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ABSTRACT

An economical two-cycle solvent extraction process has been developed on a bench scale for the separate recovery of thorium and uranium from monazite sulfate liquors. Thorium is extracted in the first cycle with a primary amine in hydrocarbon diluent and uranium in the second cycle with a secondary or tertiary amine in hydrocarbon diluent. The principal advantages of the process over conventional precipitation methods are the essentially complete recoveries of both thorium and uranium and the clean separation of these metals from each other and from rare earths and phosphate. The rare earths can also be recovered and separated from phosphate by amine extraction if desired.

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1.0 SUMMARY

The amine extraction (Amex) process provides a low-cost, efficient, continuous method for recovering thorium and uranium from monazite sulfate liquors. Recovery of both elements is essentially complete. The thorium product, which is nuclear grade with respect to uranium contamination and contains only very small amounts of rare earths and phosphate, is more amenable to final purification by TBP extraction than products obtained by available precipitation methods. After thorium and uranium have been removed from the liquor, the rare earths can be recovered and separated from phosphate by amine extraction or by precipitation as the sodium rare earth double sulfate.

The results of batch tests on extraction of thorium from monazite liquors showed that equilibrium was reached in approximately 1 min. Extraction of thorium depended strongly on the amine type and alkyl structure. Primary amines had by far the greatest affinity for thorium, 0.1 M solutions of these compounds having coefficients of 1000 or greater for extraction of thorium from typical monazite liquors. Extraction coefficients of the tertiary amines were nil, while those of certain secondary amines, e.g., di(tridecyl)amine, were high enough to allow process application. Primary amines extracted large amounts of rare earths from the liquor when thorium was not present, but only small amounts when the organic was saturated with thorium. Di(tridecyl)amine extracted only small amounts of rare earths even at low thorium loadings. With primary amines, the phosphate content of the unscrubbed extract was <0.5% based on the thorium, but with di(tridecyl)amine relatively large amounts of phosphate accompanied the thorium. Small amounts of alcohol modifier added to the kerosene diluent had little if any effect on extraction of thorium with Primene JM but a large depressing effect on extraction with di(tridecyl)amine.

Nitrate, chloride, and carbonate solutions stripped thorium from amines. Hydroxide solutions precipitated thorium directly from the solvent but separation of the phases was very difficult.

Both secondary and tertiary amines extracted uranium strongly enough from monazite liquors to be useful process extractants. The highest extraction coefficients (25-50 for 0.05 M amine) were obtained with N-benzyl branched-alkyl secondary amines.

The coefficients for extraction of rare earths from thorium- and uranium-barren monazite liquors with primary amines (0.2 M) were less than 1 but high enough to allow >98% extraction in three to four ideal extraction stages. At high rare earth loadings the phosphate content of the extract was

~1% of that of the rare earths. The rare earths were readily stripped with 3-4 M sulfuric acid, nitrate, chloride, or carbonate solutions. Addition of a sodium salt to the liquor precipitated the sodium rare earth double sulfate. Recoveries were >97% with ~3 lb of sodium chloride or ~2 lb of sodium sulfate per pound of rare earth oxides.

Flowsheet Demonstration. Continuous runs in bench-scale mixer-settler contactors successfully demonstrated a two-cycle process for recovering thorium and uranium. In three different runs, thorium recoveries were >99.9% in four extraction stages with 0.10 M Primene JM in 97% kerosene—3% tridecanol as the extractant. The extract was scrubbed in four stages with dilute sulfuric acid and stripped with either nitric acid—sodium nitrate solution or with sodium carbonate solution. Decontamination from uranium (<10 ppm uranium in the thorium product) was good when the thorium was extracted either before or after the uranium. The former approach is favored, however, owing to considerations on cross-over of extractant between processing cycles. The thorium products contained ~0.1% total rare earth oxides and <0.1% phosphate. Attempts to use di(tridecyl)amine for thorium recovery were unsuccessful owing to physical difficulties caused by carry-over of phosphate into the stripping system. In a single run with 0.05 M tri-iso-octylamine in 97% kerosene—3% tridecanol, uranium recovery was >99.9% in eight extraction stages.

On the basis of data obtained in the continuous tests, reagent costs for treating 1000 gal of monazite liquor to recover 50 lb of ThO_2, 1.9 lb of U_3O_8, and 280 lb of RE_2O_3 were estimated at about $22. This estimate assumes recovery of the rare earths by precipitation as the alkali rare earth sulfate using sodium chloride.

2.0 INTRODUCTION

The successful development of solvent extraction processes using alkyl amines for recovering uranium from ore-leach liquors[1,2] led naturally to adaptation of these extractants to the recovery of other metals, e.g., thorium, vanadium, and molybdenum. Of these elements, thorium is of particular interest because of its potential usefulness as a fertile material for breeder reactors. Monazite, which consists principally of the phosphates of rare earths and thorium, is the world's largest source of thorium. Recently, the discovery of uranium-thorium ores in the Blind River district of Canada has also signalled opportunity for recovering large tonnages of thorium as a by-product of uranium milling operations in that area. Studies have been made at the Oak Ridge National Laboratory on use of amine extraction (Amex) processes for recovering thorium from both of these important sources. This report describes the monazite studies, combining the informa-

tion previously reported[3,4] with results of more recent test work. Studies with Blind River liquors have been partially reported[5-7] and will be summarized in a separate topical report.

Previous studies of methods for treating monazite sand to recover nuclear grade thorium and to recover the uranium and rare earths in usable form have been made at Battelle Memorial Institute and Ames Laboratory. As an outcome of this work, several process schemes have been proposed. The Battelle process[8-10] uses caustic and the Ames process[11-15] sulfuric acid to open up the sands. In each case, the elements are partially separated by precipitation. The thorium-rich precipitate is redissolved in nitric acid and extracted with tributyl phosphate (TBP)[10,13] for final purification of the thorium. In general, separations of uranium and/or rare earths from the thorium in the precipitation steps of these processes are relatively poor, which complicates operation of the TBP cycle. Also, recoveries of uranium are often low.

The present amine studies were confined to treatment of sulfate liquors of the type obtained in the Ames process. However, amine extraction could probably be used in combination with the Battelle process if the hydrous metal oxides produced in the caustic digestion step were dissolved in sulfuric acid rather than the conventional hydrochloric acid. The principal objective of the program was to separately recover the thorium and uranium and to separate them from most of the rare earths and phosphate by simple solvent extraction operations. It was assumed that the thorium product would require further purification in a TBP solvent extraction system, although it was hoped that uranium contamination could be reduced to the level that no further decontamination from it would be needed. In batch tests the thorium, uranium, and rare earth extraction abilities of different amines were compared, the importance of several process variables was evaluated, and several methods of stripping thorium and rare earths from amine extracts were investigated. The thorium and uranium recovery cycles were then demonstrated in continuous countercurrent runs made in bench-scale mixer-settler equipment. Chemical reagent requirements were estimated on the basis of data obtained in the continuous tests.

Chemical and spectrographic analyses were obtained from the Y-12 section of the Oak Ridge National Laboratory Analytical Chemistry Division.

3.0 EXTRACTION OF THORIUM

The monazite liquors used in these studies were prepared by digesting Indian monazite sands in 93% sulfuric acid,

adding water to dissolve the metal sulfates, and filtering to produce a clear liquor. The procedure used is approximately the same as that recommended by the Ames Laboratory[12] and is described in detail in Sec. 11.1. Analyses of the four different liquor batches showed thorium concentrations ranging from 5.3 to 7.7 g/liter, total rare earth oxides ranging from 34 to 52 g/liter, and uranium ranging from 0.17 to 0.21 g/liter (Table 3.1). The pH of the liquors was approximately 0.05.

Table 3.1 Composition of Monazite Liquors[a]

	Analysis, g/liter				
	Spectrographic,	Chemical			
Component	Liquor A	Liquor A	Liquor B	Liquor C	Liquor D
Th	6.0	6.9	7.7	5.3	5.9
U	-	0.17	0.21	0.20	0.20
Total rare earth oxides	-	44	52	35	34
Ce_2O_3	19	22	-	-	-
La_2O_3	10	-	-	-	-
Pr_2O_3	2	-	-	-	-
Nd_2O_3	8	-	-	-	-
Sm_2O_3	1.5	-	-	-	-
Gd_2O_3	-	-	-	0.5	-
Y_2O_3	-	-	-	0.3	-
SO_4	-	129	137	128	120
PO_4	-	28	33	26	26

[a]Prepared as described in Sec. 11.1; the liquors had a pH of ~0.05 and a specific gravity at 25°C of ~1.15.

3.1 Thorium Extraction Rate

The extraction of thorium with amines was rapid. In extractions from a monazite liquor with 0.1 M Primene JM in kerosene, equilibrium was apparently reached in ~1 min:

Mixing Time, min	Th, g/liter Organic	Th, g/liter Aqueous	Thorium Extraction Coefficient[a] (E_a^Q)
0.5	3.0	1.9	1.6
1	3.0	1.5	2.0
2	3.0	1.6	1.9
3	3.0	1.6	1.9
5	3.0	1.6	1.9
10	3.0	1.6	1.9
30	3.0	1.6	1.9

[a]Coefficients were severely limited by thorium loading of the organic phase.

Contact in these tests was obtained by mixing the phases (o/a = 2/1) in a baffled mixer with a stirring speed of 600 rpm.

3.2 Effect of Amine Type and Structure

Previous studies[3,5,6,17] showed the thorium extraction power of amines in sulfate media to be strongly dependent on the amine type and structure. Primary amines have tremendous affinity and tertiary amines negligible affinity for thorium. Performance of the secondary amines is intermediate and varies greatly with the structure of the alkyl chains.

A similar pattern was obtained in extractions from monazite liquors although the magnitude of the coefficients was much lower in this case owing to the relatively high acidity and sulfate and phosphate contents of these liquors (Table 3.2). Extraction coefficients for thorium from monazite liquor A were >140 with the two primary amines (0.2 M) but <0.05 with tri-n-octylamine. The secondary amine Amberlite LA-1 (0.2 M), which has branching close to the nitrogen, extracted thorium very weakly (E_a^Q 0.3). Secondary amines (0.2 M) with branching more distant from the nitrogen, i.e., di(2-butyloctyl) and di(tridecyl), showed moderate extraction power (E_a^Q 1.8-4.6).

An isotherm (Fig. 3.1) obtained for the extraction of thorium from a monazite liquor with 0.10 M Primene JM in 97% kerosene—3% tridecanol illustrates the very strong extraction power of this amine. The extraction coefficient was 400 even at near maximum loading of the solvent, i.e., 2.8 g of thorium per liter. A recovery of >99.8% could be expected in one ideal extraction stage while loading the amine to 90% of its capacity.

Table 3.2 Extraction of Thorium from Monazite Liquor with Amines

Aqueous: liquor A, 6.9 g Th/liter (complete analysis in Table 3.1)
Contact time: 2-5 min

Amine	Diluent	Amine Conc, M	Phase Ratio, o/a	Phase Sep'n Time, sec	Th Extr. Coef. (E_a^o)
Primaries					
Primene JM	Amsco D-95[a]	0.1	3	50	> 70
		0.2	1.5	50	>140
	Kerosene	0.2	1.5	120	>140
	95% kerosene—5% capryl alcohol	0.2	1.5	90	>140
1-(3-ethyl-pentyl)-4-ethyloctyl	Amsco D-95[a]	0.1	3	45	> 70
		0.2	1.5	35	>140
Secondaries					
Amberlite LA-1	Kerosene	0.1	3	55	0.16
		0.2	1.5	75	0.3
Di(2-butyl-octyl)	95% kerosene—5% capryl alcohol	0.2	1.5	60	1.8
Di(tridecyl)	Kerosene	0.1	5	b	4.6
			2	b	2.1
		0.2	2.5	b	4.6
N-benzyl-1(3-ethylpentyl)-4-ethyloctyl	Kerosene	0.1	3	60	3.1
Tertiary					
Tri-n-octyl	95% kerosene—5% capryl alcohol	0.2	1.5	75	<0.05

[a] High-boiling aromatic petroleum product.

[b] Phase separation very slow, 5-15 min; addition of 1-2 v % tridecanol to solvent greatly improved phase separation rate.

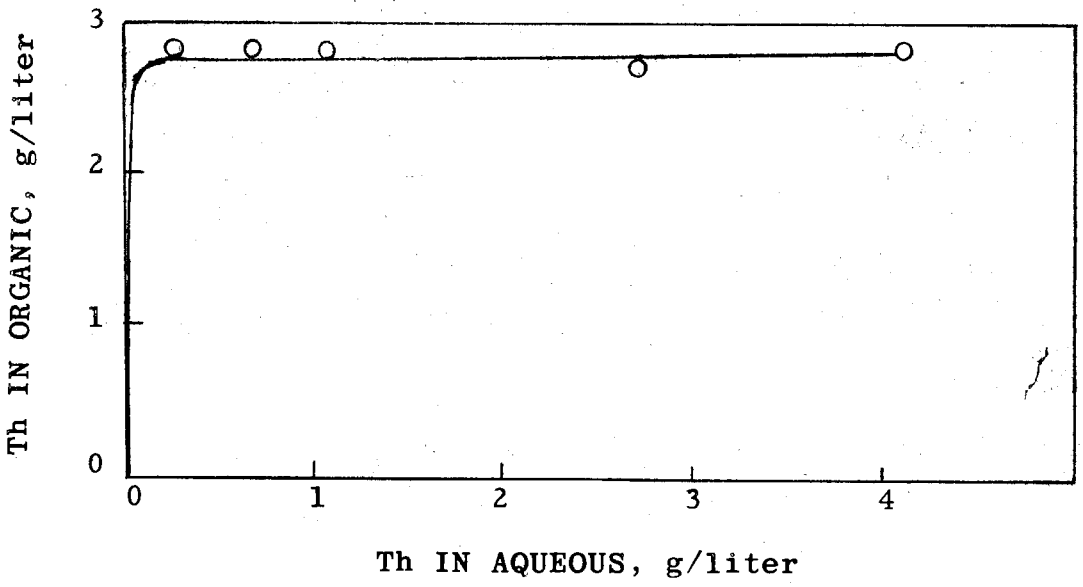

Fig. 3.1. Thorium extraction isotherm for 0.10 M Primene JM in 97% kerosene—3% tridecanol. Aqueous: uranium-barren monazite liquor containing 5.3 g of thorium per liter (uranium extracted with tri-iso-octylamine).

3.3 Selectivity of Amines

Although the primary amines extracted appreciable amounts of rare earths at low thorium loadings, rare earth contamination of the extract was limited to a low level by loading to near saturation with thorium (Table 3.3). For example, with 1-(3-ethylpentyl)-4-ethyloctyl amine (0.2 M), the cerium concentration in the extract decreased from 1.4 to <0.12 g per liter as the thorium concentration in the extract was increased from 3.1 to 6.0 g/liter. Results with Primene JM were similar. With the secondary amine di(tridecyl), only small amounts of cerium (and presumably other rare earths) were extracted at low thorium loadings. Here again, however, decontamination from cerium improved considerably with increase in thorium loading of the solvent.

3.4 Extraction of Phosphate

The amount of phosphate extracted with the thorium depended strongly on the choice of amine extractant. Large amounts of phosphate were extracted with the secondary amine, di(tridecyl), whereas a negligible amount of phosphate accompanied the thorium in extractions with the primary amine,

Primene JM. Results were essentially the same after 2 and 30 min contact time:

Amine	Diluent	Contact Time, min	Organic Analysis, g/liter Th	PO_4
Di(tridecyl)	99% kerosene— 1% tridecanol	2	2.6	1.2
		5	-	1.2
		15	-	1.2
		30	-	1.3
Primene JM	Kerosene	2	2.6	<0.01
		5	-	<0.01
		15	-	<0.01
		30	-	<0.01

These results were obtained in extractions with 0.1 M amine solutions at an organic/aqueous phase ratio of 1/1 from a uranium-barren (uranium removed from the liquor by extraction with tri-iso-octyl amine) monazite liquor containing 5.3 g of

Table 3.3 Effect of Thorium Loading on Selectivity of Amines

Aqueous: liquor A, 6.9 g Th/liter (complete analysis in Table 3.1)
Contact time: 2-5 min

Amine	Diluent	Amine Conc, M	Phase Ratio (o/a)	Final Conc, g/liter Organic Th	Organic Ce	Aqueous Th	Th/Ce Wt Ratio in Organic
Primene JM	Amsco D-95	0.2	2	3.1	1.28	<0.03	2.4
			1.5	4.4	0.48	<0.03	9.2
			1	5.8	<0.4	1.05	>14
1-(3-ethyl-pentyl)-4-ethyloctyl	Amsco D-95	0.1	3	2.1	0.46	<0.03	4.6
			2	3.1	<0.12	0.43	>26
		0.2	2	3.1	1.40	<0.03	2.2
			1.5	4.2	0.82	<0.03	5.1
			1	6.0	<0.12	0.33	>50
Di(tridecyl)	Kerosene	0.1	8	0.71	0.11	0.14	6.5
			5	1.15	0.085	0.25	13
			2	2.3	0.035	1.10	65
		0.2	4	1.42	0.20	0.22	7.1
			2.5	2.1	0.16	0.46	13
			1	4.5	0.05	1.38	90

thorium per liter.

Scrubbing Phosphate from the Extract. Phosphate was scrubbed rapidly from di(tridecyl)amine with dilute sulfuric acid:

Contact Time, min	PO_4, g/liter		Phosphate Stripping Coefficient (S_O^a)
	Organic	Aqueous	
2	0.8	2.4	3.0
5	0.8	2.4	3.0
15	0.8	2.4	3.0
30	0.7	2.4	3.4

The above data were obtained by contacting 0.1 M di(tridecyl)-amine in 99% kerosene—1% tridecanol, loaded from a monazite liquor to 2.7 g of thorium and 1.2 g of phosphate per liter, with 0.2 M H_2SO_4 at an organic/aqueous phase ratio of 5/1. Isotherms for scrubbing phosphate from the extract with 0.2 and 0.5 M H_2SO_4 were then determined (Fig. 3.2). Although all the phosphate can be scrubbed from the solvent, the isotherms indicate that, with either scrub solution, the sulfuric acid requirements would be relatively high. For example, the indicated sulfuric acid requirement for scrubbing 95% of the phosphate from the solvent with 0.5 M H_2SO_4 in four ideal stages is ~6 lb/lb ThO_2.

3.5 Effect of Alcohol Modifier

Addition of 2 or 5 v % tridecanol to the kerosene diluent had no significant effect on extraction of thorium from 1 M H_2SO_4 with Primene JM but caused a large decrease in the thorium extraction coefficients for di(tridecyl)amine (Table 3.4). Addition of a long-chain alcohol to the diluent is sometimes desirable to increase the miscibility of the amine salt in the diluent and to improve phase separation.[1,5] As shown in Sec. 6.2, addition of alcohol to the solvent has the added advantage, when using primary amines, of depressing the extraction of rare earths.

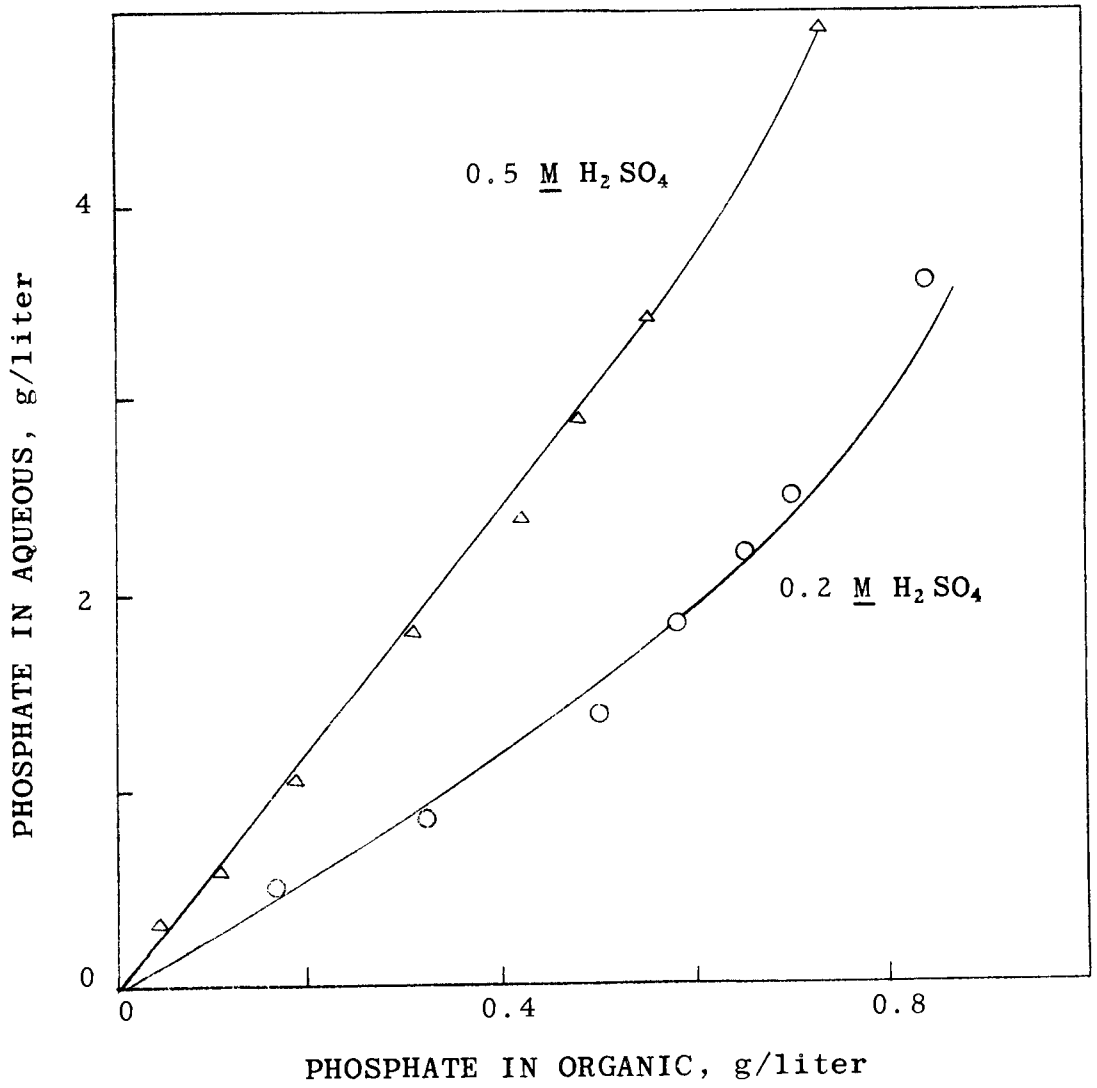

Fig. 3.2. Scrubbing of phosphate from di(tridecyl)amine with sulfuric acid. Head organic: 0.1 M di(tridecyl)amine in 99% kerosene—1% tridecanol loaded to 2.7 g of thorium and 1.2 g of phosphate per liter from a monazite liquor. Contacted 30 min with scrub solution at various phase ratios.

Table 3.4 Effect of Alcohol Addition on Thorium Extraction

Aqueous: 1 M H_2SO_4, 1.65 g Th/liter
Organic: 0.05 M amine in kerosene or kerosene-alcohol
Phase ratio, $a/\overline{o}$: 1/1

Amine	Tridecanol in Kerosene, v %	Th, g/liter Organic	Th, g/liter Aqueous	Thorium Extraction Coefficient (E_a^o)
Di(tridecyl)	0	1.39	0.26	5.3
	2	1.05	0.60	1.8
	5	0.52	1.06	0.5
Primene JM	0	1.43	0.25	5.7[a]
	2	1.45	0.26	5.6[a]
	5	1.39	0.25	5.6[a]

[a]Coefficients severely limited by saturation of the solvent with thorium.

4.0 STRIPPING OF THORIUM

Thorium was stripped effectively by treatment of Primene JM extracts* with nitric acid, acidified nitrate salt solutions, or solutions of basic reagents such as sodium carbonate, sodium hydroxide, and ammonium hydroxide. Acidified sodium chloride solution was a relatively ineffective stripping agent.

4.1 Stripping with Nitrate

The thorium is present in the extract as a thorium-amine-sulfate complex, along with excess amine sulfate and/or bisulfate. Although the actual stoichiometry of the thorium-amine-sulfate complex is not known, it is written for convenience here as $(RNH_3)_2Th(SO_4)_3$. Treatment of the extract with neutral or acidic nitrate solutions results in displacement of the thorium with the nitrate anion:

$$\underset{\cdots\cdots\cdots}{(RNH_3)_2Th(SO_4)_3} + 2NO_3^- \rightleftharpoons \underset{\cdots\cdots}{2RNH_3NO_3} + Th^{4+} + 3SO_4^{=}$$

and

$$\underset{\cdots\cdots\cdots}{(RNH_3)_2SO_4} + 2NO_3^- \rightleftharpoons \underset{\cdots\cdots}{2RNH_3NO_3} + SO_4^{=}$$

(The dotted underlines mark species in the organic phase.)

*Tests on stripping of thorium from a secondary amine, di(tridecyl), with nitrate, chloride, and carbonate solutions were described previously.[6]

Thorium stripping coefficients were considerably higher for nitric acid than for acidified nitrate salt solutions of equivalent nitrate concentration (Table 4.1). In both cases the stripping efficiency increased with increase in nitrate concentration in the range 1-3 M. With 2 and 3 M nitric acid, thorium precipitated (probably as a sulfate salt) from the pregnant strip solution on standing. The nitric acid—ammonium nitrate strip solutions were stable, however, even at thorium loadings up to 50 g/liter. Although nitric acid is a more effective stripping agent, the nitrate salt is ordinarily preferred since less base is required to precipitate thorium from the pregnant strip solution. In addition, nitrate salt

Table 4.1 Stripping Thorium from Primene JM with Nitrate

Organic extract: A, 0.2 M Primene JM in Amsco D-95 loaded to ~4.8 g Th per liter by extraction from a monazite liquor

B, 0.2 M Primene JM in kerosene loaded to 5.4 g Th and 13.4 g SO_4 per liter by extraction from a monazite liquor

Contact time: 2 min

Stripping Solution	Organic Extract	Phase Ratio (o/a)	Th, g/liter Organic	Th, g/liter Aqueous	SO_4 in Aqueous, g/liter	Thorium Stripping Coef. (S_o^a)
1.0 M HNO_3	A	1	<0.03	5.5	-	>180
		3	0.7	14.0	-	20
		5	2.0	15.0	-	7
		8	2.9	15.3	-	5
2.0 M HNO_3	A	5	0.05	24[a]	-	~500
3.0 M HNO_3	A	5	<0.03	24[a]	-	>800
0.2 M HNO_3 — 0.8 M NH_4NO_3	B	4	2.6	11.7	29	4.5
		5	2.8	12.8	31	4.6
0.2 M HNO_3 — 1.8 M NH_4NO_3	B	8	1.9	29	72	15
		10	2.4	31	78	13
0.2 M HNO_3 — 2.8 M NH_4NO_3	B	12	1.2	47	122	40
		15	1.6	51	126	32

[a]Calculated from analysis of the organic. Thorium precipitated from the strip solution on standing.

is available for use since it is produced during regeneration* of the amine.

An isotherm for stripping thorium from 0.10 M Primene JM with 0.2 M HNO_3—0.8 M $NaNO_3$ shows the maximum thorium loading of this strip solution to be approximately 17 g/liter (Fig. 4.1).

Rate of Stripping. Although most of the thorium was stripped in 1 min from Primene JM with 0.4 M HNO_3—0.6 M $NaNO_3$ solution, the final approach to equilibrium was relatively slow:

Agitation Time, min	Th, g/liter		Thorium Stripping Coefficient (S_O^a)
	Organic	Aqueous	
1	0.23	5.1	22
2	0.055	5.5	100
3	0.052	5.5	105
5	0.047	5.7	120
10	0.045	5.7	125

In this test the extract was 0.10 M Primene JM in 97% kerosene—3% tridecanol loaded to 2.9 g of thorium per liter from a monazite liquor. The phases were contacted by vigorous shaking in separatory funnels at an organic/aqueous ratio of 2/1.

4.2 Stripping with Chloride

Chloride is a much less effective stripping anion than nitrate. In stripping Primene JM with 1 M NaCl—0.05 M H_2SO_4 the maximum thorium loading of the strip solution was only

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*It is recommended that the amine nitrate be regenerated to the free base form by single-stage contact with a base, e.g., sodium carbonate or ammonium hydroxide, before recycle to the extraction system. This recovers the relatively expensive nitrate for recycle and avoids contamination of the extraction system with the nitrate anion, which may cause loss of extraction efficiency. It has not been established that the adverse effect of recycled nitrate on thorium extraction would be sufficiently large to be of concern when using primary amines but the effect on a subsequent uranium recovery cycle would undoubtedly be severe.

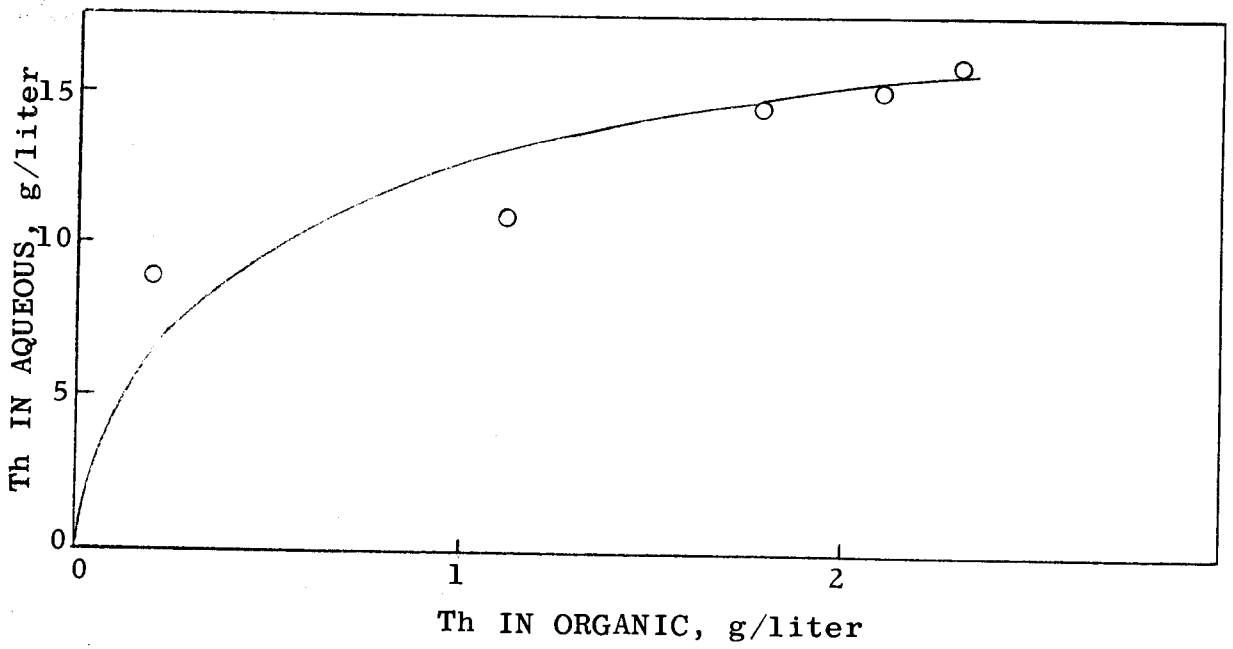

Fig. 4.1 Isotherm for stripping thorium from Primene JM with 0.2 M HNO_3—0.8 M $NaNO_3$. Organic: 0.10 M Primene JM in 97% kerosene—3% tridecanol loaded to 2.9 g of thorium per liter. Aqueous cascaded against fresh volumes of organic, 5-min contacts.

about 3.5 g/liter:

Phase Ratio, (a/o)	Th, g/liter		Thorium Stripping Coefficient (S_o^a)
	Organic	Aqueous	
1	0.24	1.1	4.6
3	0.69	1.9	2.7 (?)
5	0.71	2.9	4.1
10	1.0	3.3	3.3
15	1.1	3.4	3.1

In this test the extract was 0.05 M Primene JM in 98% kerosene—2% tridecanol loaded to 1.35 g of thorium per liter. The contact time was 2 min.

4.3 Stripping with Solutions of a Base

Hydroxide solutions precipitate thorium directly from the solvent. Simultaneously, the amine sulfate and bisulfate salts are converted to free amine which can be directly recycled to the extraction system:

$$(RNH_3)_2Th(SO_4)_3 + 6OH^- \rightarrow 2RNH_2 + Th(OH)_4\downarrow + 3SO_4^= + 2H_2O$$

and

$$(RNH_3)_2SO_4 + 2OH^- \rightarrow 2RNH_2 + SO_4^= + 2H_2O$$

Stripping of Primene JM was complete in 2 min with 2.5 M and 12.5 M sodium hydroxide solutions, using approximately 3 lb of NaOH per pound of thorium (Table 4.2). With 0.5 M

Table 4.2 Stripping of Thorium from Primene JM with Basic Solutions

Organic extracts: 0.2 M Primene JM loaded with thorium from a monazite liquor

Extract A: Amsco G diluent; 4.4 g Th/liter
Extract B: Amsco D-95 diluent; 4.8 g Th/liter

Contact time: 2 min

Stripping Solution	Extr.	Phase Ratio (o/a)	Th, g/liter Organic	Th, g/liter Aqueous[a]	Thorium Stripped,[b] %	Th Pptd,[c] % of Stripped
0.75 M Na_2CO_3	A	2	<0.03	8.5	>99	<5
		5	1.9	3.9	57	70
1.1 M Na_2CO_3	A	3	<0.03	12.5	>99	5
		7.5	1.8	9.0	59	55
1.5 M Na_2CO_3	A	4	<0.03	17.6	>99	<5
		10	2.1	17.9	52	20
12.5 M NaOH	B	35	<0.03	-	>99	-
2.5 M NaOH	B	7	<0.03	-	>99	-
0.5 M NaOH	B	1.4	permanent emulsion		-	-

[a] Analysis of the aqueous after filtration to remove thorium and rare earth precipitate. Precipitate settled rapidly in the aqueous phase.

[b] Based on analyses of the extract and stripped organic.

[c] Based on analyses of the extract, stripped organic, and filtered strip solution.

sodium hydroxide, a permanent emulsion formed, presumably because the organic/aqueous phase ratio (1.4/1) in this test was not sufficiently high to ensure organic-continuous mixing. Although no emulsions were found at higher phase ratios,

physical characteristics of the system still were not attractive since the slimy thorium precipitate did not settle in the aqueous phase but floated in the organic phase and collected at the interface. Problems were similar, although somewhat less severe, with ammonium hydroxide (results of tests not shown).

Treatment of the extract with sodium carbonate solutions also resulted in the formation of free amine but in this case the thorium went into the aqueous phase as a soluble carbonate complex provided sufficient excess of carbonate was present. Use of the carbonate stripping method affords opportunity for separating certain extracted contaminants, e.g., rare earths and titanium, since these elements are precipitated and can be filtered off prior to thorium precipitation. In some tests with Primene JM (Table 4.2), the solubilities of thorium in the carbonate solutions were exceeded and considerable precipitation* of thorium occurred. Phase separation, however, was rapid and clean, with all the precipitate settling rapidly in the aqueous phase. Owing to the favorable characteristics of the thorium precipitate, operation of the carbonate system with a low carbonate excess, i.e., allowing thorium to precipitate in the stripping system, has been considered and in bench-scale continuous tests [with di(tridecyl)amine] appeared operationally feasible. Larger scale evaluation, however, is needed. Operation of the stripping system in this way, of course, sacrifices the opportunity for obtaining separation from precipitated contaminants.

4.4 Recovery of Thorium from Nitrate Strip Solutions

More than 99.9% of the thorium was recovered from a nitrate strip solution by adding ammonia to pH 7. The thorium precipitate, after drying at 120°C, contained 69.3% ThO_2, 18% SO_4, and 0.7% CO_3 (Table 4.3). This high sulfate content is undesirable if the thorium product is to be further purified by TBP extraction, since the sulfate would adversely affect the thorium distribution coefficient.[13] Calcination at 750°C decreased the sulfate content of the product to 7.3%, and complete elimination of sulfate would be expected at still higher calcination temperatures.[6] High-temperature calcination is not attractive, however, since scouting tests indicated that the calcines could not be dissolved readily in nitric acid.

The sulfate content was reduced to 0.2-0.3% by reslurrying the precipitate in 0.5 M sodium hydroxide for 1 hr at

*Tests with di(tridecyl)amine previously reported[6] showed essentially complete precipitation of the stripped thorium under certain test conditions.

Table 4.3 Elimination of Sulfate from Thorium Precipitates

Procedure: Thorium precipitated from nitrate strip solution[a] from continuous run 1 (Sec. 7.2) by addition of ammonia to pH 7, digested 1 hr, filtered and washed; portions of the wet precipitate treated as indicated prior to calcination.

Treatment of Precipitate	Calcination Temp, °C	Analysis of Calcined Product, % ThO_2	SO_4	CO_3
None	120	69.3	18	0.7
	500	76.1	21	0.3
	750	86.8	7.3	<0.1
Reslurried with 0.5 M NH_4OH for 1 hr, filtered, and washed	120	82.8	5.0	1.1
	500	92.1	5.2	0.3
	750	95.7	2.0	0.1
Portion of filter cake from preceding test slurried with 0.5 M NH_4OH for 1 hr, filtered, and washed	120	84.4	2.7	1.4
	500	94.2	2.9	1.1
	750	95.4	1.9	<0.1
Reslurried with 0.5 M NaOH for 1 hr, filtered, and washed	120	88.0	0.3	2.7
	500	95.6	0.2	0.5
	750	98.8	0.3	<0.1
Portion of filter cake from preceding test reslurried in 0.5 M NaOH for 1 hr, filtered, and washed	120	88.1	0.2	0.6
	500	97.2	0.2	0.6
	750	99.1	0.2	0.3

[a]Analysis, g/liter: Th 10.9, U <0.0001, NO_3 33, SO_4 29, CO_3 <0.04.

room temperature (Table 4.3). Ammonium hydroxide was somewhat less effective, although the results suggest that an increase in the digestion time, or possibly in the ammonia concentration and temperature, might have been beneficial.

Filtration rates were very rapid, both after the initial precipitation and after slurrying with sodium or ammonium hydroxide.

4.5 Recovery of Thorium from Sodium Carbonate Strip Solutions

Under certain conditions, i.e., stripping with a small excess of carbonate, a high percentage of the stripped thorium may precipitate in the stripping system (Sec. 4.3) and be recovered simply by filtration. Unprecipitated thorium would not be lost, since the filtrate, after fortification with sodium carbonate, would be recycled* for further stripping. From the chemical standpoint, this flowsheet provides a direct and economical method for recovering thorium from the solvent, but, as previously mentioned, more testing is needed to prove its operational feasibility. If operational difficulties are encountered, it may prove necessary to avoid thorium precipitation by using a larger excess of carbonate. Therefore, some studies were made of thorium precipitation from a carbonate strip solution.

Thorium was recovered effectively when caustic was added to pH 12-13 or when sulfuric acid was added to pH 5-6. The pregnant strip solution used was produced in a preliminary continuous run in which a monazite liquor was extracted with Primene JM and the thorium was stripped with 1 M Na_2CO_3 solution, using a sufficient excess of carbonate to prevent thorium precipitation.

Precipitation by Addition of Caustic. Approximately 93% of the thorium was precipitated when caustic was added to the solution to pH 11.9 (1.1 lb NaOH/lb ThO_2) and the solution was digested for 0.5 hr (Table 4.4). The product, analyzing 72% ThO_2 and 16% CO_3, apparently was principally the basic carbonate salt. Thorium recovery decreased to 87% when the digestion time was extended to 18 hr. At pH >13 (1.3 lb NaOH/lb ThO_2), recovery in all tests was >99.9%; the products contained 80-84% ThO_2 and 9-11% CO_3. In all tests the sulfate content of the products was 1% or less. A very favorable separation** of thorium from uranium was obtained at pH 11.9 but not at pH >13. In the former case, <5% of the uranium initially present reported in the thorium product. In all tests, filtration of the rather gelatinous precipitates was extremely slow.

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*Some bleed would be necessary to prevent excessive buildup of sulfate in the recycle solution. The bleed solution would be recycled to the feed liquor storage tank.

**The uranium contamination of this strip solution, which was produced in a preliminary run under far from optimum operating conditions, was much higher than would be expected. Proper operation of the thorium circuit should give adequate decontamination from uranium in the extraction and scrub steps (Sec. 7.3) and further separation from uranium during precipitation should not be needed.

Table 4.4 Precipitation of Thorium from Carbonate Strip Solutions with Sodium Hydroxide

Carbonate strip solution: 18.5 g Th, 0.07 g U, 46 g CO_3, and 48 g SO_4 per liter at pH 9.0

Procedure: thorium precipitated with 10% NaOH from three portions of strip solution by addition of 0.21, 0.26, and 0.30 lb NaOH/lb ThO_2, respectively; samples of precipitate slurries withdrawn after 0.5, 2, and 18 hr, filtered, washed with water, dried at 110°C, and analyzed

NaOH Added, lb/lb ThO_2	Digestion Time, hr	pH of Filtrate	Th Precipitated, %	Dried Product, % ThO_2	U_3O_8	SO_4	CO_3
1.1	0.5	11.9	93.4	72	-	1.0	16
	2	11.8	92.6	76	<0.01	<0.2	14
	18	11.7	86.9	80	0.01	<0.2	12
1.3	0.5	>13	>99.9	80	0.12	<0.2	11
	2	>13	>99.9	82	0.12	<0.2	11
	18	>13	>99.9	84	0.17	<0.2	9
1.5	0.5	>13	>99.9	82	0.17	<0.2	11
	2	>13	>99.9	82	0.18	<0.2	10
	18	>13	>99.9	81	0.17	<0.2	10

In use of the caustic precipitation method some recycle of the filtrate would, of course, be possible after conversion of the excess NaOH to Na_2CO_3 by addition of $NaHCO_3$ or CO_2. The amount of recycle, however, would be limited by sodium sulfate buildup in the system.

Precipitation by Neutralization with Sulfuric Acid. More than 99.9% of the thorium was precipitated by adjusting the strip solution pH to 6.0 with sulfuric acid (1.7 lb H_2SO_4/lb ThO_2) and digesting for 0.5 hr (Table 4.5). As the digestion time was lengthened, the solution pH rose (owing to evolution of CO_2) and thorium recoveries decreased. When the solution was adjusted initially to pH 5.3 (2.1 lb H_2SO_4/lb ThO_2) or 4.5 (2.3 lb H_2SO_4/lb ThO_2), recoveries were not sensitive to the digestion time, being in all cases greater than 99.9%. In contrast to the very poor filtration characteristics of the precipitates obtained by caustic addition, the precipitates in these tests were granular and filtered readily.

The ThO_2 content of the products was 68-79%. At the higher pH levels, the precipitates were principally the basic carbonate salt and contained little or no sulfate. The

Table 4.5 Precipitation of Thorium from Carbonate Strip Solutions by Neutralization with Acid

Carbonate strip solution: 18.5 g Th, 0.07 g U, 46 g CO_3, and 48 g SO_4 per liter at pH 9.0

Procedure: three portions of strip solution adjusted to pH 6.0, 5.3, and 4.5, respectively, with 10% H_2SO_4 to precipitate thorium; samples of precipitate slurries withdrawn after 0.5, 2, and 18 hr digestion, filtered, washed with water, dried at 110°C, and analyzed

H_2SO_4 Added, lb/lb ThO_2	Digestion Time, hr	pH Slurry	pH Filtrate	Th Precipitated, %	Dried Product, % ThO_2	U_3O_8	CO_3	SO_4
1.7	0	6.0	–	–	–	–	–	–
	0.5	6.7	7.2	>99.9	73	<0.01	19	<0.2
	2	7.8	7.8	98.9	73	<0.01	19	<0.2
	18	8.9	8.9	93.8	68	0.02	19	2.7
2.1	0	5.3	–	–	–	–	–	–
	0.5	5.9	6.2	>99.9	79	0.16	12	<0.2
	2	6.9	7.4	>99.9	77	0.14	15	<0.2
	18	7.6	7.6	>99.9	77	0.09	13	<0.2
2.3	0	4.5	–	–	–	–	–	–
	0.5	5.2	6.0	>99.9	78	0.15	8	7.2
	2	6.0	6.5	>99.9	78	0.19	7	7.5
	18	6.8	6.8	>99.9	77	0.18	7	6.9

carbonate content decreased with increasing acid addition. At the lowest pH levels, the products contained approximately 7% CO_3 and 7% SO_4. The thorium was separated effectively from the uranium in the test in which the pH was adjusted initially to 6.0, <5% of the uranium reporting in the thorium product.

5.0 EXTRACTION OF URANIUM

A coefficient of 35-50 was obtained for extraction of uranium from a thorium-barren monazite liquor (thorium removed by extraction with Primene JM) with 0.05 M N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (Table 5.1). Two other N-benzyl secondary amines (0.05 M) gave coefficients of 20-25. Uranium extractions with Amberlite LA-1, tri-iso-octyl, and Alamine 336 amines (0.05 M) and Primene JM (0.1 M) were much weaker (E_a^o 2-5). Extraction of uranium with Primene JM (0.2 M) from a liquor containing thorium was almost negligible

Table 5.1 Extraction of Uranium from a Thorium-barren Monazite Liquor

Organic: 0.05 M amine; 97% kerosene—3% tridecanol diluent for Alamine 336 and tri-iso-octyl amines; kerosene diluent for others

Aqueous: thorium-barren monazite liquor containing 0.18 g U/liter (liquor D from which thorium had been removed by prior extraction with Primene JM)

Contact time: 5 min

Amine	Phase Ratio, a/o	Phase Sep'n Time, min	U, g/liter Organic	U, g/liter Aqueous	U Extr. Coef. (E_a^o)
N-benzyl-1-(3-ethyl-pentyl)-4-ethyl-octyl	0.5	1.2	0.10	0.003	35
	3	>5	0.50	0.01	50
N-(1-nonyldecyl)-benzyl	0.5	3.0	0.10	0.004	25
	3	5	0.47	0.02	25
N-(1-undecyldodecyl)benzyl	0.5	3.0	0.09	0.004	20
	3	>5	0.46	0.02	25
Amberlite LA-1	0.5	1.4	0.08	0.03	3
	3	>5	0.16	0.07	2[a]
Tri-iso-octyl	0.5	1.0	0.08	0.02	4
	3	>5	0.20	0.08	2[a]
Alamine 336	0.5	1.2	0.10	0.02	5[a]
	3	>5	0.30	0.05	6[a]
Primene JM	0.5	-	0.08	0.04	2[b]
	0.7	-	0.002	0.18	0.01[c]

[a] Poor material balance.

[b] 0.1 M amine in 97% kerosene—3% tridecanol.

[c] 0.2 M amine; extraction was from monazite liquor A (6.9 g Th/liter) rather than from the thorium-barren liquor.

(E_a^o 0.01), due to excessive competition from thorium. The presence of thorium would also be expected to adversely affect uranium extraction by the N-benzyl amines since these compounds are fairly effective thorium extractants (see Table 3.2), whereas uranium coefficients with Amberlite LA-1 and the

tertiary amines, particularly the latter, should not be appreciably affected by the presence of thorium.

With all the amines the rate of phase separation was slow (>5 min) at an aqueous/organic phase ratio of 3/1 but reasonably rapid (1-3 min) at 0.5/1. Presumably, an oil-in-water type dispersion resulted during contact at the high phase ratio and a water-in-oil type dispersion at the low phase ratio.*

Isotherms were determined for extraction of uranium with 0.05 M tri-n-octylamine in 97% kerosene—3% tridecanol from thorium-barren monazite liquors at two different pH levels (Fig. 5.1). As expected, uranium extractions were better at the higher pH level; e.g., uranium extraction coefficients at low loadings were approximately 3.5 at pH 0.1 and 6 at pH 0.4. The indicated maximum uranium loadings in these tests were about 0.6 g/liter at pH 0.1 and 0.7 g/liter at pH 0.4.

6.0 RECOVERY OF RARE EARTHS

6.1 Extraction with Primary Amines

Rare earths were recovered from monazite liquors and separated from phosphate by extracting with a primary amine. Extractions were improved by adjustment of the pH to 0.4 with ammonia.

Prior to the rare earth extraction tests, thorium was removed from the liquors with Primene JM and uranium was removed with a tertiary amine. Rare earth extraction isotherms for 0.2 M Primene JM in kerosene at pH 0.2 and 0.4 show a maximum loading in the range 6.5-7 g RE_2O_3 per liter (Fig. 6.1). Extraction coefficients, although low ($E_{\frac{O}{A}}$ in the dilute region is 0.3 at pH 0.2 and 1 at pH 0.4), are adequate for process use. Rough estimates from McCabe-Thiele diagrams indicate that >98% recovery of rare earths should be obtainable in ~3 ideal stages at pH 0.4 and in ~4 ideal stages at pH 0.2 with a solvent loading of 6 g of RE_2O_3 per liter.

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*In other studies[18,19] with amines and with di(2-ethylhexyl)-phosphoric acid, semipermanent emulsions were formed in treating certain liquors (particularly those containing silica) when the phases were mixed with the aqueous phase continuous (oil-in-water type dispersion), whereas phase separation was rapid when mixing was with the organic phase continuous (water-in-oil type dispersion).

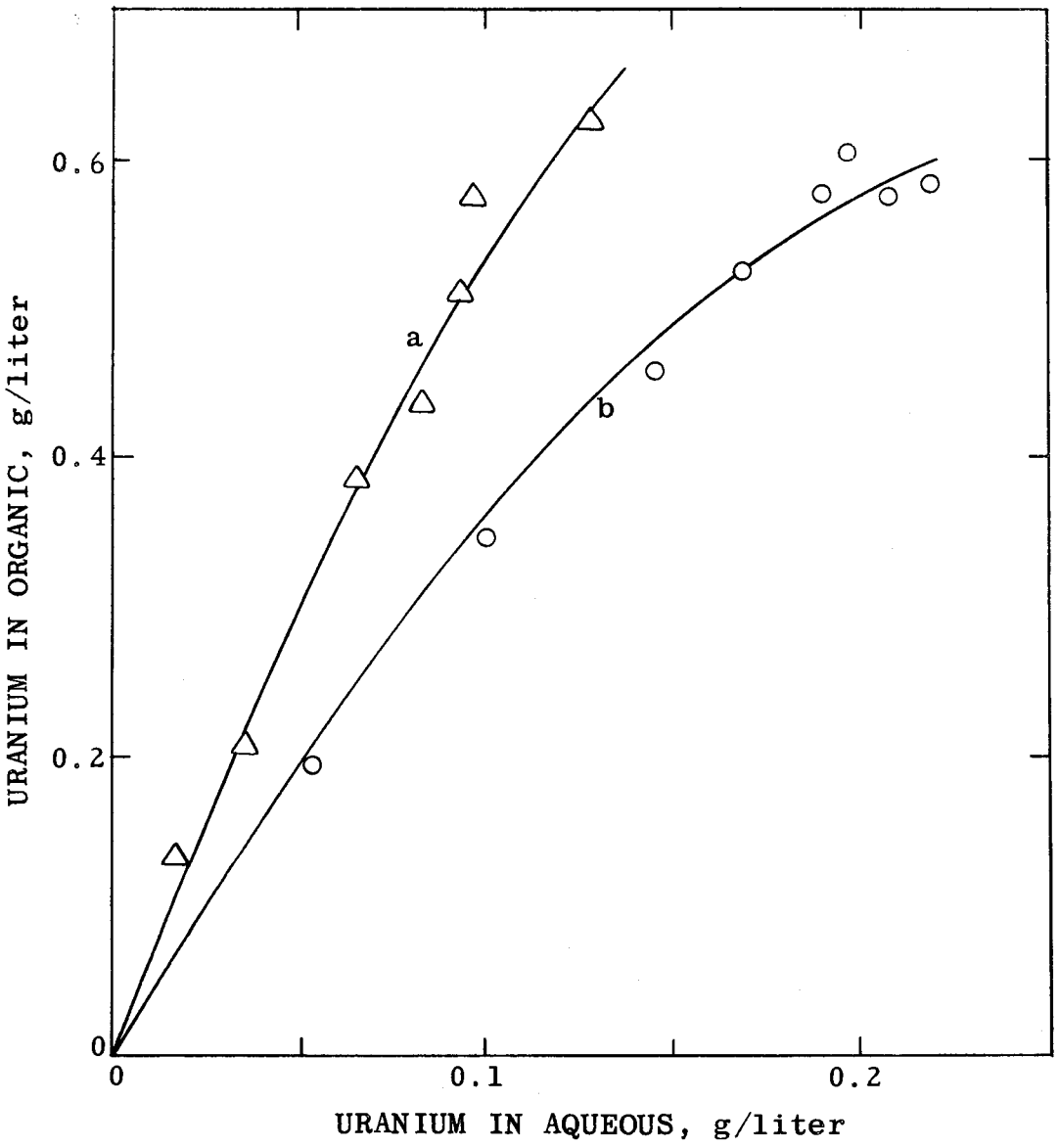


Fig. 5.1 Extraction of uranium from thorium-barren monazite liquors with 0.05 M tri-n-octylamine in 97% kerosene—3% tridecanol. Thorium removed from aqueous feeds with Primene JM; (a) liquor A, pH adjusted to 0.4 with 3 M NH_4OH, head U = 0.14 g/liter; (b) liquor B, pH 0.1, head U = 0.21 g/liter. Procedure: organic cascaded against fresh volumes of aqueous, 2 min contact per stage.

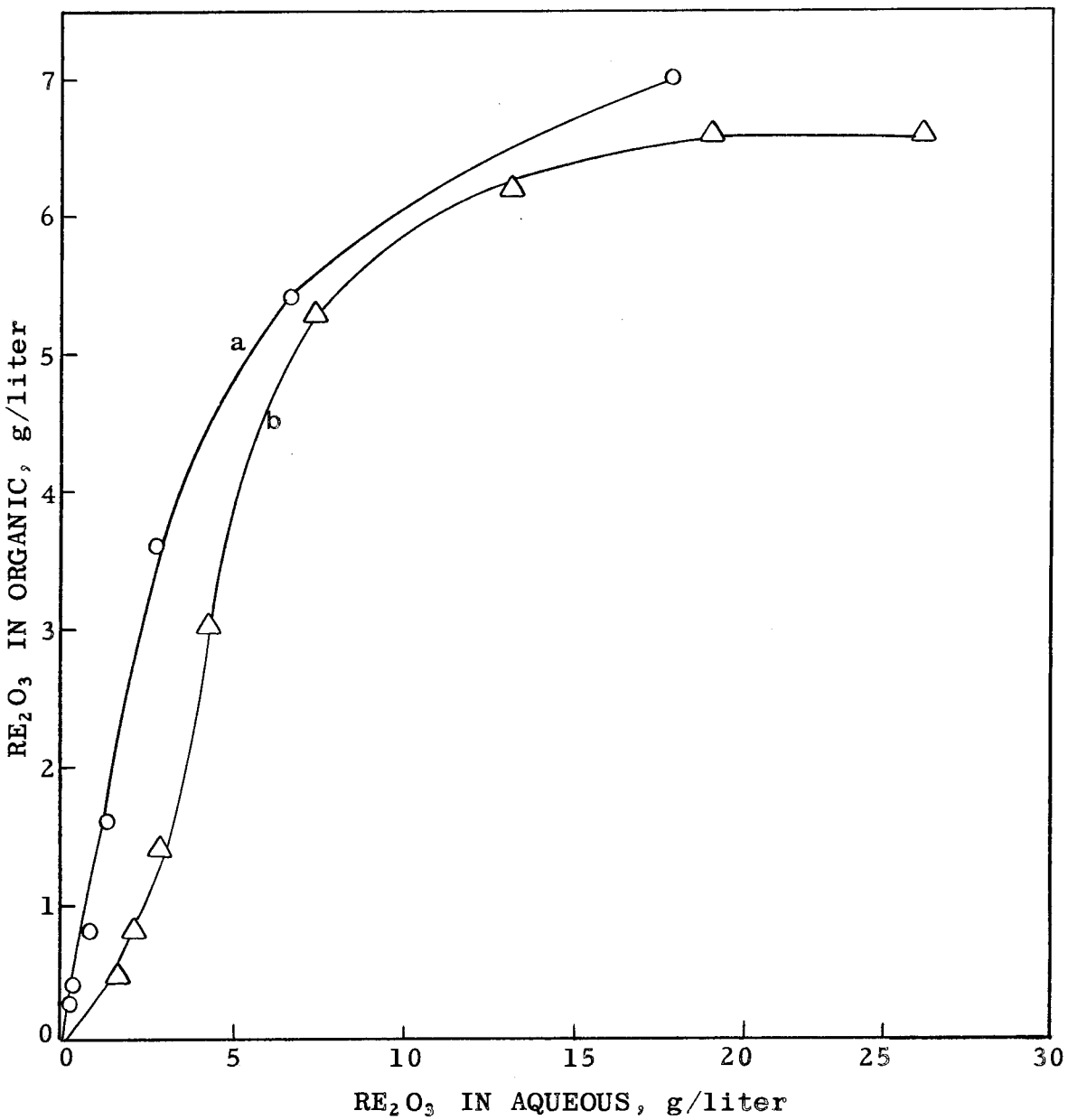


Fig. 6.1 Extraction of rare earths from thorium- and uranium-barren monazite liquor with 0.2 M Primene JM in kerosene. Aqueous: (a) thorium extracted from liquor A with Primene JM, liquor pH adjusted to 0.4 with dilute NH_4OH, and uranium extracted with tri-n-octylamine (head RE_2O_3 = 40 g/liter); (b) raffinate from thorium continuous recovery run 1 (RE_2O_3 = 29 g/liter, pH 0.2). Procedure: aqueous cascaded against fresh volumes of organic, 2 min contact per stage.

The phosphate content of the extract varied with the rare earth loading, decreasing at pH 0.4 from 0.47 g/liter at low loading to 0.055 g/liter at a loading of 7 g of rare earth oxides per liter. Further separation from phosphate could be obtained, if desired, by scrubbing the extract with dilute sulfuric acid.

6.2 Comparison of Extraction Coefficients for Individual Rare Earths

Other rare earth extraction data (Table 6.1) for two primary amines [Primene JM and 1-(3-ethylpentyl)-4-ethyloctylamine] showed significant differences in the magnitude* of the extraction coefficients for the individual rare earths (Fig. 6.2). The extraction coefficient peaked at praseodymium, falling off on both sides to lower values. The indicated separation factors, i.e., the ratio of extraction coefficients, between adjacent rare earths (La through Nd) ranged from 1.2 to 1.9 under these extraction conditions. The addition of alcohol to the solvent appreciably lowered the extraction coefficients but appeared to increase separation factors slightly.

6.3 Stripping of Rare Earths from Amines

A number of reagents, including chloride, nitrate, carbonate, and sulfuric acid, effectively stripped rare earths from Primene JM.

Stripping with Sulfuric Acid. The stripping efficiency was greatly improved by increasing the sulfuric acid concentration from 1.5 to 3.5 M (Fig. 6.3). At acid concentrations of 4 M and higher, copious precipitation of rare earth sulfates occurred during stripping. With 3.5 M acid for stripping a 0.1 M Primene JM solution loaded to 3 g of RE_2O_3 per liter, stripping coefficients ranged from 40 to 50 and the strip solution was loaded to ~60 g of RE_2O_3 per liter.

Most of the rare earths precipitated as rare earth sulfates when the strip solution was evaporated to ~8 M sulfuric acid. The supernatant was readily decanted from the crystalline precipitate, allowing recycle of this solution (after adjustment of concentration) to the stripping system. In one test with 4 M sulfuric acid solution loaded to 45 g of RE_2O_3 per liter, approximately 90% of the rare earths were precipitated by evaporation of the solution to half its

*All the coefficients were limited by saturation of the solvent with rare earths.

Table 6.1 Extraction Data for Individual Rare Earths

Organic: 0.2 M amine
Aqueous: thorium-barren monazite liquor, pH 0.1; total rare earth oxides (chemical analysis) = 40.8 g/liter
Phase ratio, o/a: 1.5
Contact time: 2 min

		Analysis, g/liter											
		Aqueous						Organic					
		Chemical, Total Rare Earth Oxides	Spectrographic					Chemical, Total Rare Earth Oxides	Spectrographic				
Amine	Diluent		La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3		La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3
Primene JM	Kerosene	30.5	6.3	12.2	0.9	4.0	0.6	8.6	1.3	3.4	0.3	0.9	0.07
	95% kerosene—5% capryl alcohol	34.0	7.1	12.6	0.9	4.0	0.6	4.5	0.7	2.1	0.2	0.5	0.05
1-3(ethylpentyl)-4-ethyloctyl	Kerosene	32.4	7.0	13.7	1.4	4.4	0.7	-	1.1	2.6	0.2	0.7	0.07
	95% kerosene—5% capryl alcohol	34.1	6.1	11.9	0.7	3.4	0.6	4.7	0.7	2.1	0.2	0.5	0.05

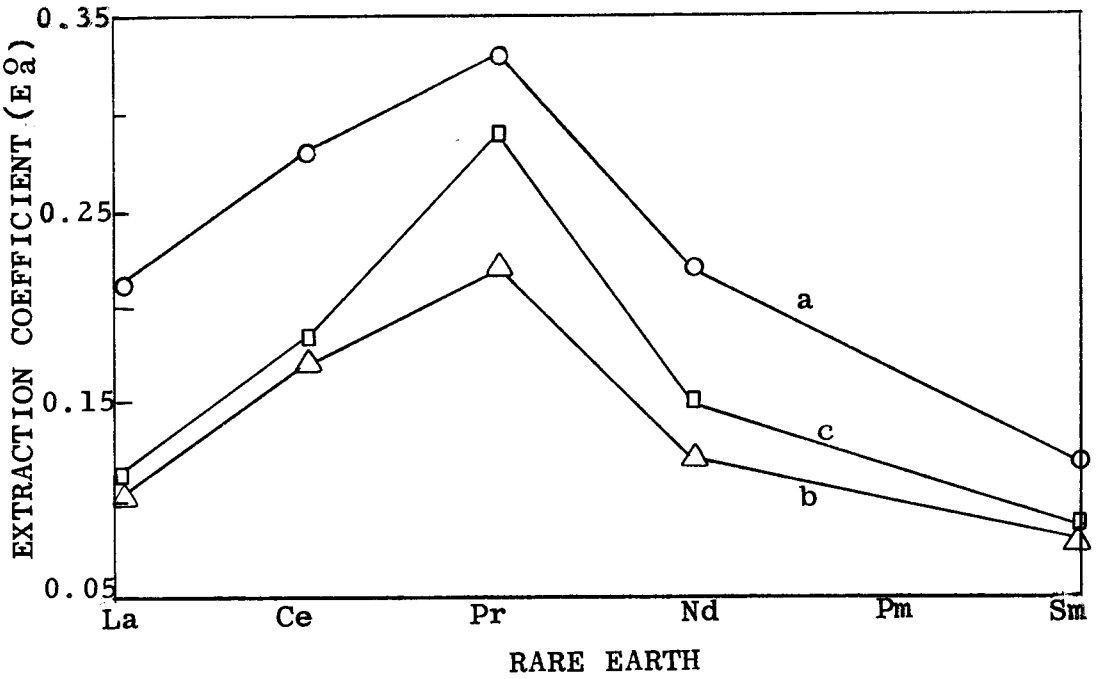


Fig. 6.2 Comparison of extraction coefficients for individual rare earths. (a) 0.2 M Primene JM in kerosene; (b) 0.2 M Primene JM in 95% kerosene—5% capryl alcohol; (c) 0.2 M 1-3(ethylpentyl)-4-ethyloctylamine in 95% kerosene—5% capryl alcohol. Extraction conditions and data listed in Table 6.2.

original volume. The supernatant was decanted and the precipitate dried on a hot plate. The dried product contained 55.9% RE_2O_3 and 48.1% SO_4.

Assuming that most of the sulfuric acid occluded by the precipitate could be recovered for recycle by a water wash* of the precipitate, the only reagent cost for this stripping method would be for sulfuric acid consumed in converting the amine from the sulfate** to the bisulfate. For stripping a 0.1 M amine solution loaded to 3 g of RE_2O_3 per liter, this quantity of sulfuric acid is estimated at ~1.7 lb per pound of RE_2O_3.

Recycle of the amine to the extraction system as the bisulfate would result in addition of an appreciable amount

*The contact time and volume of wash solution would have to be minimized to prevent excessive redissolution of rare earths.

**Most of the amine entering the stripping system would be in the form of an amine sulfate—rare earth sulfate complex.

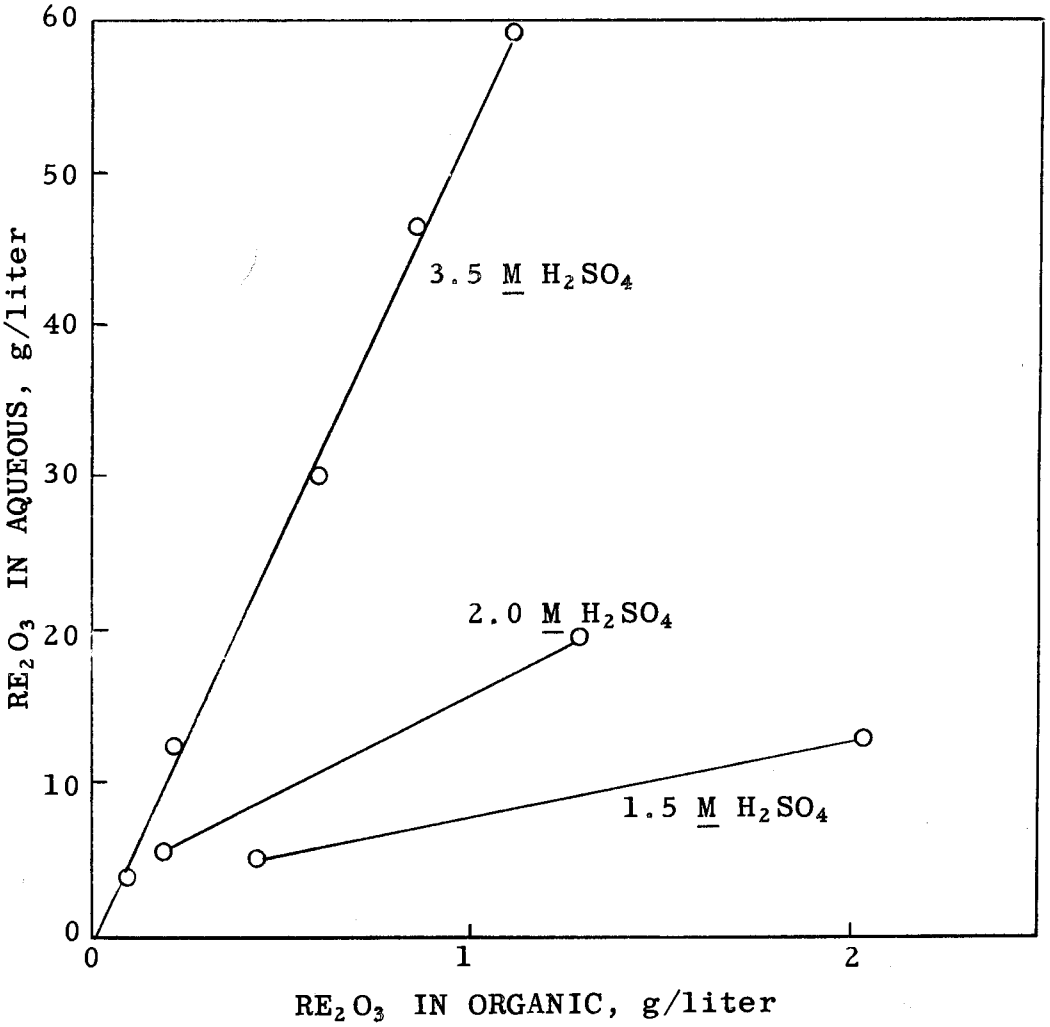


Fig. 6.3 Stripping of rare earths with sulfuric acid. Organic: 0.1 M Primene JM in kerosene loaded to 3 g of RE_2O_3 per liter from a monazite liquor; 5 min contact.

of acid to the liquor as it passed through the extraction system. The attendant drop in pH would cause some loss in rare earth extraction efficiency (see Fig. 6.1). If necessary, this effect could be compensated for by adjusting the pH of the feed liquor with ammonia.

Stripping with Nitrate and Chloride Solutions. Acidified 1 M ammonium nitrate and sodium chloride salt solutions stripped the rare earths efficiently, nitrate being the more effective stripping anion (Table 6.2). Rare earths were partially precipitated in some tests, particularly with the chloride solution. Presumably these precipitates were the

Table 6.2 Stripping of Rare Earths from Primene JM with Nitrate and Chloride Solutions

Organic: 0.2 M Primene JM in kerosene loaded with 6.7 g of RE_2O_3 per liter from a thorium- and uranium-barren monazite liquor

Contact time: 5 min

Stripping Solution	Phase Ratio, o/a	Phase Sep'n Time, sec	Final Aq pH	RE_2O_3, g/liter Aqueous	RE_2O_3, g/liter Organic	Amount Stripped, %	Stripping Coef. (S_o^a)
0.1 M HNO_3 —	1	75	1.15	6.1	<0.125	>98	>50
0.9 M NH_4NO_3	2	70	1.25	13.3	<0.125	>98	>100
	3	65	1.30	20.3[a]	<0.125	>98	>150
	4	65	1.35	25.5[a]	<0.125	>98	>200
	8	[b]	1.35	29.1[a]	3.0	55	10
0.1 M HCl—	1	30	--	[c]	<0.125	>98	>50
0.9 M NaCl	1.5	30	--	[c]	<0.125	>98	>70
	2	30	--	[c]	<0.125	>98	>90
	2.5	30	--	[c]	<0.125	>98	>120
	3	30	--	[c]	0.150	97.8	120

[a] Precipitate formed in aqueous after 15-20 min standing but redissolved readily on addition of nitric acid.

[b] Emulsion formed which was broken by centrifugation.

[c] Precipitation occurred during stripping; precipitate settled predominantly in the aqueous phase.

rare earth alkali double sulfates. Precipitation was more nearly complete in the sodium chloride system owing to the lower solubility of the sodium than the ammonium double salt.

Regeneration of the amine to the free base form by contact with a base, e.g., Na_2CO_3 or NH_4OH, would be necessary after either chloride or nitrate stripping to avoid interference from these anions in the extraction system. The nitrate or chloride salt thus formed could be recycled for further stripping.

Since the amine would be recycled as the free base, a large increase in pH would occur in the last extraction stage, which should significantly improve the rare earth distribution coefficient in that stage. In treating some liquors, however, the pH rise may be large enough to cause precipitation of some hydrolyzable metals. In such a case it might prove necessary to control the pH at a lower level by continuous addition of a small amount of sulfuric acid to the

last extraction stage.

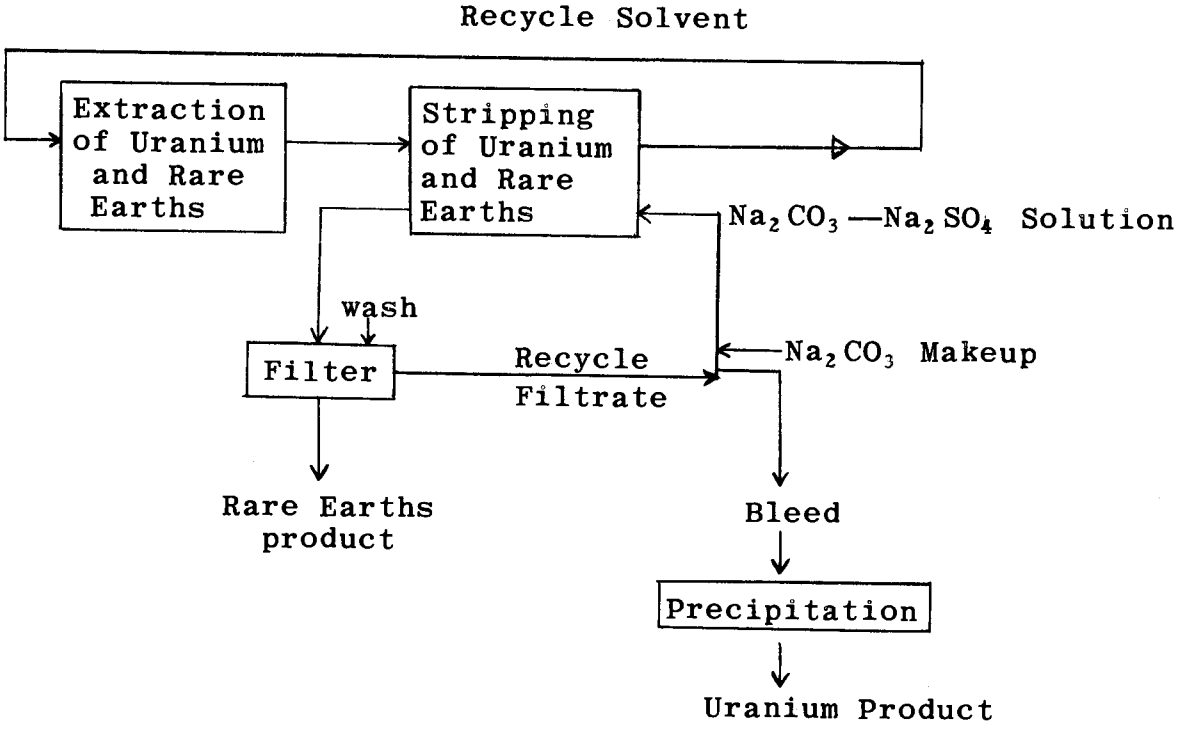
Stripping with Carbonate Solutions. Contact with carbonate solutions results in direct precipitation of rare earths from the solvent. Formation of permanent emulsions is avoided by contacting with the organic as the continuous phase (water-in-oil type dispersion). More than 80% of the rare earths were stripped from 0.1 M Primene JM in kerosene (loaded to 3.1 g of RE_2O_3 per liter) by a single 5-min contact with 0.5 M sodium or ammonium carbonate solutions (also containing sulfate salt) at an organic/aqueous phase ratio of 5/1:

Stripping Solution	RE_2O_3 in Stripped Organic, g/liter	Amount Stripped, %
0.5 M Na_2CO_3—1 M Na_2SO_4	0.45	85
0.5 M $(NH_4)_2CO_3$—1 M $(NH_4)_2SO_4$	0.59	81

Complete stripping should be obtainable by multistage contact or by increasing the amount of excess carbonate and/or the contact time. Sulfate salts were included in the carbonate strip solution since it was assumed that the stripping solution would be recycled after filtration to remove rare earths and fortification with sodium carbonate (or ammonia and carbon dioxide). Some bleed would, of course, be necessary to prevent excessive buildup of sulfate. In these tests initial separation of the organic and aqueous phases was very rapid. The separated organic phases were murky (probably owing to entrainment of aqueous) but devoid of precipitate. The precipitates were readily filtered from the strip solutions. After being washed with 0.2 M ammonium hydroxide and dried at 120°C, the precipitates were analyzed:

Stripping Solution	Analysis of Dried Precipitate, %		
	RE_2O_3	CO_3	SO_4
Na_2CO_3—Na_2SO_4	71.3	36.2	<0.2
$(NH_4)_2CO_3$—$(NH_4)_2SO_4$	74.8	29.5	<0.2

Since uranium is soluble in carbonate solutions but the light rare earths are not, it should be possible to extract the uranium and rare earths simultaneously and separate them during carbonate stripping:



A primary amine or a primary amine in combination with a small amount of tertiary amine should extract both the uranium and rare earths. The above process scheme has not yet been investigated experimentally.

6.4 Precipitation of Rare Earths from Thorium-barren Monazite Liquor

Rare earths were recovered from a monazite liquor (after amine extraction of thorium and uranium) by addition of ammonia to pH 1 or by salting out[20] the rare earth sodium double sulfate with sodium chloride or sodium sulfate. The latter method appeared the more attractive since the precipitates were more readily filtered and contained a relatively low concentration of phosphate. Rare earth recoveries were >97% using 2.9 lb NaCl, 1.8 lb Na_2SO_4, or 0.6 lb NH_3 per pound of rare earth oxides (Table 6.3).

Analyses of products obtained by precipitating rare earths with sodium chloride (4.3 lb NaCl/lb RE_2O_3), digesting 2 hr, filtering, washing, and calcining showed:

Calcination Temp., °C	Analysis of Calcined Product, %			
	RE_2O_3	Na	SO_4	PO_4
120	40	7.3	48	1.1
500	44	7.5	51	1.2
700	45	8.4	53	1.2

Table 6.3 Precipitation of Rare Earths from Thorium-Barren Monazite Liquor

Liquor: monazite liquor after extraction of uranium and thorium in continuous runs (Sec. 7.0); RE_2O_3 = 28 g/liter, pH 0.2

Procedure: indicated quantity of precipitant added, digested 2 hr, filtered

Precipitant	Precipitant Added, lb/lb RE_2O_3	Filtrate pH	RE_2O_3 in Filtrate, g/liter	Recovery,[a] %
NaCl	0.7	0.20	3.9	86.5
	1.8	0.20	1.1	96.5
	2.9	0.0	0.6	97.9
	3.6	<0.0	0.4	98.6
	4.3	<0.0	0.4	98.6
Na_2SO_4	0.7	0.30	3.7	87.2
	1.8	0.35	0.7	97.6
	2.9	0.40	0.3	99.0
	3.6	0.50	0.2	99.3
	4.3	0.50	0.2	99.3
NH_3[b]	0.6	1.1	<0.1	>99.5
	1.0	2.9	<0.1	>99.5

[a] Based on the head liquor and filtrate analyses.

[b] Added as a 10% NH_3 solution.

7.0 CONTINUOUS RUNS

The applicability of the Amex process to separation and recovery of thorium and uranium from monazite liquors was demonstrated in bench-scale continuous tests in mixer-settlers. Details of the design of the equipment and the operating conditions for the continuous runs are included in Sec. 11.3.

Two main process arrangements have been considered for the recovery of thorium and uranium. Depending on the choice of amine, either metal can be recovered in the primary cycle of a two-cycle process:

Flowsheet 1	1st cycle:	extraction of uranium with a tertiary amine
	2nd cycle:	extraction of thorium with a primary amine or with di(tridecyl)amine
Flowsheet 2	1st cycle:	extraction of thorium with a primary amine
	2nd cycle:	extraction of uranium with a tertiary or secondary amine

From the thorium- and uranium-barren liquor, the rare earths can be extracted with a primary amine (Sec. 6.1) or directly precipitated (Sec. 6.4).

In demonstrating flowsheet 1, successful runs were made with tri-iso-octylamine for uranium recovery and Primene JM for thorium recovery. Attempts to use di(tridecyl)amine for the thorium cycle were unsuccessful owing to excessive extraction of phosphate. Two successful thorium recovery runs were then made with a liquor containing uranium, with Primene JM as the extractant, as a demonstration of the first cycle of flowsheet 2. The thorium was stripped with nitrate in the first run and with sodium carbonate in the second.

The recovery of rare earths by amine extraction has not yet been demonstrated in continuous equipment.

7.1 Uranium Recovery Cycle

With 0.05 M tri-iso-octylamine* in 97% kerosene—3% tridecanol, more than 99.5% (based on head liquor and raffinate analyses) of the uranium was recovered from monazite liquor C in eight extraction stages (Table 7.1). A flow diagram for the run is shown in Fig. 7.1. The organic/aqueous flow ratio was 1.3/1. The extract was scrubbed in a single stage with 0.1 its volume of 0.1 M sulfuric acid and stripped in two stages with 0.47 M sodium carbonate solution at an organic/aqueous flow ratio of 7.5/1. Other stripping methods[1] would, of course, be applicable. The system was operated for a total of 15 hr, equivalent to approximately eight complete cycles of the organic phase.

*Probably Alamine 336, which was not available at the time of the tests, would be a better choice for treating this dilute uranium liquor, since it has equivalent or better extraction power and a lower steady-state solubility loss (<5 ppm) than tri-iso-octylamine (~25 ppm).

Table 7.1 Uranium Recovery Cycle Data

Operating conditions as shown in Fig. 7.1

Material Sampled	Sampling Time, hr	Analysis, g/liter					
		Organic			Aqueous		
		U	PO_4	Th	U	PO_4	RE_2O_3 + ThO_2
Extraction System							
Feed		-	-	-	0.2	-	41
Stage 1	5	0.15	0.10	0.04	-	-	-
8		-	-		0.0007	-	-
Stage 1	6.5	0.14	0.10	0.03	-	-	-
8		-	-		0.0008	-	-
Stage 1	8	0.14	0.08	0.02	0.082	-	-
2		0.070	-	-	0.040	-	-
3		0.046	-	-	0.020	-	-
4		0.021	-	-	0.011	-	-
5		0.012	-	-	-	-	-
6		0.006	-	-	0.0027	-	-
7		0.003	-	-	0.0014	-	-
8		0.002	-	-	0.0008	-	-
Stage 1	14	0.15	0.09	0.03	0.083	-	-
2		0.083	-	-	0.038	-	-
3		0.047	-	-	0.020	-	-
4		0.023	-	-	0.010	-	-
5		0.013	-	-	0.0045	-	-
6		0.007	-	-	0.0025	-	-
7		0.003	-	-	0.0015	-	-
8		0.002	-	-	0.0009	-	-
Total raffinate		-			0.0009	-	-
Scrub Stage							
	5	0.16	0.02	-	0.001	1.05	-
	6.5	0.17	0.02	-	0.001	0.92	-
	8	0.15	0.03	-	0.001	0.83	0.6
	14	0.17	0.02	-	0.001	0.77	0.6

Table 7.1 (Contd.)

Material Sampled	Sampling Time, hr	Analysis, g/liter					
		Organic			Aqueous		
		U	PO_4	Th	U	PO_4	$RE_2O_3 + ThO_2$
Stripping System							
Stage 1	5	-	-	-	1.18	-	-
2		0.0013		-	-	-	-
Stage 1	6.5	-	-	-	1.20	-	-
2		0.0003	-	-	-	-	-
Stage 1	8	0.031	-	-	1.19	0.13	-
2		0.0004	-	-	0.23	-	-
Stage 1	14	0.012	-	-	1.11	0.13	-
2		0.0002	-	-	0.15	-	-

The organic leaving the extraction section contained 0.15 g of uranium, 0.02-0.04 g of thorium, and 0.08-0.10 g of phosphate per liter (Table 7.1). Sixty to 80% of the phosphate was removed in the scrub. The spent scrub solution, which contained only 0.6 g of $RE_2O_3 + ThO_2$ and 0.001 g of uranium per liter, was not passed through the extraction system. In practice, this solution would probably be recycled to the ore dissolution step. Severe emulsions formed in the extraction system on one occasion when mixing was with the aqueous phase continuous (oil-in-water type dispersion). With organic-continuous mixing (water-in-oil type dispersion), phase separation in the extraction system was satisfactorily rapid at all times, and this method of contacting the phases is recommended.

Stripping of uranium was essentially complete (>99.5%), yielding a relatively low-grade strip solution containing only 1.2 g of uranium per liter. Owing to the low solvent uranium loading, the consumption of sodium carbonate was much higher than that experienced in treatment of, for example, western uranium ore liquors. The sodium carbonate costs, although relatively high, are still tolerable since the uranium is recovered as a by-product. A small amount (~1 g) of white precipitate, primarily thorium and rare earth phosphates, formed in the first stripping stage but caused no operational difficulties. Some of this precipitate was carried out in the pregnant strip solution; the balance accumulated at the interface.

Uranium was >99.9% recovered from the pregnant strip solution, after filtration to remove the white precipitate,

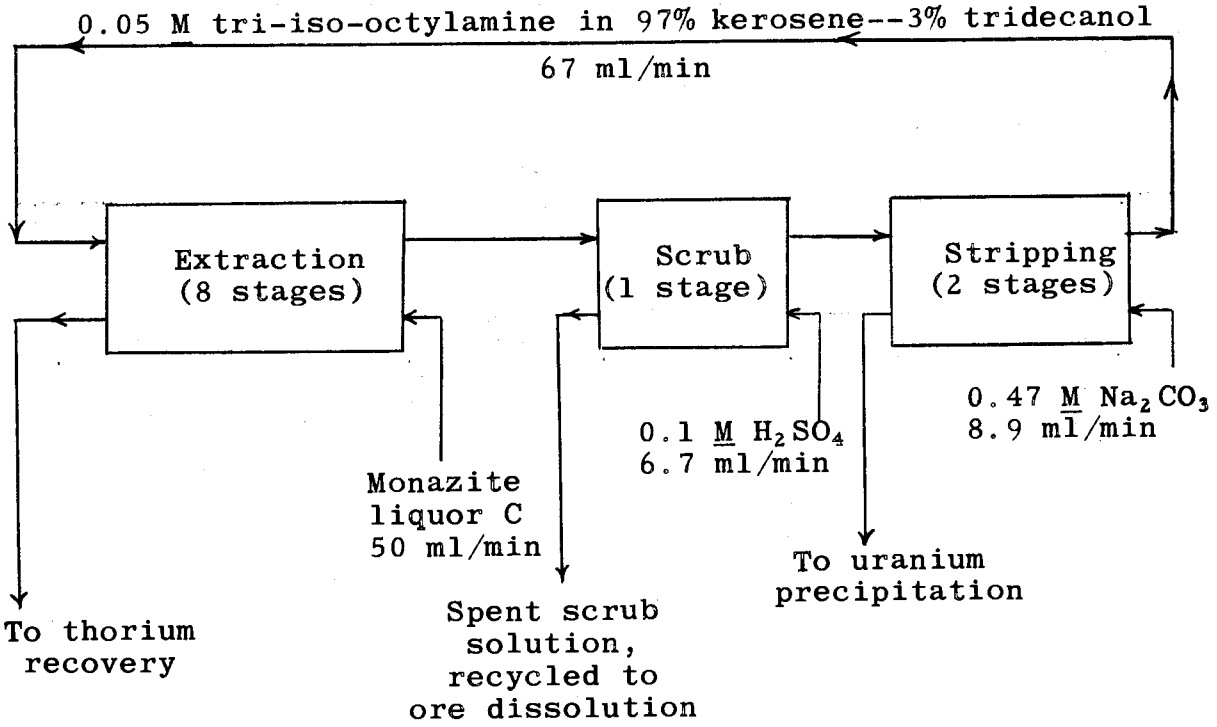


Fig. 7.1 Uranium Recovery Cycle.

by acidifying to pH 2 with sulfuric acid, boiling to remove carbon dioxide, and precipitating with ammonia. Approximately 19 lb of sulfuric acid and 1.3 lb of ammonia were consumed per pound of U_3O_8. The dried (120°C) product contained 78% U_3O_8, 8% ThO_2, <0.3% RE_2O_3, 6.5% PO_4, and 1.9% SO_4. The high phosphate content undoubtedly could be greatly decreased by adding another one or two scrub stages. The relatively high carryover of thorium into the stripping system was unexpected in view of the high selectivity of tertiary amines. However, subsequent analyses showed the solvent to be contaminated with secondary amine, equivalent to ~10% of the total amine content. Use of a purer tertiary amine or use of the preferred (Sec. 8.0) flowsheet, i.e., removal of thorium in the primary extraction cycle, would, of course, circumvent the problem of thorium contamination of the uranium product.

7.2 Thorium Recovery from Uranium-barren Liquor

Initially it was decided to use di(tridecyl)amine for recovering thorium since decontamination from rare earths would be easier with this amine than with a primary amine. A circuit was set up in which the thorium was extracted in four stages with 0.10 M di(tridecyl)amine in 99% kerosene—1% tridecanol, scrubbed in four stages with 0.2 M sulfuric

acid, and stripped in four stages with ammonium nitrate—nitric acid solution. The stripped solvent was regenerated to the free amine, for recycle to the extraction step with ammonium hydroxide, the ammonium nitrate produced being fortified with nitric acid and recycled to the stripping step.

In the stripping section physical difficulties were encountered almost immediately. Large quantities of a white precipitate, subsequently shown to be primarily thorium phosphate, formed, resulting in permanent emulsions in the stripping settlers and eventual shutdown of the system. Precipitate carried in the organic stream also fouled the regeneration system. The organic leaving the extraction section contained 1.2 g of phosphate per liter, only about half of which was removed in scrubbing. Although batch scrubbing tests (Sec. 3.4) showed that most of the phosphate could be eliminated by extensive scrubbing with sulfuric acid, this treatment was sufficiently difficult and expensive that use of di(tridecyl)amine was abandoned in favor of Primene JM which showed little tendency to extract phosphate (Sec. 3.4).

Thorium Recovery Run 1. Thorium recovery (based on feed liquor and raffinate analyses) from the uranium recovery run raffinate was >99.9% using 0.10 M Primene JM in 97% kerosene—3% tridecanol (Table 7.2). A flow diagram for the run is presented in Fig. 7.2. The extraction circuit consisted of four mixer-settler stages and was operated with the amine essentially completely saturated with thorium in order to minimize extraction of rare earths. Solvent saturation was obtained without endangering thorium recoveries by feeding ~10% more thorium to the system than the amine could accept (based on extraction isotherm data) and bleeding off a portion of the aqueous stream leaving the second stage. In practice, this bleed, equivalent in volume to ~25% of the feed liquor flow, would be recycled to feed liquor storage.

The extract, which contained 2.8 g of thorium and 0.01 g of phosphate per liter, was scrubbed in four stages with 0.2 its volume of 0.2 M H_2SO_4. Approximately half the phosphate was removed from the solvent by the scrub. The rare earth content of the extract before and after scrubbing was not determined, because of the difficulty of this analysis in the presence of relatively high concentrations of thorium, and therefore the efficiency of the scrubbing in removing rare earths cannot be calculated. The quantity of rare earths removed during scrubbing, however, was obviously small since the spent scrub solution contained <0.05 g of RE_2O_3 per liter.

The scrubbed extract was stripped in four stages with a sodium nitrate—nitric acid solution, approximately 1 M in

Table 7.2 Thorium Recovery Run 1: Extraction and Scrub Data

Operating conditions as shown in Fig. 7.2

Operating Time, hr	Stage No.	Organic Analysis, g/liter Th	U	PO_4	Aqueous Analysis, g/liter Th	PO_4	RE_2O_3
			Extraction System				
4	1	2.8	<0.0001	0.009	4.0	-	-
	2	2.8	-	-	3.3	-	-
	3	2.2	-	-	0.05	-	-
	4	0.23	-	-	<0.005	-	-
5	1	2.8	-	-	-	-	-
	4	-	-	-	<0.005	-	-
6	1	2.6	-	-	-	-	-
	4	-	-	-	<0.005	-	-
7	1	2.8	<0.0001	0.010	4.0	-	-
	2	2.8	-	-	4.2	-	-
	3	2.8	-	-	0.28	-	-
	4	0.34	-	-	<0.005	-	-
			Scrubbing System				
4	1	2.8	-	-	0.025	0.06	-
	2	2.8	-	-	0.012	-	-
	3	2.8	-	-	0.009	-	-
	4	2.8	<0.0001	0.005	0.007	-	-
7	1	2.8	-	-	0.030	0.03	<0.05
	2	2.8	-	-	0.013	-	-
	3	2.9	-	-	0.009	-	-
	4	2.9	<0.0001	0.005	0.007	-	-

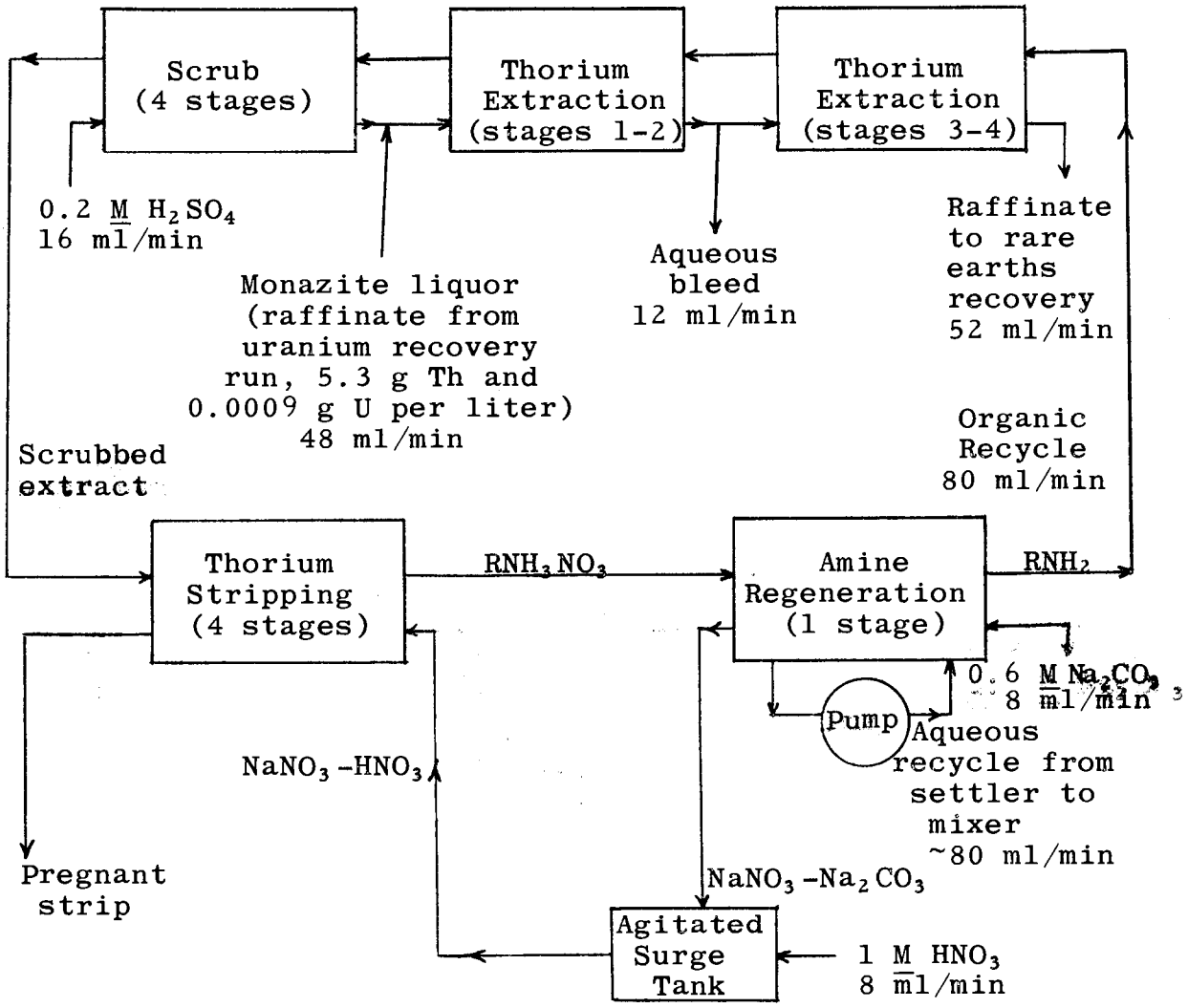


Fig. 7.2 Flow diagram for thorium recovery run 1.
Organic: 0.10 M Primene JM in 97% kerosene—3% tridecanol.

total nitrate, and regenerated to the free amine, for recycle, by a single-stage contact with 0.6 M sodium carbonate (Table 7.3). The pregnant strip solution contained approximately 13 g

Table 7.3 Thorium Recovery Run 1: Stripping and Amine Regeneration Data

Operating conditions as shown in Fig. 7.2

Operating Time, hr	Stage No.	Organic Analysis, g/liter		Aqueous Analysis, g/liter					Aq pH
		Th	NO_3	Th	U	NO_3	SO_4	CO_3	
Stripping System									
4	1	2.4	-	13.2	<0.0001	31	35	-	0.9
	2	1.5	-	9.3	-	-	-	-	0.8
	3	-	-	6.5	-	-	-	-	0.7
	4	0.4	5.2	3.3	-	-	-	-	0.7
5	1	-	-	12.0	-	30	34	-	0.9
	4	0.2	6.4	-	-	-	-	-	-
6	1	-	-	12.1	-	29	34	-	0.8
	4	0.3	6.2	-	-	-	-	-	-
7	1	2.4	-	12.7	<0.0001	29	38	-	0.9
	2	1.8	-	9.8	-	-	-	-	-
	3	1.0	-	6.6	-	-	-	-	0.8
	4	0.4	5.0	3.4	-	-	-	-	0.7
Regeneration System									
4	Single Stage	0.2	0.5	0.6[a]	-	52	-	17	9.0
5		<0.1	0.4	1.0[a]	-	42	-	20	8.7
6		0.1	0.5	1.1[a]	-	41	-	17	9.1
7		0.1	<0.2	1.1[a]	-	49	-	18	9.0

[a]Analysis after filtration to remove small amount of precipitated thorium.

of thorium per liter. Organic analyses showed 85-95% removal of thorium in the stripping system. Most of the remaining thorium was removed from the solvent during regeneration with

sodium carbonate* and recycled to the stripping system. Comparison of the stripping data with batch stripping isotherms (Sec. 4.1) suggests that stage efficiencies in the stripping system were poor, probably no higher than 40-50%, which accounts for the incomplete thorium stripping. It is believed that excessive intrastage recycle** of organic from the settlers to the mixers, which reduced the retention time of aqueous in the mixer, was an important factor in limiting stage efficiencies. Presumably, higher stage efficiencies would have resulted if the interface in the settler had been maintained below (rather than above as was done in this run) the line connecting the mixer and settler, in order to provide aqueous recycle.

The thorium product recovered from the strip solution by precipitating with ammonia, digesting the precipitate in caustic to remove sulfate, and drying at 120°C contained 91.4% ThO_2, 2.5% CO_3, <0.1% PO_4, 0.07% SO_4, and 9 ppm U (Table 7.4). This amount of uranium contamination is satisfactorily low for nuclear grade material. Spectrographic analysis showed 1070 ppm of total rare earth oxides, 10 ppm of boron, 5000 ppm of niobium, 500 ppm of silicon, and >10,000 ppm of titanium. Consumption of reagents for the precipitation and caustic digestion steps were 0.55 lb of ammonia and 0.40 lb of sodium hydroxide per pound of thorium oxide.

Precipitation of thorium from the strip solution with oxalic acid and calcination at 600°C gave a product analyzing 98.8% ThO_2, 8 ppm U, <0.1% PO_4, 50 ppm SO_4, and 0.45% CO_3 (Table 7.4). Although not determined, rare earth contamination of the product presumably was similar to that of the ammonia-precipitated product since the oxalate precipitation would not be expected to give effective separation from rare earths. Concentrations of niobium and titanium were lower than in the ammonia-precipitated product but still significant.

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*Use of sodium carbonate rather than a hydroxide solution is recommended for regenerating the amine since, in the latter case, any thorium entering the regeneration system produces a slimy precipitate which can cause severe emulsion difficulties. With sodium carbonate, part or all of the thorium remains in solution. Even when some thorium precipitates, as it did in this test, the precipitate does not cause emulsions and eventually is carried into the stripping system where it redissolves.

**Some solution recycles from the settler to the mixer through the line connecting them (Sec. 11.3). Either organic or aqueous is recycled depending on whether the interface in the settler is maintained above or below the connecting line.

Table 7.4 Thorium Products from Continuous Run 1

Procedure: Thorium recovered from the pregnant strip solution by both (a) ammonia and (b) oxalate precipitation

(a) Precipitated at pH 7 with NH_4OH, filtered and washed, reslurried in 0.5 M NaOH for 1 hr to remove sulfate, filtered and washed, dried at 120°C (digestion with caustic done in plastic rather than glass equipment to minimize contamination with silicon and boron)

(b) Solution adjusted to pH 1.5 with NH_4OH and heated to 90°C, thorium precipitated with oxalic acid (125% of stoichiometric), digested 1 hr at 90°C, filtered, reslurried twice in 0.5 M NH_4OH (in plastic equipment) to eliminate occluded sodium sulfate, filtered and washed, calcined 2 hr at 600°C

Component	Ammonia Precipitation Product	Oxalate Precipitation Product
Chemical Analysis		
ThO_2	91.4%	98.8%
U	9 ppm	8 ppm
PO_4	<0.1%	<0.1%
SO_4	0.07%	<50 ppm
CO_3	2.5%	0.45%
Loss at 1000°C	6.2%	0.8%
Spectrographic Analysis, ppm		
Al	<100	<100
B	10	20
Be	<0.1	<0.1
Cd	<100	-
Co	<5	<5
Cr	<5	<5
Cu	2	<2
Fe	20	<10
Mg	<10	<10
Mn	<5	<5
Mo	<10	<10
Ni	<10	<10
Nb	5000	2000
Pb	<10	<10
Si	500	500
Sn	<10	<10
Ti	>10,000	5000
V	<10	<10

Table 7.4 (Contd.)

Component	Ammonia Precipitation Product	Oxalate Precipitation Product
	Spectrographic Analysis, ppm	
Zn	<20	<20
Total rare earth oxides[a]	1070	-
La	56	-
Ce	425	-
Pr	125	-
Nd	225	-
Sm	54	-
Gd	26	-

[a]Separation of the rare earths from thorium prior to spectrographic analysis was made by Cyrus Feldman's group of the Oak Ridge National Laboratory Analytical Chemistry Division, using a cellulose column.[16]

7.3 Thorium Recovery from Liquor Containing Uranium

Two thorium recovery runs of relatively short duration were made with liquor D, which contained 5.9 g of thorium and 0.2 g of uranium per liter. The solvent was 0.10 M Primene JM in 97% kerosene—3% tridecanol.

Thorium Recovery Run 2. Test conditions were identical to those shown in Fig. 7.2 except that the feed liquor and aqueous bleed flow rates were changed to 43 and 10.8 ml/min, respectively, to compensate for the higher thorium concentration in the feed liquor.

Based on profile samples of the system taken after 3 hr of operation (~1.5 complete cycles of the organic phase), recovery of thorium was >99.9% (Table 7.5). The organic leaving the extraction section contained 3.0 g of thorium, 0.007 g of phosphate, and only 0.00012 g of uranium per liter. Scrubbing reduced the uranium content to <0.0001 g/liter. The pregnant strip solution contained 10.5 g of thorium and <0.0001 g of uranium per liter (<10 ppm of U based on thorium). As in run 1, stripping of thorium was incomplete, the stripped solvent containing 0.7 g of thorium per liter, which was decreased to 0.3 g/liter during amine regeneration. This relatively high recycle of thorium to the extraction system, however, did not adversely affect extraction results since, as mentioned before, recovery of thorium was essentially complete.

Table 7.5 Data for Thorium Recovery Run 2

Operating conditions as shown in Fig. 7.2 except feed liquor flow rate and aqueous bleed were 43 and 10.8 ml/min, respectively
System sampled after 3 hr of operation (~1.5 cycles of the organic phase)

Stage No.	Organic Analysis, g/liter Th	U	PO_4	Aqueous Analysis, g/liter Th	U	PO_4
			Extraction System			
1	3.0	0.00012	0.007	4.4	-	-
2	2.9	-	-	3.9	0.28	-
3	2.6	-	-	0.06	-	-
4	0.4	-	-	<0.005	-	-
			Scrubbing System			
1	2.8	-	-	0.045	0.0007	0.036
2	2.9	-	-	0.006	-	-
3	2.7	-	-	0.008	-	-
4	3.0	<0.0001	-	0.007	-	-
			Stripping System			
1	2.5	-	-	10.5	<0.0001	-
2	2.2	-	-	9.1	-	-
3	1.8	-	-	8.5	-	-
4	0.7	-	-	7.3	-	-
			Regeneration System			
Single Stage	0.3	-	-	0.7[a]	-	-

[a]Analysis after filtration to remove thorium precipitate.

Thorium Recovery Run 3. Operation of the extraction system was the same as in run 2 except that the nitrate strip was replaced by three stages of stripping with 0.75 M sodium carbonate (Fig. 7.3). Sufficient sodium carbonate was supplied to the stripping system to keep the stripped thorium in solution.

The raffinate contained <0.005 g of thorium per liter, corresponding to a thorium recovery of >99.9% (Table 7.6). The extract analyzed 3.0 g of thorium and 0.002 g of uranium per liter, the uranium concentration being decreased to <0.0001 g/liter in the scrubbing operation.

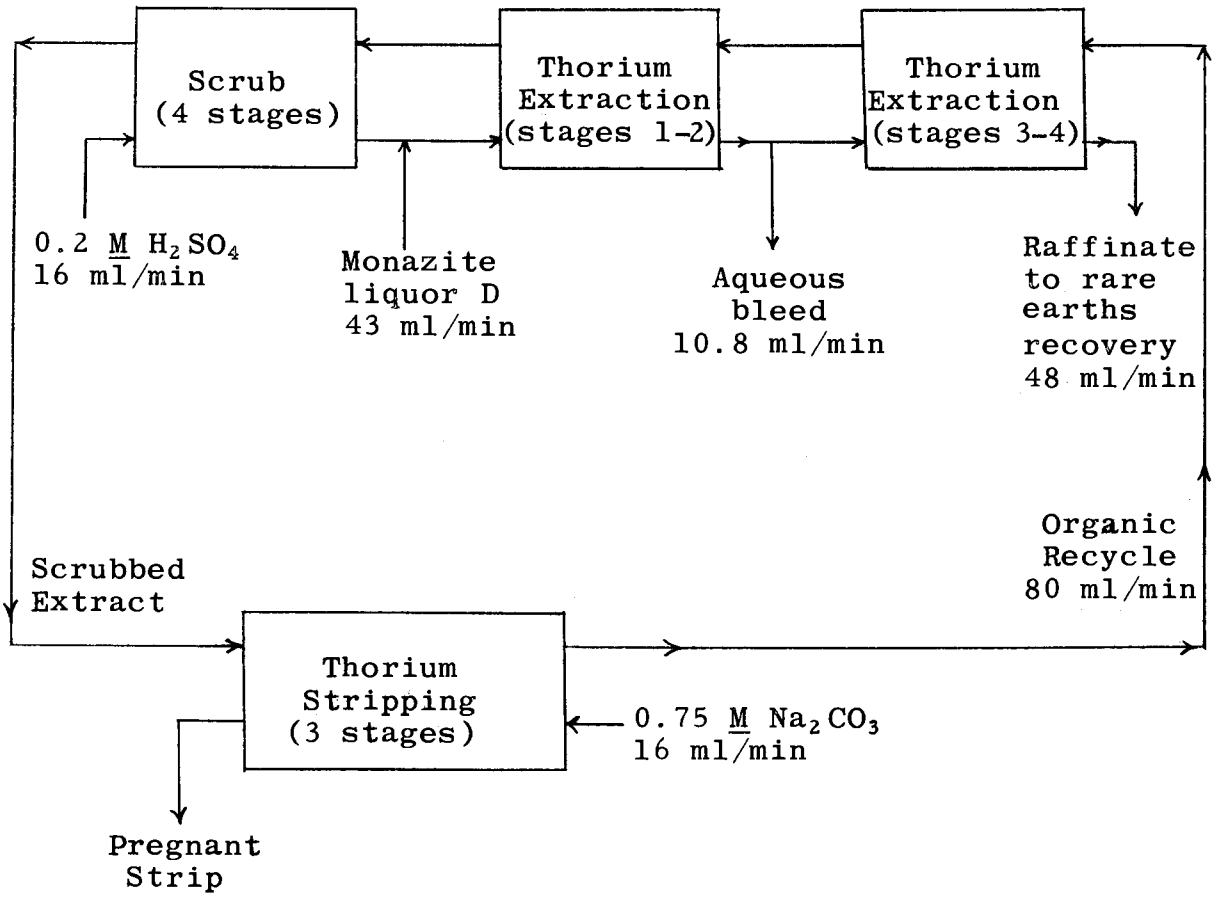

Fig. 7.3 Flow diagram for thorium recovery run 3. Organic: 0.10 M Primene JM-T in 97% kerosene—3% tridecanol.

The pregnant strip solution contained ~12 g of thorium and ~0.0001 g of uranium per liter (<10 ppm of uranium based on thorium). Thorium was recovered from this solution >99.9% by adding 1 M sulfuric acid to pH 6, digesting 30 min (final pH 7.4), filtering, and washing with 0.1 M NH_4OH. One portion of the wet cake was calcined directly while a second portion was reslurried for 1 hr with 0.5 M NH_4OH before calcining. The calcined products contained 73-94% ThO_2, 0.1-0.3% SO_4, and 2-19% CO_3:

Product	Calcination Temp. °C	Analysis, % ThO_2	SO_4	CO_3
Calcined directly	120	72.8	0.31	18.7
	500	83.7	0.19	6.8
	750	88.6	0.21	6.3
Reslurried in 0.5 M NH_4OH	120	78.3	<0.10	12.6
	500	90.7	0.12	3.7
	750	93.8	0.13	2.3

Table 7.6 Data for Thorium Recovery Run 3

Operating conditions as shown in Fig. 7.3

Operating Time, hr	Stage No.	Organic Analysis, g/liter Th	Organic Analysis, g/liter U	Aqueous Analysis, g/liter Th	Aqueous Analysis, g/liter U	Aqueous Analysis, g/liter RE_2O_3	Aqueous pH
Extraction System							
2.7	2	-	-	2.6	0.27	-	-
	4	-	-	<0.005	-	-	-
3.2	2	-	-	2.5	0.32	-	-
	4	-	-	<0.005	-	-	-
3.5	1	3.0	0.0002	4.4	-	-	0.20
	2	3.0	-	2.5	0.33	-	0.20
	3	1.6	-	0.02	-	-	0.20
	4	0.1	-	<0.005	-	-	0.25
Scrubbing System							
3.5	1	3.0	-	0.024	-	0.04	0.7
	2	3.0	-	0.012	-	-	0.7
	3	3.0	-	0.008	-	-	0.7
	4	3.0	<0.0001	0.007	-	-	0.7
Stripping System							
2.7	1	-	-	12.6	0.0001	-	9.5
3.2	1	-	-	12.5	0.0001	-	9.6
3.5	1	1.4	-	12.0	0.0001	-	9.5
	2	0.6	-	6.3	-	-	10.2
	3	0.1	-	1.9	-	-	10.9

Consumption of sulfuric acid for the precipitation step was ~2.4 lb per pound of ThO_2.

The combined total raffinates from runs 2 and 3 contained 0.08 g of uranium per liter. This is only about 55% of the concentration expected on the basis of the head liquor analysis (0.20 g of uranium per liter) and raffinate volume, assuming no uranium extraction. Examination of the stage data for runs 2 and 3 (Tables 7.5 and 7.6) shows accumulation of uranium in the second extraction stage, the concentration in the aqueous phase having increased to 0.33 g/liter at the end of run 3. It is evident that an appreciable amount of uranium was extracted in the bottom two stages and displaced

from the solvent by thorium in the upper two stages. Thus, the aqueous bleed stream from the second stage was enriched in uranium (the combined aqueous bleeds from runs 2 and 3 contained 0.28 g of uranium per liter) in comparison to the feed liquor. Since it is anticipated that the liquor bleed would be recycled to feed liquor storage and blended with fresh liquor, it is apparent that the liquor fed to the extraction system would gradually increase in uranium concentration until the amount of uranium exiting in the raffinate is equivalent to that dissolved from the ore. Although the higher uranium content of the feed liquor would result in higher uranium contamination of the thorium product stream than was obtained in runs 2 and 3, calculations show that the increase in contamination would be small and thorium products containing <15 ppm of U would still be expected.

8.0 CONSIDERATIONS ON CHOICE OF OPTIMUM FLOWSHEET

In the continuous thorium recovery runs (Secs. 7.2 and 7.3) the thorium product stream contained less than 10 ppm of uranium based on thorium when the thorium was extracted either prior or subsequent to the uranium recovery cycle. However, it appears that, in actual plant practice, adequate uranium decontamination could best be achieved by recovering thorium rather than uranium in the first extraction cycle. This conclusion, which on first thought appears incongruous, is based on the following considerations. In a two-cycle solvent extraction process, where uranium is recovered in the first cycle with a tertiary amine and the thorium in the second cycle with a primary amine, it is inevitable that the second cycle extractant will eventually become contaminated to some extent with tertiary amine carried in the raffinate stream from the first cycle.* This tertiary amine contaminant will extract most of any uranium passing the uranium extraction system. Thus, since little decontamination from uranium can be expected in the thorium extraction cycle, removal of uranium from the liquor in the uranium recovery step must be essentially complete. For example, in treating liquors containing 5 g of thorium per liter, a raffinate containing <0.0001 g of uranium per liter (approximately one order of magnitude lower than was obtained in the continuous run) must be produced to meet a requirement of <20 ppm of uranium contamination based on thorium. Since the uranium extraction coefficients of the tertiary amines in this system are relatively low, achievement of such high recoveries would require an excessive number of extraction stages and/or acceptance of very low solvent loadings.

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*Probably, the continuous demonstration runs were of too short duration to allow accumulation of a significant amount of tertiary amine in the organic used for thorium recovery.

In contrast, recovery of thorium in the primary extraction cycle allows considerable freedom in choice of conditions for the uranium recovery cycle. Since extremely high uranium recoveries are not necessary, the number of extraction stages can be appreciably decreased. In addition, the more powerful uranium extractants, the N-benzyl branched alkyl secondary amines, can be considered for recovering uranium from thorium-free liquors. The higher uranium extraction power of these compounds would allow higher loading of the solvent in fewer extraction stages. Once the thorium has been removed from the liquor, other schemes (see, for example, Sec. 6.3) involving simultaneous extraction of the uranium and rare earths (with separation during carbonate stripping) can be considered.

8.1 Preparation of Nuclear Grade Thorium Oxide

The preparation of extremely pure thorium products has not yet been attempted. However, the experimental results suggest that study of the Amex process for this purpose might be worthwhile. Probably the most favorable approach would be to precipitate thorium from the nitrate strip solution with oxalic acid. This would increase the separation from certain metal impurities and from phosphate and sulfate. A major obstacle appears to involve attainment of adequate decontamination from rare earths during the extraction and scrubbing operations, since little or no decontamination would be expected during the oxalate precipitation. The thorium product obtained in the continuous tests contained 1070 ppm of total rare earth oxides, which is 2-3 orders of magnitude higher than is allowable in nuclear grade thorium oxide. Thus a large increase in rare earth decontamination is necessary. It is expected that inclusion of a small amount of nitrate, 0.01-0.05 M, in the sulfuric acid scrub solution would greatly facilitate removal of rare earths from the solvent during scrubbing. In addition, the selective extraction of thorium with Primene JM can be greatly improved by modifying the kerosene diluent with relatively high concentrations of alcohol. For example, in extractions of cerium(III) and thorium from 0.5 M sulfate solutions at pH 1 with 0.08 M Primene JM, the cerium extraction coefficients decreased by a factor of 8 on increase of alcohol from 2 to 15 v %, whereas the thorium coefficients were virtually unchanged. These approaches will be followed in future tests.

The oxalate-precipitated product also was contaminated with significant concentrations of silicon, boron, niobium, and titanium. It is anticipated that, in preparing thorium metal, silicon and boron would be eliminated effectively during hydrofluorination of the thorium oxide to thorium fluoride. Niobium and titanium, however, might be only partially eliminated during hydrofluorination and could represent a limiting problem.

9.0 ESTIMATED REAGENT COSTS

Based on the data from the continuous runs, total reagent costs for treating 1000 gal of liquor to recover 50 lb of ThO_2, 1.9 lb of U_3O_8, and 280 lb of RE_2O_3 are estimated at approximately $22 (Table 9.1). About 46% of these costs are for thorium recovery, 14% for uranium recovery, and 40% for rare earth recovery. It should be emphasized that this estimate is for only one set of process circumstances. Other processing arrangements are possible, for example, choice of different stripping methods or type of liquor treated, which could lead to costs different from those presented. The above estimate assumes a feed liquor the same as that of liquor C (Table 3.1); operation of the thorium recovery cycle as in run 1 (nitrate stripping method), the thorium being precipitated with ammonia and digested with caustic to remove sulfate, with an overall thorium recovery of 99.5%; operation of the uranium cycle as in the continuous test, with an overall uranium recovery of 99%; and rare earth recovery as the sodium rare earth double sulfates by precipitation with sodium chloride, with an overall rare earth recovery of 97%.

Table 9.1 Estimated Chemical Reagent Costs

Basis: treatment of 1000 gal of leach liquor containing 5.3 g of Th, 0.20 g of U, and 35 g of RE_2O_3 per liter to recover 50 lb of ThO_2, 1.9 lb of U_3O_8 and 280 lb of RE_2O_3

Chemical	Consumption	lb per 1000 gal liquor	Unit Cost, ¢/lb	Cost per 1000 gal liquor
	Thorium Recovery Cycle			
H_2SO_4	Organic scrub	59	1.4	$0.83
HNO_3	Th stripping	95	4.5	4.30
Na_2CO_3	Amine regeneration	95	2.2	2.10
NH_3	Th pptn	26	5.0	1.30
NaOH	Sulfate removal from Th ppt	20	4.7	0.94
Primene JM	Distribution loss to raffinate (50 ppm)	0.6	70[a]	0.42
Organic phase	Entrainment and spillage	0.5 gal	38¢/gal[b]	0.19

Table 9.1 (Contd.)

Chemical	Consumption	lb per 1000 gal liquor	Unit Cost, ¢/lb	Cost per 1000 gal liquor
		Uranium Recovery Cycle		
H_2SO_4	Organic scrub	10.9	1.4	0.15
Na_2CO_3	U stripping	74	2.2	1.63
H_2SO_4	U pptn	38	1.4	0.54
NH_3	U pptn	2.5	5.0	0.13
Tri-iso-octyl-amine	Distribution loss to raffinate (25 ppm)	0.4	125	0.50
Organic phase	Entrainment and spillage	0.5 gal	40¢/gal[b]	0.20
		Rare Earths Recovery		
NaCl	Rare earths pptn	870	1	8.70
			Total	$21.93

[a]The selling price of Primene JM is actually ~50¢ per pound. However, it is a mixture of primary amines, some of which are of relatively low molecular weight and are readily lost to acid liquors. Thus, the price is taken as 70¢ per pound to allow for loss of this readily soluble fraction (25-30% of the total amine content).

[b]Assumes kerosene cost of 14¢/gal and tridecanol cost of 23¢/lb.

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11.0 APPENDIX

11.1 Preparation of Leach Liquors

The monazite liquors (analyses in Sec. 3.0) were prepared from Indian monazite sands (9.7% ThO_2, 59% RE_2O_3) in approximately the same manner as recommended by Ames Laboratory.[12] The procedure used in preparing liquor A was as follows:

Three hundred grams of sand was added slowly to 462 g of 93% H_2SO_4 in a 4-liter beaker heated to 150°C with a Glas-Col heating mantle. The reaction mixture was agitated by a glass stirrer driven by a Ful-Tork laboratory motor. After addition of the sand, the temperature was raised to 200°C and the digestion was continued for 2 hr. Stirring was continued until the mixture became too viscous for further agitation. After digestion, the mixture was cooled to room temperature and diluted slowly with 3 liters of water. As soon as sufficient water was added to soften the mixture, stirring was started and continued for 1 hr. After 18-hr aging the slurry was filtered. The filter paper was precoated with Celite to increase the filtration rate and to improve the clarity of the filtrate. The above procedure was performed several times and the liquors from the various batches were combined.

Liquor B was prepared identically except that, instead of diluting the digestion mixture with 3 liters of water, sufficient water was added to bring the volume of the slurry to 3 liters. Since the amount of water added was smaller in the latter case, the liquor was somewhat more concentrated in thorium and rare earths.

Liquors C and D were prepared in the same way as liquor A but the size of the batches was increased fourfold, while maintaining the same proportions of sand, acid, and dilution water. Based on the liquor analyses, dissolution of thorium and rare earths was less complete than in the preparation of liquor A. This can probably be attributed to poorer agitation of the digestion mixture in the preparation of the larger sized batches.

11.2 Description of the Amine Reagents

Description of the amine compounds and discussion of their purity, losses to aqueous liquors, diluent compatibility, etc. have been presented previously.[3,5-7,17,21-23] It was shown that many of the reagents contained appreciable amounts of lower molecular weight amines (some of which were amines of a different type), which caused higher distribution losses to the aqueous phase than did the major component. In process use these more soluble constituents would be effectively removed from the organic phase in relatively few cycles.

In laboratory batch experiments, however, the presence of these impurities could cause spurious conclusions with regard to reagent performance. Therefore, in order to obtain a more representative evaluation of the compounds with reference to process application, the amine solutions were scrubbed prior to testing. The amine was dissolved in the diluent at a concentration higher than that desired for use and scrubbed by contact with 2% sulfuric acid (10-15 vol). The scrubbed organic phase was contacted with a solution of sodium carbonate to convert the amine salt to free amine, washed with water, and titrated to determine its amine concentration. The concentration was then adjusted, by addition of diluent, to the level desired for test purposes.

Prior to batch extraction tests, the amine was converted to the amine salt by contact with dilute sulfuric acid. This was done to prevent excessive pH changes in contacts at high organic/aqueous phase ratios.

Information on structure, source of supply, and present availability of the amine compounds is given in Table 11.1

11.3 Design and Operation of the Mixer-Settler Contactors

The mixer-settler equipment used in the continuous tests utilizes the hydraulic head developed by the mixer impeller to advance the phases between stages, requiring no interstage pumps. In most of the contacting stages, round mixers and settlers, fabricated from glass and connected with Tygon tubing, were used. The arrangement of a typical stage is shown in Fig. 11.1. One blade of the mixer impeller is placed directly in line with the tube connecting the mixer and settler. This provides a difference in liquid levels between the mixer and settler of 0.75-1.25 in., which is adequate to allow good interface control. In addition to the glass equipment, a six-stage partitioned-box mixer-settler, made of Plexiglas, was used. This unit, which had internal gravity legs, operated on the same principle as the glass equipment but had the advantage of requiring less bench space and no outside tubing connections between stages.

Information on the size of the mixers and settlers used in each of the continuous runs and the residence times of the phases in the mixer is shown in Table 11.2. It should be noted that the residence times listed are only a calculated average based on the total solution flow to the stage. In operation there is considerable surging of solution back and forth between the mixer and settler, which results in some recycle of organic from the settler to the mixer when the liquid interface in the settler is below the connecting tube, and recycle of aqueous when the interface is above the connecting tube. Consequently, the volume ratio of the phases

Table 11.1 Description of Amine Reagents

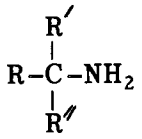
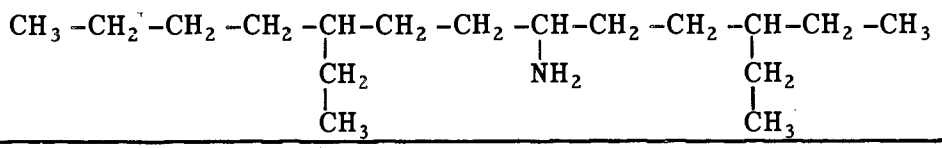
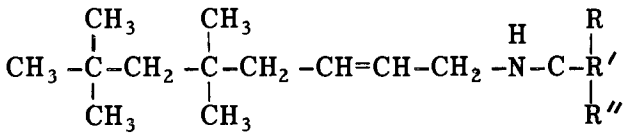
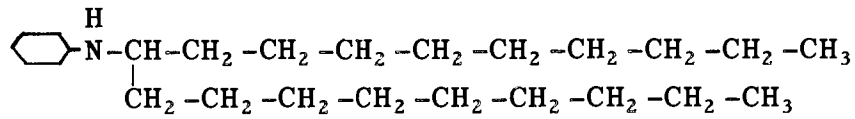
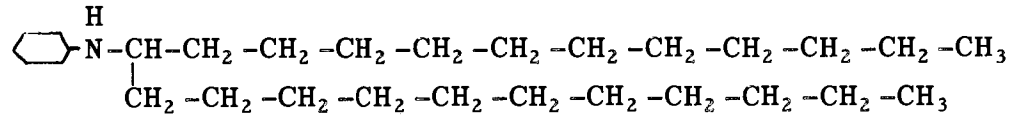
Amine	Structure	Supplier	Availability
	Primary Amines		
Primene JM	Mixture of primary amines  where R + R′ + R″ = 15-21 carbon atoms	Rohm and Haas	a
1-(3-ethylpentyl)-4-ethyloctyl (amine 21F81)		Carbide	b
	Secondary Amines		
Amberlite LA-1 (formerly identified as amine EB-765-2 and 9D-178 amine)	 where R + R′ + R″ = 11-14 carbon atoms	Rohm and Haas	a
N-benzyl-(1-nonyldecyl)		Armour	c
N-benzyl-(1-undecyldodecyl)		Armour	c

Table 11.1 (Contd.)

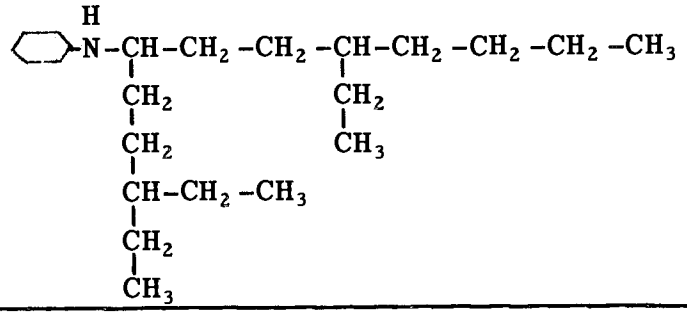
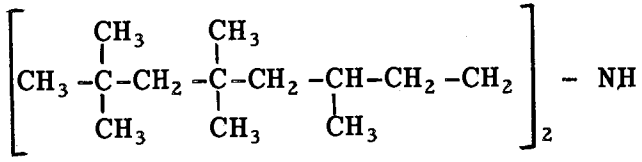
Amine	Structure	Supplier	Availability
	Secondary Amines (Contd.)		
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl		Carbide	b
	Tertiary Amines		
Alamine 336 (formerly identified as mixed tertiary amine)	Mixture of straight-chain tertiary amines, 55% octyl—45% decyl	General Mills	a
tri-n-octyl	self-evident	Carbide	b
tri(iso-octyl)	branching reported to be no closer to the nitrogen than the third carbon	Carbide	b
di(tridecyl)	alkyl group derived from tetrapropylene 	Carbide	b

Table 11.1 (Contd.)

Amine	Structure	Supplier	Availability
	Tertiary Amines (Contd.)		
di(2-butyloctyl)	$\left[CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{\vert}{CH}}-CH_2\right]_2-NH$	Carbide	b

[a]Commercially available.

[b]Obtained in experimental quantities; manufacturer should be contacted for information on supply.

[c]Available in experimental quantities.

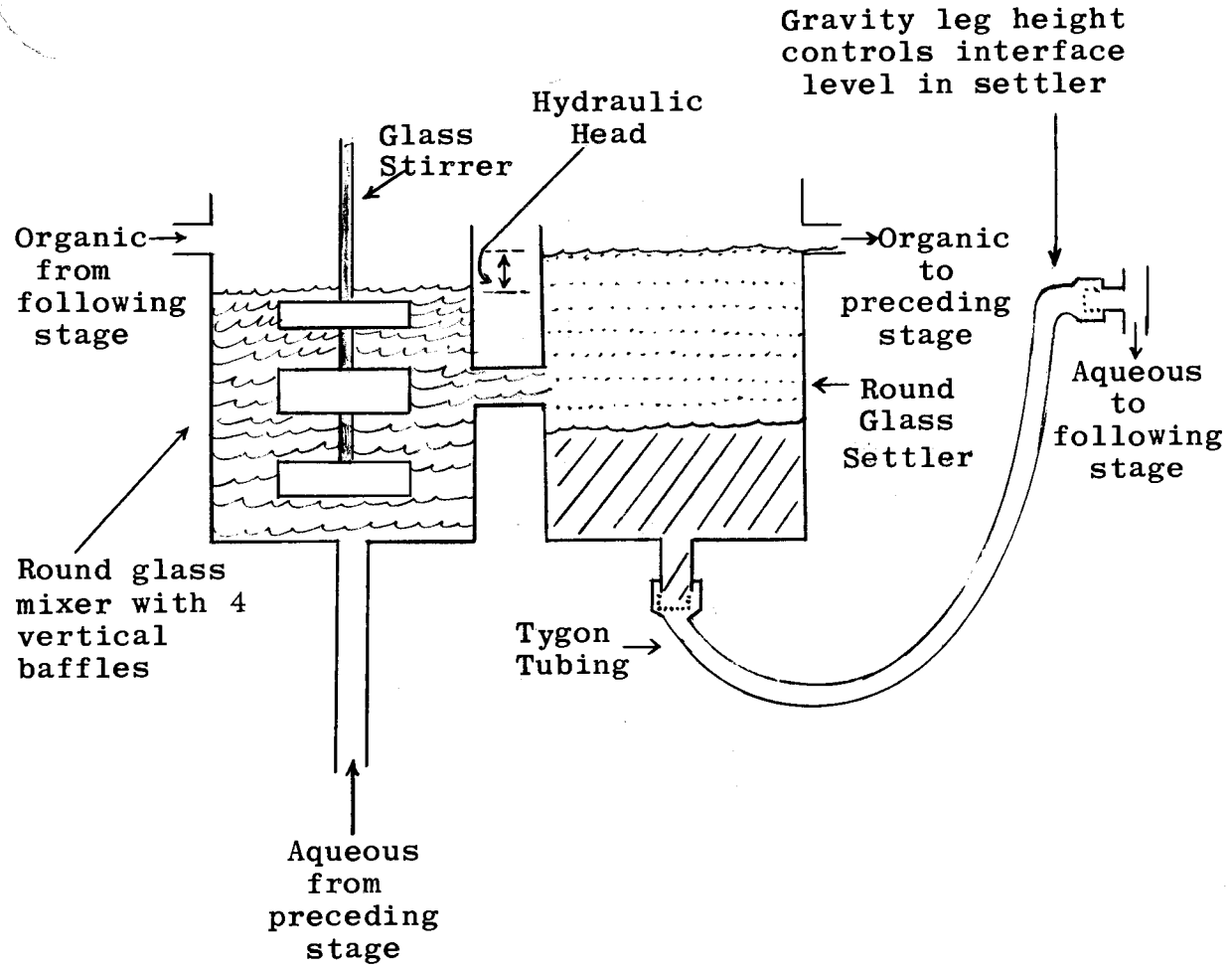


Fig. 11.1 One mixer-settler stage connected for operation (drawing not to scale).

in the mixer can vary appreciably from the feed phase ratio, and thus the actual residence time in the mixer of a particular phase can also differ appreciably from the calculated average residence time.

To avoid formation of troublesome emulsions in the extraction system, the phases were contacted with the organic as the continuous phase. Organic-continuous mixing conditions were established at startup by filling the mixers with organic only and starting the agitators before starting the flow of aqueous. Interface levels in the extractor were maintained below the opening connecting the mixer and settler in order to ensure that any intrastage recycle was organic rather than aqueous.

Table 11.2 Description of Mixer-Settlers Used in Continuous Runs

Step	Mixer-Settler Type	Mixer Working Vol, ml	Mixer Sol'n Resid. time,[a] min	Settler Settling Area, in.^{2}
Uranium Recovery Cycle				
Extraction				
Stages 1-2	Round glass	260	2.2	6
Stages 3-8	Plexiglas box	590	5.0	15
Scrub (1 stage)	Round glass	260	3.5	6
Strip (2 stages)	Round glass	260	3.4	6
Thorium Recovery Runs 1 and 2				
Extraction (4 stages)	Plexiglas box	590	4-4.5	15
Scrub (4 stages)	Round glass	260	2.7	6
Stripping (4 stages)	Round glass	260	2.7	6
Regeneration (1 stage)	Round glass	720	4.3	11
Thorium Recovery Run 3				
Extraction (4 stages)	Plexiglas box	590	4-4.5	15
Scrub (4 stages)	Round glass	260	2.7	6
Stripping				
Stage 1	Round glass	720	7.5	11
Stages 2-3	Round glass	260	2.7	6

[a] Calculated on the basis of the total solution fed to the mixer. Actually, as explained on p. 57, individual phase residence times probably varied appreciably from this value.

The solution contacting times and settling areas used in these tests (Table 11.2) are not meant to represent those that would be used in actual practice. The choice of flow rates was dictated primarily by the size of the pumps available.

Engineering studies adequate to define mixer and settler scaleup factors for the Amex-monazite liquor system have not been made. However, a few batch settling tests made in a 6-in.-dia plastic cell allow a crude approximation of settling requirements. With organic-continuous contacting conditions, the indicated nominal settler capacity with either 0.05 M tri-iso-octylamine or 0.10 M Primene JM

in 97% kerosene—3% tridecanol and monazite liquor raffinate from the thorium recovery runs was about 0.7 gpm of liquor/sq ft. This is approximately the same capacity obtained with these solvents (and other amine-diluent combinations) in treating western ore uranium liquors.

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