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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C
Monthly Progress Report

July 1959

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U. S. Atomic Energy Commission

ABSTRACT

Effect of Nitrate on Thorium Extraction by Primary Amines

Nitrate contained in raffinates from Canadian Blind River mills interferes seriously with thorium extraction by secondary amines. With primary amines, however, the effect is negligible and these compounds are the preferred process extractants.

Effect of Alcohol on Selectivity of Primene JM

Primary amines are less selective extractants for uranium over trivalent metals such as iron and rare earths than are the secondary or tertiary amines. Selectivity of the primary amines can be greatly improved, however, by adding alcohol to the kerosene diluent. The better separations obtainable permit production of higher grade products in thorium recovery processes.

Flow Capacity of Settlers for Sodium Chloride Stripping in the Amex Process

The flow capacity of settlers for sodium chloride stripping in the Amex process was determined in a 6-in. settler for alcohol-modified and unmodified 0.1 M Rohm and Haas LA-1 amine in kerosene. At a phase ratio (a/o) of 1/6, which is typical of most flow sheets, the flow capacity is limited by aqueous entrainment in the solvent. The nominal solvent flow capacity was 2 gpm/sq ft for either modified or unmodified solvent. Aqueous entrainment in the solvent was 10 gal/1000 gal at the nominal flow rate. Recycle of aqueous to obtain a phase ratio (a/o) of 1/1 or 2/1 reduced entrainment, but also reduced the nominal flow capacity to 0.7 gpm/sq ft. Entrainment of solvent in aqueous was consistently less than 0.2 gal/1000 gal of aqueous.

Uranium-Plutonium Recovery from Sulfuric Acid Decladding Solution

A process scheme is proposed for the recovery of uranium and plutonium from sulfuric acid stainless steel decladding solutions, by extracting U(IV) and Pu(III) or (IV) with successive streams of 0.1-0.3 M primary amine and stripping the combined extracts with dilute nitric acid. Any U(VI) in the feed is reduced with, e.g., iron metal or chromous sulfate. The uranium extraction coefficient $E_{\text{U-IV}}$ varies with the cube of the uncomplexed amine concentration, and is ~10,000 with 0.1 M Primene JM from 3 M H_2SO_4 . The plutonium(IV) extraction coefficient is >1000 from oxidized

solution. However, complete oxidation of the solution is not necessary. Addition of a relatively small amount of oxidant after the uranium extraction, equivalent to oxidation of only 1-2% of the Fe^{++} present, permits effective extraction of Pu(III) or (IV) with coefficients approaching 100.

Structural Effects on Thorium and Uranium Extraction with Neutral Organophosphorus Reagents

Variation in the organic side chains of neutral phosphates and phosphonates, while not producing much change in the uranium extraction ability of the reagents, caused wide variation in thorium extractability, and consequently in the uranium-thorium separation factors. Best separation was achieved with di-secondary-alkyl phenylphosphonates and tri-secondary-alkyl phosphates. Branched primary alkyl groups contributed to intermediate separation ability and compounds with straight alkyl chains, including TBP, gave the poorest separation. Tributyl phosphate gave better separation factors when diluted in xylene than in Amsco 125-82.

Purification of Promethium

A flowsheet has been developed for the separation of promethium from mixed fission-product rare earths by continuous multistage countercurrent extraction between tributyl phosphate and nitric acid. Data from single-stage extractions have been confirmed by samarium-neodymium separation in glass equipment with 11 stages. Samarium-promethium separation in 34 stages of the Knowles-type mixer-settlers to be used for promethium production has equaled the theoretical value.

Anomalous Equilibria in Uranium Extraction by Amine Sulfates

It has been shown that previously anomalous dependences of uranium extraction coefficients on reagent concentration in the amine sulfate extractant systems are due to metastable conditions induced by violent agitation during equilibration. Nearly theoretical results are obtained by slow equilibration through quiescent interfaces.

Aggregation in the Amine Extractant Systems

In light scattering measurements at 546 m μ the normal sulfates of tri-n-octylamine, trilaurylamine, di(1-isobutyl-3,5-dimethylhexyl)amine, 1-(3-ethylpentyl)-4-ethyloctylamine, and di-n-decylamine showed aggregation numbers of 1, 1, 2, 6, and 12, respectively, in n-nonane containing 3% tridecanol.

Kinetic Behavior of the Amine Extractants

A kinetic study of uranyl sulfate extraction by tri-*n*-octylamine sulfate in benzene has shown that the uranyl ion is three times as effective as the neutral monosulfate complex in transferring uranium to the organic phase, and that the neutral complex, in turn, is twice as effective as the dinegative disulfate complex.

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1.0 RAW MATERIALS PROCESSING

1.1 Effect of Nitrate on Thorium Extraction by Primary Amines (D. J. Crouse, W. D. Arnold)

Previous studies¹ on extraction of thorium with di(tri-decyl)amine from waste sulfate liquors from the Blind River district of Canada showed severe interference from small concentrations (1-2 g/liter) of nitrate ion introduced into the liquor by the anion exchange uranium recovery process. Recently it has been found that this problem can be circumvented by using primary amines as the extraction agent since these compounds show insignificant interference from nitrate.

In extractions of thorium from synthetic liquors with 0.05 M Primene JM solutions, results were essentially equivalent when the liquor contained 0, 1, and 2 g/liter of nitrate (Table 1). In a comparative test with the last liquor, thorium extraction results with another primary amine, 1-nonyldecyl, were nearly the same as those obtained with Primene JM.

Table 1. Effect of Nitrate on Thorium Extraction

Aqueous: In grams per liter, Th 0.20, Fe(II) 1.0, Fe(III) 1.0, Al 1.5; 0.2 M SO₄, pH 1.4; nitrate added as NaNO₃

Organic: 0.05 M amine in kerosene + 2 v % tridecanol

Amine	NO ₃ ⁻ in Liquor, g/liter	Phase Ratio, a/o	Thorium, g/liter		Thorium Extraction Coefficient, E _{Th}
			Organic	Aqueous	
Primene JM	0	2	0.4	<0.005	>80
		5	1.0	<0.005	>200
		10	1.4	0.070	20
	1.0	2	0.4	<0.005	>80
		5	1.0	<0.005	>200
		10	1.3	0.069	19
	2.0	a	0.8	<0.005	>160
			1.1	<0.005	>220
			1.4	0.093	15
			1.3	0.20	6
			1.3	0.20	6
1-nonyldecyl	2.0	a	0.8	<0.005	>160
			1.0	<0.005	>200
			1.3	0.070	19
			1.3	0.19	6
			1.3	0.20	6

^aOrganic cascaded against fresh aqueous, sampled after each contact.

1.2 Effect of Alcohol on Selectivity of Primene JM

(D. J. Crouse, W. D. Arnold)

Tests on separate extractions of thorium, uranium(VI), iron(III), and cerium(III) from sulfate solutions indicated that the selectivity of Primene JM for thorium over iron(III) and rare earths could be greatly improved by modification of the kerosene diluent with relatively high concentrations of alcohol. The indicated separation of thorium from uranium, at least when the solvent was nearly saturated with metals, was not appreciably affected by alcohol addition. Primary amines have been used successfully for recovering thorium from monazite sulfate liquors^{2,3} and from thorium-containing liquors from the Blind River district of Canada.⁴ The improved separations obtainable by modifying the solvent with alcohol should permit preparation of higher grade thorium products in these applications.

In tests (Table 2) where the amine was nearly saturated with thorium (aqueous/organic, a/o, phase ratio = 4/1), thorium extraction coefficients for 0.08 M Primene JM remained virtually the same as the tridecanol concentration in the kerosene diluent was varied from 0 to 15 v %. Tests at lower (~30% of saturation) thorium loadings (a/o = 1/1), both at pH 0.1 and 1.0, also showed no effect of varying the tridecanol concentration in this range. These tests, however, were not conclusive since, in all cases, the thorium concentration in the aqueous phase was below the point of detection by the analytical method used.

Uranium extraction results (Fig. 1) at ~25% of saturation loadings (a/o = 1/1) showed an increase in the extraction coefficient from 10 to 35 as the tridecanol concentration was increased from 0 to 6 v %. Further addition of tridecanol to 15 v % lowered the coefficient to ~20. At near saturation loadings (a/o = 4/1), the effect of alcohol addition was less pronounced and the maximum extraction coefficient was obtained at ~4% tridecanol.

Addition of tridecanol severely depressed extractions of iron(III) (Fig. 1). For example, the extraction coefficient decreased by a factor of ~17 at low loadings (a/o = 1/1) and by a factor of ~5 at higher loadings (a/o = 4/1) as the tridecanol concentration was increased from 0 to 15 v %.

In tests (Fig. 1) at high loadings (a/o = 4/1), the cerium(III) coefficient was decreased by a factor of 2.5 by adding 15 v % tridecanol. At low loadings (a/o = 1/1), the coefficient increased from 13 with no tridecanol to 20 with 2 v % tridecanol and then dropped off to 2.5 as the tridecanol concentration was raised to 15 v %.

Fig. 1. Effect of Tridecanol Concentration on Extractions of Uranium(VI), Iron(III), and Ce(III): Aqueous: 0.5 M SO_4 , pH 1 solution containing 1.05 g U, 0.2 g Fe(III), or 1.0 g Ce(III) per liter. Organic: 0.08 M Primene JM in kerosene-tridecanol diluent.

Table 2. Effect of Alcohol on Thorium Extraction
by Primene JM

Organic: 0.08 M Primene JM in kerosene-tridecanol
Aqueous: 0.95 g Th/liter, 0.5 M SO₄

pH	Phase Ratio, a/o	Tridecanol Concentration, v %	Th Analysis, g/liter		Extraction Coefficient, E _a ⁰
			Organic	Aqueous	
1.0	1/1	0	0.95	<0.001	>900
		2	0.96	<0.001	>900
		4	1.0	<0.001	>900
		6	1.0	<0.001	>900
		10	0.93	<0.001	>900
		15	0.97	<0.001	>900
1.0	4/1	0	2.1	0.42	5.0
		2	2.2	0.41	5.4
		4	2.1	0.42	5.0
		6	2.2	0.42	5.2
		10	2.2	0.41	5.4
		15	2.2	0.43	5.1
0.1	1/1	0	0.97	<0.001	>900
		2	0.95	<0.001	>900
		4	1.0	<0.001	>900
		6	0.95	<0.001	>900
		10	0.97	<0.001	>900
		15	0.94	<0.001	>900

1.3 Flow Capacity of Settlers for Sodium Chloride

Stripping in the Amex Process (A. D. Ryon, R. S. Lowrie)

Most of the data necessary for mixer design for the Amex process have been reported previously.^{5,6,7} The basis for design of settlers for the extraction section has also been reported.⁸ In further tests, continuous flow runs were made in a 6-in. dia settler to determine the flow capacity and entrainment values for the sodium chloride stripping section of the Amex process. The equipment and test procedures were the same as those used in the settler tests for the extraction section.⁸

The solvent was a 0.1 M solution of Rohm and Haas amine LA-1 (formerly identified as 9D-178) in kerosene modified where noted with 3 v % tridecanol. The aqueous feed was a 1.0 M sodium chloride--0.05 M sulfuric acid solution at pH 1.0. The physical properties of the phases were:

Phase	Density, g/ml	Viscosity, centistokes	I.T., dynes/cm	Batch Break Time in 12x12 in. tank at a/o = 1/1, sec.	
				Oil-in-Water	Water-in-Oil
Unmodified solvent	0.82	3.0	8.8	140	260
Modified solvent	0.82	3.0	8.8	190	200
Aqueous feed	1.04	0.97	-	-	-

The flow capacity of the settler was measured for oil-in-water type dispersions at a/o phase ratios of 2/1 and 1/1, and for water-in-oil dispersion at a/o ratios of 1/1 and 1/6. The latter phase ratio of 1/6 is typical for most flowsheets. The other conditions provide a broader base for design, showing the effect of aqueous phase recycle on flow capacity and entrainment.

At steady state a distinct dispersion band existed at the interface similar to that previously observed in tests of the extraction section of both the Amex and Dapex processes. Measurement of the band thickness as a function of flow rate made possible the determination of nominal flow capacity of the settler at various phase ratios for both types of dispersions. The data for modified and unmodified solvent are shown in Table 3. Dispersion band thickness increases exponentially with solvent flow rate per unit settler area (Fig. 2), resulting in nearly parallel lines for different phase ratios with the exception of data obtained at a/o phase ratio of 1/6, where a thin band was formed which did not change in thickness with flow rate. The nominal solvent flow capacity at the other phase ratios was read from Fig. 2 at a band thickness of 5 in., which had been previously shown to be approximately one-half of the flooding point of the settler.

In the case of a/o phase ratio of 1/6, the flow capacity of the settler was limited by entrainment of the aqueous phase in the solvent leaving the settler. Entrainment increased from 1 to 150 gal per 1000 gal of solvent over the flow range tested. The high value is nearly equivalent to the phase ratio of the dispersion entering the settler, showing flooding of the settler. In Fig. 3, entrainment as a function of solvent flow rate increases slowly to an inflection point at a flow rate of about 3 gpm/sq ft and then increases rapidly to complete flooding at 4 gpm/sq ft. Allowing a safety factor of 2, the nominal solvent flow capacity is 2 gpm/sq ft. The aqueous entrainment at this flow rate is approximately 10 gal/1000 gal of solvent which

Table 3. Summary of Data in 6-in. Settler

Phase Ratio, a/o	Solv. Flow Rate, gpm/ft ²	Dispersion Thickness, in.		Entrainment, gal/1000 gal			
		Unmod.	Modif.	Solv. in Aq		Aq in Solv.	
		Solvent	Solvent	Unmod.	Modif.	Unmod.	Modif.
Oil-in-water type dispersions							
2/1	0.33	0.8	0.4	0.08	0.12	<0.07	<0.07
	0.87	-	5.3	-	0.16	-	<0.07
	0.93	9.5	8.0	0.08	0.10	0.35	<0.07
1/1	0.33	0.9	0.6	<0.04	<0.04	<0.07	<0.07
	0.80	-	4.8	-	<0.04	-	<0.07
	1.03	10.8	11.0	<0.04	<0.04	<0.07	<0.07
Water-in-oil type dispersions							
1/1	0.27	0.8	0.8	<0.04	<0.04	<0.07	0.2
	0.68	5.8	4.9	<0.04	<0.04	0.14	1.1
	0.87	13.3	10.3	<0.04	<0.04	0.07	1.1
1/6	0.80	0.3	0.5	<0.04	<0.04	1.2	1.3
	1.60	-	0.5	-	<0.04	-	6.3
	2.40	1.0	1.5	<0.04	<0.04	19.0	12.0
	3.47	0.8	-	<0.04	-	92.0	-
	4.00	1.0	1.0	<0.04	<0.04	150.0	150.0

is low enough to avoid loss of stage efficiency due to back-mixing of aqueous and the resultant loss of sodium chloride entrained in the solvent is not economically significant.

The nominal solvent flow capacity (Table 4) is nearly the same (0.6 to 0.8 gpm/sq ft) for both modified and unmodified solvent at a/o phase ratios of 2/1 and 1/1 for either oil-in-water or water-in-oil type dispersions. This is approximately one-third of the nominal flow capacity at typical flow sheet phase ratio of 1/6. Consequently, there apparently is no advantage to be gained by intrastage recycle of the aqueous phase in the sodium chloride strip section unless entrainment is significant.

Entrainment of aqueous in solvent was lowest for the oil-in-water type dispersion, being less than 0.1 gal/1000 gal with one exception. For water-in-oil dispersion, entrainment was less than 0.2 gal/1000 gal for unmodified solvent and 1.0 gal/1000 gal for modified solvent at a/o phase ratio of 1/1, and at nominal flow rate the entrainment at 1/6 was 10 gal/1000 gal for both modified and unmodified solvent.

Entrainment of solvent in aqueous was low for all run conditions, being less than 0.04 gal/1000 gal for water-in-oil dispersions and less than 0.2 gal/1000 gal for oil-in-water dispersions.

Solvent		Dispersion Type	Phase Ratio, a/o
Unmod.	Modif.		
○	●	Oil-in-water	2/1
□	■	Oil-in-water	1/1
△	▲	Water-in-oil	1/1

Fig. 2. Throughput Capacity of 6-in. Settler for Sodium Chloride Stripping of 0.1 M Rohm and Haas LA-1 Amine.

Fig. 3. Aqueous Entrainment at a/o Phase Ratio of 1/6.

Table 4. Nominal Flow Capacity of Settler for Sodium Chloride Stripping in Amex Process

Dispersion Type	Phase Ratio, a/o	Nominal Solvent Flow Capacity, gpm/ft ²	
		Unmodified Solvent	Modified Solvent
Oil-in-water	2/1	0.7	0.8
	1/1	0.7	0.8
Water-in-oil	1/1	0.6	0.7
	1/6	2.0	2.0

2.0 SOLVENT EXTRACTION TECHNOLOGY

2.1 Uranium-Plutonium Recovery from Sulfuric Acid Decladding Solution (C. F. Coleman, D. E. Horner)

2.11 Uranium(IV) and Plutonium(IV) Extraction by Primary Amine. Of several possible extraction methods for recovery of the uranium and plutonium that may be lost to sulfuric acid stainless steel decladding solutions, extraction with a primary amine appears at present to be the most promising. Primary amines are strong extractants for the sulfates of both uranium(IV)⁹ and plutonium(IV),¹⁰ even at fairly high concentrations of sulfate and sulfuric acid (Table 5).

The uranium(IV) extraction coefficient from 3 M sulfuric acid with 0.1 M Primene JM, a commercial primary amine, was too high for accurate direct measurement. The best estimate obtained from a series of measurements at different uranium levels, using the relationships that the extraction coefficient varies with the cube of the uncomplexed amine concentration¹⁰ and that the molar association ratio is U/amine = 1/8,⁹ was $E_a^0(\text{U-IV}) \approx 10,000$ with 0.1 M amine, at low loading. An extraction isotherm calculated on this basis, i.e., $\frac{M_{\text{U(org)}}}{M_{\text{U(aq)}}} = 10,000 [(0.12 - 8 M_{\text{U(org)}})/0.1]^3$, is shown as the solid curve in Fig. 4. (The curve shown is calculated for 0.12 M rather than 0.10 M amine, since 0.12 M was used in the following tests.) The validity of this calculated extraction isotherm was confirmed by two-stage batch extractions carried through 4 cycles (Table 6). Two tests were run at different phase ratios, corresponding to molar ratios of U/amine = 1/10 and 1/7, i.e., slightly below and slightly above the expected loading limit. At the 1/10 ratio the uranium recovery was >99%. At the 1/7 ratio it dropped to 93%, with about the expected amount of uranium lost to the raffinates. The individual points from these tests are also shown in Fig. 4, in reasonably close agreement with the calculated curve.

Table 5. Plutonium Extraction by Amines from Sulfate Solutions

Initial Pu concentration, 10-20 mg/liter
Organic diluent, Amsco 125-82
Phase ratio a/o = 1/1, room temp.

Amine	M	Extraction Coefficient, E_a^O (Pu-IV)	
		3 M H_2SO_4	3 M SO_4 , pH ~1
Primene JM ^{a,b}	0.1	>1000	>1000
	0.4	>8000	
Di(tridecyl)amine ^a	0.1	0.8	6
Bis(1-isobutyl-3,5-dimethylhexyl)amine	0.1	<0.1	0.2
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctylamine	0.1	6	>20
	0.4	20	100
N-Benzyl-1-undecyl-laurylamine	0.1	5	
Tri-iso-octylamine	0.1	<0.001	<0.01

^aDiluent modified by addition of tridecanol.

^bPrimene JM is a commercial primary amine.

Table 6. Two-Stage Countercurrent Uranium Extraction

Feed: 3 M H_2SO_4 , 0.5 M Na_2SO_4 , 3.1 g U(IV)/liter
Extractant: 0.12 M Primene JM in 90% Amsco
125-82--10% tridecanol
10 min contact in Burrell shaker, room temp.

Cycle	Stage	Uranium Distribution, g/liter					
		a/o = 1.34 ^a			a/o = 0.94 ^b		
		Aqueous In	Organic Out	Aqueous Out	Aqueous In	Organic Out	Aqueous Out
1	1	3.1	3.5		3.1	2.9	
	2	3.1		0.58	3.1		0.008
2	1	3.1	3.4		3.1	3.5	
	2			0.018			0.005
3	1	3.1	3.6		3.1	3.0	
	2			0.43			0.018
4	1	3.1	3.5	(2.61)	3.1	3.5	(2.09)
	2		(1.7)	0.020		(0.005)	0.006
Material Balance, %		99		103			
Uranium Loss to Raffinate, %		7		0.3			

^aPhase ratio 1.34 to give steady-state mole ratio U/amine = 1/7.

^bPhase ratio 0.94 to give steady-state mole ratio U/amine = 1/10.

Fig. 4. Uranium(IV) Extraction Isotherm with 0.12 M Primene JM from 3 M H₂SO₄--0.5 M Na₂SO₄ Solution.

2.12 Chemical Flowsheet. While uranium(IV) and plutonium(IV) are the oxidation states desired for extraction by a primary amine, they do not ordinarily exist together in solution. Hence, the flowsheet was set up for recovery by successive extractions, first of U(IV), and then of Pu(IV) after oxidation (Fig. 5). After the two separate extractions, the extracts can be combined for stripping. The decladding solution is expected to be 2-3 M H_2SO_4 containing stainless steel sulfates totaling $\sim 1 \text{ M}$.¹¹ Arbitrary assumption of $\sim 1\%$ loss from the core of a typical fuel element led to concentrations of $< 3 \text{ g U/liter}$ and $\sim 0.001 \text{ g Pu/liter}$. This solution is to be treated with a reductant, e.g., iron metal or chromous sulfate, as necessary to ensure that essentially all of the uranium is reduced to U(IV). The amine concentration was set at 0.3 M on consideration of both extractant volume and viscosity. The phase ratio in the uranium extraction section is set at a/o $\approx 100/35$ by the limiting loading ratio of 1/8, with only a little margin of uncomplexed reagent required. With plutonium at 1 mg/liter, physical operation rather than the stoichiometric plutonium loading limit will limit the phase ratio in the plutonium extraction section.

Fig. 5. Plutonium and Uranium Recovery from Sulfuric Acid Decladding Solution by Extraction with Primary Amine.

This was arbitrarily set at $a/o = 100/5$ in the flowsheet. The extraction isotherm calculated for 0.3 M amine shows an even steeper rise and sharper knee than that in Fig. 4, so that a single stage (at high stage efficiency) can give high recovery, and two extraction stages should be sufficient for >99% recovery of U(IV) even at loading close to the limiting ratio.

It was not necessary to oxidize the solution completely in order to extract the plutonium. The extraction conditions shown in Fig. 5 gave effective plutonium recovery, with extraction coefficients variable but typically up to and above 100, using as an oxidant only 0.01 M ferric iron, which was much higher than the plutonium concentration but much lower than the ferrous concentration already present. This ability to extract plutonium(III) in the presence of Fe(II) is tentatively ascribed to enhancement of oxidation from Pu(III) to (IV), during extraction, by the complexing action of the sulfate and the amine.

For the first countercurrent testing of the plutonium extraction, a combined flow system (Fig. 6) rather than the separate flow system was used, since it is closely parallel to the flowsheet of Fig. 5 in the uranium and plutonium extraction sections considered separately, and in addition provided a test of the ability of the plutonium, once extracted, to be retained in the organic phase during uranium extraction. Four extraction stages of this flowsheet were tested through five cycles of countercurrent batch extraction (Table 7). Five preliminary cycles without plutonium in the feed were used to bring the macro components into approximately steady state distribution. Tenth-molar amine and phase ratio $a/o = 1/1$ were used, instead of 0.3 M and 100/35 as in Fig. 5, for convenience in the glove box operation. Air was displaced from the separatory funnels with carbon dioxide immediately after each transfer to minimize air adsorption and thus provide a better test of the need and sufficiency of the ferric sulfate oxidant.

As expected, uranium extraction was nearly complete in the first stage, and less than 0.1% of it remained in the aqueous stream leaving the second stage. The plutonium re-fluxed almost completely in the first stage, and had not reached steady state. Its extraction was high in the third stage, $E_a^O = 70$, and in spite of its buildup in the upper stages less than 0.1% of it was lost in the 4th stage raffinate. Thus, removal of the organic stream leaving stage 3 as a product, according to Fig. 2, would have given high plutonium recovery.

Fig. 6. Countercurrent Batch Equilibration Test of Combined Extraction of Uranium(IV) and Plutonium(III) or (IV) with Primary Amine: Final Distribution Coefficients and Concentration Profiles.

Table 7. Countercurrent Test of Combined Extraction
of Uranium and Plutonium by Primary Amine

Batch equilibration, double diamond pattern

Feed: 2.4 M H_2SO_4 , 1.5 M s.s. sulfates, 3.1 g U(IV)/liter;
9.4 mg Pu(III)/liter in feed for cycles 6-10 only

Extractant: 0.113 M Primene JM in 90% Amsco 125-82--
10% tridecanol

Phase ratio a/o = 1/1, 10 min contact in Burrell shaker,
room temp.

Cycle	Stage	U Distn., g/liter			Pu Distn., mg/liter		
		U	U Out		Pu	Pu Out	
		In	Org	Aq	In	Org	Aq
1-4	1	4x3.1	4x(3.0) ^a		0		
	4			0.0004			
5	1	3.1	3.0	0.007	0		
	2		0.009	0.0003			
	3		0.0009	0.0002			
	4		<0.0004	0.0004			
6-9	1	4x3.1	4x(3.8) ^a		4x9.4	4x(0.09) ^a	
	4			0.0012 ^b			<0.01
10	1	3.1	3.6	0.063	94	0.4	21.8
	2		-	0.0027		13.7	2.5
	3		0.0034	0.0020		2.1	0.03
	4		0.0008	0.0015		0.013	<0.01
<hr/>							
Material Balance, %		~110			87		
Loss in Raffinate, %							
--from stage 2		0.09			-		
--from stage 4		0.05			0.07		

^aComposites, cycles 1-4 and 6-9.

^bUranium in raffinates from cycles 6, 7, and 8 was 0.0014, 0.0014, and 0.0016 g U/liter.

2.2 Structural Effects on Thorium and Uranium Extraction with Neutral Organophosphorus Reagents (C. A. Blake, J. M. Schmitt, W. E. Oxendine)

Twenty-two trialkylphosphates and dialkyl alkyl- or aryl-phosphonates were examined for their ability to extract uranium and thorium from separate acid solutions ranging from 1.5 to 9.0 M nitric acid at equilibrium (Table 8).

Thorium-Uranium Separation. Highest uranium-thorium separation factors were indicated by phosphates and phosphonates with secondary alkyl side chains. Calculated separation factors were 5-40 times greater than those obtained with TBP under the same conditions. The effect of secondary branching has also been observed by other investigators.¹² Reagents with branching further along the chain (e.g., 2-ethylhexyl, 2-methylbutyl) or with a mixture of normal and cyclohexyl or phenyl groups were only slightly better than TBP, by ratios of separation factors up to 5. Phosphonates with straight alkyl chains were poorer than TBP by ratios down to 1/2. The separation factors and extraction coefficients are listed in Table 8.

(Also tested were tri(hexyl-2)phosphate, tri(1,3-dimethylbutyl)phosphate, tri(2-ethylbutyl)phosphate, didecyl decylphosphonate, triphenylphosphate and tri(tert-butyl-phenyl)phosphate. The first four gave erratic behavior indicative of impurity in the reagent. They still, however, fit into the pattern described above. Of the last two, the first gave extractions of uranium and thorium too low to measure and the latter in Amsco 125-82 precipitated both metals.)

Uranium Extraction. Uranium extraction coefficients varied by a factor of ~35 through the range of reagent structure. The dialkyl alkylphosphonates gave very similar extractions, all within a factor of 2, even though the structures incorporated such groups as cyclohexyl, isopropyl, 2-ethylhexyl, octyl-2, and straight alkyl chains. Also falling in a rather close grouping were the trialkylphosphates, but the level averaged an order of magnitude lower. Introduction of the phenyl group resulted in a noticeable lowering of the phosphonate extraction, the decrease being greater when the remaining alkyl groups were secondary than when they were straight primary.

Thorium Extraction. The same compounds gave a much wider range of thorium extraction coefficient (x4000). Here the principal effect was to distribute the extractability of the phosphonates over this whole range, with the di(n-alkyl) alkylphosphonates at the top and with thorium coefficients decreasing with increasing complexity of branching and the

Table 8. Structural Effects on Uranium and Thorium Extraction
with Neutral Organophosphorus Compounds

Aqueous phase: 0.002 M U(VI) or 0.002 M Th; HNO₃ concentration is that at equilibrium
Separation factor (SF) is calculated from E_U/E_{Th}

Type of Side Chain	Reagent, 1 M in Amsco 125-82 (* 1 M in xylene)	Uranium and Thorium Extraction and Separation											
		2 M HNO ₃			4 M HNO ₃			6 M HNO ₃			9 M HNO ₃		
		E _U	E _{Th}	SF	E _U	E _{Th}	SF	E _U	E _{Th}	SF	E _U	E _{Th}	SF
Branched Secondary	Di(octyl-2) phenyl-phosphonate*	14	0.02	700	20	0.02	1000	17	0.02	850	9.4	0.02	470
	Di(sec-butyl) phenyl-phosphonate*	42	0.12	370	60	0.17	370	51	0.20	250	26	0.19	140
	Tri(octyl-2)phosphate	59	0.19	310	95	0.25	370	100	0.32	320	44	0.37	120
	Tri(sec-butyl)-phosphate	36	0.16	230	63	0.26	240	59	0.31	190	32	0.36	90
	Di(isopropyl) 2-ethyl-hexylphosphonate	-	-	-	620	6.2	100	-	-	-	-	-	-
	Di(octyl-2) 2-ethyl-hexylphosphonate	300	5.4	55	330	6.0	55	-	-	-	-	-	-
Branched Primary and Straight Primary + Cyclohexyl or Phenyl	Di(2-ethylhexyl) 2-ethylhexylphosphonate	420	21	20	490	18	27	350	12	29	180	7.0	26
	Tri(2-ethylhexyl)-phosphate	35	1.2	29	62	2.2	28	56	2.1	27	35	1.6	22
	Di(n-butyl) cyclohexyl-phosphonate	280	23	12	400	18	22	300	12	25	150	9.8	15
	Tri(2-methylbutyl)-phosphate	22	2.0	11	46	2.6	18	48	2.7	18	32	2.2	15
	Tri(isobutyl)phosphate	16	0.9	19	37	1.9	20	40	2.1	19	22	2.1	10
	Di(n-butyl) phenyl-phosphonate*	56	3.2	18	115	6.0	19	100	6.2	16	50	6.0	8.3
Straight Primary	Tri(n-butyl)phosphate*	32	1.2	26	55	2.1	26	46	2.0	23	25	1.6	16
	Tri(n-butyl)phosphate	17	1.6	11	36	3.4	11	38	4.0	10	22	4.1	5.4
	Di(n-hexyl) hexyl-phosphonate	300	48	6.5	440	54	8.1	400	40	10	170	29	5.9
	Di(n-pentyl) n-pentyl-phosphonate	340	76	4.4	460	85	5.4	400	75	5.3	170	61	2.8
	Di(n-butyl) n-butyl-phosphonate	460	39	12	540	43	13	300	63	4.8	150	77	1.9

positioning of the point of branching nearer the central phosphorus atom. Much less of an effect was seen with the trialkyl phosphates.

Effect of Diluent. The dialkyl phenylphosphonates were tested in xylene since the uranium-organophosphorus complex is difficultly soluble in aliphatic hydrocarbons. When comparison tests with TBP were run in both types of solvents, better (x2.3-2.9) uranium-thorium separation was obtained in xylene.

2.3 Purification of Promethium by Solvent Extraction

(Boyd Weaver, F. A. Kappelmann, J. P. Eubanks)

A flowsheet has been developed for the purification of promethium by continuous multistage countercurrent extraction between tributyl phosphate and nitric acid. This process is an outgrowth of previous work on the separation of natural rare earths by liquid-liquid extraction. Its immediate use will be in the production of kilocurie quantities of rare earths by the Isotopes Division. The later part of the development has been in cooperation with members of the Isotopes Division, using the actual equipment which will be used in production.

The process is based on the fact that in extraction by TBP from concentrated HNO_3 , the extraction coefficients of the fission product rare earths differ by a factor of 1.8-1.9 between adjoining elements. Fig. 7 is a plot of recent data on extraction coefficients of Pm^{148} and Nd^{147} over a wide range of acidities. It is evident that greatest separation is possible at high acidities and that effective stripping from the organic phase is easily attained below about 9 N HNO_3 . Extraction data for samarium, using Sm^{153} tracer, in the 12 N HNO_3 region indicate an equal separation between Sm and Pm.

The high specific activity of Pm^{147} permits the processing of kilocuries of activity in a reasonable volume while limiting concentrations to levels where reagent loading does not cause any appreciable departure from ideal extraction. Such departures are a limiting factor in the separation of natural rare earths by liquid extraction. With dilute solutions the overall separation to be expected from continuous multistage systems at equilibrium is $\alpha^{\frac{n}{2}}$, where α is the single-stage separation factor, and n is the number of stages. The optimum organic/aqueous flow ratio is $(E_1 E_2)^{-1/2}$, where E_1 and E_2 are the respective extraction coefficients of the two elements to be separated. The distribution of the separative power, $\alpha^{\frac{n}{2}}$, of the system between high yield and high purity is determined by the feed point.

Fig. 7. Extraction of Pm, Nd, and Sm by TBP from HNO_3 .

In an experiment with an 11-stage glass system with a mixture of natural rare earths containing no promethium, an overall separation was attained which indicated a single stage separation factor of 3.42 between Sm and Nd. By interpolation the Sm/Pm and Pm/Nd factors would be 1.85. There was apparently ~100 percent stage efficiency. At about this point the original plan to use the process for removal of yttrium activity prior to ion exchange separation and a second plan to reduce the bulk of the material to be placed on ion exchange columns were combined, with the hope of performing the complete separation by liquid-liquid extraction. Further activities were devoted to obtaining more data regarding optimum flow ratios and feed points and testing the stripping circuit of the system. Experiments were performed with 20 and 34 stages, as it became definite that the two production cycles to be set up by the Isotopes Division would have these respective numbers of stages.

Figure 8 is a flowsheet derived from experimental data. The final production flowsheet will differ only slightly in flow rates, and feed points are nearly established. The use of 13.6 N commercial HNO₃ in the first cycle will result in a further adjustment. The stripping ratios are based on calculations and have been successfully tested.

Table 9 shows the quantities and compositions of materials to be expected at various stages in the processing of one kilo of cerium-free fission-product rare earths. The quantity has already been reduced to 910 grams by loss of yttrium and some other elements during the removal of cerium by extraction with di(2-ethylhexyl)phosphoric acid. The predicted element distributions are based on an arbitrary distribution of the total separative power between yield of promethium and removal of neodymium in the first cycle and between yield of promethium and removal of samarium in the

Table 9. Predicted Products from Promethium Purification

	1st Cycle			2nd Cycle	
	Feed, g	Waste, g	Product, g	Waste, g	Product, g
La	129	129	-	-	-
Pr	130	130	-	-	-
Nd	489	480	9.4	-	9.4
Pm	57	5.7	51	0.04	51
Sm	98	0.4	97.6	94.6	3
Eu	3.3	-	3.3	3.3	3x10 ⁻⁶
Gd	0.6	-	0.6	0.6	-
Y	3	-	3	3	-
	910	745	165	102	63

Fig. 8. Promethium Purification Flowsheet

second cycle. It is to be noted that the purity of the promethium is limited by the number of stages in the first cycle. An additional 5 stages would reduce the neodymium content by half and give a somewhat higher yield.

The process is now being tested by the Isotopes Division in the actual production equipment. The larger mixer-settlers for the first cycle were designed for much larger flows than those of the present flowsheet and have required modification. They are at present under test of the promethium and neodymium distributions at equilibrium. The small equipment for the second cycle has been tested, first with Sm^{153} and then with Pm^{148} . In the samarium test, only 2 parts in 1000 of the Sm^{153} appeared in the raffinate. In the promethium test, 1 part in 100 of the Pm^{148} was in the organic phase at equilibrium under the same conditions. The indicated overall separation factor is 50,000, the α for Sm/Pm is 1.88, and the process efficiency is ~100 percent.

3.0 FUNDAMENTAL CHEMISTRY

3.1 Anomalous Equilibria in Uranium Extraction by Amine Sulfates (K. A. Allen, W. J. McDowell)

As previously described,¹³⁻¹⁵ uranium extraction coefficients obtained by the usual violent agitation procedures have varied approximately linearly with the uncomplexed amine sulfate concentrations, although the molar association ratios (amine sulfate/uranium) have been in the range 2/1 to 3/1, never as low as 1/1. A hypothesis which could account for this is that metastable conditions are induced by the agitation itself, such as organic droplets sufficiently small so that all the extractant is adsorbed at the interface. On coalescence, the clear phase analyses obtained would thus reflect an interfacial adsorption equilibrium rather than a true extraction equilibrium, because of the slowness with which true equilibrium is established through the quiescent interface. In order to test this hypothesis, long term equilibrations through quiescent interfaces have been run. With respect to this variable (reagent concentration dependence of the uranium extraction coefficients) the differences in the results obtained by the two techniques have been startling. Thus, while di-n-decylamine sulfate (DDAS) and tri-n-octylamine sulfate (TOAS) had both shown approximately linear dependences on violent agitation, it had been predicted from particle size determinations that the former should have shown none or only very little dependence at all¹⁶ (i.e., the uranium extraction coefficients should have been nearly constant, independent of the uncomplexed DDAS concentration) and that the dependence for TOAS should have been at least as high as square, and possibly third power at

low uranium loadings. On slow equilibration through quiescent interfaces the coefficients remained constant, within experimental error, over a 32-fold range of DDAS concentration, and for TOAS the dependence varied from third power below 0.05 N down to nearly first power at higher concentrations (Fig. 9).¹⁷ The slow equilibration technique has thus definitely established metastability due to violence of agitation as an important factor in the anomalous "equilibria" observed in at least one definitive parameter in the amine extractant systems. Also, it has replaced the previously anomalous dependences with nearly theoretically ideal results over a considerable range, and it shows promise of becoming a new and generally valuable tool in obtaining true thermodynamic equilibria in any extraction system where violence of agitation during equilibration may be leading to spurious results.

3.2 Aggregation in the Amine Extractant Systems (K. A. Allen, W. J. McDowell, G. N. Case)

In continued study of the aggregation behavior of the amine sulfate extractants in hydrocarbon diluents, light-scattering measurements have been extended to solvents other than benzene. The following table shows molecular weights and aggregation numbers for six amine salts in *n*-nonane containing 3% tridecanol, along with the previous results in benzene for comparison.¹⁸ Except for the 1-undecyldodecyl amine sulfate, for which the measurements were made on dry solutions and, therefore, do not apply to the corresponding two phase equilibria, it remains generally true that in no case are the particles of sufficient size to provide a basis for the apparent (and probably spurious) constant activity observed in some of the equilibria previously studied¹⁹ (see preceding section for an important example).

	Benzene		<i>n</i> -Nonane (1 3% tridecanol)	
	M	N	M	N
Tri- <i>n</i> -octylamine sulfate	900	1	900	1
Trilaurylamine sulfate	1100	1	1300	1
Di(1-isobutyl-3,5-dimethyl- hexyl)amine sulfate	3600	4	1800	2
1-(3-Ethylpentyl)-4-ethyl- octylamine sulfate	8000	11	4200	6
Di- <i>n</i> -decylamine sulfate	30,000	40	3300-8100*	5-12
1-Undecyldodecylamine sulfate**	140,000	180	800,000	1000

*The DDAS results in modified nonane showed a smooth curvature corresponding to a continuous change in the avg. mol. wt. from 3300 at $c = 0.005$ g/ml to 8100 at $c = 0.036$ g/ml.

**The 1-undecyldodecylamine sulfate measurements were made on dry solutions, and the *n*-nonane did not contain tridecanol.

Fig. 9. Anomalous Equilibria due to Violence of Agitation with Di-n-decylamine Sulfate (DDAS) and Tri-n-octylamine Sulfate (TOAS).

A preliminary study of the dielectric behavior of these solutes in benzene has been completed.²⁰ The absence of a frequency dispersion for the large di-n-decylamine sulfate particle suggests that it is the individual molecules rather than the entire aggregates which respond to the electric field, which, in turn, indicates that the bonds holding the micelles together may be quite weak, possibly only a few kilocalories per mole. At a fixed frequency of 1 Mc, the dependences of the dipole moments of this and other amine sulfates on concentration have shown that aggregation results in some cancellation of the moments due to the individual molecules.

3.3 Kinetic Behavior of the Amine Extractants (K. A. Allen, G. N. Case)

In view of the rather startling results obtained on slow equilibration through quiescent interfaces, a kinetic study has been made of acid and uranium extraction by amine sulfates in benzene, using an all-glass apparatus in which the phases could be stirred separately in opposite directions at controlled speeds. All the extractions run so far appear to be first order, suggesting that the rate controlling step is Fick's First Law diffusion through the stationary layers at the interface. Under constant mechanical conditions, and at constant amine, uranium, and acid activity, but varying the aqueous sulfate ion concentration,¹³ a series of uranyl sulfate extractions by tri-n-octylamine sulfate in benzene has shown that the uranyl ion is three times as effective as the neutral monosulfate complex in transferring uranium to the organic phase, and that the neutral complex, in turn, is twice as effective as the dinegative disulfate complex.²¹

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