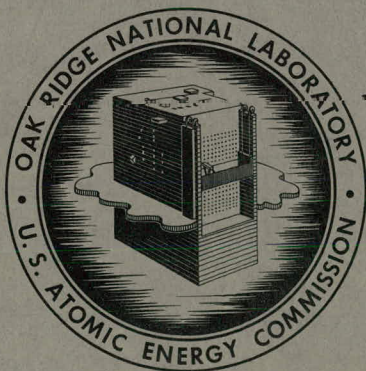


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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT
SECTION C
MONTHLY PROGRESS REPORT
AUGUST 1959



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OAK RIDGE NATIONAL LABORATORY

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ORNL CF-59-8-45

CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C
Monthly Progress Report

August 1959

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Date Issued

SEP 8 1959

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. Atomic Energy Commission

ABSTRACT

Solvent Extraction of Uranium from Carbonate Solutions

Uranium extractions from carbonate solutions were effective and phase separation rates were rapid using a new commercial quaternary extractant, Alamine 336. Extraction coefficients were approximately proportional to the quaternary concentration. Addition of ~0.5 mole tridecanol/mole quaternary to the solvent gave optimum extraction efficiency and phase separation rates. Small concentrations of nitrate or chloride in the liquor severely depressed uranium extractions but the depressing effect of sulfate was relatively minor. Both vanadium and molybdenum were extracted fairly strongly by Alamine 336 and represent difficult contamination problems in process operation. Uranium was stripped very effectively with dilute nitrate or chloride salt solutions or precipitated directly from the solvent with sodium carbonate--sodium hydroxide solutions. Uranium stripping efficiency with the latter, however, was seriously impaired by the presence of vanadium and molybdenum in the solvent. Preliminary tests with an ore carbonate leach liquor indicated that organic matter dissolved in the liquor may seriously interfere with the solvent extraction process.

Prevention of Silica Stabilized Emulsions by Solvent-Continuous Mixing

Emulsion difficulties in the Amex and Dapex solvent extraction systems have been encountered when silicic acid is present in the aqueous feed. The emulsion is an oil-in-water type which can be prevented by controlling the mixing to form water-in-oil (solvent-continuous) dispersions which separate readily. The utility of solvent-continuous mixing has been demonstrated in uranium mills where feed liquors containing in the order of 2 g silica per liter have been successfully processed.

Uranium-Plutonium Recovery from Sulfuric Acid Decladding Solution (Continuous Countercurrent Extraction with Primary Amine)

The chemical flowsheet previously proposed for recovery of uranium and plutonium from sulfuric acid stainless steel decladding solution by extraction with a primary amine was confirmed by continuous countercurrent extraction in a six-stage bank of laboratory-scale mixer-settlers. Separate streams of 0.3 M RNH₂ extracted U(IV) in stages 1-2 and Pu(III-IV) in stages 3-6, both with >99.5% recovery, from 2 M H₂SO₄ containing 1 M s.s. sulfates, 3 g U/liter, and 0.0005 g

Pu/liter. A small amount of ferric sulfate added after stage 2 aided plutonium extraction. Extraction with a single organic stream, with ferric sulfate added after the third stage, gave nearly as good results as the separate streams.

Estimates based on the extraction results indicated that uranium and plutonium recovery should be feasible with a single stage extraction for each, assuming that the efficiency of single-stage equilibration would approach 100%.

Uranium-Plutonium Recovery from Sulfuric Acid Decladding Solution (Nitric Acid Stripping from Primary Amine)

In continued testing of the chemical flowsheet previously proposed for plutonium and uranium recovery from sulfuric acid stainless steel decladding solution by extraction with a primary amine, four-stage batch countercurrent stripping with 5 M HNO₃ at a/o = 1/10 removed 97-99.8% of the uranium and >99.9% of the plutonium from 0.3 M Primene JM. Variable plutonium reflux occurred in the first two stages, but showed no significant effect on the 4th stage.

Uranium-Plutonium Recovery from Sulfuric Acid Decladding Solution (U(VI) Extraction by Primary Amine)

The extraction coefficients for U(VI) from 3 M H₂SO₄ -- 0.5 M Na₂SO₄ with Primene JM were nearly proportional to the free amine concentration calculated as $\frac{M}{M} \text{RNH}_2 - 6 \times \frac{M}{M} (\text{U})_{\text{org}}$, with $E \approx 0.5$ at 0.1 M free amine. From this, 30-80% recovery of any small amount of unreduced or reoxidized uranium in the feed was estimated for the previously proposed U(IV)-Pu(III-IV) extraction flowsheets.

Uranium Recovery from Sulfuric Acid Decladding Solution (Uranium Extraction by Dialkylphosphoric Acid)

Uranium recovery was >95% in 8 stages of continuous countercurrent extraction with a di(2-ethylhexyl)phosphoric acid-TBP synergistic extractant, at a/o = 10/1, from a synthetic sulfuric acid stainless steel decladding solution containing 0.07 g U/liter and ~2 g Th/liter. About 2% of the thorium was extracted with the uranium. The extracted metals were stripped with sodium carbonate to give after acidification a product solution containing (g/liter) 4.5 U, 1.5 Th, 0.2 Fe, $\approx 0.03 \text{ SO}_4$, in 1.8 M NaNO₃ -- 0.5 M HNO₃.

Removal of Americium from Plutonium

Plutonium was effectively freed from americium contamination by extraction from 2 M HNO₃ with 0.1 M di(2-ethyl-

hexyl)phosphoric acid, $E_a^O(\text{Pu-IV}) > 10^4$ and $E_a^O(\text{Am-III}) < 10^{-2}$. Plutonium in which ~3% of the α -activity was from Am^{241} was recovered at a concentration of ~1 g Pu/liter in 2 M HNO_3 -- 1 M NaNO_3 solution, with <0.03% of the α -activity due to Am.

Electrical Coalescence in Solvent Extraction

Electrical coalescence of water-in-oil type dispersions, which is used commercially in the petroleum industry, is being investigated for application in radiochemical solvent extraction systems.

Emulsion Stabilization by Silicic Acid

Silicic acid apparently stabilized emulsions in oil-in-water (aqueous-continuous) solvent extraction systems, such as those encountered in the Amex processes for uranium purification, by forming links between the organic droplets through the intervening aqueous phase. Additives to the organic phase which have active hydrogen atoms show promise of preventing such emulsions, presumably by competing with the silicic acid hydrogens for bonding sites on the organic solutes.

Activities in Solvent Extraction Systems

A vapor pressure apparatus, capable of measurement to within a few microns, has been constructed and is being tested. The data obtained with this apparatus will allow calculation of much-needed activity coefficients for organic solvent-solute extractant systems.

Thorium Extraction by Amines

Thorium sulfate extractions from aqueous sulfate solutions by di(tridecyl P)amine sulfate in benzene indicate, from the isotherm plateau, a complex containing three amine sulfates per thorium, in close analogy with corresponding ratios for uranium loading by a number of the amine extractants. Di-n-decylamine and di-l-isobutyl-3,5-dimethylhexylamine behaved similarly.

Interfacial Tensions in Amine Extractant Systems

Interfacial tension measurements of several salt forms of 0.1 N tri-n-octyl and di-n-decylamines in benzene vs. the corresponding 0.01 N aqueous acid have shown that sulfate affects the surface activity most markedly, followed by Cl^- , NO_3^- , and ClO_4^- in order of decreasing effect.

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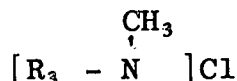
1.0 RAW MATERIALS PROCESSING

1.1 Solvent Extraction of Uranium from Carbonate Solutions

(D. J. Crouse, F. G. Seeley)

In previous studies¹⁻³ effective extraction of uranium from carbonate solutions was obtained with certain quaternary ammonium compounds but the phase separation properties of the commercially available compounds was extremely poor. Recent commercial availability of a new quaternary ammonium compound (Aliquat 336) with good phase separation properties has renewed interest in the processing of uranium ore carbonate leach liquors by solvent extraction. Thus far this compound has been evaluated with regard to (1) effect of diluent type and liquor composition on uranium extraction, (2) extraction of unwanted contaminating elements such as vanadium and molybdenum, and (3) stripping methods.

Aliquat 336, which is shipped by the manufacturer (General Mills) in the chloride form, has the following structural formula, where the alkyl groups are mixed n-octyl and n-decyl (~55% octyl and 45% decyl):



Prior to testing, an approximately 0.15 M solution of the Aliquat 336 in 95% kerosene--5% tridecanol was scrubbed by repeated contact with sodium carbonate solution to convert the quaternary to the carbonate form. The scrubbed solvent was then diluted with kerosene and tridecanol to the level desired for test purposes. Modification of the kerosene diluent with alcohol is necessary to prevent formation of emulsions.

1.1.1 Effect of Quaternary and Tridecanol Concentration. Isotherms for uranium extraction from 0.5 molar carbonate solution were obtained at four quaternary concentrations in the range 0.02-0.10 M and with varying amounts of tridecanol added to the kerosene diluent (Fig. 1). Comparison of tests in which the solvent contained the same alcohol/quaternary ratio shows the uranium extraction coefficient and maximum uranium loading to be nearly proportional to the quaternary concentration. An increase in tridecanol concentration from 5 to 15 v % with 0.083 M Aliquat 336 and from 2.5 to 10 v % with 0.042 M Aliquat 336 appreciably depressed the extraction efficiency in regions of higher uranium loadings. For example, the indicated maximum uranium loading for 0.083 M extractant was reduced from 3.5 to 2.7 g/liter by increase in tridecanol concentration from 5 to 15 v %. Since, in the dilute uranium region, the effect of alcohol

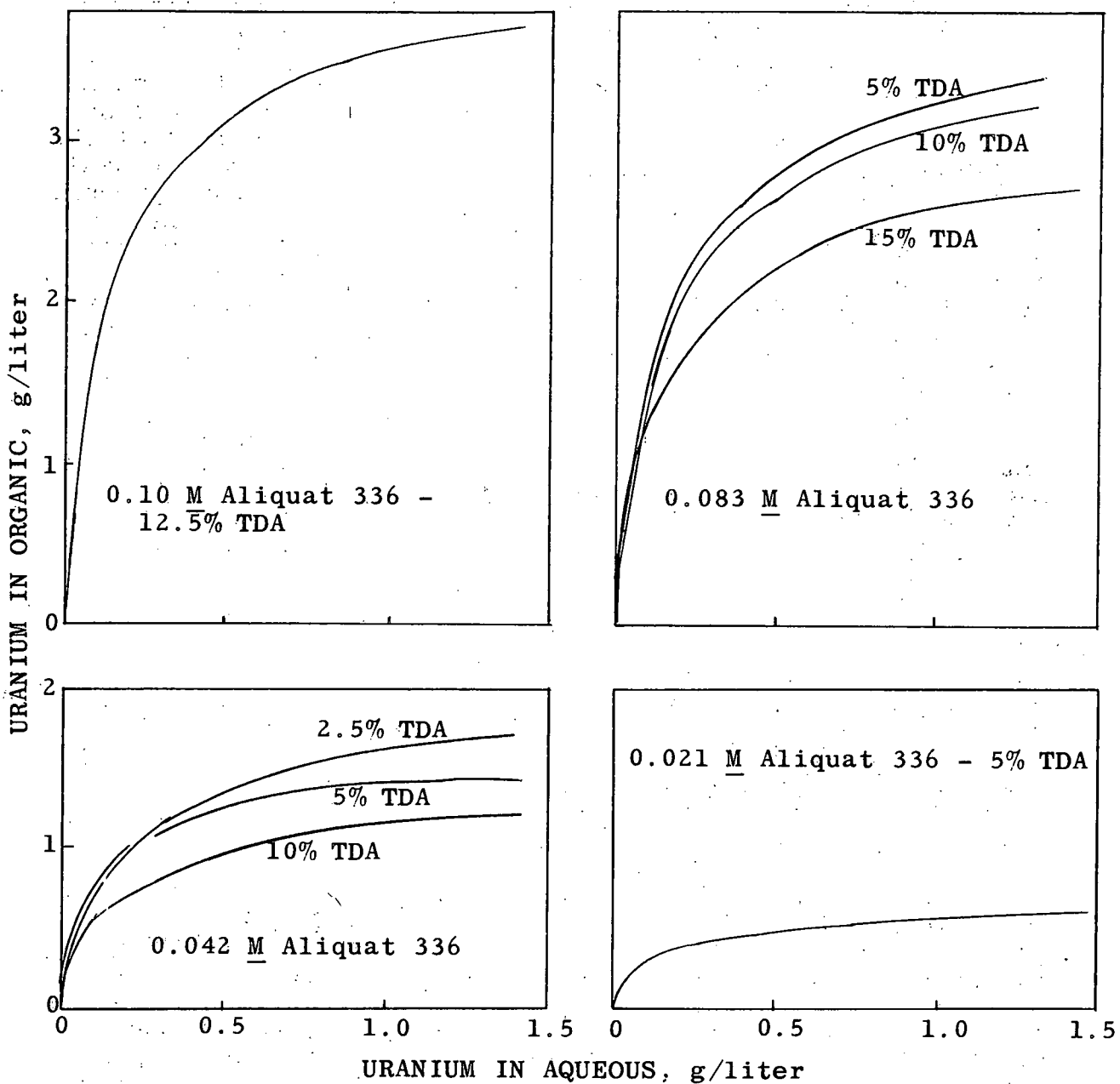


Fig. 1. Isotherms for Extraction of Uranium from Carbonate Solution with Aliquat 336 (carbonate form) in Kerosene-Tridecanol (TDA) Diluent. Aqueous: $0.4 \text{ M Na}_2\text{CO}_3$ -- 0.1 M NaHCO_3 , pH ~ 10 .

concentration is masked by convergence of the isotherms, this data is replotted in Fig. 2. At both extractant concentrations, the extraction coefficient reached a maximum at an alcohol/quaternary mole ratio of about 0.5, i.e., 10 v % tridecanol for 0.083 M Alamine 336 and 5 v % tridecanol for 0.042 M Alamine 336.

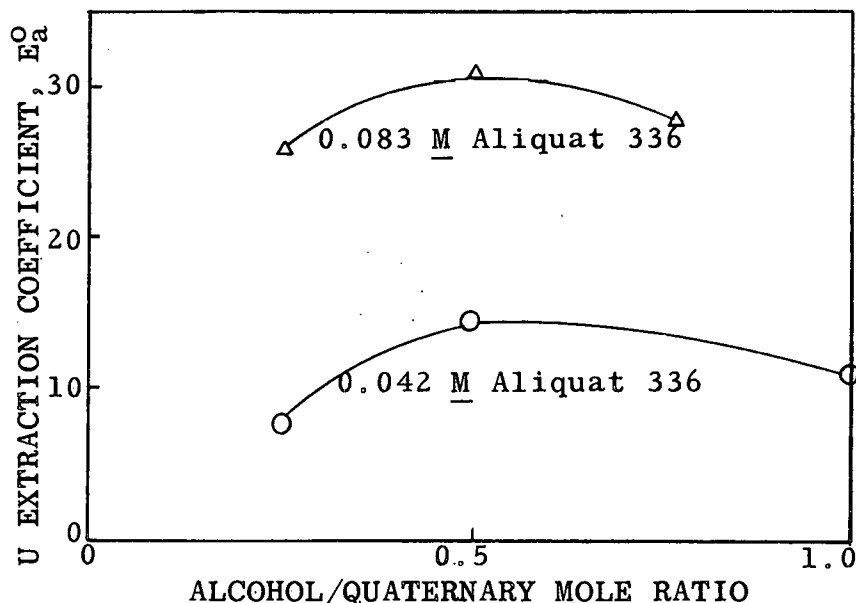


Fig. 2. Effect of Tridecanol Concentration on Uranium Extraction at Low Loading. Aqueous: 0.4 M Na_2CO_3 -- 0.1 M NaHCO_3 . Organic: Aliquat 336 in kerosene-tridecanol diluent; solvent ~15% loaded with uranium.

The rate of phase separation was reasonably rapid (2 min or less) in all tests but appreciably faster with alcohol/amine mole ratios of 0.5 or greater than with a ratio of 0.25. For example, the times (average of 5 tests) for complete disengagement of the phases with 0.083 M Alamine 336 were 1.5 min, 0.9 min, and 0.9 min for solvents with alcohol/quaternary ratios of 0.25, 0.5, and 0.75, respectively.

On the basis of the extraction and phase separation results, an alcohol/quaternary mole ratio of about 0.5 appears to be optimum.

1.1.2 Effect of Sulfate, Chloride, and Nitrate on Uranium Extraction. The presence of sulfate in the carbonate liquor lowered extraction coefficients, but with as much as 0.09 M sulfate the interference was not prohibitive (Fig. 3). Both chloride and nitrate, particularly the latter, caused a

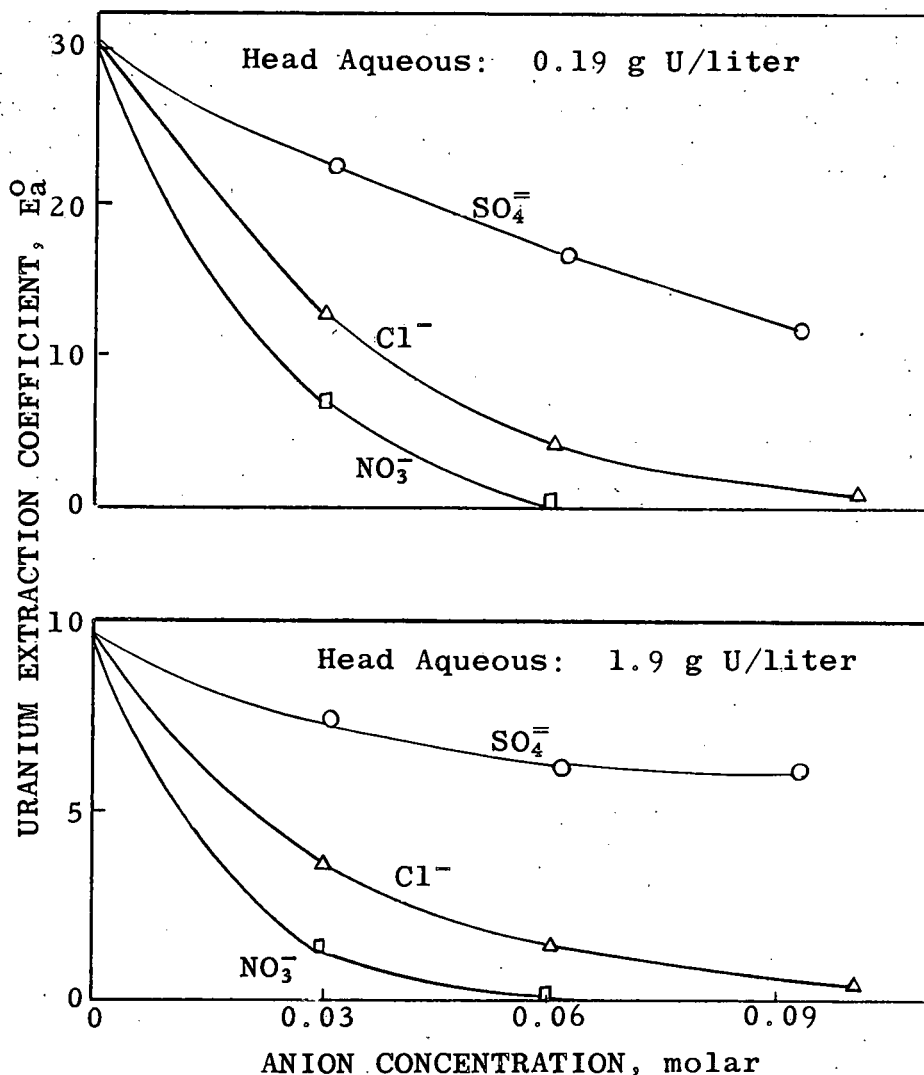


Fig. 3. Effect of Sulfate, Chloride, and Nitrate on Extraction of Uranium from Carbonate Solutions with 0.095 M Aliquat 336 in Kerosene + 9.5 v % Tridecanol. Aqueous: 0.4 M Na_2CO_3 --0.1 M $NaHCO_3$ containing 1.9 or 0.19 grams of uranium per liter; sulfate, chloride, and nitrate added as sodium salt; phase ratio, a/o = 1.5/1.

serious loss of extraction efficiency. Addition of 0.06 M nitrate decreased extraction coefficients by a factor >100 . Some sulfate is usually present in carbonate liquors owing to oxidation of sulfide minerals during leaching. Chloride or nitrate can be introduced into the extraction circuit if chloride or nitrate salts are utilized for stripping (see Sect. 1.1.7) and the extractant is recycled without regeneration to the carbonate form.

1.1.3 Extraction of Vanadium and Molybdenum. Both vanadium and molybdenum, which are common contaminants of ore carbonate leach liquors, were extracted fairly strongly by Alamine 336 from 0.4 M Na_2CO_3 --0.1 M NaHCO_3 solution. An isotherm for extraction of vanadium (Fig. 4) had the same unorthodox shape which is characteristic of vanadium extraction by amines in an acid system.⁴

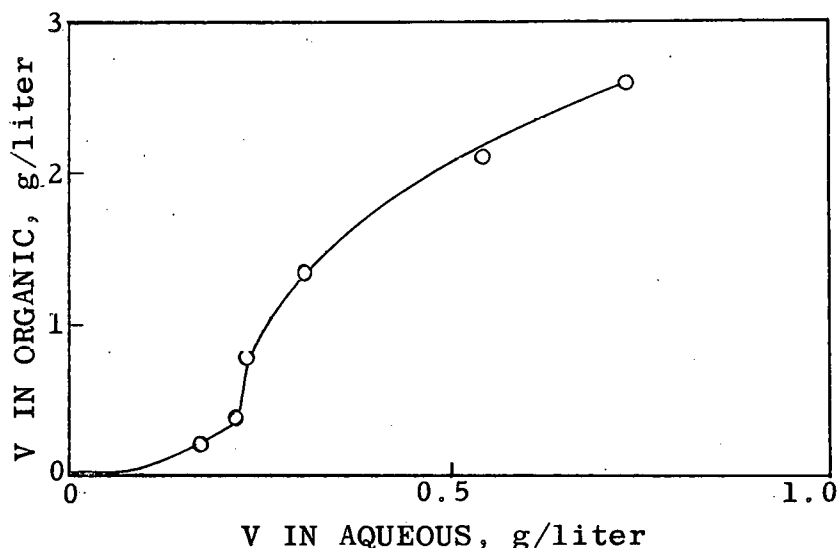


Fig. 4. Extraction of Vanadium(V) from Carbonate Solution with 0.075 M Aliquat 336 in Kerosene + 7.5 v % Tridecanol. Aqueous: 0.4 M Na_2CO_3 --0.1 M NaHCO_3 , 1 g V per liter. 5 min contact time.

Extractions from 0.4 M Na_2CO_3 --0.1 M NaHCO_3 solution containing both uranium and vanadium showed more effective extraction of vanadium than of uranium at high solvent loadings.

Phase Ratio, a/o	Analysis, g/liter				Extraction Coefficient, E_a^0	
	Organic		Aqueous		U	V
	U	V	U	V		
1/4	0.50	0.20	0.018	0.16	28	1.2
1/2	0.81	0.32	0.54	0.19	15 ^a	1.7 ^a
1/1	1.5	0.70	0.46	0.30	3.3	2.3
2/1	1.46	1.15	1.25	0.41	1.2	2.8
5/1	0.84	1.88	1.80	0.59	0.5	3.2
10/1	0.47	2.5	1.98	0.75	0.2	3.3

^aPoor material balance.

These extractions were with 0.075 M Alamine 336 in kerosene + 7.5 v % tridecanol from 0.4 M Na₂CO₃--0.1 M NaHCO₃ solution (pH 10.2) containing 2 g U and 1 g V per liter. Control of vanadium contamination by saturating the solvent with uranium obviously is not feasible in treating a liquor of this composition. However, a repeat of the test, after adjustment of the aqueous solution to pH 11.1 with sodium hydroxide, showed displacement of vanadium from the solvent by uranium under these conditions:

Phase Ratio, a/o	Analysis, g/liter				Extraction Coefficient, E _a ^o	
	Organic		Aqueous		U	V
	U	V	U	V		
1/4	0.50	0.17	0.016	0.28	31	0.60
1/2	0.95	0.28	0.032	0.41	30	0.68
1/1	1.8	0.33	0.14	0.58	13	0.57
2/1	2.8	0.22	0.57	0.70	4.9	0.32
5/1	3.5	0.14	1.4	0.90	2.5	0.16
10/1	3.4	0.11	1.6	0.93	2.1	0.12

Coefficients of 1-2 were obtained in extraction of molybdenum from 0.4 M Na₂CO₃--0.1 M NaHCO₃ solution containing 1 g Mo/liter with 0.095 M Aliquat 336 in kerosene + 9.5% tridecanol:

Phase Ratio, a/o	Mo Analysis, g/liter		Molybdenum Extraction Coefficient, E _a ^o
	Organic	Aqueous	
0.25	0.21	0.099	2.1
2	0.82	0.57	1.4

1.1.4 Removing Extracted Vanadium by Scrubbing. Attempts to scrub vanadium from uranium-vanadium extracts with sodium carbonate, sodium hydroxide, and mixtures of sodium hydroxide and sodium carbonate were only partially successful (Table 1). Best results were obtained with 1 M Na₂CO₃--0.2 M NaOH which removed 70% of the vanadium (and 5% of the uranium) in a single contact at an organic/aqueous phase ratio of 4/1. However, the residual vanadium contamination of the extract, i.e., ~10% V₂O₅ based on U₃O₈, was still above the specification limit (2% V₂O₅) for uranium concentrates.

1.1.5 Stripping Uranium with Nitrate, Chloride, and Sulfate Solutions. Dilute solutions of chloride and nitrate, particularly the latter, were effective stripping agents. Stripping isotherms (Fig. 5) indicate that >98%

Table 1. Scrubbing Extracted Vanadium from Alamine 336

Organic: 0.075 M Alamine 336 in kerosene + 7 v %
tridecanol loaded from carbonate solution
to (A) 1.95 g U and 0.5 g V per liter, or
(B) 2.5 g U and 0.45 g V per liter

Phase ratio, o/a: 4/1

Contact time: 5 min

Organic	Scrub Solution	Organic		Aqueous		Removed by Scrub, %	
		U	V	U	V	U	V
A	0.5 M Na ₂ CO ₃	1.85	0.40	0.25	0.45	3.2	22
	0.5 M Na ₂ CO ₃ -- 0.1 M NaOH	1.91	0.30	0.17	0.81	2.1	40
	0.1 M NaOH	1.97	0.47	<0.001	0.09	<0.1	4
B	0.1 M NaOH	2.5	0.44	<0.001	0.13	<0.1	7
	0.3 M NaOH	2.4	0.45	0.06	0.10	0.6	5
	0.6 M NaOH	2.2	0.44	0.49 ^a	0.16	~12	8
	1.0 M NaOH	2.4	0.34	0.18 ^a	0.46	~5	25
	0.2 M Na ₂ CO ₃ -- 0.2 M NaOH	2.4	0.34	0.06	0.44	0.6	25
	1 M Na ₂ CO ₃ -- 0.2 M NaOH	2.2	0.15	0.46	1.3	5	70

^aSome uranium precipitation; filtered before analysis.

stripping could be obtained in a single ideal stage while loading 1 M sodium nitrate solution to 30 g U/liter or 1 M sodium chloride solution to 20 g U/liter. A 1 M sodium sulfate solution was an ineffective stripping agent. In spite of the efficient stripping obtained with nitrate and chloride solutions, process use of these reagents does not appear attractive since the quaternary chloride or nitrate salt must be regenerated to the carbonate form prior to recycle in order to avoid serious interference from chloride or nitrate in the extraction system (see Sect. 1.1.2). Since displacement of nitrate and chloride with carbonate is difficult, other stripping methods appear to offer more promise.

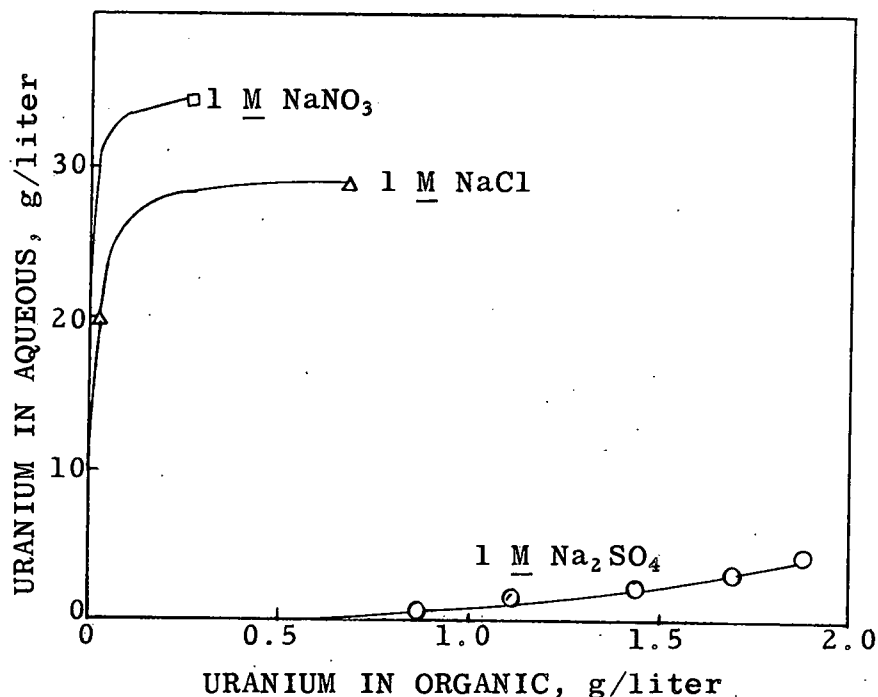


Fig. 5. Stripping Uranium from Aliquat 336 with Sulfate, Nitrate, and Chloride Solutions. Organic: 0.075 M Aliquat 336 in Kerosene + 7.5 v % Tridecanol loaded with 2.5 g U per liter.

1.1.6 Stripping Uranium with Sodium Carbonate--Sodium Hydroxide Solutions. Uranium was >95% stripped by a 20 min contact of a uranium extract with 1 M Na₂CO₃--0.6 M NaOH or 0.5 M Na₂CO₃--1 M NaOH at an organic/aqueous phase ratio of 4/1 (Table 2). Stripping with these solutions in a 5 min contact was only slightly less efficient. Sodium carbonate solutions (0.5-1 M) containing 0.3 M NaOH stripped only 15-30% of the uranium. With the latter strip solutions only 70-90% of the stripped uranium precipitated but with 0.6-1 M NaOH, precipitation of the stripped uranium was >99% complete. In all tests the phases separated in <1 min, with the precipitate settling fairly rapidly in the aqueous phase.

1.1.7 Separation of Uranium from Vanadium and Molybdenum. To determine whether the alkaline stripping cycle would give separation of uranium from vanadium and molybdenum, two extracts (0.075 M Aliquat 336 in kerosene + 7.5% tridecanol) were prepared, the first containing 2.0 g U and 0.5 g V per liter and the second 2.0 g U and 0.16 g Mo per liter. Each was scrubbed 5 min with 0.5 M Na₂CO₃--0.1 M NaOH at an organic/aqueous phase ratio of 4/1 and then stripped by two 5 min contacts with 0.5 M Na₂CO₃--1 M NaOH solution, the first contact at 4/1 and the second contact at 2/1 organic/aqueous phase ratio. In the uranium-vanadium

Table 2. Stripping Uranium from Aliquat 336 with
Na₂CO₃-NaOH Solutions

Organic: 0.075 M Aliquat 336 in kerosene +
7.5 v % tridecanol loaded to 2.5 g
U/liter

Phase ratio, o/a: 4/1

Strip Solution	Contact Time, min	Uranium in Stripped Organic, g/liter	Uranium Stripped, %
0.5 <u>M</u> Na ₂ CO ₃ -- 0.3 <u>M</u> NaOH	5	2.1	16
	20	2.0	20
0.5 <u>M</u> Na ₂ CO ₃ -- 0.6 <u>M</u> NaOH	5	0.56	78
	20	0.58	77
0.5 <u>M</u> Na ₂ CO ₃ -- 1 <u>M</u> NaOH	5	0.23 ^a	91
	20	0.08	97
1 <u>M</u> Na ₂ CO ₃ -- 0.3 <u>M</u> NaOH	5	1.9	24
	20	1.8	28
1 <u>M</u> Na ₂ CO ₃ -- 0.6 <u>M</u> NaOH	5	0.14	94
	20	0.11	96

^aA second 5 min contact with fresh 0.5 M Na₂CO₃ -- 1 M NaOH at an organic/aqueous phase ratio of 2/1 reduced the uranium concentration in the organic to 0.05 g/liter.

test, 38% of the vanadium and 2% of the uranium were removed by the scrub. The first strip contact increased uranium removal to 85% and vanadium removal to 88%. After the second strip contact the organic still contained 8% of the uranium and 3% of the vanadium. Uranium stripping was much less complete than in earlier tests (see Table 2) with vanadium-free extracts, suggesting an adverse effect from the presence of vanadium. The washed uranium precipitate contained 5% V₂O₅ based on U₃O₈ indicating appreciable but still inadequate separation from vanadium during stripping. A duplicate test using 20 min contacts during scrubbing and stripping gave approximately the same results.

In treatment of the uranium-molybdenum extract, 20% of the molybdenum and 1.4% of the uranium were removed in the scrub step. Uranium stripping was only ~50% complete after the first strip and 70% after the second strip indicating a strong adverse effect from the presence of molybdenum.

Approximately 40% of the molybdenum originally present in the extract was removed in the first strip contact and an additional 13% in the second contact. A favorable separation from molybdenum was obtained during uranium precipitation since the washed uranium precipitate contained <0.4% Mo based on U_3O_8 . In a duplicate test using 20 min contacts during scrubbing and stripping, uranium removal from the solvent increased to 83% whereas the amount of molybdenum stripped remained about the same.

1.1.8 Effect of Organic Matter in Carbonate Liquors. Preliminary extraction tests with an ore carbonate leach liquor from a western mill indicated that organic matter (possibly sodium humates) in the liquor seriously interfered with the extraction process. When the liquor was contacted with Alamine 336 in kerosene-tridecanol diluent the organic matter transferred from the liquor to the organic phase. The organic matter, however, was not extracted by the diluent alone, indicating extraction occurred as a result of reaction with the quaternary extractant. In some tests copious amounts of a brown crud separated from the solvent and it is suspected, but not confirmed, that the crud is a quaternary-organic complex which has very limited solubility in the kerosene-tridecanol diluent. The organic matter was removed effectively from the liquor prior to solvent extraction by passing the liquor through a column of 20-50 mesh activated carbon but more data is needed to determine if such a treatment is economically attractive.

1.2 Prevention of Silica Stabilized Emulsions by Solvent-Continuous Mixing (A. D. Ryon, R. S. Lowrie, F. L. Daley)

A number of sulfuric acid leach liquors from uranium mills contain emulsifying agents which stabilize oil-in-water (aqueous-continuous) dispersions when mixed with either Amex or Dapex process solvents. Emulsion difficulties are avoided by controlling the mixing to form water-in-oil (solvent-continuous) dispersions which are not stabilized. Batch phase separation tests (Table 3) show the relative effect of type of dispersion on primary break time for different plant liquors vs. typical 0.1 M solvents at 1/1 phase ratio.

For aqueous-continuous, emulsion formation appears to be a function of the concentration of soluble silica in the liquor which cannot be removed by filtration or centrifugation. No difficulty was encountered at silica concentrations less than 0.7 g SiO_2 /liter. At concentrations greater than 1.0 g/liter, the break time was greater than 300 sec and some stable emulsion (24 hr. or more) was formed; the amount generally increased with increased silica concentration. Addition of silicic acid to sodium sulfate solutions caused similar emulsification demonstrating that silica is probably the main cause of difficulty with plant liquors.

Table 3. Batch Break Time of Plant Liquors Containing Silica vs. 0.1 M Solvents

Settler: 3 in. x 3-5/8 in.
Phase ratio: 1/1

Plant Liquor	SiO ₂ g/l	Di(2-ethylhexyl)- phosphoric Acid 3% TBP		Rohm and Haas LA-1 Amine, 3% TDA		Ditridecyl P Amine, 5% TDA		Alamine 336 3% TDA	
		Aq	Solv.	Aq	Solv.	Aq	Solv.	Aq	Solv.
		Cont.	Cont.	Cont.	Cont.	Cont.	Cont.	Cont.	Cont.
Slime ^a	<0.1	81	53	120	110	120	100	-	-
KM-11 ^b	<0.1	64	79	120	160	110	130	73	120
Shiprock ^b	0.3	110	68	110	130	96	130	-	-
Sect 10 ^c	0.7	120	80	150	130	120	80	-	-
Holly ^c	1.0	>300	62	>300	170	130	110	-	-
C-19 ^a	1.0	>300	87	>300	>300	>300	120	-	-
Old Rifle ^d	1.6	>300	54	>300	120	150	51	-	-
St. Anthony ^c	2.2	>300	62	>300	130	210	130	-	-
New Rifle ^d	2.5	>300	75	>300	160	>300	77	>300	150

^aClimax Uranium Co., Grand Junction, Colo.

^bKerr-McGee Oil Industries, Shiprock, New Mexico.

^cKermac Nuclear Pilot Plant, Golden, Colo.

^dUnion Carbide Nuclear Co., Rifle, Colo.

Emulsion formation was less with di(tridecyl P)amine than with other solvents. Only two liquors gave break times greater than 300 sec and the amount of stable emulsion was much less than that formed with either Rohm and Haas LA-1 amine or di(2-ethylhexyl)phosphoric acid. The reason for this is not known, and the data are not conclusive enough to recommend routine use of di(tridecyl P)amine for aqueous-continuous mixing with silica liquors. However, its use would seem to provide an additional safeguard as compared to other solvents in case phase inversion occurred in a plant designed for solvent-continuous mixing.

For solvent-continuous mixing, primary break times were all considerably less than 300 sec, with one exception where only a small amount of emulsion was formed. Although the break times for each solvent varied with different liquors, there was no apparent dependence on silica concentration.

The importance and utility of controlled mixing for handling feed liquors containing in the order of 2 g of silica per liter has been successfully demonstrated in uranium mills. The ratio of solvent to aqueous in the mixer is usually maintained in the range of 1/1 to 2/1 to prevent inversion to aqueous-continuous in case of surges in flow rates. In the usual case where aqueous feed rate into the plant is greater than the solvent flow, proper phase ratio in the mixer is attained by recycling solvent from each settler.

2.0 SOLVENT EXTRACTION TECHNOLOGY

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

2.1.1 Uranium(IV) and Plutonium(IV) Extraction by Primary Amine. The chemical flowsheet previously proposed⁵ for recovery by successive extractions, first of U(IV), and then of Pu(III) or (IV) after supplying some oxidant, was confirmed by continuous countercurrent extraction in a six-stage bank of laboratory-scale mixer-settlers. The results, Table 4 and Fig. 6, show >99.5% recovery of the uranium and plutonium from synthetic decladding solution. A brief test was included of extraction of both U(IV) and Pu(III) or (IV) with a single extractant stream. The results, also shown in Table 4 and Fig. 6, were essentially as satisfactory as with the separate extractant streams.

The mixer-settlers used have been described by Boyd Weaver.⁶ Their holdup was about 40 ml of organic and 160 ml of aqueous phase each. They were set up in a glove box for the tests with plutonium. The aqueous stream at 45.5 ml/min and the first extractant stream at 19 ml/min (see Fig. 6)

Table 4. Uranium and Plutonium Recovery from Sulfuric Acid-Stainless Steel Dissolver Solution by Extraction with Primary Amine

Feed (synthetic): 2 M H₂SO₄, 1 M s.s. sulfates, ~3 g U/liter, ~0.5 mg Pu/liter

Extractant: ~0.3 M Primene JM in 85% Amsco 125-82--
15% tridecanol

Continuous countercurrent extraction in 6 mixer-settlers;
see Fig. 6

Cycle ^a	U, g/liter			Pu, mg/liter			
	Feed	Raff.	U-Extr.	Feed	Raff.	U-Extr.	Pu-Extr.
1.3 ^b	3.2	3.0x10 ⁻³	5.2				
2.6	2.6	1.6x10 ⁻³	7.5				
3.9	2.8	1.4x10 ⁻³	7.8				
1.3 ^c	2.6	0.3x10 ⁻³	6.5	0.48	7x10 ⁻³	0.44	4.4
2.6	2.2	0.5x10 ⁻³	6.0	0.48	3x10 ⁻³	0.48	6.9
3.9	2.4	1.6x10 ⁻³	6.0	0.49	2x10 ⁻³	0.79	4.9
5.2	2.3	1.2x10 ⁻³	5.9	0.48	1x10 ⁻³	0.52	5.5
7 ^d	2.3	3.8x10 ⁻³	6.0	0.48	1x10 ⁻³		1.2

^aOne cycle = 1 estimated displacement of the slowest stream through the extraction system.

^bCold run with U only, starting with barren aqueous in the settlers. Feed/U Extr./Pu Extr. = 50/17.5/2.5, 0.35 M amine.

^cConsecutive U and Pu extraction with separate organic streams, starting with barren aqueous in the settlers. Feed/U Extr./Pu Extr. = 45.5/19/2.4, 0.29 M amine.

^dCombined U-Pu extraction, starting with the solutions present at the completion of the consecutive extraction test. Feed/Extr. = 45.5/19, 0.29 M amine.

were metered by bellows pumps located outside of the glove box, the former by pumping an inert hydrocarbon stream to move the feed solution by displacement. The slower flows, i.e., the second extractant stream at 2.4 ml/min and the ferric sulfate oxidant stream at 1 to 2 ml/min were metered by pinch clamp and gravity head.

The synthetic decladding solution was made up in several batches to the composition of approximately 2 M H₂SO₄, 1 M stainless-steel sulfates, 3 g U/liter, and 0.5 mg Pu/liter.

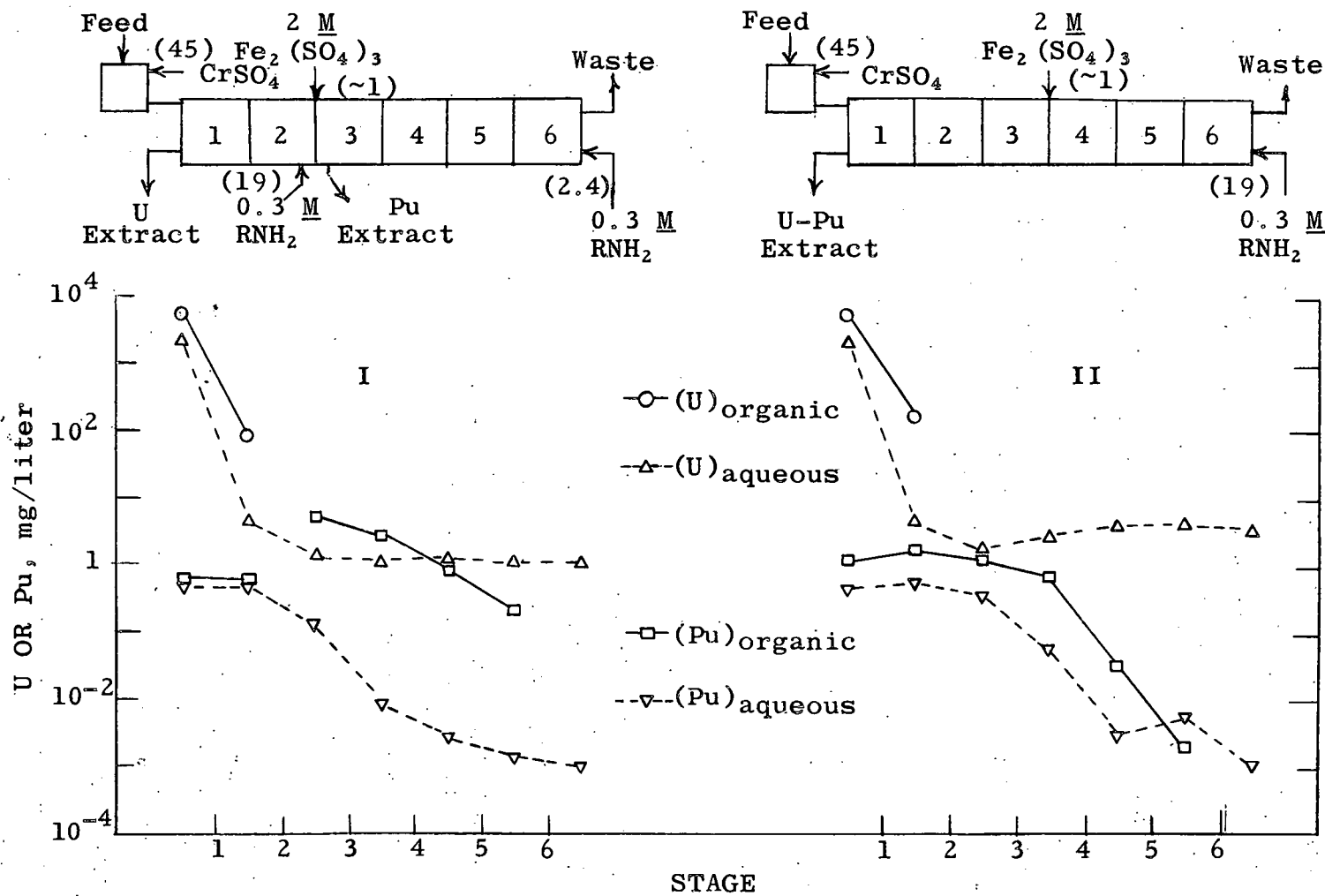


Fig. 6. Concentration Profiles through Extraction System

I, Consecutive U and Pu extraction with separate organic streams, after five cycles.

II, Combined U and Pu extraction, after seven cycles.

Each batch was reduced to -200 mv* with chromous sulfate solution (~1 M $\text{Cr}_2(\text{SO}_4)_3$ reduced with Zn/Hg), using 50-100 ml per liter. The amine solution was washed with 25 volumes of 0.2 M H_2SO_4 to remove the more water-soluble components, so that the resulting extractant would approximate the properties to be expected after long recycle.

Troublesome emulsions formed in the mixers until a surfactant, Victawet 12, was added to the aqueous feed at a concentration of about 100 ppm. Slight emulsification was still observed at times when a mixer stirrer was running too fast.

The extraction coefficients through the extraction system corresponding to the profiles shown in Fig. 6 were as follows:

Stage:	1	2	3	4	5	6
I. Consecutive U and Pu extraction streams:						
$E_a^O(\text{U})$	1300	60				
$E_a^O(\text{Pu})$	1	4	70	1000	680	>150
II. Combined U and Pu extraction:						
$E_a^O(\text{U})$	1200	100				
$E_a^O(\text{Pu})$	2	5	20	250	60	5

The small quantity of uranium in the aqueous stream after the second stage was probably rapidly oxidized to the poorly-extractable U(VI) by the ferric iron added. The plutonium extraction coefficient was low in the first stage because the extractant was loaded to a considerable extent with uranium and probably also because oxidation was prevented by the U(IV). It was appreciably higher in the second stage where there was negligible loading, and much higher in the next subsequent stages where a small amount of oxidant was available. (Besides the added ferric sulfate, air-oxidation probably had some effect after the U(IV) was gone.)

The flow ratio in uranium extraction, and hence the uranium loading and concentration factor, was appreciably lower in the uranium-plutonium test than indicated in the proposed flowsheet (Ref. 5, Fig. 2), a/o = 2.4/1 instead of 100/35 \approx 2.9/1 with ~0.3 M amine. The mixer-settlers available for these tests had been designed and used for flow ratios close to 1/1, and significantly low stage efficiency

*Potential between platinum and saturated calomel electrodes. The sign is that of the platinum electrode, so that a higher positive emf indicates higher oxidation.

was suspected at much different flow ratios. Hence, the uranium extraction flow ratio was decreased to avoid the possibility of interference with the testing of the plutonium extraction. The resulting uranium concentration of 0.025 M in the extract was 70% of the stoichiometric loading. While the first stage extraction coefficient of 1200 as compared with 6000-7000 from the extraction isotherm (Ref. 5, Fig. 1) does indicate stage efficiency appreciably below 100%, it also shows a considerable margin of safety for adjustment to higher uranium loading.

Single-Stage Recovery. With confirmation in continuous countercurrent extraction of the ability to extract Pu(III-IV) from ferrous sulfate solution containing only a slight amount of oxidant, estimates were made of expected single stage performance which indicated feasible operation. Use of single stage continuous or batch extraction instead of countercurrent extraction should permit a considerably simpler and cheaper installation for the scavenging process. The main consideration is the balancing of recovery against extract loading, especially as loading affects the amount of sulfate accompanying the recovered metals.

High single-stage recovery of U(IV) is readily available even at relatively high loading. Assuming close to 100% equilibration, at 85% loading of 0.3 M amine the extraction coefficient expected from the extraction isotherm is 1000, corresponding to 99.7% extraction at a/o = 2.5/1. As previously described,⁵ the apparent extraction coefficient measured for Pu(III-IV) has varied considerably, and is expected to be affected more by minor variations in the system than are the coefficients for, e.g., U(IV), or Pu(IV) in oxidized solution. Hence a value from the lower part of the range observed, $E_a^Q(\text{Pu-III, IV}) \approx 100$ with 0.3 M amine, was used for the following estimates rather than the higher values found in the continuous extraction tests.

One extraction system envisaged is to mix a batch of the reduced feed with a specified volume of extractant, let settle in the same vessel, draw off the extract, add a small amount of oxidant, repeat extraction with a fresh (probably smaller) volume of extractant, collecting the extracts for stripping with dilute nitric acid. The metal and sulfate extractions calculated on basis of 3 g U/liter, 0.0005 g Pu/liter, and 0.3 M amine (Table 5) show that the minimum sulfate accompanying the recovered metals, at the highest uranium loading, will be about 2.4 g SO₄/g U. Without a second (plutonium) extraction, the theoretical uranium recovery can be raised to 98% with an increase only to 2.5 g SO₄/g U. Plutonium can be recovered at ~90% (theoretical) with a further increase to 3.5 g SO₄/g U, and at ~95% with 4.5 g SO₄/g U. Thus, most of the plutonium can be expected to be recovered in a single stage extraction, without a very great increase in the sulfate carry-over.

Table 5. Effect of Phase Ratio on Calculated Metal Recovery and Sulfate Carry-Over

Consecutive batch U and Pu extractions
 Feed: 3 g U and 0.0005 g Pu/liter
 Extractant: 0.3 M amine

U Extraction				Pu Extraction			SO ₄ /U g/g in Product
A/O	g U/liter	% Loading	Theor. % Recy	A/O	Theor. % Recy	Net A/O	
100/28	8.70	97.5	80	(no Pu extrn.)		100/28	2.4
100/35	8.4	94	98	100/35	97	100/70	6.0
				100/20	95	100/55	4.5
				100/10	91	100/45	3.5
				100/5	83	100/40	3.0
				(no Pu extrn.)		100/35	2.5
100/40	7.5	84	99.7	100/40	98	100/80	6.9
				100/20	95	100/60	4.9
				100/10	91	100/50	3.9
				100/5	83	100/45	3.4
				(no Pu extrn.)		100/40	2.9

2.1.2 Nitric Acid Stripping from Primary Amine. In continued testing of the chemical flowsheet proposed for plutonium and uranium recovery by extraction with a primary amine,⁵ batch countercurrent stripping of the loaded extract with 5 M HNO₃ showed a maximum of ~3% of the uranium and 0.1% of the plutonium left in the stripped organic. However, the plutonium concentration in the aqueous product solution varied considerably, indicating varying internal reflux.

The combined uranium-plutonium extract from the continuous countercurrent extraction with 0.3 M Primene JM (Sect. 2.1.1) was stripped in a four-stage batch countercurrent system with 5 M HNO₃ at phase ratio a/o = 1/10. Single-diamond contact pattern was used, carried through 18 cycles. Analysis of the consecutive exit solutions (Table 6) and the final profile across the system (Table 7) showed that uranium was carried over into the second stage until the aqueous concentration there was higher than in the product solution, but carried over much less to the third and fourth stages. After the first 6 cycles, during which the uranium reflux was presumably building up, the uranium concentration was nearly constant in the product solution. The fraction of the uranium remaining in the stripped organic started near 1%, rose to ~3%, and then dropped to <0.2%. Plutonium stripping was more complete than

Table 6. Uranium and Plutonium Stripping from Primary Amine

Extract: 0.3 M Primene JM in 85% Amsco 125-82--15%
tridecanol, 6.5 g U/liter, 0.00155 g Pu/liter

Strip: 5 M HNO₃

Four-stage countercurrent batch equilibration, single-diamond pattern

Phase ratio a/o = 1/10, 5 min contact in Burrell shaker, R.T.

Cycle ^b	U or Pu, g/liter				% of U Left
	Loaded Strip ^c		Stripped Organic ^d		
	Pu	U	Pu	U	
1	0.0142	30			
2					
3	0.0163	47			
4			<10 ^{-6a}	0.054 ^a	0.8
5	0.0120	57			
6			<10 ⁻⁶	0.035	0.5
7	0.0141	70			
8			<10 ⁻⁶	0.040	0.6
9	0.0246	67			
10			<10 ⁻⁶	0.057	0.9
11	0.0002	74			
12			<10 ⁻⁶	0.171	2.6
13	0.0037	76			
14			1.4x10 ⁻⁶	0.182	2.8
15	0.0422	79			
16			<10 ⁻⁶	0.010	0.15
17	0.0173	74			
18			<10 ⁻⁶	0.012	0.18
Material Balance	105%	115%			

^aThe stripping system was started with one 50 ml batch of organic extract contacting successive 5 ml batches of aqueous solution adjusted to 3 M HNO₃--2 M H₂SO₄, 4 M HNO₃--1 M H₂SO₄, 4.5 M HNO₃--0.5 M H₂SO₄, and 5 M HNO₃, and leaving the system in the 4th cycle as the first stripped organic.

^bCycles 1-11 were run in one day, 12-18 after a lapse of 2 days.

^cLoaded strip = aqueous leaving the first stage.

^dStripped organic = organic leaving the 4th stage.

Table 7: Concentration Profiles Across Stripping System

Aqueous strip solution: 5 M HNO₃, a/o = 1/10
 Four-stage batch countercurrent system, single-diamond pattern

Stage ^a :	Organic In	Organic Out			Aqueous Out		
	1	2	3 ^b	4 ^c	1 ^d	2	4
U, g/liter:	6.5	0.74	0.05	0.012	74	89	0.40
Pu, mg/liter:	1.55	0.34	<0.01	<0.001	17	7.5	0.005
H ⁺ , <u>M</u>					5.6	4.5	4.5
NO ₃ ⁻ , <u>M</u>					0.25	0.8	4.5
SO ₄ ⁼ , <u>M</u>	0.25 ^e	<0.01			2.4	2.2	<0.02

^aLast cycle = cycle 17 for stages 1 and 3, cycle 18 for stages 2 and 4.

^bConcentrations in organic leaving stage 3, cycle 17, calculated from concentration in organic and aqueous leaving stage 4, cycle 18.

^cStripped organic for recycle.

^dProduct solution.

^eSulfate in loaded organic extracted estimated from R₃U(SO₄)₆ + RHSO₄, R = 0.3 M amine.

uranium stripping, with less than 0.1% remaining after the fourth stage in all cycles, and without indication in the final profile of reflux buildup. However, the product solution analyses showed that a large internal reflux was built up and dissipated between the 11th and 15th cycles. Less than 2% of the input plutonium appeared in the product solution from the 11th cycle, and only ~25% in that from the 13th; then essentially all of the plutonium held up appeared in the product solution from the 15th cycle. Thus, considerable plutonium may have refluxed into the 3rd stage of the 13th cycle, but still only a trace appeared in the stripped organic from the 4th stage of the 14th cycle. The nitrate concentration in the final aqueous product solution was lower than expected, and varying nitrate-sulfate displacement in the first two stages may have caused the varying plutonium distribution. If so, it seems likely that the sulfate effect would not carry beyond the second or third stage, so that four stages should provide a sufficient operating margin.

The product solution from the last cycle contained 74 g U/liter, 17 mg Pu/liter, 0.25 M NO₃, and 2.4 M SO₄. This

represents a recovery of >99% and concentration by a factor >30 for both uranium and plutonium, from the synthetic decladding solution containing 2.3 g U/liter and 0.48 mg Pu/liter (Sect. 2.1.1).

Rate of Stripping. Equilibration time in the foregoing countercurrent batch stripping test was arbitrarily set at 5 min. A separate stripping test indicated that this was more than enough time for equilibration: A 2-liter batch of uranium-loaded extract was stripped with 5 M HNO₃ at a/o = 1/10 by stirring in a 4-liter beaker with a 2x1/2-inch flat paddle at a constant speed of ~2000 rpm, which gave considerably milder agitation than does shaking. The uranium distribution was close to equilibrium within 2 min (Table 8). After 60 min contact the phases were separated. A second 1/10 volume of 5 M HNO₃ stripped 95% of the remaining uranium.

Table 8. Rate of Stripping

Loaded extract: 0.33 M Primene JM in 90% Amsco
125-82--10% tridecanol, 4.4 g U/liter
Strip: 5 M HNO₃, a/o = 1/10, stirred, R.T.

Strip Stage	Contact Time, min	U Distribution, g/liter		U Stripped, % of Total	Approach to Equilibrium, %
		Aq	Org		
1	0	-	4.4	0	0
	1	24	1.96	56	75
	2	26	1.57	64	87
	4	28	1.44	67	91
	10	29	1.40	68	92
	~60	32	1.15	74	(100)
2	10	12	0.055	99	

2.1.3 Uranium(VI) Extraction by Primary Amine. In the proposed process for uranium and plutonium recovery by extraction with a primary amine (Fig. 5 in Ref. 5), nearly complete extraction of U(IV) is expected in the first stage. Extraction coefficients for U(VI) were measured from sulfuric acid solution (Table 9) to determine whether or not unreduced or reoxidized uranium would also be recovered in the countercurrent system. The observed extraction coefficients plotted against calculated free reagent concentration (Fig. 7) indicate extraction coefficients of ~0.5 at 0.1 M and ~1 at 0.3 M free reagent. Thus, with 0.3 M amine in separate uranium and plutonium extraction streams, a/o ≈ 3/1 in two uranium extraction stages and ≈ 20/1 in two to four plutonium extraction stages, somewhat less than half of any small amount of

U(VI) initially present should be recovered (none in the highly loaded first stage, ~25% in the second uranium stage, and 10-20% in 2-4 plutonium stages). In the alternate flow-sheet suggested using a single extractant stream at a/o \approx 3/1 through four plutonium and two uranium extraction stages, the recovery of a small amount of U(VI) should approach 80%.

Table 9. U(VI) Extraction from Sulfuric Acid
Solution by Primene JM

3 M H_2SO_4 -- 0.5 M Na_2SO_4 ; 1 to 10 g U/liter
 Diluent: 90% Amsco 125-82 -- 10% tridecanol
 A/O = 1/1, R.T.

<u>M Amine</u>	<u>E_a</u>	<u>M(U)_{org}</u>
0.03	0.06	0.0022
0.03	0.10	0.0004
0.1	0.47	0.0013
0.3	1.1	0.0017

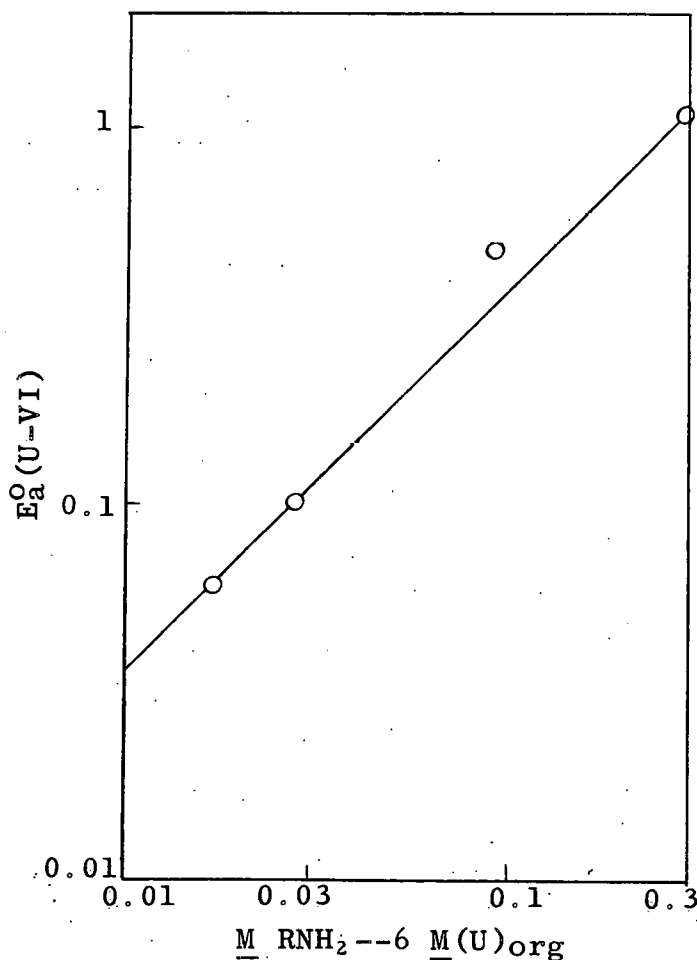


Fig. 7. U(VI) Extraction by Primene JM in 90% Amsco 125-82 -- 10% Tridecanol from 3 M H_2SO_4 -- 0.5 M Na_2SO_4 .

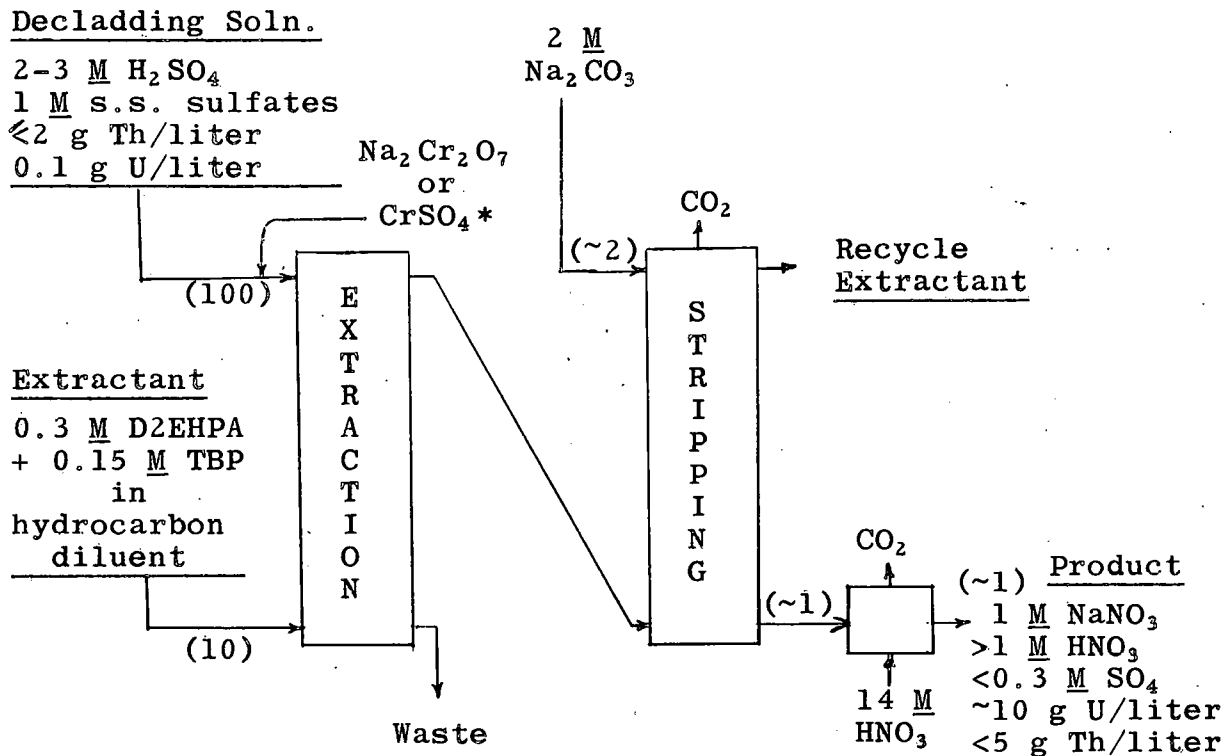
2.1.4 Uranium Extraction by Dialkylphosphoric Acid. A chemical flowsheet for recovery of uranium alone from sulfuric acid stainless steel decladding solution by extraction with dialkylphosphoric acid plus TBP was tested in continuous countercurrent extraction in laboratory-scale mixer-settlers. The uranium recovery from a synthetic decladding solution containing thorium and uranium was >95% in 8 stages. About 2% of the thorium was extracted with the uranium.

Di(2-ethylhexyl)phosphoric acid (D2EHPA) in synergistic combinations with TBP and related compounds extracts U(VI) from sulfate solutions even at fairly high sulfuric acid concentrations. This type of extractant offers a potential advantage in uranium recovery from decladding solutions in that much less sulfate accompanies the uranium than in recovery by amine extraction (above). D2EHPA also extracts Pu(IV) from 2-3 M H_2SO_4 and from oxidized sulfuric acid decladding solution, but it extracts Fe(III) from oxidized decladding solution sufficiently to interfere with plutonium extraction. Reduction of the iron to non-extractable Fe(II) would also reduce plutonium to the poorly-extracted Pu(III), whereas uranium can be kept at U(VI) with essentially all the iron reduced. Accordingly, the use of this extractant was directed mainly toward solutions containing negligible plutonium, e.g., from decladding of fully-enriched UO_2-ThO_2 fuels.

The chemical flowsheet (Fig. 8) consists of redox adjustment of uranium to U(VI) and iron to Fe(II), countercurrent extraction with D2EHPA-TBP in a hydrocarbon diluent, either countercurrent or batchwise stripping with sodium carbonate, and destruction of carbonate with nitric acid for return of the recovered uranium to a Purex or Thorex cycle. The reagent concentration and flow ratios were fitted to an assumed feed composition of 2-3 M H_2SO_4 , 1 M stainless steel sulfates, 2 g Th/liter, and 0.1 g U/liter. Synthetic feed solutions approximating this composition (Table 10) gave uranium extraction coefficients approaching 25 in batch equilibrations with 0.3 M D2EHPA--0.15 M TBP in Amsco 125-82, in fair agreement with previous extraction coefficients from 3 M H_2SO_4 . A McCabe-Thiele diagram constructed on basis of $E = 25$ with 0.3 M reagent, and flow ratio a/o = 10/1, indicated about 6 ideal stages required for 99% uranium extraction.

Continuous extraction was tested in a bank of 8 laboratory-scale mixer-settlers of the same type as used in the continuous amine extraction (Sect. 2.1.1). The aqueous stream at 50 ml/min and the extractant stream at 5 ml/min were metered by bellows pumps. Each batch of feed solution was reduced to 100-200 mv* with ~100 ml chromous sulfate

*Pt-SCE, higher + emf indicating higher oxidation.



Numbers in parentheses represent relative flows.

*Na₂Cr₂O₇ or CrSO₄ as required to adjust all of U to U(VI) and most of Fe to Fe(II).

Fig. 8. Uranium Recovery from Sulfuric Acid Decladding Solution by Extraction with Di(2-ethylhexyl)phosphoric Acid.

solution per liter (~1 M Cr₂(SO₄)₃ reduced with Zn/Hg). Less than 2% of the iron remained at Fe(III), as shown by comparison of batch extractions with and without addition of a 2% Fe(III) spike. The four batches were run in succession. At the completion of each, the mixers were stopped and the separated phases were sampled. There was no flow between units with the mixers stopped, so that the concentration profile was not lost during change-over and sampling.

The end concentrations for the four profiles measured are shown in Table 11, indicating ~95, 95, 97, 97% recovery at 1.2, 2.5, 3.8, and 5.0 cycles.* The final profile (Fig. 9) shows a nearly constant extraction of 60-65% per stage, E_g ≈ 17. The

*One cycle = 1 estimated displacement of the organic phase through the extraction system.

Table 10. Feed Solutions

Four-liter batches, each used for ~1.3 cycles of continuous extraction (see Table 11).

	1	2	3	4
U, mg/liter	70	69	75	76
Th, g/liter	1.77	1.68	1.44	1.46
Fe, \underline{M}^a	0.67	0.60	0.53	0.55
Cr, \underline{M}^b	0.46	0.46	0.48	0.52
Ni, \underline{M}	0.09	0.08	0.08	0.08
H ⁺ , \underline{M}	5.5	4.9	4.7	4.1
NO ₃ ⁻ , \underline{M}^c	0.03	0.03	0.025	0.025
SO ₄ ⁻ , \underline{M}^d	4.2	4	3.5	3.5
E _a ^o (U) ^e	17	18	24	25
E _a ^o (Fe) ^e	-	<0.001	<0.001	<0.001

^a>98% of Fe reduced to Fe⁺⁺.

^bCr includes CrSO₄ used to reduce Fe.

^c~0.03 \underline{M} NO₃ from addition of thorium as Th(NO₃)₄.

^dSulfate concentrations calculated.

^eUranium and iron extraction coefficients were measured with each batch of feed solution by batch equilibration at a/o = 1/1 with 0.3 \underline{M} D2EHPA--0.15 \underline{M} TBP.

final profile is also shown in a McCabe-Thiele diagram (Fig. 10) for comparison with the calculated uranium extraction isotherm. Significantly low stage efficiency was expected, because the mixer-settlers used were not designed to handle flow ratios far from 1/1. The failure of the upper points in Fig. 10 to reach the equilibrium curve appears to confirm this. The failure of the lower points to reach the operating line suggests that some back-mixing between stages occurred. The apparent stage efficiency* averaged ~50%. Thus, in an extraction system with high stage efficiency, nearly complete uranium recovery could be expected in rather fewer than 8 stages. However, high recovery could not be obtained in a single stage, unless the feed/extractant ratio approached 1/1.

A portion of the composited organic product from the extraction test was stripped in two batch stages (not

*The ratio (uranium concentration increment between aqueous samples)/(corresponding uranium concentration increment between operating line and equilibrium curve).

Table 11. Uranium Recovery from Sulfuric Acid Stainless

Steel Dissolver Solution by Extraction with D2EHPA-TBP

Feed (synthetic): 2-3 M H₂SO₄, ~1 M s.s. sulfates, ~1.5 g Th/liter, ~0.07 g U/liter
 Extractant: 0.3 M D2EHPA + 0.15 M TBP in Amsco 125-82
 Continuous countercurrent extraction in 8 mixer-settlers; see Fig. 9
 Feed/extractant = 50/5
 Run started with barren aqueous in the settlers

Cycle ^a	U Distribution, mg/liter			E _g (U)	
	Feed	Raffinate	Extractant	1st Stage	2nd Stage
1.2	70	3.7	590	12	12
2.5	69	3.5	710	16	14
3.8	75	2.1	790	19	21
5.0	76	2.1	775	17	19

^aOne cycle = 1 estimated displacement of the slower (i.e., organic) stream through the extraction system.

countercurrent) with 2 M Na₂CO₃ at a/o = 87.5/500 initial, 58/530 final in the first stage and 87.5/530 in the second stage. The phase ratio changed in the first stage because of extraction of water along with Na⁺.⁸ About 90% of the uranium was removed by the first strip, and <1% remained in the organic after the second strip (Table 12). A small amount of water-soluble thorium-bearing precipitate separated during the first strip, indicating that with this much thorium present (0.24 g/liter organic) a larger volume of less concentrated sodium carbonate solution should be used. The first strip was acidified with 1/5 its volume of 14 M HNO₃, giving a product solution containing 4.5 g U/liter, 1.5 g Th/liter, 0.2 g Fe/liter, and <3x10⁻⁴ M SO₄ in ~2 M NaNO₃, 0.5 M HNO₃.

2.2 Removal of Americium from Plutonium (C. F. Coleman, D. E. Horner)

High plutonium extraction coefficients, measured by α -counting, are affected by contamination with even small amounts of nonextractable α -activity. For example, the measured extraction coefficient for plutonium(IV) sulfate by 0.1 M primary amine appeared to be ~40 (actual coefficient >1000) when ~3% of the initial α -activity was due to americium²⁴¹ instead of plutonium.

It has been found possible to eliminate the americium satisfactorily from plutonium stock solution by extracting the plutonium with di(2-ethylhexyl)phosphoric acid (D2EHPA).

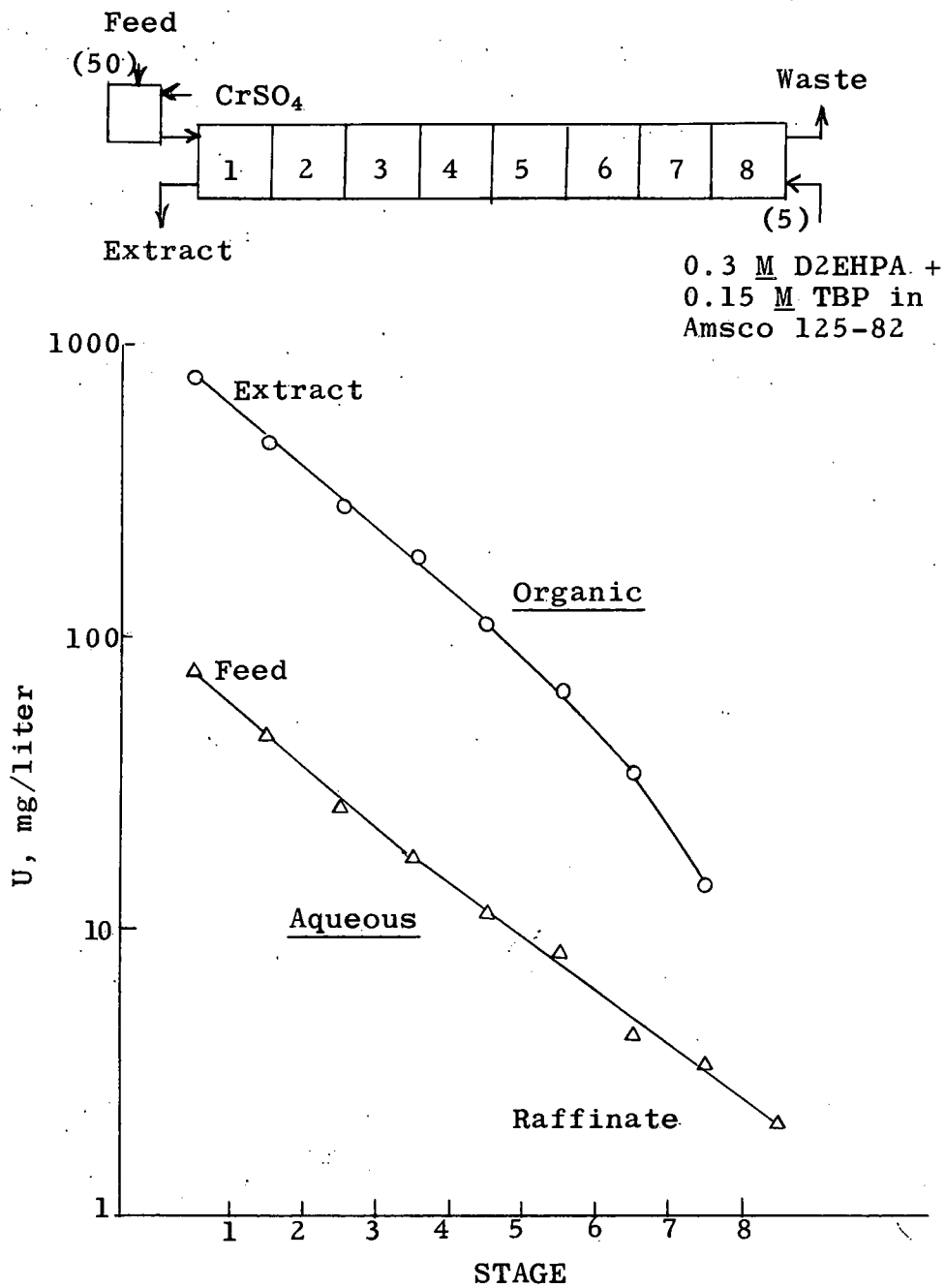


Fig. 9. Concentration Profile through Extraction System. Uranium extraction by D2EHPA-TBP, after 5 cycles.

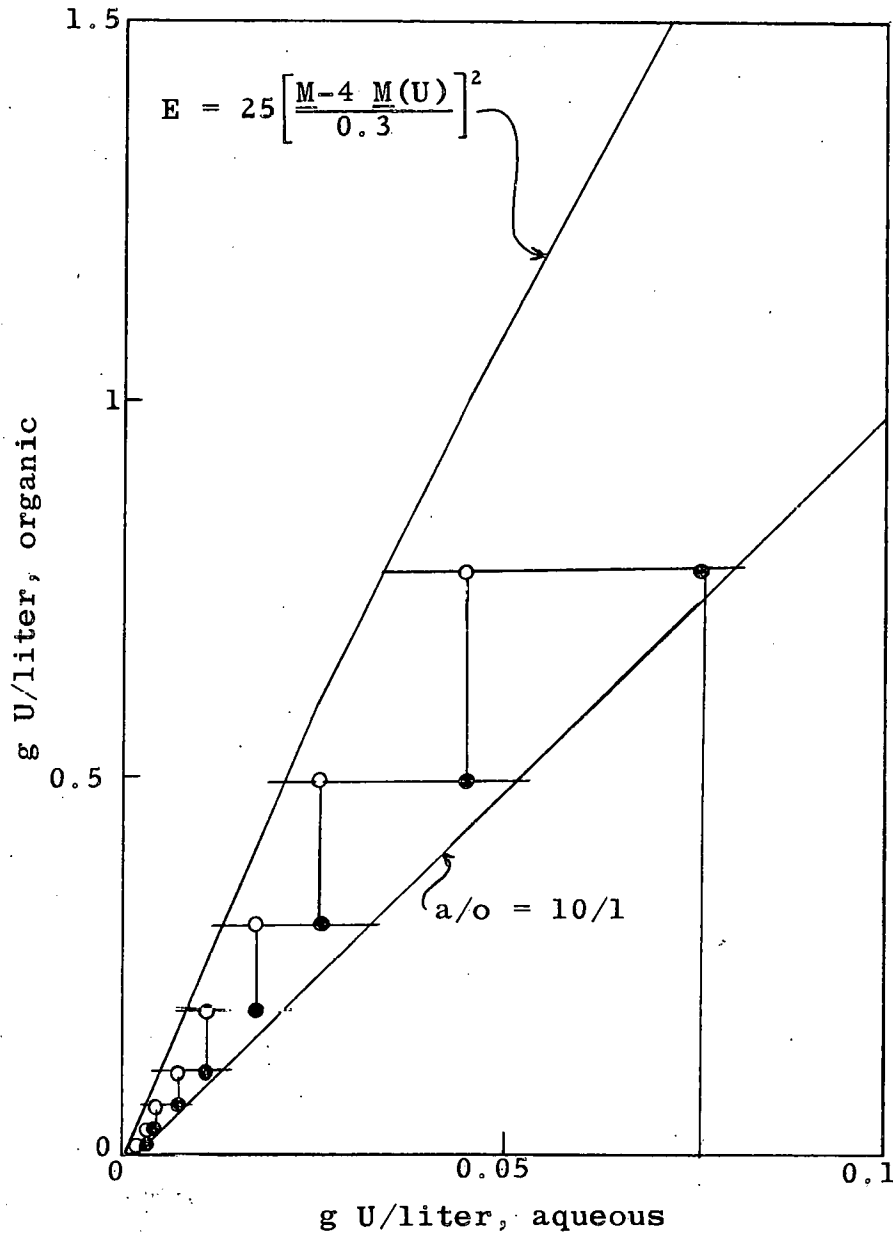


Fig. 10. Comparison of Concentration Profile with Calculated Extraction Isotherm. Uranium extraction by D2EHPA-TBP.

Table 12. Sodium Carbonate Strip of D2EHPA-TBP Extract

Extract: 0.3 M D2EHPA + 0.15 M TBP in Amsco 125-82, loaded composite from countercurrent extraction test
 Strip: 2 M Na₂CO₃, two-stage batch contact
 Contact: Hand-shaking in stoppered cylinder, 3 min, R.T.

Phase	Volume ml	U	Th	Fe	SO ₄	U Distribution %
Organic Extract	500	0.70	0.24	0.025		(100)
Strip-1	58 ^a	5.3				89
Strip-2	87.5	0.56				14
Stripped Organic	530	0.0055				0.8
Strip-1 Acidified ^b		4.5	1.5	0.2	<0.03	

^aInitial volume 87.5 ml; decreased by ~30 ml and organic volume increased by ~30 ml because of water extracted on conversion of D2EHPA to its sodium salt.

^b25 ml of strip-1 + 5 ml 14 M HNO₃; final gross composition 1.8 M NaNO₃--0.5 M HNO₃.

In extraction from 2 M nitric acid with 0.1 M D2EHPA, E_a^O(Pu-IV) >10⁴ and E_a^O(Am-III) <10⁻². Plutonium was extracted from stock solution at ~2 g Pu/liter in 2 M HNO₃ with 0.1 M D2EHPA--2% tridecanol in Amsco 125-82, scrubbed twice with 2 M HNO₃, and stripped twice with 1 M Na₂CO₃. The phase ratios feed/extrac-tant/scrub/strip = 100/200/100/100. The strip solution was acidified with nitric acid to give a stock solution containing ~1 g Pu/liter, 2 M HNO₃, and 1 M NaNO₃. Americium²⁴¹ in this purified solution was too low to interfere detectably with direct measurement of extraction coefficients up to at least 3000; i.e., less than 0.03% of the α-activity was due to americium.

2.3 Electrical Coalescence in Solvent Extraction (A. D. Ryon)

Electrical coalescence of water-in-oil type dispersions is used commercially for desalting petroleum crudes, separation of caustic and acid emulsions in distillate treating, and removal of abrasive solids from crude oil. The success of electrical treatment in the petroleum industry suggested that it might be useful in solvent extraction processes:

- 1) Systems which separate slowly under gravity

2) Radiochemical processes where low residence time is required to minimize radiation damage to the solvent

3) Processes using critically safe equipment where rapid phase separation would increase the throughput

4) Processes where entrainment of aqueous in solvent causes contamination of the product

5) Removal of small particulate matter in the solvent which may cause product contamination

Preliminary tests with a small electrical source (150,000 cps, 50,000 volts, low amperage) showed that electrical coalescing of a 1/1 (a/o) phase ratio water-in-oil dispersion increased the flow capacity of a 0.2 sq ft gravity settler about 5 times.

In order to further explore the possibilities, a 10 KV, 30 MA maximum, AC or DC source was constructed and tests are underway to evaluate the effect of electrical coalescence on the maximum throughput capacity of a conventional mixer-settler unit.

3.0 FUNDAMENTAL CHEMISTRY

3.1 Emulsion Stabilization by Silicic Acid (K. A. Allen, W. J. McDowell)

A study was made of the effects of silica on emulsion formation in the Amex processes for uranium, with a view toward the prediction and testing of specific remedies.⁹ It was found that with a given amine (vs. an aqueous phase containing silicic acid) the stability of the emulsion formed was dependent on the anion present in the order SO_4^- (most stable) > Cl^- > ClO_4^- (least stable). Emulsion stability increased with silica concentration and with the age of the silicic acid solution. Other organic solutes that also had electron-donating tendencies (e.g., oxygen atoms) showed smaller but real emulsion forming abilities when contacted with silicic acid liquors. Organic additives with active hydrogen atoms decreased phase separation times of a typical silica liquor--amine sulfate solution dispersion by factors of 2 or more, presumably by competing with the silicic acid hydrogen atoms for bonding sites on the amine sulfate oxygens. It is suggested that silicic acid stabilizes oil-in-water type emulsions by hydrogen bonding to electron-donating groups adsorbed on the surfaces of the organic droplets and by forming typical silicic acid networks in the aqueous phase.

3.2 Activities in Solvent Extraction Systems (K. A. Allen, A. L. Myers)

In interpreting the equilibration behavior of the organo-nitrogen and organophosphorus extractants,^{10,11} it has become increasingly apparent that serious limitations are imposed by a lack of accurately and unambiguously determined activity coefficients for the organic (and often the aqueous) solutes. Isopiestic measurements have partially met this need,¹² but since the isopiestic results depend on the nonideal behavior of a reference solute, there still exists a need for measurements of a more absolute nature. Accordingly, an apparatus for obtaining accurate vapor pressure data has been constructed and is now being tested. This equipment will allow pressure readings to within a few microns ($\pm 2 \mu$ should be obtainable). This method has the further advantage of being very general: it is applicable to any two-component system of solvent and solute provided only that the former is volatile and that the latter is not, both of which requirements are met by most organic extractant systems.

3.3 Thorium Extraction by Amines (W. J. McDowell, G. N. Case)

Four hundred and sixteen grams of very pure di-n-decylamine (neutralization equivalent 298, 0.8% primary, 99.2% secondary) has been obtained and is being used in the thorium extraction studies in place of di(tridecyl P)amine. The di-n-decylamine is purer and in addition gives lower extraction coefficients than the di(tridecyl), allowing more accurate analyses. Extraction of varying amounts of thorium with 0.05 M benzene solutions of di-n-decylamine sulfate from 0.75 M Na_2SO_4 -- 0.25 M H_2SO_4 and 0.995 M Na_2SO_4 -- 0.005 M H_2SO_4 resulted in equilibration curves with plateaus indicating an amine sulfate-thorium combining ratio of 3:1.

Experiments designed to investigate the thorium-amine coordination number by acid transfer and the dependence of the extraction coefficients on reagent concentration and on aqueous sulfate concentration have been performed. However, analytical data necessary to interpret the results are not yet available.

3.4 Interfacial Tensions in Amine Extractant Systems (W. J. McDowell, K. A. Allen)

An important question in interpreting solute transfer data in the amine extractant systems is whether the amine molecules adsorbed at the organic-aqueous interface are mostly in the ionized alkyl ammonium form or whether the anions are held closely enough to affect the surface activity of the adsorbed layer. The interfacial tension measurements shown in

Table 13, obtained by the ring method with a Cenco-Du Nouty Interfacial Tensiometer, leave no doubt whatever that the anions do indeed affect the surface activity markedly. Parallel with its complex forming tendencies, sulfate shows the most pronounced effect, especially with the ring moving from aqueous to organic. The same is true in the other direction, but to a lesser degree. The reasons for the differences between the two methods are not understood.

Table 13. Interfacial Tension Measurements

System		Interfacial Tension (dynes/cm)	
Organic	Aqueous	Up	Down
Benzene	H ₂ O	33.2 ^a	29.1
Benzene	0.01 N HCl	33.4	27.9
Benzene	0.01 N HNO ₃	33.2	27.9
Benzene	0.01 N HClO ₄	28.7	26.4
Benzene	0.01 N H ₂ SO ₄	30.9	24.9
DDA ^b	H ₂ O	25.2	27.9
DDA NO ₃	0.01 N HNO ₃	21.3	23.0
DDA SO ₄	0.01 N H ₂ SO ₄	3.6	13.3
TOA	H ₂ O	28.0	29.6
TOA ClO ₄	0.01 N HClO ₄	25.0	25.9
TOA NO ₃	0.01 N HNO ₃	21.1	23.2
TOA Cl	0.01 N HCl	13.0	17.9
TOA SO ₄	0.01 N H ₂ SO ₄	8.1	14.5

^aEach number shown is the average of at least three determinations; the average deviation from the average was ≤ 0.2 dyne/cm for all except benzene-H₂O up (0.4) and TOA SO₄-0.01 N H₂SO₄ up (0.8).

^bDDA = di-n-decylamine, TOA = tri-n-octylamine; the amines were 0.1 N in benzene.

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