sheet iron pick-up in the zinc solvent extraction circuit, and if so how do you get rid of this iron?

S.O.S. Andersson: In the controlled neutralization in the leaching step, iron levels are brought down to about 10 ppm. The small iron pick-up that occurs seems to reach some kind of equilibrium with the stripping. Significant iron build-up in the organic was not observed during our pilot tests. We have made the same observation in the commercial plant of the Valberg process for zinc recovery from rayon effluents using DEHPA. Originally a separate iron removal step was designed but no significant iron build-up was found.

CONFERENCE SUMMARY AND CLOSING REMARKS

G.M. Ritcey, ISEC '77 Conference Chairman

We have had successive international solvent extraction conferences in the United States, Sweden, Israel, United Kingdom, Netherlands and now Canada, each with its own specific format and themes. This particular ISEC '77, although attempting to cover all aspects of solvent extraction, had its theme directed toward the industrial side of metals recovery. I believe that objective was achieved.

The conference dwelt much on the elaboration of the information provided earlier at ISEC '74 at Lyons as well as other meetings. This included the areas of dispersion, coalescence, mass transfer, reagents, diluents, modifiers, equipment and environment. No real major breakthroughs were reported, but an improved understanding was, I believe, generally achieved.

With the large industrial audience in attendance there has been a definite increase in the application to an integrated process. The conference marked the first time that the majority of delegates were housed in the same hotel. This provided the setting for renewed friendships as well as new ones. Such communication that resulted was, I am certain, valuable in the technical sense as well as the social, for one can often learn as much outside the formal session as inside. Lively discussions were held in the poster sessions and in the several panel discussions on organic reagents, mass transfer, inorganic processes, mixer settlers, uranium and copper. These panel discussions were a real asset to ISEC '77, but I think that in the future, if we were to do this, we should allow more time for such panel discussions.

To attempt to summarize a technical conference of this size in any detail requires more time than we have here. I should mention, however, in the summary that I will give in the next few minutes, that I was assisted by the various session co-chairmen throughout the conference who provided me with their summaries and from which I have abstracted.

With respect to the reagents, again as in previous conferences the major emphasis was on copper with no real departure in reagent type or configuration. The modifications were slight. Both basic and applied research were demonstrated in the reagent sessions and effectively presented the current state of the art.

Reagents of the sulphoxides and dialkyl sulphides, methyl phosphates and crown ethers, for example, appear to offer future potential uses, as well as do the solvent extraction-bridged ion exchange resins. The physical aspects of the extraction system were discussed which showed that application of physical chemistry together with the incorporation of knowledge from other fields can provide a broader horizon necessary to achieve the full potential and practical application of solvent extraction.

The addition of certain alcohol modifiers, such as an alkylphenol, to hydroxyoximes or hydroxyquinolines was shown to influence the equilibrium and kinetics of copper extraction. Additives, as accelerators to improve the rates of copper extraction, were described for the salicylaldoxime extractants. No substantially new work was presented on improving the understanding of the diluent and its role in the solvent extraction process.

Mass transfer studies continued in the examination of the hydroxyoximes for copper. The consensus was that the rate of such extraction could not always be assumed

to be chemically controlled. Diffusion effects play a role whose importance varies, depending on the type of apparatus used for the kinetic studies, and a number of models were put forward for that area. An important point that was brought out was the need to use extremely pure compounds in the laboratory studies of extraction mechanisms.

Some general aspects of mass transfer were covered including axial mixing in columns, a special sampling probe for columns which permits the direct measurement of mass transfer driving forces at any position, the effect of interfacial absorption on mass transfer phenomena, and the development of an air-agitated packed extraction column.

Papers presented in the modelling sessions continued to show a trend from the purely theoretical appraisal of modelling in solvent extraction to its practical realization in industrial processes. We had this week, for example, the bringing together of the physics or the hydrodynamics of the process, the thermodynamic concepts of mass transfer and an appraisal of the problems of scale-up. Methods of predicting coefficients, being the basis of all solvent extraction work, were covered by several contributors where the methods used varied from semi-empirical to fully thermodynamic approaches to the problem, the mathematical complexity of the approach being consistent with the theoretical nature of the model. For the future, it would seem that work is still required to place the solvent extraction process on a sound thermodynamic footing and to include in this work a still better understanding of the physical behaviour of the extraction devices.

On the equipment side, with respect to mixer-settlers work was carried out on laboratory, pilot, and commercial scales, highlighting points such as the mixer-settlers in series, rather than single mixers per stage. These were reported to improve the performance both theoretically and in practice. Of considerable interest were the experimental results with a vertically baffled settler to substantially reduce the solvent loss, the settler size and entrainment. A settler designed for settling three immiscible liquids has also been developed. A session on mixer-settlers demonstrated an increasingly rational approach towards determination of equipment design parameters. Regarding differential contactors — the reciprocating plate, the sieve plate, pulse and spray columns were described and there were also papers on mixer-settler coalescence aids and centrifuges. In general, any data on the performance of equipment is to be welcomed but comparisons of the work discussed at this conference with previously published data is not possible. The design of solvent extraction columns is a difficult matter, and the small amount of information on mass transfer coefficients and flow phenomena as a function of scale is a major problem. The papers on industrial equipment may encourage the future use of columns and centrifuges by virtue of the performance data supplied. However, it is notable that interpretation of data is not very profound. Much industrial data is rendered of little value for re-interpretation using transfer units, if equilibrium data and operating conditions are not given fully.

Use of centrifuges for metals recovery is of interest but the problems associated with the use of precision-made equipment in the mining industry must be considered carefully. There are situations where they can be used but they should be thoroughly studied. The use of mobile equipment for processing leach liquors from small ore bodies, particularly uranium, is of considerable interest and perhaps centrifuges might be used in these circumstances.

The problems related to coalescence of dispersions can

be considered in the three main stages involved in the overall separation. Thus, the flocculation of droplets to form a close dispersion band, coalescence within the dispersion band, and phase disengagement after primary coalescence were considered in papers during the week dealing with these three important aspects.

There were many papers during the conference describing processes for extraction of organics or inorganics. The organic papers included the diphenols, cyclohexanol, asphaltenes and caprolactam as well as other mixtures. The inorganic papers included extraction of boron, gallium, cobalt, arsenic, phosphorus, zinc, tantalum, columbium, alkali metals, manganese, thorium, protactinium, platinum and osmium. Flowsheets were also described for aluminum, chromium and vanadium.

Of interest in the copper processing was the pilot plant evaluation of LIX 34. Also of interest was the sensitivity to costs of copper solvent extraction plants using two different reagents, due to the various design parameters such as flow rate, plant capacity and copper concentration. And, of course, we had the very interesting panel, just finished, on the copper plants.

The uranium processing session was an excellent overview of the application of solvent extraction for uranium recovery in the South African gold mining industry. No two solvent extraction plants are identical in design or operation, being suited to the particular conditions of the mine concerned. The plant operating efficiencies are similar to whatever method was used. The session covered the Purlex and the Bufflex processes and discussed the high purity at lower cost that is obtained in the Purlex operation. Also, comparisons of solvent extraction with continuous ion exchange for the recovery of uranium were presented showing that continuous ion exchange offers substantial advantages for certain operations. Following the three papers, the panel discussed aspects in Canada and South Africa.

Regarding nuclear processing, even after twenty-five years of development improvements are still being made in the solvent extraction processing with TBP. For example, at this meeting improvements have been reported in the design of safe mixer-settlers, the processing of enriched uranium fuels, the prevention of unwanted solids formation, methods of cleaning up the used solvent, methods for achieving valence change in the processes, methods for stripping or partitioning metals from the solvent phase, and a knowledge of extraction kinetics.

A new area for potential solvent extraction development has risen in the last few years, and this is in the handling of nuclear wastes. The extremely high decontamination factors pose a real challenge to the ingenuity of the solvent extraction experts. A number of interesting papers were presented in that field.

Recent work in the analytical area concerning solvent extraction methodology was required to determine small amounts of solvent components and has involved thin layer chromatography, high-pressure liquid chromatography and gas chromatography. While progress has been made in some areas, considerably more is required both in sampling and analysis if we are to understand and combat solvent losses.

Solvent extraction techniques in analytical chemistry are still of particular interest especially in determining low-level metal concentrations. Techniques that involve sub-stoichiometric solvent extraction procedures in neutron activation and the use of solid-liquid systems in rare earth determinations provide two important areas. The development of analytical and sampling methodology from the bench to the plant is an area in which considerably more

effort is required which can provide knowledge for environmental control, process control and finally the optimization of the solvent extraction process.

In the important area of considering the environmental aspects of solvent extraction processing, this session was interesting in that more research is gradually in evidence.

Economics is thus not the main overlying theme in the development of the process but the cost of effluent treatment is also a major constraint. One paper dealt with treating waste solutions arising from sulphuric acid leaching or from ammoniacal carbonate leaching, for the recovery of metal values. We also had a discussion of solvent extraction applied to waste water treatment. But to use the solvent extraction process for the recovery or removal of any material also implies that the process itself releases a pollutant to the effluent stream which can have an adverse toxicity effect on the aquatic life. One paper described the decomposition of the organic phase, decomposition products, soluble losses and evaporation losses resulting from mixer-settler plant operations using LIX 64 for copper.

That summarizes the conference. I would like to say now where I think we should be going from ISEC '77. I, as well as others in this room, believe that we have reached a plateau in the learning process concerning solvent extraction technology. If we are to influence that progress and the progress to higher limits, and therefore assist in the implementation of solvent extraction for the optimization of process technology, we must be prepared to do more work in certain areas. More integrated and applied research is thus required if the technology is to advance at a rapid pace.

We now have a multitude of reagents, most of them designed for copper. All have their respective advantages and disadvantages. We still lack reagents specific for other metals and capable for use at a low pH. Much research in the past has dwelt on the examination of these reagents, but it seems to me that much further research is only of academic value. Either the manufacturers must develop other reagents for specific extraction purposes if other plants are to be developed or we must make use of such reagents, as the alkyl phosphates, which are capable of use in many situations, and modify the capabilities of those reagents to suit our needs. Perhaps we require more research on the use of solvents bridged with ion exchange resins. Certainly the combination of the two unit operations can be of definite benefit. Our understanding of diluents and their effects on mass transfer, kinetics, etc., has improved and would only warrant further work in the optimization for specific process applications.

Many types and designs of contactors are now available. Also, there have been much data produced on mass transfer aspects, dispersion and coalescence, modelling and design, as well as redesign, of equipment. The industry now requires all this excellent work to be put in its proper perspective where the physical and engineering aspects of the process design can be meaningful and helpful in the ultimate optimization of the plant design. Real systems, under proper pilot conditions, will be required to improve our understanding of this very interesting, but complex, area of solvent extraction. Thus, an integrated R & D approach must be taken with less work in isolation.

I mention the tying together of the technology for the ultimate plant, but at these and other conferences we really do not hear much about the design of plants, their economics, their problems or how these problems were solved. We have had a few sessions this week on the panels which attempted to get involved in that area. Such problems involve the chemical and physical aspects as

well as those resulting from corrosion problems due to the materials selected for the equipment in the plant. Studies related to the plant would be of real benefit to the many researchers working on the details concerning the design of the process, which also includes the selection of the materials of construction as well as the process chemistry and engineering. In recent years many materials of construction have become available so that even corrosive chlorides can be considered for metal recovery processes. Such systems offer increased kinetics and selectivity, the ability to recycle leach liquor and the possibility of producing elemental sulphur during the process instead of noxious sulphur dioxide. Serious thought should therefore be given to the use of the chloride route.

Energy, economics and environment: — These three "E's" are major factors in the final decisions and implementation of the solvent extraction process. Because of the energy situation and the increasing costs of that commodity, it is therefore evident and essential that all aspects of the process design be concerned with the utilization and conservation of energy. Such concern should therefore affect the choice of equipment and plant design. With respect to economics, naturally the process design must be economically viable. But with the rapidly changing economic situation, that factor is often a difficult one. Nevertheless, a process should be studied early in the

R & D work to determine its economic viability before proceeding further. A process that costs more than the product is worth is of very little use to anybody. Finally, we must become more concerned with the environmental aspects of the process. While some research has been performed over the last few years on acute toxicity tests with fish, organic removal and biodegradability of organics, much more research has to be done in this important area. We must not only convince plant management of an economic process but the process will have to meet the environmental constraints of that particular country. If we, as the solvent extraction community, are not prepared to devote an effort towards establishing and solving the environmental problems then we can only anticipate the eventual imposing of environmental restrictions by the respective governmental agencies.

In conclusion we have seen at this conference data demonstrating better knowledge of not only the fundamentals of solvent extraction but also that of the practical applications. We have convinced each other of the value of these scientific truths. Now we must convince more in the industry to implement our ideas and processes. We must become better salesmen — as well as scientists.

I now declare ISEC '77 closed.

G.M. Ritcey,
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