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ABSTRACT

Thorium Recovery from Blind River Mill Liquors by Amine Extraction

Thorium was extracted effectively from Blind River ion exchange mill effluents with two primary amines, 1-nonyl-decylamine and Primene JM. Stripping of thorium from Primene JM with sodium chloride solutions was operable at a utilization of only ~6 pounds NaCl/pound ThO₂ by recycling the strip solution, after heating to precipitate thorium sodium double sulfate. 1-Nonyldecylamine showed poor response to the chloride stripping method.

Technetium and Neptunium Recovery from Fluorination Plant Residues

Continuous countercurrent testing of the process for recovery of Tc, Np, and U by tertiary amine extraction from uranium hexafluoride transfer cylinder wash solutions, in a laboratory-scale mixer-settler system, showed good recoveries with relatively high mutual separations from both simulated and actual plant feeds. Addition of a new step, stripping of most of the nitrate from the extractant stream before technetium stripping, permitted a higher technetium concentration to be reached in the product. More than 99.9% of the uranium was recovered from the actual plant feed, at ~30 g U/liter in 1 M HNO₃, contaminated with 0.6 g Th, 0.002 g Np, and 0.001 g Tc/liter. More than 90% of the Np was recovered (plus ~6% to be recycled with the uranium), at 90 mg Np/liter in ~0.3 M HNO₃; the major contaminant was Th at 1.2 g/liter. More than 97% of the Tc was recovered, at 1.87 g Tc/liter in 3 M NaNO₃--0.8 M NaOH, contaminated with 0.002 g U and 0.007 g Np/liter.

Plutonium Nitrate Extraction by D2EHPA

Di(2-ethylhexyl)phosphoric acid (D2EHPA) in hydrocarbon solution extracts Pu(IV) from dilute nitric acid solutions much more strongly than do amines or phosphine oxide. The order of extractability is Pu(IV) > Pu(VI) > Pu(III). The extraction coefficient with 0.01 M D2EHPA is ~2500 from 1 M HNO₃ and ~3000 from 1 M HNO₃ + 5 M NaNO₃. It varies with the square of the D2EHPA concentration and close to the inverse square of the acidity, indicating extraction of a divalent Pu(IV) cation, probably

The Pu(VI) extraction coefficient from ~4 M HNO₃ was ~10 with 0.1 M D2EHPA in Amsco 125-82, ~6 in the presence of 2

vol % tridecanol (decreasing slightly with decreasing acidity), and ~60 in the presence of 0.05 M tri-n-octylphosphine oxide (increasing with decreasing acidity. These results resemble the extraction of U(VI), including a marked synergism with the D2EHPA-phosphine oxide combination. Extraction from reduced solutions was low, but there appeared to be some oxidation to and extraction of Pu(IV) in spite of all precautions. Calculations from extraction-scrub tests indicated Pu(III) extraction coefficients on the order of 10^{-2} .

Separation of Transplutoniums from Lanthanons

In a study of relative extractabilities of americium and lanthanons from aqueous solutions by several reagents, the only preferential extractions of americium over the fission product rare earths were with phosphate (TBP) and phosphonate esters from concentrated lithium chloride solutions. The other reagents tested were a primary amine, a tertiary amine, a quaternary ammonium compound, and a mono-alkylphosphoric acid. A batch countercurrent extraction with TBP gave promising separation of americium from europium in 10 N LiCl--0.1 N HCl, although extraction coefficients and separation factors varied during the test.

Solvent Screening

Sec-butyl benzene, dibutyl carbitol, n-butyl ether, and di-isobutyl ketone have been examined as diluents for certain extraction reagents (D2EHPA, TOA, DDA, and TBP) of potential use in radiochemical processing. In addition to the advantage of being single compounds rather than mixtures (and therefore of reliably reproducible characteristics) these solvents are reasonably satisfactory with respect to the following criteria: (1) commercial availability at reasonable cost, (2) compatibility with several typical extraction reagents, both with and without uranium, (3) acceptable flash point, toxicity, aqueous solubility, volatility, and physical behavior characteristics.

Solubility of DSBPP and TBP Complexes of Uranyl and Thorium Nitrates in Sec-butylbenzene

Scouting tests with 1 M DSBPP and 1 M TBP in sec-butylbenzene have shown appreciable solubility of the uranium and thorium complexes with DSBPP or TBP, suggesting physical feasibility of sec-butylbenzene as a diluent in process applications.

Diluent Nitration and Its Contribution to the Problem of
Solvent Cleanup

Nitrohydrocarbons have been identified as a major nitration product of Amsco 125-82 based on (1) infrared measurements, (2) similarity of extraction properties of degraded diluent with those of diluent spiked with separately synthesized nitrohydrocarbons, and (3) the fact that the observed properties of the degraded diluent are consistent with the known chemical properties of nitrohydrocarbons. Identification of these compounds as a major reason for poor diluent performance gives positive direction to methods of attacking the problem of solvent cleanup.

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1.0 RAW MATERIALS PROCESSING

1.1 Thorium Recovery from Blind River Mill Liquors by Amine Extraction (D. J. Crouse, W. D. Arnold)

Since small concentrations of nitrate ion (introduced into the liquor by the anion exchange resin uranium recovery process) severely interfere with thorium extractions by di(tridecyl)amine¹ but do not affect extractions with primary amines,² recent effort on recovering thorium from Blind River waste liquors has been concentrated on use of the latter extractants. Additional extraction data were obtained for 1-nonyldecylamine and Primene JM and the solubility loss of Primene JM was found to be lower than had previously been estimated. In addition, an economical chloride stripping flowsheet was developed for Primene JM.

1.1.1 Extraction Isotherms

Thorium was extracted effectively (Table 1) from an actual Blind River ion-exchange effluent and from a synthetic liquor of similar composition by Primene JM and 1-nonyldecylamine (0.03 M). Considerable iron and some titanium were extracted at low thorium loadings but these elements were rejected when the solvent was saturated with thorium. With 1-nonyldecylamine, change of the tridecanol concentration from 1 to 6 v % (addition of at least 1 v % TDA to the kerosene diluent is needed to speed phase separation) had no significant effect on extraction of thorium and iron but depressed titanium extraction.

1.1.2 Distribution Loss of Primene JM to the Aqueous Phase

The loss of Primene JM (0.15 M in kerosene diluent) on scrubbing with 30 volumes of 2% H_2SO_4 was ~33%. In subsequent measurements with the scrubbed amine solution, the loss rate of Primene JM to synthetic thorium-barren Blind River liquor did not reach a constant value but was still decreasing slowly after contact with 2000 liquor volumes. The average amine loss to the 2000 liquor volumes was ~10 ppm, a loss rate which is much lower than was estimated previously,^{3,4} at lower aqueous/organic phase ratios. This lower loss allows application of Primene JM to treatment of liquors more dilute in thorium than had previously been considered economically practicable.

1.1.3 Thorium Stripping by Chloride Solutions

In previous studies with di(tridecyl)amine,⁵ thorium was stripped efficiently with acidified sodium chloride solution, consumption of sodium chloride being only ~3 pounds per pound

Table 1. Extraction of Thorium with Primary Amines

Aqueous: A - Ion exchange effluent (pH 1.8) from Stanleigh Uranium Mining Corporation, Ltd. containing in grams per liter: 0.15 Th, 1.9 Fe(II), 1.0 Fe(III), 0.9 Al, 0.033 Ti, 0.10 Si, 0.4 Cl, 0.03 F, 1.0 NO₃, and 15 SO₄

B - Synthetic ion-exchange effluent (pH 1.8) containing in grams per liter: 0.15 Th, 2.4 Fe(II), 0.5 Fe(III), 0.9 Al, 0.03 Ti, 0.03 F, 0.4 Cl, 1.0 NO₃, and 15 SO₄

Organic: 0.03 M amine in kerosene with indicated concentration of tridecanol (TDA)

Procedure: Organic cascaded against fresh aqueous, 5 min contacts

Amine	TDA, v %	Head Aqueous	Concentration, g/liter				Thorium Extraction Coeff. (E _a)
			Organic			Aqueous	
			Th	Fe	Ti	Th	
1-Nonyldecyl	1	A	0.29	0.19	0.02	<0.005	>58
			0.45	0.16	0.02	<0.005	>90
			0.72	0.054	0.01	0.009	80
			0.81	0.029	<0.01	0.066	12
			0.83	0.023	<0.01	0.14	6
	6	A	0.29	0.18	<0.01	<0.005	>58
			0.44	0.14	<0.01	<0.005	>88
			0.72	0.056	<0.01	<0.005	>140
			0.82	0.030	<0.01	0.068	12
			0.83	0.014	<0.01	0.13	6
Primene JM	0	B	0.15	0.22	0.02	<0.005	>30
			0.29	0.17	0.03	<0.005	>58
			0.61	0.068	0.02	<0.005	>120
			0.76	0.029	0.01	<0.005	>150
			0.80	0.010	<0.01	0.13	6

of ThO₂. The primary amines, however, are much less responsive to the chloride stripping method and, in the usual arrangement of the process flowsheet, consumption of sodium chloride would be excessive. This is shown in Fig. 1 for tests in which Primene JM was stripped with 1 M NaCl--0.05 M H₂SO₄. With 0.05 M amine in kerosene-tridecanol diluent, maximum thorium loading of the strip solution was only ~3.5 grams per liter. From these data, sodium chloride consumption for stripping 90% of the thorium in three ideal stages is estimated at ~18 pounds per pound of ThO₂. Higher loading of the strip solution was obtained in the test with 0.03 M amine in kerosene (presumably

Fig. 1. Stripping Thorium from Primene JM with 1 M NaCl--0.05 M H_2SO_4 . Head organic: a) 0.05 M Primene JM in 98% kerosene--2% tridecanol loaded to 1.35 g Th/liter, b) 0.03 M Primene JM in kerosene loaded to 0.85 g Th/liter.

because tridecanol was not present; see below) but predicted sodium chloride consumption for equivalent stripping efficiency would still be high (~16 pounds per pound of ThO_2).

Higher loading of the strip solution and effective utilization of the stripping reagent can be obtained by using more concentrated sodium chloride solution and recycling most of this solution to the strip section after precipitation of thorium. Under these conditions, sodium sulfate accumulates in the strip solution, the buildup in sulfate concentration being controlled by bleeding a minor fraction of the recycle solution from the system. In batch tests (Fig. 2) stripping of 0.03 M Primene JM in kerosene was efficient with 2 molar sodium chloride. Results were essentially the same with either 0.6 M or 1 M Na_2SO_4 present in the strip solution (curve c vs curve b). Addition of 1 v % tridecanol to Primene JM-kerosene severely depressed the stripping efficiency. Stripping of 0.03 M 1-nonyldecylamine in 99% kerosene--1% tridecanol was even

Fig. 2. Stripping Thorium from Primary Amines with Acidified Sodium Chloride-Sodium Sulfate Solutions. Head organic: 0.03 M amine in kerosene or kerosene-tridecanol diluent loaded to 0.85 g Th/liter. Head aqueous: 2 M NaCl--0.05 M H₂SO₄ plus 0.6 M or 1 M Na₂SO₄.

Curve	Amine	TDA, v %	Na ₂ SO ₄ , M
a	Primene JM	1	1.0
b	Primene JM	0	1.0
c	Primene JM	0	0.6
d	1-nonyldecyl	1	1.0

more difficult and too inefficient to be of interest. Some thorium sulfate precipitated from strip solutions containing >5 grams of thorium per liter after standing overnight but no precipitation occurred during any of the stripping tests.

1.1.4 Thorium Recovery from Chloride Strip Solutions

Thorium can be recovered completely from the strip solution by hydrolytic precipitation at pH ~7 and the filtrate from the precipitation operation can be recycled to the strip-

ping section. More economical recovery of thorium is obtained, however, by heating the strip solution to precipitate thorium sulfate. This procedure has the added advantage of providing effective separation from certain metal contaminants, principally iron(III), which are not precipitated with the thorium but accumulate in the recycle solution and are eventually removed by the bleed.

Effect of Temperature. In continuous precipitation tests with a synthetic strip solution containing 6 grams of thorium per liter in 2 M NaCl--0.6 M Na₂SO₄ solution (pH 1.6), ~90% of the thorium was recovered by heating the solution for 1.7 hr at 45, 60, or 75°C (Table 2). The settling rate of the precipitate decreased slightly with increasing temperature. The residual thorium content of these solutions was sufficiently low to allow recycle to the stripping system.

Table 2. Effect of Temperature on Thorium Precipitation

Head solution: 6 g Th/liter, 2 M NaCl, 0.6 M Na₂SO₄, pH 1.6

Heating time: ~0.85 hr in each of two co-current mixers

Temp., °C	Thorium Precipitated, ^a %		
	First Mixer	Second Mixer	Total
45	79	9	88
60	83	5	88
75	86	5	91

^aBased on head solution and supernate analyses.

Effect of Heating Time. Further studies with the same solution at 60°C showed an increase in recoveries from 89 to 94% as the total residence time of the solution in the mixers was increased from 0.8 to 3.2 hr:

Total Residence Time in the Mixers, hr	Thorium Precipitated, %		
	First Mixer	Second Mixer	Total
0.8	80	9	89
1.2	79	10	89
1.6	85	7	92
3.2	87	7	94

Some of the precipitate from the above tests (after being washed with water and dried at 110°C) analyzed 28.4% Th, 13.1% Na, and 51.1% SO₄, indicating a thorium sodium double sulfate salt. Sulfate can be eliminated from the precipitate, if desired, by digestion with dilute caustic.

1.1.5 Continuous Thorium Recovery Run

On the basis of the foregoing results, a continuous system was set up and thorium was recovered from a synthetic Blind River waste liquor by extraction with 0.03 M Primene JM in kerosene, stripping with sodium chloride-sodium sulfate solution, continuous precipitation of thorium by heating at 60°C, and recycling most of the precipitation supernate to the stripping system (Fig. 3). The feed liquor (pH 1.8) contained in grams per liter: 0.15 Th, 0.003 U, 2.4 Fe(II), 0.5 Fe(III), 0.9 Al, 0.03 Ti, 0.4 Cl, 1.0 NO₃, and 15 SO₄. Thorium extraction in three mixer-settler stages was >99% (Fig. 3). Although considerable iron extracted in the last stage, most of it was displaced by thorium in the upper stages. In the stripping system, ~95% of the thorium but only about one-half of the iron and one-third of the titanium were removed from the solvent. The pregnant strip solution, containing ~5.5 grams of thorium and 1.2 grams of iron per liter, was heated in two co-current mixers (total solution residence time of 1.7 hr), precipitating ~75% of the thorium but essentially none of the iron. The precipitate was separated continuously from the supernate in two co-current decanters (total solution residence time of 1.5 hr), producing a clear solution for recycle to the stripping system. The volume of slurry withdrawn from the bottom of the decanters was regulated at the value which limited sodium sulfate buildup in the recycle solution to ~0.6 M. Under these conditions, sodium chloride consumption was approximately 6 pounds per pound of ThO₂ recovered. Filtration of the precipitate slurry was rapid. Presumably, the filtrate, which contained ~5% of the original thorium, would be recycled to the extractor. Analyses of the thorium product from the run are not yet available.

2.0 SOLVENT EXTRACTION TECHNOLOGY

2.1 Technetium and Neptunium Recovery from Fluorination Plant Residues: Continuous Countercurrent Runs (C. F. Coleman, F. A. Kappelmann, B. Weaver, J. P. Eubanks)

Solvent extraction methods are being studied to develop a process for recovery of the technetium that occurs in some fluorination plant residues. The process should either be compatible with or satisfactorily replace existing processes for recovery of neptunium and uranium from these residues. Studies leading to a tentative chemical flowsheet (Fig. 4) for recovery and separation of Tc, Np, and U by tertiary amine extraction were previously reported.^{6,7,8} Several continuous countercurrent runs have now been completed in laboratory-scale mixer-settlers. These runs, using both simulated and actual plant feed, showed good recoveries and

Fig. 3. Thorium Recovery from Synthetic Blind River Liquor with 0.03 M Primene JM in Kerosene. Numbers in blocks show concentrations in grams per liter at steady-state.

Fig. 4. Schematic Flowsheet for Recovery and Separation of Tc, Np, and U from Nitric Acid-Aluminum Nitrate Solutions of Fluorination Plant Residues. Feed adjustment: reduction to Np(IV), and dilution to the approximate nitrate concentration and acidity shown. Circled numbers represent relative flows.

relatively high mutual separations of Tc, Np, and U. Addition of a new step, stripping of most of the nitrate from the extractant stream before technetium stripping, permitted a relatively high technetium concentration to be reached in the product.

The continuous extraction system was described previously.⁸ Briefly, a series of small glass mixer-settlers⁹ were set up so as to be divisible into any combination of extraction, partition, and stripping banks; e.g., as illustrated in Fig. 5. The series consisted at first of 21 units, later increased to 24. The holdup of each unit was about 250 ml organic + aqueous. Feeds were metered by bellows pumps, calibrated and repeatedly checked by using tubulated graduated cylinders for the feed reservoirs.

The operating conditions are shown in Table 3 for the series of runs with the simulated and actual solutions described in Table 4. The first, Run "U-1," was a "cold" run to test the system and bring it to steady state, and to confirm the uranium extraction and stripping behavior. No radioactive tracer was used in this run; however, there was considerable activity from the daughter products of the

Fig. 5. Continuous Countercurrent Test of Tc-Np-U Recovery Process in Laboratory-Scale Mixer-Settler Bank. Runs Plant-1 and Plant-2, Table 3.

reagent-grade uranium (see below). Run "Tc-1" continued without significant interruption after Run "U-1," the only change being the addition of Tc-95m tracer to the adjusted feed solution. In Run "Tc-2" the banks were rearranged to test nitrate removal in a partial stripping step, and technetium stripping at (in effect) a very high O/A ratio obtained by recirculating the strip solution in closed circuit from settler to mixer of the same unit. No profiles were measured in the following "cold" Run "U-2," which served primarily to flush out the technetium tracer. Np-238 tracer was added to the adjusted feed solution for Run "Np." However, the amount of the tracer available at that time was not sufficient to give neptunium activity usefully higher than the uranium daughter product activity, except at the neptunium product stage. The uranium profiles rechecked in this run showed that uranium was gradually building up in the extraction section. Accordingly, the feed/extraction ratio was decreased for the last two runs, as indicated in Table 3. At the lower ratio, the feed no longer supplied sufficient acid to acidify the recycled base-form amine, and a small acid stream was introduced into the raffinate stage. Whether or not such additional acid is needed depends primarily on the uranium/acid ratio in the feed. When needed, it is better added at the raffinate stage than to the feed, and this will probably be more convenient in plant operation than a separate acidification of the recycled amine.

2.1.1 Uranium Distribution

The uranium extraction and stripping profiles from the successive runs are compared in Tables 5 and 6, and those from

Table 3. Operating Conditions, Continuous Countercurrent Tests

Cf. Fig. 5

Extractant: 0.3 M Alamine 336 in 90% Amsco 125-82, 10% tridecanol, entering at Stage No. 1, 290-300 ml/hr

Feed Compositions: Solutions as listed in Table 4 made 0.1 M in ferrous sulfamate and diluted to twice original volume

Run	Coextraction	U Partition	Np Partition	NO ₃ Removal	Tc Stripping	Hours
U-1	Stages: 1-6 Streams In: Syn. Feed ml/hr: 230-260	7-12 1 N HNO ₃ 150-160	13-19 0.05 N HNO ₃ 50		20-21 1 N NH ₄ OH 140-160	42
Tc-1	Stages: 1-6 Streams In: Syn. Feed ^a ml/hr: 240-260	7-12 1 N HNO ₃ 150	13-19 0.05 N HNO ₃ 40-50		20-21 1 N NH ₄ OH 140-160	27
Tc-2	Stages: 1-6 Streams In: Syn. Feed ^a ml/hr: 240-260	7-12 1 N HNO ₃ 140-150	13-14 0.05 N HNO ₃ 45-55	15-20 0.5 N NH ₄ OH ^d 140-180	21 2 N NH ₄ OH Static ^e	18
U-2	Stages: 1-6 Streams In: Syn. Feed ml/hr: 250-260	7-12 1 N HNO ₃ 150	13-19 0.05 N HNO ₃ 50		20, 21 2 N NH ₄ OH Static ^e	14
Np	Stages: 1-6 Streams In: Syn. Feed ^b ml/hr: 250-260	7-12 1 N HNO ₃ 140-155	13-19 0.05 N HNO ₃ 45-50		20, 21 1 N NaOH Static ^e	20
Plant-1	Stages: 1-7 Streams In: PCF-1 ^c ml/hr: 175-210	8-13 1 N HNO ₃ 145-155	14-19 0.05 N HNO ₃ 50	20-23 0.5 N NH ₄ OH ^d 150-160	24 4 N NaOH Static ^e	46
Plant-2	Stages: 1-7 Streams In: PCF-1 ^c ml/hr: 180-200	8-13 1 N HNO ₃ 150-160	14-19 (0.05 N HNO ₃ (1% H ₂ O ₂ 50-55	20-23 0.5 N NH ₄ OH ^d 160	24 4 N NaOH Static ^e	13

Table 3 (Notes)

- a) Tc-95m tracer added to the synthetic feed, giving 433 γ /sec ml in Run Tc-1 and 353 γ /sec ml in Run Tc-2.
- b) Np-238 tracer added to the synthetic feed, giving ~40 γ /sec ml.
- c) Extra stream of 2 N HNO₃ at 16 ml/hr added to the raffinate stage (stage No. 1) to maintain acid balance.
- d) Plus 5 to 10 ppm Victawet 12.
- e) In "static" operation of the Tc stripping stages, the aqueous underflow from the settler was returned continuously to its mixer. At intervals, the entire aqueous batch was replaced with fresh solution.

Table 4. Unadjusted Feed Solution Compositions

	Typical Composition ^a	PCF ^b	PCF-1 ^b	Simulated Solution
Tc, g/liter	0.1	0.113	0.08	none
Np	0.03	0.045	0.057	none
U	40	42	40	39.8
Th	2	1.13	-	2.5 ^e
Al	45	48.4	-	44.8
s.s. ^c	5	-	-	6.75 ^{c,e}
Cu	0.5	-	-	0.5 ^e
Mg	0.2	-	-	none
Na	-	2.5	-	none
H ⁺ , M	1	0.91	0.74	0.82
NO ₃ ⁻	6	6.8	-	6 ^e
F ⁻	0.5	0.26	-	0.5 ^e
SO ₄ ²⁻	-	<0.003	-	none
Sp. Gr.	-	1.41	-	-
Gross β /min mld ^d	-	1.3x10 ⁵	-	-
Gross γ /min mld ^d	-	2.5x10 ⁴	-	4.5x10 ³

^acf. Typical ash compositions, References (10) and (21).

^bTwo portions obtained from nominally the same batch of leach solution.

^cStainless steel metals. In the simulated solution (g/liter): Fe, 2; Cr, 1; Ni, 1; Mn, 0.125.

^d β counts at ~10% geometry, γ counts at ~25% efficiency.

^eConcentrations calculated from quantities used, instead of from analysis.

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Table 5. Uranium Extraction Profiles
Effect of Loading Ratio

		Uranium Distribution, g/liter					
Run ^a :		<u>"U-1"</u>	<u>"Tc-2"</u>	<u>"Np"</u>	<u>"Plant-1"</u>		<u>"Plant-2"</u>
Stream	Stage No.	Stage No.					
Feed		20	20	20		21	21
	6-A	19.4	23.0	20.5	7-A	9.9	8.6
	5-A	17.6	23.0	19.6	6-A	2.1	1.8
	4-A	14.6	19.7	17.4	5-A	0.36	0.33
	3-A	10.1	14.9	12.9	4-A	0.033	0.035
	2-A	5.3	10.0	6.8	3-A	0.007	0.007
Raffinate	1-A	1.6	2.3	1.7	2-A	0.001	-
					1-A	0.0005	0.001
Extract	6-O	15.3	16.8	15.2	7-O	14.9	13.1
	5-O	15.6	16.0	16.0	6-O	6.7	5.3
	4-O	14.1	14.8	14.8	5-O	1.4	1.1
	3-O	10.7	13.7	13.1	4-O	0.21	-
	2-O	7.7	9.9	9.6	3-O	0.005	-
	1-O	3.6	5.0	4.3	2-O	0.007	-
					1-O	-	0.003
Feed Ratio, Feed/Extractant		$\frac{245}{300}$	$\frac{250}{300}$	$\frac{245}{300}$		$\frac{200}{300}$	$\frac{200}{300}$

^aSee Table 3.

Run "Plant-1" are shown graphically in Fig. 6. The feed/ex-
tractant flow ratio of ~250/300 used in the runs with simu-
lated feed proved to be too high, so that the top 3 stages of
the extraction section became nearly saturated, and the raffi-
nate loss was as high as 10%. With the feed/extractant ratio
decreased to ~200/300 (and only a slight change in the uranium
feed concentration) in the runs with the actual plant feed,
this saturation hump disappeared. The uranium concentrations
in the successive stages now decreased in approximately con-
stant ratio (Fig. 6), and reached ~1 ppm (<0.01% loss) in the
raffinate. The uranium concentration in the loaded extract
decreased only a little, to 13-15 from 15-17 g/liter. The
stripping profiles were similar in all the runs, with a con-
stant ratio of decrease in each stage and <0.1% of the uranium
remaining in the organic stream after six stages. The uranium
extraction isotherm for Run "Plant-1" (Fig. 7) shows that the
stage efficiency was close to 100%. The uranium recovery
reached >98% in 3 stages and >99.8% in 4 stages, which should
thus be sufficient for plant operation. Additional stages

Table 6. Uranium Stripping Profiles

Stream	Stage No.	Uranium Distribution, g/liter					
		Run ^a : "U-1"	"Tc-2"	"Np"	"Plant-1"	"Plant-2"	
Extract	6-O	15.3	16.8	15.2	7-O	14.9	13.1
	7-O	4.3	3.9	3.4	8-O	4.1	3.7
	8-O	1.25	1.19	0.9	9-O	0.93	0.93
	9-O	0.15	0.46	0.35	10-O	0.35	-
	10-O	0.049	0.043	0.045	11-O	0.07	-
	11-O	0.12	0.012	0.012	12-O	0.024	-
Stripped Extractant ^b	12-O	0.009	0.004	0.005	13-O	0.001	0.009
U Product	7-A	31.4	35.0	29.9	8-A	28	26
	8-A	8.2	16.6	6.7	9-A	7.2	7.7
	9-A	2.5	2.1	1.7	10-A	1.9	-
	10-A	1.3	0.7	0.6	11-A	0.6	-
	11-A	0.41	0.27	0.06	12-A	0.13	-
	12-A	0.025	0.12	0.006	13-A	0.037	0.038

^aSee Table 3.^bTo Neptunium Stripping Section, etc.

would give a useful margin of holdup capacity to tolerate periods of excessive feed rate, as occurred in the present runs with the simulated feed.

2.1.2 Neptunium Distribution

As mentioned above, the amount of Np-238 tracer available for Run "Np" proved to be insufficient (in the presence of the uranium daughter products) for more than a qualitative indication that most of the neptunium did report to the neptunium product stream. The profiles from the runs with actual plant solution are compared in Table 7. Extraction, and retention in the extract during uranium partition, were similar in the two runs. The aqueous neptunium concentration dropped below the analytical limit (>99.8% extracted) within 2 stages. The steep slope of the extraction profile (>95% per stage, Fig. 8) reflects the considerably greater extractability of neptunium than of uranium (~80% per stage, Fig. 6). Neptunium partition with 0.05 N HNO₃ appeared to be feasible, although much less effective than partition with 0.1 N H₂SO₄.⁷ With addition of 1% H₂O₂ to the 0.05 N HNO₃, at the same volume ratio, the neptunium partition was much more effective (Fig. 8). Less than 1% remained in the organic stream after 3 stages. The level found did not decrease much further (Table 7); this might actually be 0.1-0.2 ppm of unstrippable neptunium, or it may have been the effective analytical limit for analysis of these small organic samples.

Fig. 6. Uranium Extraction and Stripping Profiles from Continuous Countercurrent Run Plant-1, Table 3.

2.1.3 Nitrate Removal

The last step of the process is stripping of technetium, and all other anions present, by complete hydrolysis of the amine salt with a basic solution. This type of stripping is conducive to obtaining a high concentration factor, provided a high O/A ratio can be handled. The extract leaving the neptunium partition section carries 0.3 M nitrate as its major anion, which is stripped along with the technetium and sets a lower limit on the product volume. The selectivity for technetium over nitrate in extraction suggested that selective stripping might permit discard of a major fraction of the nitrate without significant technetium loss. A series of batch equilibrations (Table 8) confirmed this possibility, and a nitrate removal section was incorporated in the mixer-settler bank for Runs "Tc-2," "Plant-1," and "Plant-2." A 0.5 N NH_4OH solution was arbitrarily chosen for the strip solution, with flows set to hydrolyze 80-90%

Fig. 7. Uranium Extraction Isotherms

- Continuous countercurrent Run Plant-1, Table 3;
0.3 M Alamine 336 in 90% Amsco 125-82, 10%
tridecanol
- From 1 N HNO_3 --0.5 N $\text{Al}(\text{NO}_3)_3$, CF-60-1-119, Fig. 3⁶
- I 0.5 M trilaurylamine, 90% Amsco 125-82, 10% tridecanol
- II 0.3 M trilaurylamine, 94% Amsco 125-82, 6% tridecanol
- III 0.1 M trilaurylamine, 98% Amsco 125-82, 2% tridecanol

Table 7. Neptunium Extraction and Stripping Profiles

	Run ^a :	Neptunium Distribution, mg/liter			
		"Plant-1"		"Plant-2"	
		Aq	Org	Aq	Org
Feed		28		28	
Coextraction	1	<0.04 ^b	<0.04	<0.04 ^b	-
	2	<0.04	<0.04	-	-
	3	-	-	-	-
	4	-	-	-	-
	5	<0.04	<0.06	-	-
	6	<0.04	1.4	<0.04	0.4
	7	1.2	28 ^c	0.7	18 ^c
U Partition	8	1.9	17	2.8	17
	9	1.3	16	2.4	18
	10	1.4	16	-	-
	11	1.4	15	-	-
	12	1.2	16	-	-
	13	0.7	16	0.8	18
Np Partition	14	80 ^d	-	130 ^d	17
	15	80	9	130	4.2
	16	67	2.8	54	0.1
	17	32	0.8	9	0.17
	18	14	0.2	1.6	0.16
	19	4.1	-	0.34	0.12
NO ₃ Removal	20	1.2	0.4	0.11	0.10
	21	1.2	0.4	-	-
	22	-	-	-	-
	23	0.6	0.4	0.06	<0.04
Tc Stripping	24	9	<0.04	9 ^e	-

^aSee Table 3.^bRaffinates.^cLoaded Extracts.^dNeptunium Product Solutions.^eIncludes Np in Tc product from Run "Plant-1."

of the amine nitrate. Closer control, or a narrower margin of unhydrolyzed amine salt, was not attempted in these runs, but should not be difficult since the performance here was very good even though the conditions were rather arbitrarily chosen. A tendency toward emulsification (typical at very

Fig. 8. Neptunium Extraction and Stripping Profiles from Continuous Countercurrent Runs, Table 3.

Run Plant-1, Np stripped with 0.05 N HNO_3

Run Plant-2, Np stripped with 0.05 N HNO_3 -1% H_2O_2

Table 8. Nitrate Removal from Technetium Extract

Organic: 0.291 M Alamine 336 in 90% Amsco 125-82--1% tri-decanol, equilibrated with 0.05 N HNO_3 , containing extracted Tc-95m tracer at 325 $\gamma/\text{sec ml}$

Aqueous: 0.3 N NH_4OH

One volume of organic extract equilibrated with successive varying volumes of hydroxide solution

Cumulative A/O	Σ % RHNO_3 Hydrolyzed ^a	Aqueous pH	Σ % Tc Removed	$D_a^O(\text{Tc})$	$\frac{D_a^O(\text{Tc})}{M(\text{RH}^+)}$
0.5	51.7	5.2	0.6	75	530
0.8	82.7	5.6	2.1	16	320
0.9	93.1	5.8	3.5	6	300
0.95	98.2	5.8+	6.1	1.6	310
1.05	-	-	74	0.003	-
1.15	-	-	87	0.001	-

^a = % of nitrate removed from organic phase. Calculated assuming quantitative reaction.

low ionic concentrations) was eliminated by addition of a surfactant, Victawet 12, at 10 ppm. This was later decreased to 5 ppm without reoccurrence of emulsification; lower concentrations were not tested. The degree of nitrate removal was monitored by titration of organic stream grab samples. Preliminary tests suggest that a simpler pH control test may be feasible. As shown below, the partial strip caused only a minor reflux of technetium, which was contained within two stages.

2.1.4 Technetium Distribution

The technetium profiles are compared in Table 9, with one run illustrated in Fig. 9. In each case the aqueous technetium concentration dropped below analytical limit (>99.5% extracted) within 3 stages. It is to be noted that these are the same stages that were excessively loaded with uranium (cf. Table 5). Thus, the technetium extraction was not impaired by the excessive feed rate which led to ~10% loss of the uranium. The extracted technetium was well retained through the partition sections, in spite of some refluxing (as expected) in the nitrate removal section. Recirculation of the basic strip solution within the mixer-settler unit until the base was nearly all converted to nitrate worked smoothly with either 2 M NH_4OH or 4 M NaOH . One batch initially 4 M NaOH was used through the latter part of Run "Plant-1" and all of Run "Plant-2." At the termination of that run it contained 1.87 g Tc/liter in 3.2 M NaNO_3 --0.84 M NaOH solution, suggesting that with continuation of the same conditions it would have reached ~2.3 g Tc/liter when the hydroxide was all converted to nitrate. With flows adjusted to a higher percent nitrate removal in the nitrate-removal section, the limiting technetium concentration could have been correspondingly higher. The organic stream leaving the single stripping stage carried ~1 mg Tc/liter (~3% not stripped) when the sodium hydroxide concentration had dropped to 0.84 M. Hence, two such stages should be used in series to obtain the maximum technetium product concentration without recycle of some unstripped technetium.

2.1.5 Distribution of Radioactive Contaminants

The simulated feed contained considerable activity from the uranium daughter products introduced with the reagent grade uranium. Figure 10 shows the distribution of the γ activity. Most of it accompanied the uranium, about two-thirds as much accompanied the neptunium, and only about one-tenth as much accompanied the technetium. Figure 11 shows several points from the distributions of both γ and β after processing of the actual plant solution. Here the chief activity (besides technetium β) was from protoactinium, which went mostly with the neptunium.

Table 9. Technetium Extraction and Stripping Profiles

Run ^a :	Technetium Distribution										
	γ counts/sec ml						mg Tc/liter				
	"Tc-1"			"Tc-2"			"Plant-1"		"Plant-2"		
	Stage No.	Aq	Org	Stage No.	Aq	Org	Stage No.	Aq	Org	Aq	Org
Feed		433			353			40		40	
Coextraction	1	- ^b	-	1	- ^b	-	1	<0.1 ^b	<0.1	<0.1 ^b	<0.1
	2	-	-	2	-	-	2	<0.1	<0.1	-	-
	3	-	-	3	-	2	3	-	-	-	-
	4	-	12	4	2	12	4	-	-	-	-
	5	16	78	5	15	104	5	<0.1	0.4	<0.1	0.2
	6	99	333 ^c	6	66	262 ^c	6	0.5	4.5	0.4	2.8
							7	8	23 ^c	4.3	15 ^c
U Partition	7	10	344	7	11	260	8	1.0	23	1.2	23
	8	9	337	8	8	269	9	0.8	22	0.8	24
	9	9	335	9	6	262	10	-	-	-	-
	10	11	331	10	8	266	11	-	-	-	-
	11	9	351	11	8	264	12	-	-	-	-
	12	8	338	12	6	268	13	0.6	21	0.8	27
Np Partition	13	4	338	13	4	252	14	0.2	24	0.1	27
	14	3	334	14	-	240	15	-	-	-	-
	15	10	334				16	-	-	-	-
	16	2	338				17	<0.1	58	-	-
	17	-	334				18	-	-	-	-
	18	2	335				19	<0.1	25	-	26
	19	4	350								
NO ₃ Removal				15	3	240	20	0.2	22	0.2	24
				16	2	250	21	0.2	27	0.3	39
				17	1	251	22	0.4	29	16	141
				18	1	238	23	6.2	34	140	9
				19	7	1160					
				20	1335	107					
Tc Stripping	20	734 ^d	6	21	5240 ^d	10 ^e	24	1600 ^d	0.9 ^e	1870 ^e	1 ^e
	21	96	- ^e								

Table 9 (Notes)

- a) See Table 3.
- b) Raffinates.
- c) Loaded Extracts.
- d) Technetium Product Solutions (cumulative through Runs "Plant-1" and "Plant-2").
- e) Stripped Extractant.

Fig. 9. Technetium Extraction and Stripping Profiles from Continuous Countercurrent Run "Plant-1," Table 3.

Fig. 10. Distribution of Gamma-Activity (Uranium Daughter Products) after Cold Run "Np." Activities counted (~25% efficiency) 28 days after termination of run.

Fig. 11. Distribution of Beta (O) and Gamma (O) Activity after Run "Plant-2" with Actual Plant Solution. Activities counted (β ~10% geometry, γ ~25% efficiency) 21-26 days after termination of run.

2.1.6 Products

Table 10 summarizes the distributions of technetium, neptunium, and uranium among the product and discard streams of Run "Plant-1," and partial analyses in Table 11 show the degree of separation. More than 99.9% of the uranium was recovered (based on total in the feed less holdup in the system), at ~30 g U/liter in 1 M nitric acid, contaminated with 0.6 g Th, 0.002 g Np, and 0.001 g Tc/liter, or 2% Th, 0.007% Np, and 0.003% Tc based on the uranium content. More than 90% of the neptunium was recovered (plus ~6% to be recycled with the uranium), at 90 mg Np/liter in ~0.3 M nitric acid. The major contaminant in the neptunium product was thorium at 1.2 g/liter, which is about the same ratio of thorium to neptunium as in the product from the TBP U-Np process. More than 97% of the technetium was recovered, at 1.87 g Tc/liter in 3.2 M NaNO₃--0.84 M NaOH solution contaminated with 0.002 g U and 0.007 g Np/liter.

Table 10. Distribution of Uranium, Neptunium and Technetium
From Final Profile of Continuous Countercurrent
Test with Plant Feed

	% of Feed ^a		
	Tc	Np	U
Raffinate	<0.2 ^b	<0.1 ^b	0.003
U Product	2	6	104
Np Product	0.1	96	0.05
NO ₃ Discard	0.3	0.3	0.002
Tc Product	104	<0.1 ^{b,c}	<0.001
Material Balance	107	103	104

^aNot adjusted for material balance.

^bBelow analytical limits.

^cLess than 0.1% of the Np to the Tc product when H₂O₂ was used in the Np strip solution; ~1% when H₂O₂ was not used.

2.2 Plutonium Nitrate Extraction by D2EHPA (C. F. Coleman, D. E. Horner)

Di(2-ethylhexyl)phosphoric acid (D2EHPA) extracts plutonium(IV) from dilute nitric acid solutions much more strongly than do either amines or phosphine oxide. While the mechanism of extraction must be different, i.e., extraction of a simple cation or a cationic complex instead of a neutral or anionic complex, the extractability varies in the same order with plutonium oxidation state, Pu(IV) > Pu(VI) > Pu(III).

Table 11. Product Solution Analyses
From Continuous Countercurrent Test with Plant Feed

	Tc Product ^a	Np Product ^b	U Product ^c
Tc, g/liter	<u>1.87</u>	0.001	0.001
Np, g/liter	0.007	<u>0.09</u>	0.002
U, g/liter	0.002	0.04	<u>29</u>
Th, g/liter	-	1.2	0.6
HNO ₃ , M	-	0.3	1
NaNO ₃ , M	3.2	-	-
NaOH, M	0.8 ^d	-	-
Gross β /min ml ^e	3x10 ⁶	1.5x10 ⁴	5x10 ³
Gross γ /min ml ^e	1x10 ⁴	5x10 ⁴	4x10 ³
Cross Contamination, % ^f			
Tc	-	0.1	0.003
Np	0.4	-	0.007
U	0.1	45	-

^aProduct fraction collected after 16th hr of 58 hr run.

^bProduct fraction collected for last 12 hrs of run.

^cProduct collected for entire run.

^dNaOH remaining unconsumed at the arbitrary termination of the test. In plant operation essentially complete consumption of the NaOH would be expected.

^e β Counts at ~10% geometry, γ counts at ~25% efficiency.

^f% Cross contamination values based on the quantities of Tc, Np, and U in the respective products, not on weight of solution nor weight of total solids.

2.2.1 Plutonium(IV)

As expected on the basis that the extraction involves plutonium-hydrogen cation exchange, plutonium(IV) extraction coefficients decreased with increasing acidity over most of the nitric acid concentration range (Fig. 12). The slope, presumably corresponding to the charge of the plutonium cation and the number of hydrogen ions exchanged, changed with increasing acidity from ~1/2 near 1 M HNO₃ to 2, and then to >4 above 6 M HNO₃. The slopes lower than 4

Fig. 12. Plutonium(IV) Extraction by Di(2-ethylhexyl)phosphoric Acid: Effect of nitric acid and sodium nitrate concentrations.

suggest extraction of an oxygenated or a nitrate-complexed plutonium(IV) cation.* At ~0.1 M HNO₃ (the only acidity tested at less than 0.3 M) the extraction coefficient dropped by a factor of 10, suggesting major interference by plutonium hydrolysis. Addition of sodium nitrate to the nitric acid to maintain 6 M total nitrate had little effect on the extraction from 1-6 M HNO₃. It increased the extraction from 0.3 M HNO₃, bringing that point more nearly into line with the points at the higher acidities.

Extraction with a concentration of D2EHPA higher than 0.01 M was measured only at >6 M HNO₃ (Fig. 12), since trials at lower acidity indicated extraction coefficients too high to measure.

Extractions over a range of D2EHPA concentrations (Fig. 13) showed the extraction coefficient varying with close to the square of the D2EHPA concentration. This was corrected for the amount tied up by the extracted plutonium, calculated on the basis (explained below) of 4 organophosphorus anions per plutonium. While some of the corrections were appreciable, up to 30% at the lowest D2EHPA concentration, ignoring them would have shifted the apparent slope only to ~2.4, with still nearly as close a fit to linearity. Hence, the conclusion of second power dependence does not depend strongly on the correctness of the assumed 4:1 ratio. Conversely, the resulting good fit gives only a little additional support to that assumption.

Since D2EHPA is dimeric in hydrocarbon solutions,¹² second power dependence on its concentration indicates complexing at a mole ratio anion:metal ion of 4:1. As both neptunium and plutonium results indicated 2 hydrogen ions exchanged per metal ion, the indicated extraction reaction is

*The slopes below 6 M HNO₃ (Fig. 12) are uncertain, since they depend on the accuracy of extraction coefficients measured at >>1000, where the raffinates were approaching analytical limits. However, the observations are also supported by comparison with extraction of neptunium(IV), which generally parallels plutonium(IV). Neptunium(IV) extraction coefficients with 0.01 M D2EHPA showed a reproducible slope of ~2 between 1 and 8 M HNO₃, and scatter attributed to variable hydrolysis below 1 M HNO₃.¹¹ There was less uncertainty in the neptunium than in the plutonium measurements, both because the neptunium coefficients were not so extremely high, and because many more equilibrations were measured, taking advantage of the ready analysis of Np-238 tracer.

Fig. 13. Variation of Plutonium(IV) extraction coefficient with di(2-ethylhexyl)phosphoric acid concentration from nitric acid solutions. Diluent, Amsco 125-82

where dotted underlines indicate the organic phase, X represents the dialkylphosphoric anion, and the cation M^{++} is probably PuO^{++} or possibly $Pu(OH)_2^{++}$, $Pu(NO_3)_2^{++}$, etc. This formulation of the extracted complex is analogous to the formulations (at low loading) proposed for uranyl, $UO_2X_4H_2$, iron(III), $Fe(OH)X_4H_2$, rare earths, REX_6H_3 , and thorium, ThX_6H_4 .¹³

2.2.2 Plutonium(VI)

The extraction coefficient for plutonium(VI) with 0.1 M D2EHPA from ~4 M HNO₃ was ~10 (Fig. 14), nearly 3 orders of magnitude lower than for plutonium(IV). As generally found in the extraction of uranium(VI),^{14,15} the plutonium(VI) extraction coefficient was lower with an

Fig. 14. Plutonium(VI) extraction from nitric acid solutions by 0.1 M D2EHPA in Amsco 125-82 plus -

- × No modifier
- 2 v % Tridecanol
- △ 0.05 M TOPO

* Uranium(VI) extraction with 0.1 M D2EHPA in kerosene plus 2% 2-ethylhexanol.¹⁴

✕ Uranium(VI) extraction with 0.1 M D2EHPA in kerosene plus 0.1 M TBP.¹⁵

alcohol (tridecanol) and higher with phosphine oxide added to the extractant.* With the Amsco-alcohol diluent, the extraction coefficients rose with increasing nitric acid concentration from 2 to 8 M, parallel to uranium(VI) extraction.¹⁴ With tri-*n*-octylphosphine oxide (TOPO) present, the

*The effect of these additives is of interest because some such additive is needed when the extracted plutonium is to be stripped with carbonate solution,¹⁶ to maintain miscibility of the organophosphate salt in a diluent like Amsco 125-82 (see also Sect. 2.4, below).

extraction coefficients were much higher, although dropping sharply from 2 to 4 M HNO_3 . This is qualitatively similar to, but steeper than, the curve for uranium(VI) extraction with D2EHPA + TBP.¹⁵ At ~2 M HNO_3 , the plutonium(VI) extraction coefficient with 0.05 M TOPO is <100.¹⁶ Since the coefficient with 0.1 M D2EHPA alone is 4, the coefficient of 360 with the combination shows a synergistic enhancement of plutonium extraction corresponding to that in uranium extraction.¹⁵

2.2.3 Plutonium(III)

The extraction coefficients for plutonium(III) with 0.1 M D2EHPA from nitric acid solutions are much lower than for plutonium(IV), but it has not been possible to measure exactly how low. Direct extraction under a carbon dioxide atmosphere from solution reduced with ferrous sulfamate in the presence of excess sulfamic acid gave extraction coefficients ranging around 10^{-1} from nitric acid solutions 0.5 to 6 M and >1 from 8 M (Fig. 15). However, these extractions were suspected to involve some plutonium(IV) in spite of the precautions, in view of very low extraction coefficients with D2EHPA for RE(III) and for Am(III),¹⁷ and (2) experience encountered in extractions of reduced plutonium with amines¹⁸ and phosphine oxide.¹⁶ To test this, some of the extracts were scrubbed with 1 M HNO_3 , containing sulfamic acid to avoid oxidation by nitrite. A small fraction of the extracted plutonium was removed, as shown by the upper points in Fig. 15, indicating that most of the plutonium in the extract was plutonium(IV)* at the time of the scrub. However, it was not all indicated to be plutonium(IV), for which the expected distribution coefficient would have been $\sim 10^5$. The extreme assumption that the plutonium removed by the scrub was all that had been originally extracted as plutonium(III) permitted calculation of the extraction coefficients shown at the bottom of Fig. 4, which lie between 10^{-3} and 10^{-4} .

The entire extraction-scrub test series was repeated using hydrazine instead of excess sulfamic acid with the ferrous sulfamate reductant. This combination has been reported to be more effective in reducing and stabilizing plutonium(III).¹⁹ The results (Fig. 15) were similar to the previous results. Again the limiting assumption, that all the plutonium originally extracted as plutonium(III) remained at (III) and was removed in the scrub, led to calculated extraction coefficients for plutonium(III) lying between 10^{-3} and 10^{-4} . Since it is more likely that some plutonium(III) was oxidized before or during the extraction and some more was oxidized afterwards in the extract, the actual plutonium-

*An alternative possibility cannot yet be ruled out, that some new and nonstrippable species of plutonium(III) might have been formed in the organic phase.

(III) extraction coefficients probably lie between the limits indicated in Fig. 15, i.e., somewhere around the order of 10^{-2} .

Fig. 15. Plutonium extraction from reduced solution by 0.1 M D2EHPA in Amsco 125-82.

- Distribution in direct extraction.
- △ Distribution in subsequent scrub with 1 N HNO₃ containing 0.5 M NH₂SO₃H.
- Calculated distribution of Pu(III) in the original extraction.

Original aqueous solution reduced with -

- 0.1 M Fe(NH₂SO₃)₂ + 0.5 M NH₂SO₃H
- 0.1 M Fe(NH₂SO₃)₂ + 0.1 M N₂H₄

2.3 Separation of Transplutoniums from Lanthanons

(Boyd Weaver and J. P. Eubanks)

A study of the extraction of americium and some of the lanthanons by various solvents has been made in a search for new methods of separating the transplutonic elements from fission product lanthanons. From practical considerations the most desirable solvent system is one in which the transplutoniums are extracted considerably better than the fission product lanthanons and yttrium. This is because the heavier transplutoniums are generally more extractable than americium. Hence, in systems where americium is less extractable than the lanthanons, the extractabilities of the more valuable heavier transplutoniums will be closer to those of the lanthanons and may overlap, preventing separation. The corresponding difficulty may exist to some degree in systems where americium is more extractable than the light lanthanons in that heavier lanthanons may be produced in parallel to production of the heavier transplutoniums, and the extractability of these might overlap that of americium and even the heavier transplutoniums. However, the fact that Gd^{158} has a low thermal neutron absorption cross section will impede the production of the heavier lanthanons, and they may prove to be negligible.

2.3.1 Experimental Procedures

Reagents which have been studied include amines and organophosphorus compounds. The study of an individual compound was continued only as long as it appeared promising for use in separations. Therefore, in several instances where results were not reproducible, attention was soon shifted to more promising reagents instead of continuing attempts to resolve the inconsistency. Also, little work was done with systems in which the extraction of americium was between those of cerium and europium. For example, a single test was made to determine that americium behaves almost exactly like neodymium²⁰ in extraction by TBP from nitric acid. This system, which gives good separation of fission product lanthanons on a multistage basis²⁰ and has been used for separation of americium from lanthanum,²¹ appears to have no applicability to the present problem. Other systems involving nitrates and one sulfate system were also soon eliminated on the basis of low distribution coefficient or lack of separation. As a result of this process of elimination, continued studies were made almost entirely with highly concentrated chloride solutions. Since concentrated HCl is undesirable, the necessary chloride concentration was obtained from LiCl. The diluent for most tests was Amsco 125-82, which gave organic solutions compatible with concentrated LiCl solutions of low acidity.

A 10 N LiCl solution is viscous and hygroscopic. Since pipettes deliver less of this solution than their calibrated delivery volume, distribution coefficients obtained by counting radioactivity in "TD" pipetted samples of organic and aqueous solutions are larger than the actual coefficients unless the organic phase is equally viscous. Since the chief interest in this study has been in separation factors, or ratios of coefficients under identical conditions, absolute values for coefficients were usually unnecessary. The determination of optimum flow ratios for multistage countercurrent tests does require accurate coefficients. Coefficients for Am should be free of such bias since the Am samples were total volumes in "TC" micropipettes. The net result is that the actual Am/RE separation factors may be higher than the apparent separation factors where Am is the most extractable element.

Prolonged exposure of the LiCl-HCl solutions to the atmosphere was carefully avoided to prevent absorption of water, and also to prevent loss of HCl, which has a high vapor pressure over 10 N LiCl.

Solid LiCl is very hygroscopic. Weight loss measurement of fresh bottles of Baker's Analyzed Reagent LiCl indicated H₂O contents up to 6%. Analysis of a bottle which had been opened previously showed 14% H₂O. A considerable number of the initial tests reported here were made with aqueous solutions prepared from nominally 10 M LiCl which was probably actually only 9.0 to 9.5 M LiCl. Since comparisons of elements were made simultaneously with identical solutions, the only errors are in absolute values of coefficients, not in separation factors, unless the separation factors are affected significantly by LiCl concentration differences. Recent tests were made with solutions prepared from LiCl which had been thoroughly dried at 120°C.

Lithium chloride and HCl are extracted by several of the reagents. For example, 1 M tributylphosphate (TBP) in Amsco 125-82 was 0.5 N in LiCl when in equilibrium with 10 N LiCl, 0.1 N HCl. Undiluted TBP had a LiCl content of 1.27 N under the same conditions. Inaccuracies due to changes in concentration resulting from extraction were avoided by pre-equilibration of the organic phase with the test solution and/or a similar solution free of acidity. Since distribution coefficients with some of the reagents are impracticably low except at very low acidities, an attempt was made to control acidity by glass electrode pH measurement. The indicated pH of a 10 N LiCl solution was ~6.5. Indication of some precipitation of europium in such a solution suggested that the pH reading was about right. Addition of sufficient HCl to reduce the pH reading to 3 removed all trace of precipitation. However, the pH reading was reduced to zero by adjustment to only 0.0025 N HCl instead of to

1 N HCl. Thus, the pH readings have a very limited range of usefulness in acidity adjustment. Most of the work on extraction by TBP was performed with acidity of 0.1 N HCl, since useful coefficients are obtained in this range.

In most of the tests 10 ml volumes of the organic phase were contacted with equal volumes of the appropriate aqueous solution. The active isotopes were introduced into the aqueous phase without diluting it, by first evaporating to dryness and then dissolving in the aqueous phase. Isotopes used were Ce¹⁴⁴, Nd¹⁴⁵, Pm¹⁴⁸, Eu¹⁵², Y⁹¹ and Am²⁴¹. Relative rare earth concentrations were determined by counting the γ activity of 2-ml samples in a well-type scintillation counter. Americium coefficients were determined by counting the α activity of 0.1 ml aliquots of samples dried on metal plates. Preliminary separations by coprecipitation with LaF₃ were made to remove salts from the Am and give nearly weightless samples.

2.3.2 Tests with Primary Amine

Extractions of Am, Ce and Eu from 0.1 N H₂SO₄ by 0.4 M Primene JM-T in Amsco 125-82 were essentially identical with distribution coefficients, E_a^O , of about 100. Extractions of Ce, Nd, Pm, and Eu from 1 N H₂SO₄ also showed no useful differences, with E_a^O of about 2. Extractions of Eu from 10 N LiCl with or without 1 N HCl gave $E_a^O < 0.001$. From 10 N LiNO₃ the E_a^O was about 0.02. The reagent was partially stripped from the solvent by contact with LiCl solutions and almost completely by LiNO₃.

2.3.3 Tests with Tertiary Amine

Extractions of Am, Ce, and Eu from 8 N LiNO₃, 0.1 N HNO₃ by 0.3 M trilaurylamine (TLA) in xylene indicated preferential extraction of Ce, with the order Eu:Am:Ce $\approx$ 1:1.5:8. In addition to the unfavorable position of Am, coefficients were not constant but decreased with successive extractions (probably because of imperfect acid pre-equilibration for the initial extractions).

2.3.4 Tests with Quaternary Ammonium Compounds

Extractions of Am, Ce, and Eu from 8 N LiNO₃, 0.1 N HNO₃ by 0.1 M tetra-*n*-heptyl ammonium nitrate (THAN) were in the order Ce:Am:Eu $\approx$ 1:5:8. This is the reverse of trilaurylamine in order and magnitude. Extractions from 10 N LiCl, 0.01 N HCl by 0.1 M tetra-*n*-heptyl ammonium chloride (THACL) were in the order Ce:Am:Eu $\approx$ 1:2.7:3.5.

2.3.5 Tests with Monoalkylphosphoric Acid

Study of monododecylphosphoric acid (MDDPA) was started for comparison with mono(2-ethylhexyl)phosphoric acid

(M2EHPA), which was known to extract lanthanons preferentially to Am, but with very little separation between cerium and lanthanum.^{22,23} However, neither extraction coefficients nor separation factors for Ce and Eu were reproducible on repeated equilibrations, and no tests were made with Am. The results that were obtained showed preferential extractions of Eu over Ce by factors of 1.5 to 5, in distribution between 1 M MDDPA in Amsco 125-82 and 10 N LiCl with acidities ranging from pH 3 to 0.2 N HCl. This extraction preference is in the same direction as that with M2EHPA, but does not provide a direct comparison.

2.3.6 Tests with Dialkyl Phosphonates

Dialkyl Alkylphosphonates. In tests with 1 M diamyl amylphosphonate (DAAP) in Amsco and slightly acid 10 N LiCl solutions, maximum separations obtained were in the order Ce:Eu:Am $\approx$ 1:1.5:6. There was considerable variability. Results with di-n-butyl butylphosphonate were similar.

Dialkyl Arylphosphonate. The first results with di-n-butyl phenylphosphonate (DnBPP) gave separations in the order Ce:Eu:Am $\approx$ 1:4:8. Yttrium was similar to Eu. Several series of distribution experiments gave consistent results, but later there were variations by a factor of 10 under apparently identical conditions. Conditions may have been too difficult to control with acidities around 0.01 N. The possibility of impurities in the reagent was considered, but exhaustive treatment with Na₂CO₃ and mixtures of Na₂CO₃ and Al₂O₃ did not give consistent changes. Decreases in coefficients with successive contacts with LiCl solutions suggested stripping of a highly extracting impurity, but such decreases did not always occur.

Because of the indicated high separations in the desired direction, and in spite of the inconsistencies encountered, multistage separation was tested with DnBPP. On the basis of what appeared to be the best data, a batch countercurrent experiment was set up for the separation of Am from Eu in 12 separatory funnels. The organic stream was purified 1 M DnBPP in 80% Amsco--20% xylene. The aqueous stream was nominally 9.9 M LiCl, 0.1 M HCl, and the feed was a mixture of Am and Eu in 9.8 M LiCl, 0.1 M HCl. On the basis of EQ's of 2.0 for Eu and ~6 for Am, the volumes in each funnel were set initially at 5 ml organic and 15 ml aqueous. The feed was introduced batchwise as 1 ml in the 6th stage from the top (giving 16 ml aqueous in stages 6-12). Phases were contacted and transferred in a diamond pattern with takeoff of organic and aqueous at either end. When analyses of the organic at the top and aqueous at the bottom showed that the Eu was moving predominately upward, the organic volumes were changed to 4 ml and the aqueous to 20 ml. After 54 additions of feed, analyses showed a high degree of reflux toward the

feed point. E_a^0 for Eu was 3.2 at both ends of the system and 4.4 at the feed stage. E_a^0 's for Am were 5.4 and 6.5 at bottom and top stages. Single-stage separation factors were 1.7 and 2.0. These data are inconsistent with the refluxing which occurred.* Because of these uncertainties about the system, the experiment was discontinued at this point.

2.3.7 Tests with Tributylphosphate

Preliminary distribution coefficients for Ce, Eu and Am between 1 M TBP in Amsco 125-82 and 9.9 M LiCl--0.1 M HCl were 0.20, 0.38, and 1.35, respectively. A 12-stage separation experiment was set up on this basis. Volumes were 20 ml organic, 15 ml aqueous, and 0.5 ml feed. The experiment was continued until 125 batches of feed had been added. The 12-stage system was predicted to give a separation of 3.4^6 or ~1550. The apparent factors found by analysis were near 2000 early in the test, but fluctuated as low as 300 and as high as 17,000. Toward the end of the test the separation factor appeared to decrease systematically, dropping finally to ~300 again.* (The value of 300 is about the separation expected in 10 stages.) At the end, 98% of the Am was leaving in the organic stream, and 87% of the Eu was leaving in the aqueous. The extraction coefficients for Eu were 0.45 at the ends and 0.9 at the feed stage. In spite of the unexplained variations, these results confirm this system as a promising one for the americium-lanthanum separation.

Europium is a minor constituent of fission-product rare earths and can be removed from Am well enough with only a moderate separation factor in each stage. Any process with good separations between Am and Eu and between Eu and Ce should give high separation between Am and the abundant but inactive lanthanons as well as from the very active and abundant promethium. However, it will not separate Am from abundant Y unless Y falls within the light lanthanum series. In comparison of TBP extractions of Am, Eu, and Y from LiCl solutions, it was found that Y behaved almost exactly like Eu. Thus Y can be separated from Am, but it must be considered as an abundant element with a rather small separation factor in calculating stage requirements.

Of the heavier lanthanons, only lutetium, the most readily available as a tracer, Lu^{177} , has been studied.

*Tests in progress indicate significant degradation of TBP in contact with acidic 10 N LiCl, suggesting that buildup of degradation products during prolonged contact in the batch countercurrent test may have contributed to the shifting separation factor with TBP, and also with DnBPP.

Surprisingly, this showed separation factors of 20 or more from Eu. This indicates higher separation factors between adjoining heavy lanthanons than between the lighter elements. In all extraction systems which have been studied previously, the reverse is true. In the present case, further study should include tests of intermediate elements.

Extraction of Am and lanthanons from LiCl is greatly increased by the addition of a small amount of nitrate. E_A^0 for Eu between 1 M TBP and 8.9 M LiCl, 0.1 M HCl, 1.0 M LiNO₃ was about 3000. Acidity must be kept low to avoid reactions between the chloride and nitrate. TBP and phosphonates also give very high extraction of rare earths from concentrated LiNO₃ of low acidity. While such high extractions are not useful for separations, they can be useful in concentrating the values.

2.3.8 Summary

The information above is summarized graphically, along with some data from other sources, in Fig. 16. Where only a few elements have been tested, there is no certainty that intermediate elements fall on a straight line, but reversals in direction are unlikely within the first half of the lanthanide series. The chart shows that extractabilities of Am by M2EHPA and TBP are respectively entirely below and above the fission product (light) lanthanons. Extraction of Am by DAAP appears to be higher than all the lanthanons. Extractions by DnBPP and TBP are greater for Am than for any lanthanon likely to be present in significant amounts in the transplutonics. With the other reagents, extraction of Am is intermediate in the fission products.

Of the apparently useful reagents, M2EHPA appears satisfactory for separation of Am from the lanthanons. However, it does not separate the other transplutonics, Leuze having found that Cm and La extract alike. This reagent may be useful for separations within the transplutonic group, such as between Cm and Cf. Berkelium can be separated by extraction after oxidation, unless this is prevented by the extremely high radioactivity from considerable amounts of these elements. The phosphonates appear to be adaptable to separations between the transplutonics and all the lanthanons which are likely to be present. However, experience with the phosphonates has given many inconsistencies, which have not yet been investigated enough to determine whether they are characteristic of the reagents, or were fortuitous in these tests. The most promising results thus far have been obtained by extraction from concentrated LiCl by TBP. The phosphonates and TBP can also be useful in transferring values from one phase to another with a large reduction in volume.

Fig. 16. Relative Extractabilities of Rare Earths and Americium in Various Systems

- Lanthanons, as indicated on abscissa
- Elements (Y, Cm) outside of lanthanons

2.4 Solvent Screening (K. A. Allen, W. J. McDowell, G. N. Case)

Attempts to find a solvent which would keep the sodium salt of di(2-ethylhexyl)phosphoric acid (NaD2EHP) in solution in the organic phase under a wide variety of aqueous phase conditions have led to a study of the solubility of NaD2EHP under various conditions in several solvents, and a general search for a solvent extraction diluent of better characteristics than those commonly in use. The major faults of the kerosene type solvents now used appear to be poor solubilization power for the reagents under some conditions (e.g., separation of NaD2EHP, precipitation of amine nitrates and bisulfates, separation of thorium-nitrate-TBP complex) and the presence of components, varying from batch to batch, which can seriously affect the affinity of the organic phase for certain fission products.

For a practical solvent the following are desirable characteristics: (1) low solubility in water, (2) flash point $\geq 140^{\circ}\text{F}$, (3) low volatility (B. P. $>100^{\circ}\text{C}$), (4) low toxicity, (5) partially aromatic structure, (6) a pure chemical compound, (7) reasonable cost (probably 50¢/gal or less), (8) adequate solubilization power for the reagents, and (9) no adverse effects on the extraction ability of the reagents.

With NaD2EHP in a nitrate system the aqueous salt concentration which produces the most serious solubility problem is ca. 1 M at pH ≥ 10 . At this aqueous composition NaD2EHP remains insoluble in the aqueous phase but neither is it sufficiently soluble in the organic phase when benzene or kerosene is used as a solvent. Instead, a large portion of the NaD2EHP forms a third phase containing mostly NaD2EHP with small amounts of water and benzene. The solubility of NaD2EHP in benzene as a function of aqueous NaNO_3 M at an aqueous pH of ca. 10 may be seen in Table 12.

Table 12.. Solubility of Sodium Di(2-ethylhexyl)phosphate in Benzene when Solution is in Equilibrium with 0.05 M NaOH - Various Concentrations of NaNO_3

Conc. of NaNO_3	Solubility of NaD2EHP in Benzene
0.4	0.001 M
1.0	0.013
2.0	0.057
3.0	>0.5
4.0	>0.5
6.0	>0.5

Using as a test the system 1 M NaNO₃ at pH vs an organic phase containing NaD2EHP, various solvents which were available and which might have a possibility of fulfilling the requirements outlined above were screened. The results may be seen in Table 13. Of these solvents n-butyl ether, dibutyl carbitol and di-isobutyl ketone were chosen as most nearly approaching the desirable properties listed previously and at the same time having good solubility properties. For further checking, these three, plus sec-butylbenzene representing the substituted benzenes and n-nonane as a kerosene-like compound, were tested as solvents for the following four extraction reagents: tri-n-octylamine (TOA), di-n-decylamine (DDA), tri-n-butylphosphate (TBP) and di(2-ethylhexyl)phosphoric acid (D2EHPA). These reagent-solvent combinations were tested in contact with typical aqueous phases used with the various reagents. The performances of the solvents are recorded in Table 14. Comparison of the extraction coefficients for uranium with each type of reagent in the different systems may be seen in Table 15.

The n-nonane was the least versatile of the five solvents from the standpoint of reagent solubility, being insufficient for either the nitrate or the sulfate of either amine, or for NaD2EHP. None of the solvents held as much as 0.02 M DDA nitrate. Excluding n-nonane, the solubilities of DDA nitrate were nearly alike, slightly higher in the ketone

Table 13. Solubility of Sodium Di(2-ethylhexyl)phosphate in Various Solvents

Solvent	Solubility of D2EHPA	Phase Separation
Toluene	0.017 M	
Xylene	<0.002	
Ethylbenzene	0.009	
Sec-butylbenzene	<0.002	
Tert-butylbenzene	<0.002	
N-butylbenzene	<0.002	
Mesitylene	0.019	
2-Ethylbutyl cellosolve	>0.10	Poor
3-Phenyl-1-propanol	0.096	Poor
Diisobutyl ketone	>1.0	Good
n-Butyl ether	>1.0	Excellent
1-Chloronaphthalene	<0.002	
p-Chlorotoluene	<0.002	
Chlorobenzene	0.025	
n-Hexyl chloride	<0.002	
Ethylene dichloride	<0.002	
Dibutyl carbitol	>1.0	

Table 14. Solubility of Some Reagents in Selected Solvents under Various Conditions

Reagent Solubility (M) in Equilibrium with					
1 M SO ₄ , pH 1			1 M NO ₃ , pH 1		
U Free	3/4 U Loaded	U Free	3/4 U Loaded	10% Na ₂ CO ₃	
Sec-Butylbenzene					
TOA	>0.2	>0.2	>0.2	>0.2	>0.2
DDA	>0.2	>0.2	0.0122	0.0130	>0.2
TBP	>0.2	-	>0.2	>0.2	>0.2
D2EHPA	>0.2	>0.2	>0.2	>0.2	0.002
n-Butyl Ether					
TOA	>0.2	>0.2	>0.2	>0.2 ^a	>0.2
DDA	>0.2	>0.2	0.0122	0.0140	>0.2
TBP	>0.2	-	>0.2	>0.2 ^a	>0.2
D2EHPA	>0.2	>0.2	>0.2	>0.2	>0.2
Nonane					
TOA	0.011	0.065	0.011	0.028	>0.2
DDA	<0.0005	<0.0005	<0.0005	<0.002	>0.2
TBP	>0.2	>0.2	>0.2	>0.2	>0.2
D2EHPA	>0.2	>0.2	>0.2	>0.2	0.002
Dibutyl Carbitol					
TOA	>0.2	>0.2	>0.2	>0.2	>0.2
DDA	>0.2	0.0906 ^b	0.0134	0.0130	>0.2
TBP	>0.2	-	>0.2	>0.2	>0.2
D2EHPA	>0.2	>0.2	>0.2	>0.2	>0.2
Isobutyl Ketone					
TOA	>0.2	>0.2	>0.2	>0.2	>0.2
DDA	>0.2	>0.2	0.0177	0.0190	>0.2
TBP	>0.2	-	>0.2	>0.2	>0.2
D2EHPA	>0.2	>0.2	>0.2	>0.2	>0.2

^aU ppt in aqueous.

^bU ppt at interface.

Phase separation on TOA and DDA was slower than other two reagents; DDA being slower of the two.

Table 15. Uranium Extraction Coefficients
in Various Solvents

Solvent	Reagent (0.2 M)			
	D2EHPA from Nitrate	D2EHPA from SO ₄	DDAS from SO ₄	TBP from NO ₃
Sec-Butylbenzene	900	8.3	34	0.73
n-Butyl ether	1200	7.0	5.8	0.73
Nonane	2900	19.3	10	0.41
Isobutyl ketone	1000	7.5	17	0.65
Dibutyl carbitol	1300	4.3	ppt in aq	ppt in aq

All aqueous phases 1 M in the anion at pH ca. 1.

than in the others. Both hydrocarbons held only 0.002 M NaD2EHP, while all three oxygenated solvents held the maximum tested (0.2 M). All five held the 0.2 M maximum tested of TBP*, of acid-form D2EHPA, and of free-base form amines. The physical properties of the solvents listed in Table 16 indicate that most of the other requirements listed above are reasonably well met by all of them (remembering that a higher homolog of the nonane would be required to meet 140°F flash point).

In summary, four commercially available solvents, each normally a single compound rather than a mixture have shown evidence of meeting certain requirements for potential utility in general solvent extraction technology. Additional groups of compounds suggested by the behavior of these four include other substituted benzenes, the phenyl-alkyl ethers, and the phenyl alkyl or diphenyl carbitols or cellosolves.

Table 16. Physical Properties of Solvents

Solvent	Solubility, %		Flash Pt	BP, °C	Toxicity
	in water	water in	Open Cup, °F		
Sec-Butylbenzene	<0.01	<0.01	~140	173	Low
n-Butyl ether	0.03	0.19	100	142	Moderate
Nonane	<0.01	<0.01	88	151	Low
Dibutyl carbitol	0.3	1.4	245	255	Low
Isobutyl ketone	0.05	0.75	140	169	Low

*Note also satisfactory performance of >1 M di-sec-butyl-phenylphosphonate in sec-butylbenzene, Sect. 2.5 (below).

2.5 Solubility of Di-sec-butyl Phenylphosphonate (DSBPP) and Tributylphosphate (TBP) Complexes of Uranyl and Thorium Nitrates in Sec-butylbenzene* (A. T. Gresky, R. G. Mansfield)

Organic phases of 1.12 M DSBPP-sec-butylbenzene were contacted and equilibrated with crystalline (1) $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in one case, and (2) $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in the other to effect uranium and thorium saturation of the DSBPP reagent. After centrifugation the two organic phases were found to contain uranium and thorium concentrations of 0.492 M $\text{UO}_2(\text{NO}_3)_2$ and 0.358 M $\text{Th}(\text{NO}_3)_4$, respectively. Assuming an organic volume increase of 10%, the values correspond to complexes of 2.04 DSBPP· $\text{UO}_2(\text{NO}_3)_2$ and 2.8 DSBPP· $\text{Th}(\text{NO}_3)_4$. A small amount of crystallization occurred after standing a few weeks, but resolution was effected by warming.

Parallel saturation tests with 1.03 M TBP-sec-butylbenzene and the two crystalline salts produced centrifuged organic phases of 0.496 M $\text{UO}_2(\text{NO}_3)_2$ and 0.449 M $\text{Th}(\text{NO}_3)_4$. These data, assuming a 10% volume increase of the organic phases, suggested soluble TBP complexes of 2.0 TBP· $\text{UO}_2(\text{NO}_3)_2$ and 2.1 TBP· $\text{Th}(\text{NO}_3)_4$.

Little or no objectionable nitration by-product was formed in one test in which the 1 M TBP-sec-butylbenzene was boiled under reflux with 2 M HNO_3 for 4 hr. After removal of low molecular weight degradation products of TBP and diluent into sodium carbonate, extraction of Zr-Nb⁹⁵ was low and about the same as with undegraded solution. If nitrohydrocarbons, preferentially soluble in the organic extract, had been formed, appreciable Zr-Nb extraction would be expected (cf. Sect. 2.6).

These scouting tests indicate that sec-butylbenzene may be feasible as a TBP or DSBPP diluent for uranium and thorium process applications insofar as complex solubility and stability are concerned.

2.6 Diluent Nitration and Its Contribution to the Problem of Solvent Cleanup (C. A. Blake, J. M. Schmitt, W. E. Oxendine)

Previous reports have described experiments which show that many of the difficulties encountered in cleaning up used TBP-Amsco 125-82 solvent stem from degradation of the Amsco 125-82 diluent.^{6,24} Most of the degradation products

*Cf. Sect. 2.4

of TBP, which accounted for much of the extraction of contaminating fission products, are rather easily removed by simply washing the solvent with sodium carbonate or sodium hydroxide. This procedure, however, does not remove the diluent degradation products which, if left in the solvent, can act in combination with TBP to give strong, apparently synergistically enhanced, extraction of zirconium-niobium. Previous studies at ORNL and by other investigators²⁵ have shown these diluent degradation products to be nitrogen-containing compounds. Recent studies have been conducted at ORNL to determine more specifically the types of nitrogen compounds that are most responsible for the diluent behavior.

In the tests described below, three nitrogen-containing hydrocarbon compounds, a nitrite (R-ONO), a nitrate (RONO₂), and a nitro-compound (RNO₂), were synthesized and compared to Amsco 125-82 which had been degraded by refluxing with concentrated nitric acid. It was found that the nitro compound (RNO₂) gave the same infrared spectrum and performed in extraction tests similarly to nitric acid-degraded diluent as well as a nitrogen-bearing component that had been separated from degraded diluent. In addition, the observed behavior of the degraded diluent in extraction operation is consistent with the known chemical properties of nitrohydrocarbons.

This identification of the most probable of the "bad actors" in process solvents gives a positive direction to studies of means to circumvent the problem. Selection of diluents with few sites active to nitration is an obvious suggestion and such diluents are being sought. In the event that sufficiently stable diluents are not available, studies are being made of methods for removing nitrohydrocarbons such as taking advantage of their acid-base properties to form aqueous soluble salts.

2.6.1 Isolation and Identification of Amsco 125-82 Degradation Products

A sample of Amsco 125-82 was severely degraded by boiling with an equal volume of 8 M nitric acid under total reflux for ~6 hr. In accordance with procedures studied previously²⁴ a part (possibly all) of the organonitrogen products from the degradation reaction were sorbed on chromatographic grade alumina. The alumina was washed first with petroleum ether to remove undegraded diluent, and next with acetone to remove the sorbed material. Acetone was removed from the wash by evaporation, leaving a product which analyzed 75.2% C, 12.6% H and 2.7% N.

Infrared analysis, made by C. A. Horton of the ORNL Analytical Chemistry Division, showed the following bands with the degradation product which did not occur with the original Amsco 125-82:

Band (μ)	Relative Strength	Possible Vibration
6.4	Very strong	Nitro ($-\text{CNO}_2$)
7.4	Moderately strong	Nitro ($-\text{CNO}_2$)
5.8	Moderately strong	Carbonyl ($-\text{C}=\text{O}$)
2.8	Moderately weak	Carboxyl ($-\text{COOH}$) or hydroxyl ($-\text{OH}$)

The 6.4 and 5.8 μ bands could also represent nitroso ($-\text{CNO}$) and lactam ($\text{NH}(\text{CH}_2)_n\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$) groups, respectively. However,

these groups are unlikely products of the degradation treatment since (1) each requires trivalent nitrogen to be present in a highly oxidizing medium and (2) hot aqueous acidic conditions are not conducive to either the formation or the stability of lactams. The moderately strong absorption in the region characteristic of carbonyl groups may be misleading in that acetone was used in the isolation of this product and would, if not completely removed, affect the strength of this band. On the other hand, the presence of some oxidation products is definitely indicated by the weak band at 2.8 μ . In addition to the bands listed, both untreated Amsco and the nitrated product showed strong bands representative of branched aliphatic hydrocarbons.

The presence of aliphatic nitrohydrocarbons and oxidation products has been confirmed by the infrared absorption studies of W. H. Baldwin, ORNL Chemistry Division.²⁶ In a further test Baldwin dissolved some of the nitrated product in a mixture of sodium hydroxide and sodium nitrite. Upon acidification a faint blue-green color was developed typical of that given by secondary nitro groups (RR_1CHNO_2). Although this test cannot be considered conclusive (the molecular weight of the compounds tested are probably much higher than those of the compounds for which the test was developed), it bears considerable significance in combination with the weight of infrared evidence.

Preparation, Identification and Properties of Three Nitrogen-Containing Aliphatic Hydrocarbons. Three nitrogen-containing aliphatic hydrocarbons were synthesized to compare their effect on the extraction performance of TBP-Amsco 125-82 solutions with that of the chemically degraded Amsco 125-82. Adaptation of standard methods were used by H. L. Holsopple of the ORNL Analytical Chemistry Division to prepare nitrooctane²⁷ ($\text{C}_8\text{H}_{17}\text{NO}_2$), decyl nitrite²⁸ ($\text{C}_{10}\text{H}_{21}\text{ONO}$), and octyl nitrate²⁹ ($\text{C}_8\text{H}_{17}\text{ONO}_2$). Although the purity of the compounds has not been established, infrared spectra prove the presence of major amounts of the groups characteristic of the three compounds named, with little or no cross contamination. Only the nitrooctane showed the characteristic band at 6.4 μ which occurred in the nitrated Amsco product.

The chemical literature, while generally describing properties of compounds of low molecular weight, supports the conclusion that nitrohydrocarbons are among the most likely products of nitration of Amsco 125-82. A few pertinent observations from the literature follow: (1) The direct introduction of nitro groups into aliphatic hydrocarbons is usually possible by means of dilute or concentrated nitric acid. The nitration is particularly easy with hydrocarbons containing secondary and tertiary carbon atoms;³⁰ (2) Primary hydrogens on methyl groups attached to tertiary carbon atoms have been substituted by nitro groups;³¹ and (3) Nitrites (and nitrates) are easily hydrolyzed by alkalies or acids whereas the nitro compounds cannot be hydrolyzed.³⁰

2.6.2 Comparison of Nitrated Hydrocarbons and Degraded Amsco 125-82

In experiments described in previous reports the presence of diluent nitration products was best detected by Zr-Nb extraction behavior after treatment of the solvent with calcium hydroxide. TBP-fresh diluent solutions became poorer extractants of Zr-Nb after the calcium hydroxide scrub while TBP-degraded diluent solutions became stronger extractants. The extraction strength increased with the severity of degradation or, presumably, with increasing nitration product concentration.

The three compounds synthesized as described in the previous section and the nitrated hydrocarbon product extracted from degraded Amsco 125-82 were added to fresh Amsco 125-82 and each solution was made one molar in TBP. These solutions were compared in Zr-Nb extraction tests with 1 M TBP in fresh Amsco and in nitric acid-degraded Amsco. As shown in Table 17, only the nitrooctane and the nitrated Amsco product performed like the degraded Amsco in the tell-tale calcium test. Because of the uncertainty in concentrations of the various compounds, their relative effects cannot be evaluated. However, the nitrooctane solution is considered likely to be the most concentrated in nitrohydrocarbon compounds, and this solution showed the largest effect.

In further tests the nitrooctane-spiked solvent was treated after an alkaline scrub with 200 g activated alumina/liter solvent. Following the treatment Zr-Nb extraction was lower than after the alkaline scrub alone, indicating removal of some of the nitrohydrocarbon; e.g., activity in the organic phase after alkaline scrub and alumina treatment was ~180 γ c/s/ml, but after the alkaline scrub alone the activity was ~260 γ c/s/ml. In addition, the activity remaining after three 2 M nitric acid scrub stages was lowered by the alumina treatment, 20 vs 70 γ

Table 17. Zr-Nb⁹⁵ Extraction Tests with 1 M TBP in
Diluents Containing Nitrated Hydrocarbons

Description of Material	Activity in 1 M TBP Organic Phase (γ c/s/ml)					
	Fresh Amsco	Degraded Amsco	95% Amsco 5% Nitrated Amsco Product	90% Amsco 10% Nitrooctane	90% Amsco 10% Octyl- nitrate	90% Amsco 10% Decyl- nitrite
Alkaline Scrub						
Extraction stage	95	220	930	260	160	130
3rd Scrub stage	9	30	470	70	1	27
Ca(OH) ₂ Treatment						
Extraction stage	58	2300	2800	8200	89	94
3rd Scrub stage	1	370	720	6900	10	15

Alkaline scrub: Either 0.2 M Na₂CO₃ or 0.5 M NaOH, equal volumes aqueous and organic phases, 2 contacts, 10 min ea.

Ca(OH)₂ treatment: Alkaline scrub, followed by contact for 1 hr with Ca(OH)₂ solid, 200 g/liter organic phase.

Extraction: From 2 M nitric acid containing 1×10^4 c/s/ml Zr-Nb⁹⁵ γ activity, equal volumes, 10 min contact.

Scrub: Three successive scrubs, equal volumes aqueous and organic phases, with 2 M nitric acid.

c/s/ml. The sorption of the nitrated species on alumina has been observed previously,²⁴ and as described above, was the basis for the isolation of the nitrohydrocarbon fraction from degraded Amsco. [Additional tests, similar to those described in Table 17 but for which data are not reported, were made with two small samples of purified 1-nitrooctane and 2-nitrooctane which had been prepared at Purdue University.* Both were found to be adversely affected by the calcium hydroxide treatment with the former extracting slightly more Zr-Nb activity and retaining 5 times as much after 3 successive nitric acid scrub stages. It was also established that the 1-nitrooctane at the same concentration in the Amsco 125-82, but without TBP, showed no extraction ability.]

Solutions of 1 M TBP in Amsco 125-82 containing nitro-octane or the nitrated Amsco product were also examined at concentrations below those shown in Table 17. The dependence of Zr-Nb extraction on dilution is shown in Fig. 17. Each reagent extracts more Zr-Nb with increasing concentration. At low concentrations of the nitro compounds treatment with calcium hydroxide after alkaline scrubbing is more effective in decreasing Zr-Nb extraction than alkaline scrubbing alone, but with increasing reagent concentration higher extraction eventually results. More of the nitrated Amsco product is required for this to happen than of the nitrooctane, which is reasonable in view of the higher probable nitrohydrocarbon content of the latter. The acid scrub data show the same trends.

Ruthenium extraction by the initial Amsco product was also tested briefly. Previous experiments⁸ with Ru¹⁰⁶ showed degraded diluent to have no immediate effect on extraction or stripping, but after aging of the pregnant extract the Ru was stripped with difficulty. In the current tests Ru¹⁰⁶ was extracted by several 1 M TBP solutions, the first in fresh Amsco only, the second in Amsco degraded 4 hr with 2 M HNO₃ at 107°C, and third in 95% fresh Amsco-5% nitrated Amsco product. The samples were aged for 50 days. Table 18 shows the difficulty encountered in stripping the treated diluents with 2 M nitric acid. While 88% of the Ru¹⁰⁶ was stripped from the fresh Amsco sample, only 40-60% was stripped from the other two. Actually, stripping was achieved more easily from the untreated Amsco sample after 50 days than at 0 days. A shift of the extractable Ru complex toward less extractable varieties, and at the same time a very gradual complexing of some of the Ru with degradation

*Supplied by Prof. A. L. Myers, Carson-Newman College, who obtained them originally from Prof. Nathan Kornblum, Purdue University. Prepared and purified by students of Prof. Kornblum during summer of 1958.

Fig. 17. Extractions with 1 M TBP-Amsco Solutions Containing Nitrohydrocarbon Compounds.

Extraction from 2 M HNO_3 , 1×10^4 c/s/ml Zr-Nb^{95} γ , equal vol, 10 min contact

— Scrub with equal volume of 0.2 M Na_2CO_3 or 0.5 M NaOH , 2 contacts, 10 min ea.

- - - Scrub with alkaline solutions as above, also with $\text{Ca}(\text{OH})_2$ at 200 g solid/liter organic phase for 1 hr.

Table 18. Ruthenium Stripping from Aged 1 M TBP Extracts

Diluent	Days Aged	Ru ¹⁰⁶ γ Activity in Organic Phase (initially 400 c/s/ml)			
		Remain after 2 M HNO ₃ Scrub			Percent of Initial Activity after 3rd Scrub Stage
		1st Stage	2nd Stage	3rd Stage	
Fresh Amsco	0	235	160	120	30
	50	125	70	45	12
Degraded Amsco	50	230	195	160	40
95% Fresh Amsco- 5% Nitrated Product	50	300	260	240	60

products, is indicated. The latter complex is very strong, resisting stripping with even 8 M nitric acid.

On the basis of the tests described above it is generally apparent that the Zr-Nb and Ru extraction patterns with the nitrohydrocarbons correspond to those of Amsco 125-82 degraded with nitric acid. Preliminary indications from current tests show that irradiation of TBP-Amsco 125-82-nitric acid solutions (Co⁶⁰ γ source) produces compounds behaving similarly.

Comments on Extraction Properties of Nitrohydrocarbons.
The extraction behavior of degraded diluent can be explained in terms of several known reactions of the nitrohydrocarbons. One important reaction is the ability of the primary and secondary derivatives to exist in tautomeric forms,

(Because it lacks the necessary hydrogen atom, a tertiary nitro-compound would be incapable of this isomerization.) A slow approach to equilibrium is characteristic of the tautomeric shift. The literature³² describes one case where in the absence of a catalyst nitro camphor required 6 years for tautomeric equilibrium to be established in N/10 trichloroacetic acid in chloroform. Treatment with basic reagents catalyzes the forward reaction of equation 1 and the salt of the acid is formed, e.g.,

Reactions in both directions of equation 2 proceed at a measurable rate.

Another and possibly most significant reaction is between TBP and nitrohydrocarbons. Previous experiments indicated such a reaction showing that only when both components were present was there strong Zr-Nb⁹⁵ extraction. Further evidence of the reaction has now been obtained. In these tests Amsco 125-82 was degraded by contact with 2 M nitric acid at 107°C for 4 hr. The degraded diluent was used to prepare a 1 M solution of TBP. Extraction of Zr-Nb⁹⁵ activity from 2 M nitric acid was measured immediately after preparation of the 1 M solution and at intervals up to ~30 days. (The solution was scrubbed with 0.2 M sodium carbonate prior to each extraction.) Zr-Nb extraction increased 5-fold during the first 24 hr but showed little increase thereafter (Fig. 18). During the first 24-hr period, extraction was higher when the solution was scrubbed with both sodium carbonate and calcium hydroxide than when it was scrubbed with the sodium carbonate only, but it was approximately the same after the first 24-hr period. These data are taken as demonstrating a reaction between diluent nitration products and TBP which occur at a slow rate. Possible explanation lies in preferential complexing of TBP and the aci- or salt forms of the nitrocarbons, complexing similar to those with TBP and other acids and salts. Depletion of the free aci- form forces the tautomeric equilibrium in its favor. As long as the neutral form is present further treatment with strong base catalyses this shift, and enhancement of the extraction results.

These reactions of low rate are essential to the explanation of the extraction behavior of nitrated solvents, and emphasize the need for caution in comparison of results obtained under even mildly varying experimental conditions.

Comments on Solvent Cleanup. The identification of nitrohydrocarbons as principle "bad actors" in nitric acid degraded Amsco 125-82 suggest reasons for the appearance of conflicting data in the description of solvent treatment experiences at different places. Thus, the main TBP processing plants use different diluents, diversely characterized by substantial quantities of cyclic paraffins, by high aromatic hydrocarbon content, or by relatively high degrees of unsaturation, and all have differing chain lengths and types of branching. The resulting wide variation in susceptibility to nitration (and probably, for some, to reactions of entirely different type) coupled with the wide variation in processing conditions, make comparison of solvent cleanup data difficult. As an example, samples of Amsco 125-82 and a randomly selected kerosene were treated with 4 M nitric acid for 4 hr at 107°C. Following sodium hydroxide scrubbing, the usual Zr-Nb⁹⁵ tracer extractions were made (no TBP). The extraction coefficients were, for the Amsco $E_A^0 \sim 0$ (<1 c/s/ml extracted), for the kerosene, $E_A^0 = 0.17$. Further, the activity extracted by the kerosene was difficult to strip with nitric acid.

Fig. 18. Extraction of Zr-Nb⁹⁵ Activity by 1 M TBP Solutions in Degraded Amsco. Extraction conditions: Equal vol aqueous and organic phases, 10 min contact; aqueous feed: 2 M HNO₃, Zr-Nb⁹⁵ 1.3×10^4 γ c/s/ml; Na₂CO₃ scrub: contact 2 times for 10 min with equal volume 0.2 M Na₂CO₃; Na₂CO₃-Ca(OH)₂ scrub: same Na₂CO₃ treatment followed by contact with 200 g Ca(OH)₂/liter organic phase for 1 hr.

Wide variations in properties of the "same" diluent may also occur from lot to lot. At this laboratory large differences have been observed in Zr-Nb⁹⁵ extraction tests and in gas chromatographic examination with two different lots of Amsco 125-82 (Fig. 19). Batch A, the more susceptible to degradation, shows the presence of a number of components not found in Batch B and these, as indicated by their higher retention time, have the highest molecular weights and probably the most complex structures. This supports experiments reported previously⁶ in which the highest boiling fractions of Batch A Amsco 125-82 were most severely degraded with nitric acid. Significant differences in the gas chromatograms, densities and radiation stabilities of several batches of Amsco 125-82 have also been observed at the Stanford Research Institute.³³ It would be unexpected if similar variations did not occur in many other diluents.

Identification of the most probable "bad actors" in process solvents give a positive direction to studies of means to circumvent the problem. For example, diluents which are stable toward nitration reactions may be utilized. If this is not possible, knowledge of the chemistry of the nitrocarbons may suggest methods of removing these compounds by converting to water-soluble salts, amines, aldehydes, etc.

Fig. 19. Gas Chromatograms of Different Lots of Amsco 125-82 Diluent. Conditions: 4 ft column, 25 wt % dinonylphthalate on J. M. Celite 545, 140°C, 0.1 std ft³/hr He flow, 140 mamp detector filament current.

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