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CHEMICAL DEVELOPMENT SECTION C

PROGRESS REPORT FOR

DECEMBER 1959 AND JANUARY 1960

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section C

Progress Report for December 1959 and January 1960

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ABSTRACT

Recovery of Thorium from Blind River Ion Exchange Barrens with Di(2-ethylhexyl)phosphoric Acid

Thorium was extracted effectively from reduced uranium-barren Blind River liquors with 0.05 M di(2-ethylhexyl)phosphoric acid in kerosene. Extractions decreased only slightly when the solvent was modified with tridecanol, but seriously when the liquor contained ferric iron. Thorium was readily stripped from the solvent with 3-5 M H_2SO_4 and recovered from the strip solution by crystallization as thorium sulfate.

Technetium and Neptunium Recovery from Fluorination Plant Residues

Extraction of Tc(VII) from nitric acid-aluminum nitrate solution was studied, with emphasis on extraction by a tertiary amine, to determine its applicability to technetium recovery from fluorination plant residues. Leach solutions from the residues typically contain U and small amounts of Tc and Np in ~1 N HNO_3--5 N $Al(NO_3)_3$ solution. The results indicated that Tc(VII) and Np(IV) can be coextracted by 0.3 M trilaurylamine. Np can be partitioned with 0.1 N H_2SO_4, and Tc can be stripped with 1 N NH_4OH. Dilution of the feed improved Tc extraction, but dilution below ~2 N NO_3 impaired Np extraction. At low nitrate concentrations the U can be left in the raffinate; at higher nitrate it can be coextracted, and partitioned with dilute HNO_3. A batch countercurrent extraction test showed essentially complete coextraction and complete stripping, with good separation of Tc and Np from each other. It indicated that a back extraction step may be required to prevent loss of Np with the U.

Extraction of Np(IV) by Quaternary Ammonium Nitrates

Tetraheptyl ammonium nitrate at 0.1 M in xylene extracted Np(IV) with coefficients >20 from 0.1 to 10 N HNO_3 solutions. The coefficient was highest (>2000) at 1 N HNO_3 and decreased sharply with increasing acidity, in contrast to increasing coefficients (380 at 2 N to 760 at 8 N HNO_3) with 0.2 M didodecenyl dimethyl ammonium nitrate.

Sodium Carbonate-Alumina Procedure for Solvent Recovery: Solids Removal Study

A solvent recovery procedure involving successive use of Na_2CO_3-washing and alumina-adsorption has been demonstrated in laboratory tests as a possible method for the purification and decontamination of organophosphorus process solvents. However, the use of solid sorbants will, in plant practice,

require installation of some method for clarifying the solvent prior to its return to the extraction cycle. Preliminary scouting tests have been performed to determine whether countercurrent water-washing (and interfacial accumulation of solids) may provide a useful method for clarification. It was shown that fine Al_2O_3 suspensions in the treated solvents were readily removed by such a procedure: most of the fines (probably less than 325 mesh) transferred readily into the aqueous phases to form light slurries, while small quantities collected at interfaces near the feed stage.

Countercurrent Tests with TBP and DSBPP: Effect of Nitrite-Acetone Treatment of Purex Aqueous Feeds on Ru and Zr-Nb Decontamination

Previously reported laboratory data described the use of a nitrite-acetone treatment of Purex aqueous feeds and its effect on Ru and Zr-Nb decontamination in the co-decontamination cycle. Additional countercurrent tests, employing tributyl phosphate (TBP) and di-sec-butyl phenylphosphonate (DSBPP) as Purex process extractants, have shown that the feed treatment procedure accounts for significant increases of both Ru and Zr-Nb DF's, e.g., by factors of 10 to 40, in comparisons with control systems where no aqueous treatment was employed. Ru DF's of 1.3×10^4 and 1.1×10^4, respectively, were obtained in the 1 M TBP-Solvesso-100 and 1 M DSBPP-Solvesso-100 systems. Zr-Nb DF's were 1.2×10^4 and 2.3×10^4, respectively.

Effect of Nitrated Fractions of Amsco 125-82 on Zr-Nb Extractions by TBP

Continued study has confirmed previous observations that nitration products of diluents such as Amsco 125-82 can contribute adversely to Zr-Nb decontamination factors obtained in the TBP extraction process. The highest boiling fraction of Amsco 125-82 apparently contains a higher proportion of the components that are most susceptible to reaction with nitric acid, such as unsaturates and tertiary hydrogen atoms.

Chemical Degradation of TBP-Amsco 125-82 Systems

Treatment of TBP-Amsco 125-82 solutions with 2 M HNO_3 at 60°C for 1-48 hr showed that under these mild conditions the TBP degradation products were more important than those from Amsco as contributors to Zr-Nb extraction and as affecting efficiency of solvent clean-up. Scrubbing with aqueous alkaline solutions effectively removed the degradation products from solution, and little advantage was gained by further treatment with solids.

Interfacial Tensions in Amine Extractant Systems

The interfacial tensions between benzene solutions of several amine salt and alkyl phosphate extractants and aqueous solutions have been examined as functions of the solute concentrations. The interfacially adsorbed solute populations estimated from the data via the Gibbs equation are in reasonable accord with predictions based on the approximate cross sectional area requirements of the carbon chains.

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1.0 RAW MATERIALS PROCESSING

1.1 Recovery of Thorium from Blind River Ion Exchange Barrens with Di(2-ethylhexyl)phosphoric Acid (D. J. Crouse, W. D. Arnold)

Isotherms (Table 1) for extraction of thorium with 0.05 M di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene from synthetic uranium-barren Blind River liquors showed effective thorium extraction, provided essentially all of the iron in the liquor was in the ferrous form. The presence of as little as 0.23 g Fe(III) per liter in the liquor seriously limited thorium loadings. Addition of tridecanol to D2EHPA-kerosene lowered the thorium extraction coefficient and thorium loading of the solvent slightly. As would be expected for a cation exchange reagent, addition of nitrate to the liquor did not affect extractions. This is in contrast to the performance of di(tridecyl)amine[1] where 1-2 g/liter of nitrate (introduced into the liquor during ion exchange recovery of uranium) seriously interfered with thorium extraction. [Extractions with primary amines[2] were not affected by nitrate.]

In Table 2, the results of tests made over a wider range of ferric iron concentration show serious loss of thorium extraction power due to iron competition and emphasize that almost complete reduction of the iron in the liquor would be required for effective thorium recovery. All of these extraction tests were made with two minutes contact time, and iron extraction, which is usually slow (ORNL-1903), would be expected to be greater for longer contact times.

Thorium was stripped effectively from D2EHPA with 3-5 M sulfuric acid (Table 3). Stripping efficiency increased with increasing acid concentration, but poor phase separation, caused by precipitation of thorium sulfate, was obtained with 5 M acid. The precipitate appeared to contain a considerable amount of organic and tended to cling to the walls of the flask and collect at the interface rather than settle in the aqueous. Phase separation was rapid and clean at the lower acid concentrations. Precipitation did not occur from the 3 M acid and only after prolonged standing from the 4 M acid when both solutions were loaded to about 17 g Th/liter. Precipitation from the 4 M acid started after about 2-1/2 hr and 85% of the thorium had precipitated after several days standing. Thus, it should be possible to recover thorium and most of the strip acid simply by aging the loaded strip solution to precipitate thorium sulfate and recycling the filtrate to the stripping system. Preliminary tests indicate that the hold-up time for precipitation might be greatly reduced by heating and/or seeding the strip solution.

Table 1. Extraction of Thorium from Synthetic Leach Liquors with Di(2-ethylhexyl)phosphoric Acid

Organic: 0.05 M D2EHPA in kerosene or kerosene-tridecanol diluent

Aqueous: Synthetic leach liquors containing 0.2 g Th, 0.01 or 0.23 g Fe(III), 2.0 g Σ Fe, 1.5 g Al, 0-1 g NO_3, and 15 g SO_4 per liter at pH 1.40

Liquor	g Fe(III)/liter	g NO_3/liter
A	0.01	0.0
B	0.01	1.0
C	0.01	0.0
D	0.23	1.0

Contact time: 2 min
Temperature: 24-28°C

Diluent	Liquor	Phase Ratio, a/o	Th Conc., g/liter Org	Th Conc., g/liter Aq	Thorium Extraction Coefficient (E_a^o)	Fe in Organic, g/liter
Kerosene	A	1	0.21	<0.005	>40	0.010
		3	0.60	<0.005	>120	0.009
		5	0.97	0.014	70	0.009
		10	1.48	0.040	37	0.009
		15	1.52	0.083	18	0.010
	B	1	0.21	<0.005	>40	0.009
		3	0.57	<0.005	>115	0.010
		5	0.93	<0.005	>180	0.010
		10	1.52	0.041	37	0.010
		15	1.59	0.086	18	0.011
98% Kerosene-- 2% tridecanol	C	1	0.21	<0.005	>40	-
		3	0.60	0.005	120	-
		5	1.05	0.023	46	-
		10	1.30	0.121	11	-
		15	1.43	0.158	9	-
	D	1	0.20	<0.005	>40	0.06
		3	0.56	0.012	47	0.18
		5	0.83	0.086	10	0.26
		10	0.90	0.180	5	0.34
		15	0.80	0.220	4	0.42

Table 2. Effect of Ferric Iron on Thorium Extraction with D2EHPA

Organic: 0.05 M D2EHPA in kerosene
Aqueous: Synthetic leach liquors containing 0.2 g Th, 0-1.7 g Fe(III), 2.0 g Σ Fe, 1.5 g Al, 1.0 g NO_3, and ~20 g SO_4 per liter at pH 1.40
Contact time: 2 min
Phase ratio, a/o: 5/1

Fe(III) in Liquor, g/liter	Thorium, g/liter Organic	Thorium, g/liter Aqueous	Fe in Organic, g/liter	pH	Thorium Extraction Coefficient (E_a^o)
0.0	1.00	0.004	0.07	1.50	250
0.23	0.80	0.044	0.25	1.40	18
0.46	0.69	0.086	0.34	1.40	8
0.70	0.57	0.087	0.41	1.40	7
0.84	0.48	0.100	0.46	1.40	5
1.4	0.32	0.132	0.60	1.40	2
1.7	0.28	0.153	0.65	1.45	2

Table 3. Stripping Thorium from D2EHPA with Sulfuric Acid

Organic: 0.05 M D2EHPA in kerosene loaded to 1.7 g of thorium per liter
Contact time: 10 min

H_2SO_4 Conc., M	Phase Ratio, o/a	Phase Sep'n. Time, min	Thorium, g/liter Org	Thorium, g/liter Aq	Thorium Stripped, %	Thorium Precipitated in 1 hr, % of Stripped
3	4	0.5	0.054	-	97	<1
	6	0.5	0.090	10.5	95	<1
	8	0.6	0.153	13.3	90	<1
	10	0.5	0.173	16.6	90	<1
4	4	0.5	0.021	7.5	99	<1
	6	0.5	0.072	10.1	96	<1[b]
	8	0.5	0.100	13.4	94	<1[b]
	10	0.5	0.089	16.9	95	<1[c]
5	4	a	<0.005	4.8[a]	>99.5	28
	6	a	<0.005	2.4[a]	>99.5	84
	8	a	<0.005	4.0[a]	>99.5	69
	10	a	<0.005	2.2[a]	>99.5	87

[a]Copious precipitate in aqueous which stuck to walls of flask and accumulated at interface; aqueous was filtered (1 hr after stripping) before analysis.

[b]Precipitate formed after standing overnight.

[c]Precipitate formed in ~2-1/2 hr.

2.0 SOLVENT EXTRACTION TECHNOLOGY

2.1 Technetium and Neptunium Recovery from Fluorination Plant Residues (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. Principal attention has been given to extraction of pertechnetate ion with a tertiary amine. Promising results were obtained in coextraction of Tc, Np, and U, partition of U with dilute nitric acid, partition of Np with very dilute sulfuric acid, and stripping of Tc with ammonium hydroxide.

2.1.1 Feed Composition. Fluorination ash, and nonvolatiles accumulated in uranium hexafluoride transfer cylinders, are the principal pertinent residues in the Paducah fluorination plant.[3] Uranium and other values are leached from either residue with acid aluminum nitrate giving solutions containing on the order of 1 N HNO_3 and 5-6 N $Al(NO_3)_3$. The major constituents in a typical solution[4] are shown in Table 4, together with partial analyses of two solution samples received from Paducah.[5] One of these (PCF) was a sample of transfer cylinder wash, and the other (PCR) was the corresponding raffinate after TBP extraction of uranium and neptunium.[6] The neptunium concentration in PCR was <0.2% of that in PCF, and the technetium concentration, 23%. The latter may be a lower percent than is typical after the TBP U-Np extraction.[6]

2.1.2 Relation to Existing Processes. Fluorination ash in the Paducah plant[3] is leached, and the dissolved uranium is recovered for recycle by TBP extraction in a mixer-settler system. Ash leach solutions containing significant neptunium, and cylinder wash solutions, are processed in a separate system (four pulse columns, 15 to 30 ft) by extraction with 15% TBP at 1.2 N HNO_3--4.8 N $Al(NO_3)_3$, neptunium partition at 1.1 N HNO_3, and uranium stripping at 0.05 N HNO_3, followed by evaporator concentration of the product streams.[6] The obvious means of incorporating a technetium recovery step include (1) extraction from the raffinate after the Np-U recovery process, (2) prior extraction, by a method not extracting U or Np and leaving the solution suitable for the existing process, (3) extraction of Tc and Np together, leaving U, and (4) extraction of all three together. Another consideration for any process intended to be applicable at Paducah is that little or no additional equipment should be required.[6] This appears more likely to be possible with (3) or (4) than with (1) or (2), or with any other likely combination of steps.

Table 4. Feed Solution Compositions

	Typical Composition[4]	Solution PCF[5]	Solution PCR[a] [5]
Tc, M	-	1.14×10^{-3}	2.6×10^{-4}
Np	1.0×10^{-4}	1.9×10^{-4}	$<3 \times 10^{-7}$
U	0.16	0.176	2×10^{-5}
Th	0.01	5×10^{-3}	3×10^{-4}
Al	1.7	1.79	1.76
Fe	0.05	0.06	0.07
Cr	0.02	-	-
Ni	0.02	-	-
Mn	0.003	-	-
Cu	0.008	-	-
Mg	0.01	-	-
Na	-	0.11	0.08
H^+	1	0.91	1.39
F^-	0.5	0.26	0.77
NO_3^-	6	6.84	6.23
Sp. Gr.	-	1.410	1.287
Gross β[b]	-	1.3×10^5	2.9×10^4
Gross γ[c]	-	2.5×10^4	2.3×10^3

[a]After extraction of U and Np.

[b]Counts/min ml at ~10% geometry.

[c]Counts/min ml at ~23% efficiency.

Coextraction of Tc and Np by an amine, with or without U, was chosen for first trial, on basis of the foregoing considerations together with the extraction data already available, which are briefly summarized in the following section.

2.1.3 General Extraction Behavior. Technetium chemistry has been studied extensively by Boyd and Larson, who provided much unpublished information in discussions and by allowing use of manuscript drafts,[7] in addition to published information.[8] Tc(VII) is extracted from acid solution by dilute amines, 50-100% TBP, ketones, and alcohols, in about that order of extraction power. Extraction by the last three is maximum at ~1 M acid, while extraction by amines continues to increase with decreasing acidity until the amine salt itself begins to hydrolyze. With each of these extractants, the other aqueous anions present compete with $HTcO_4$, the severity of the competition varying $H_2SO_4 < HCl < HNO_3 < HClO_4$. The technetium should be readily held at Tc(VII) in the solutions described above, as Fe(II) is not sufficient to reduce it in acid solution, and even if reduced in (non-complexing) acid solution it would probably form TcO_2, which is

oxidizable to Tc(VII) by air. Behavior is different in HCl from that in the other common acids, high chloride concentration reducing Tc(VII), and stabilizing Tc(IV) by complex formation.[7]

The extracted technetium can be stripped from alcohols, ketones, or diluted TBP with water, from 100% TBP with strong cationic reductants like Cr(II), and from amines with basic solutions.[7]

For coextraction with technetium by TBP, neptunium should preferably be at Np(VI), and the Np(V)-Np(VI) equilibrium is rapid in solutions containing >4 M HNO_3 plus 0.001 M NO_2^-.[9] For coextraction with technetium by an amine, neptunium should be at Np(IV), and it is readily reduced to (IV) in solutions containing >5 N $Al(NO_3)_3$, even at very low acidity.[10,11] If not to be coextracted, neptunium should be adjusted to Np(V), perhaps with hydrogen peroxide, or else a low nitrate concentration should be obtained. Extracted neptunium can be stripped from TBP with water or with peroxide solution,[9] from amine with very dilute sulfuric acid solution.[10]

Both amine and aqueous nitrate concentrations should be low for rejection of uranium, or high for coextraction.[12,13]

2.1.4 Extraction with Amines from Nitric Acid-Aluminum Nitrate Solutions. Boyd and Larson found the technetium extraction coefficient from nitric acid solutions with 0.01 M tri-n-octylamine (TOA) in cyclohexane to reach a maximum of ~75 at 0.03 M HNO_3. The extraction coefficient decreased linearly with increasing acidity to ~0.5 N HNO_3, and then decreased more rapidly to 2 N HNO_3. At 1 N and 2 N HNO_3, the extraction coefficient varied linearly with amine concentration.[7]

These coefficients with 0.01 M TOA, multiplied by 30, are included in Fig. 1 for comparison with extractions by 0.3 M trilaurylamine (TLA).* The agreement at acidities above 0.1 M HNO_3 was close. The extraction coefficients with 0.3 M TLA at 0.1 and 0.01 N HNO_3 scattered considerably, as indicated in Fig. 1. (Since acidities this low were not ex-

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*Except where otherwise noted, Eastman Kodak trilaurylamine was used in the present extraction tests. It assayed 524 neutral equivalent vs 522.0 theoretical; <1% primary, <2% secondary, >98% tertiary amine by differential titration. The diluent was Amsco 125-82, usually modified with oxo-process mixed tridecanols (TDA). Technetium-95m tracer was used in tests with reagent chemical solutions for analysis by γ-counting. Technetium in tests with actual plant solutions was analyzed polarographically.

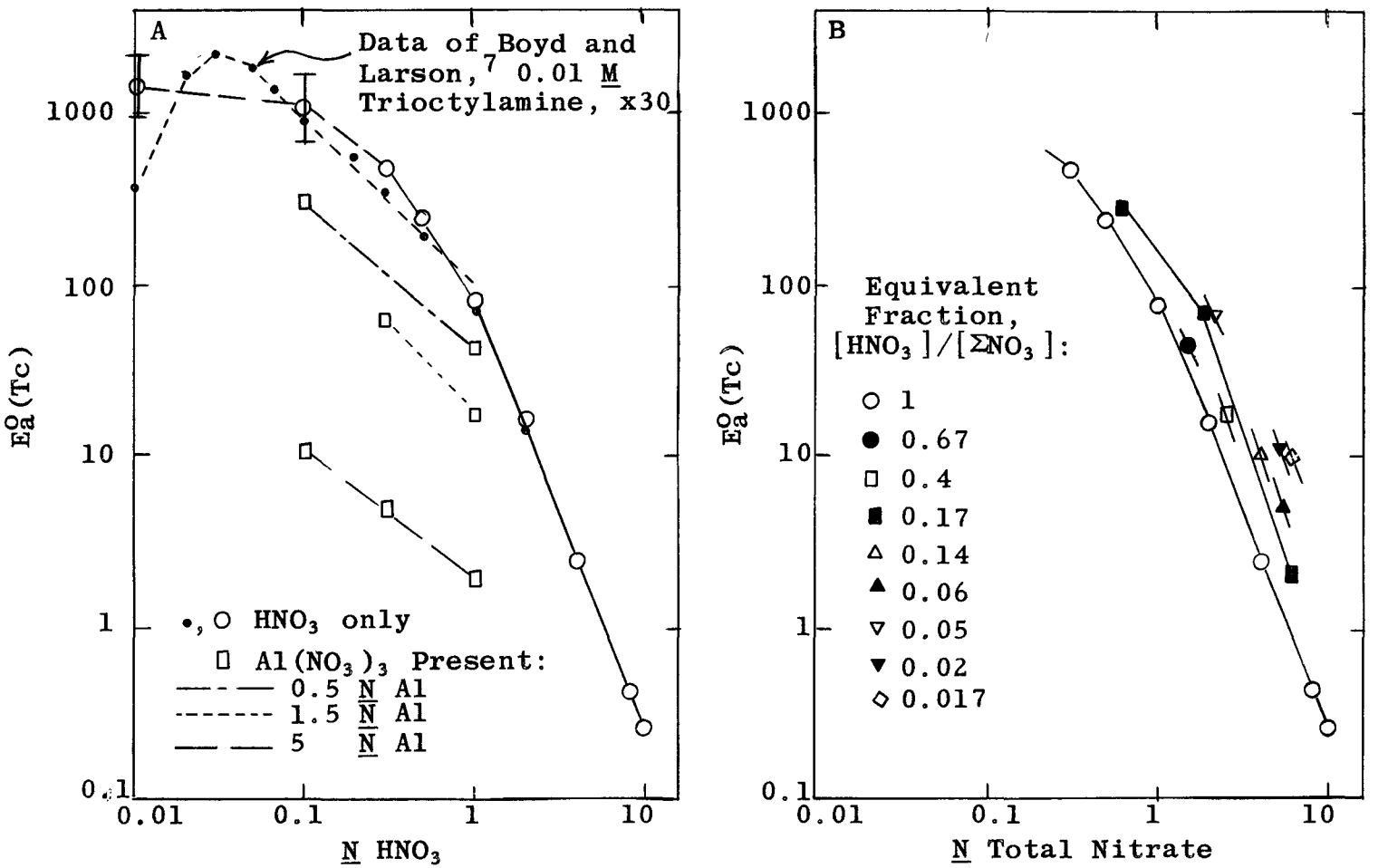


Fig. 1 Tc(VII) extraction by 0.3 M trilaurylamine in Amsco 125-82 from nitric acid and acidic aluminum nitrate solutions.

pected to be encountered in the process development, no attempt was made either to improve the precision or to account for the variations.) Reproducibility was good at the higher acidities. Addition of aluminum nitrate impaired the technetium extraction nearly as much as did adding the equivalent amount of nitric acid. At a constant aluminum nitrate level (0.5, 1.5, or 5 N), the extraction coefficient varied linearly with the inverse of the acidity. When both aluminum nitrate and nitric acid were varied, at a constant $[HNO_3]/[\Sigma NO_3]$ mole ratio, the resulting curve was closely parallel to the steeper portion of the HNO_3-only curve.

The data of Fig. 1 permitted estimation of the technetium extraction coefficient over a wide range of nitric acid-aluminum nitrate solutions. With the assumption that the technetium extraction coefficient remains directly proportional to the amine concentration over all of this range, they indicated that useful coefficients could be obtained with 0.5 M TLA from the undiluted PCF solution (~5 N $Al(NO_3)_3$, ~1 N HNO_3), with 0.3 M TLA after some dilution, and with 0.1 M TLA after considerable dilution.

Neptunium and uranium extractions depend on nitrate salting, so that their extraction coefficients decrease while the technetium extraction coefficient increases with dilution of the nitrate feed solution. The neptunium data (Fig. 2) indicate usefully high coefficients with 0.3 M amine even with dilution to considerably below ~6 N NO_3^-, but indicate little dilution permissible with 0.1 M amine. The uranium data (Table 5) indicate coefficients suitable for uranium extraction from undiluted PCF solution with 0.1 M amine, and from undiluted or 1:1-diluted PCF with 0.3 M amine. They indicate coefficients low enough for uranium rejection (with the aid of a scrub) on dilution to less than 2-3 N NO_3^-.

Table 5. U(VI) Extraction from HNO_3-$Al(NO_3)_3$ Solutions

Trilaurylamine in Amsco 125-82 modified with tridecanol

Nitrate, N			$E_a^o(U)$	
HNO_3	$Al(NO_3)_3$	Total	0.3 M TLA[a]	0.1 M TLA[b]
1.0	5.0	6.0	30	10
0.67	3.33	4.0	10	3
0.5	2.5	3.0	5	1.7
0.63	1.67	2.3	1.5	0.5
1.0	0	1.0	0.2	0.06
0.5	0	0.5	0.1	0.03

[a]Modified with 6 v % tridecanol.

[b]Estimated on basis of $E \propto M$ (amine).

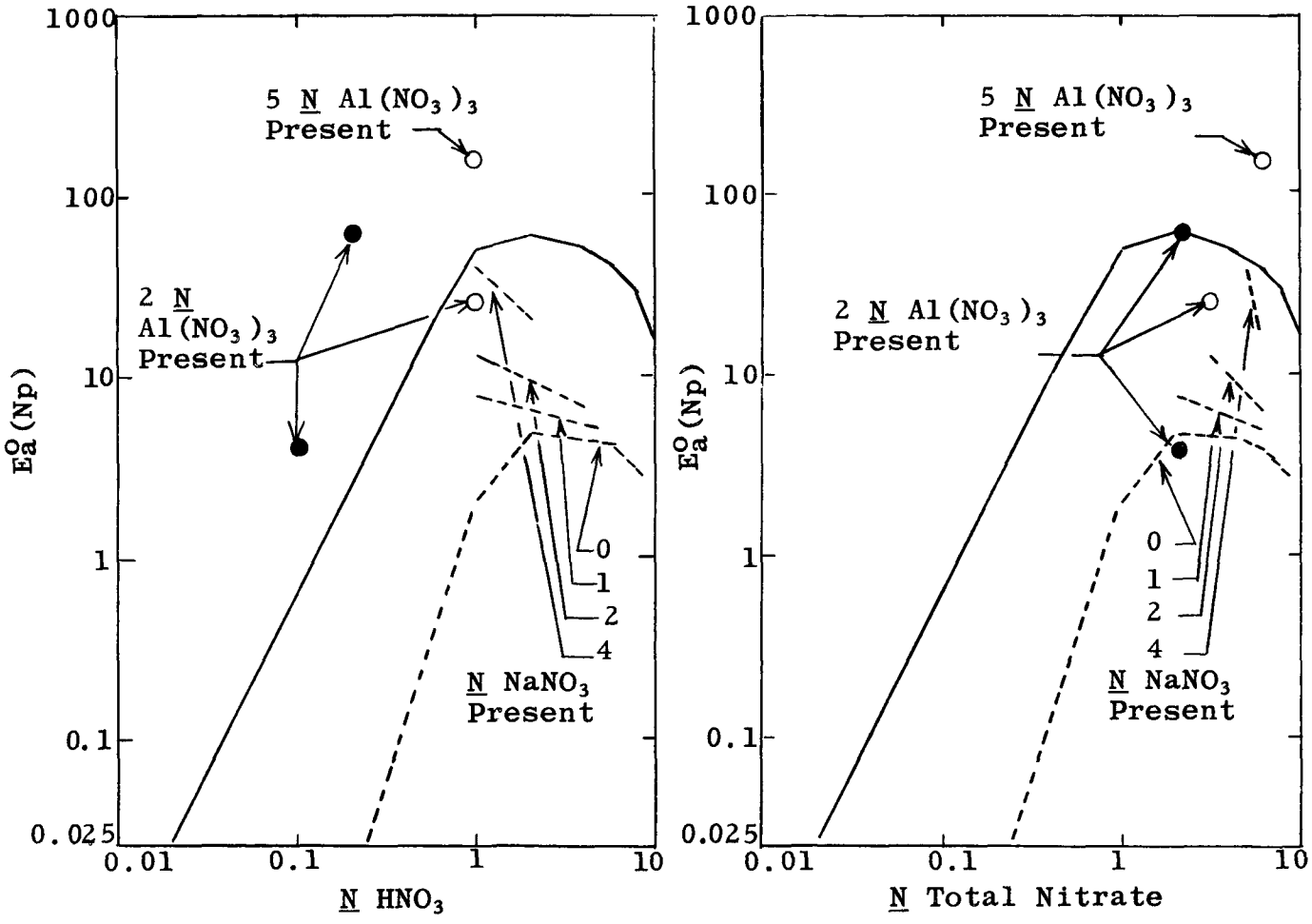


Fig. 2. Np(IV) extraction by tertiary amines from nitric acid and acidic nitrate salt solutions. = 0.3 M TLA in Amsco-5% TDA; others 0.3 M (—) and 0.1 M (---, ○) TIOA in xylene.[10]

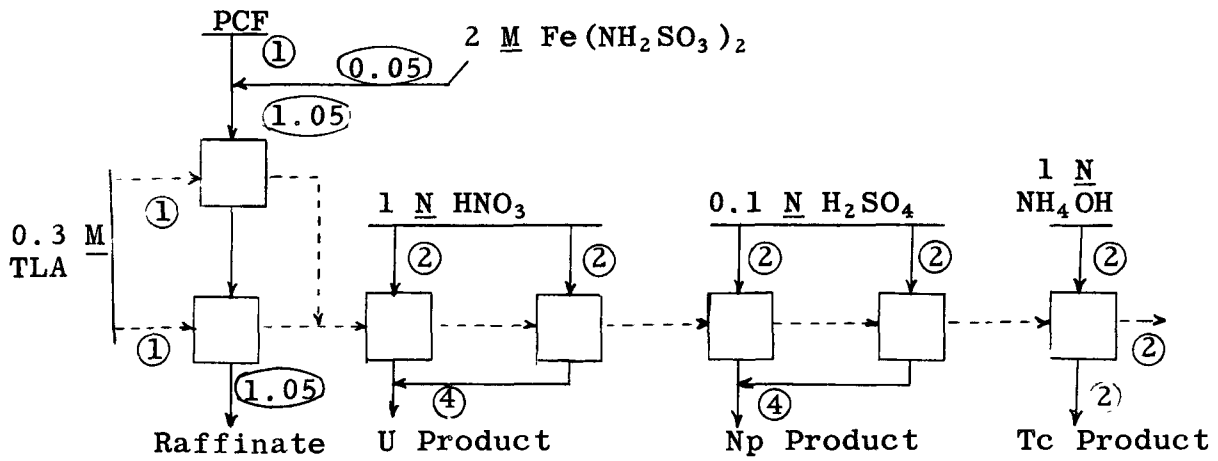
These combinations of extraction coefficients suggested extraction of both Tc and Np from the PCF solution, either with dilution to between 1/2 and 1/4 of the original nitrate concentration and scrubbing with dilute nitric acid to hold back uranium, or with little or no dilution, and coextraction of the uranium followed by a dilute nitric acid uranium partitioning strip. These possibilities were tried with the actual process solution, using 0.3 M TLA for extraction from undiluted PCF, 1 N HNO_3 for uranium scrub, 0.1 N H_2SO_4 for neptunium partition, and 1 M NH_4OH for technetium stripping. The test procedure is summarized in Table 6. Since this was not a countercurrent test and the dilute nitric acid scrub solution did not return to the extraction step, its results (Table 6) were pertinent to both of the alternative uranium paths being considered. They showed nearly complete extraction of the neptunium and uranium and ~75% extraction of the technetium. (The extent of uranium extraction was underestimated in choosing the phase ratio for the extraction, so that excessively high uranium loading impaired the technetium extraction. Subsequent calculation of the free amine concentration by means of the uranium extraction isotherms below showed that 75% Tc extraction was consistent with its measured extraction coefficients (Fig. 1), and with complete Tc extraction at somewhat lower A/O). More than 99% of the uranium was removed by the 1 M HNO_3, together with ~10% of the neptunium and ~4% of the technetium. More than 99% of the neptunium was removed by the 0.1 N H_2SO_4, together with <0.1% of the technetium, and <0.2% of the neptunium accompanied the technetium in the final strip with 1 N NH_4OH. These were considered promising results for a non-countercurrent test, and they were considered to favor extraction and partitioning of the uranium over rejection of it to the raffinate.

Since uranium is the only major component extracted, the system will follow the uranium extraction isotherm. Accordingly, portions of the uranium extraction isotherms were measured using 0.1-0.5 M TLA and several different aqueous nitrate levels (Fig. 3-5). In addition, two of the most highly-loaded organic products were used for uranium stripping cascades with 0.5 N HNO_3 (Fig. 6).

2.1.5 Chemical Flowsheet. A chemical flowsheet was set up (Fig. 7) for coextraction and partition of uranium, neptunium, and technetium, with tentative concentrations based on the foregoing results. The feed solution is adjusted to 0.3-1 N HNO_3 and 2-6 N $Al(NO_3)_3$. The extractant is 0.3 M tertiary amine, at phase ratio A/O set to give 15-20 g U/liter in the loaded organic phase. No scrub section is used. The uranium is partitioned with 0.5-1 N HNO_3. A back extraction with a separate smaller solvent stream might be needed, if too much neptunium or technetium is lost with the uranium. The neptunium is partitioned with 0.1 N H_2SO_4. The

Table 6. Tc-Np-U Extraction and Separation

Extractant: 0.3 M TLA in Amsco 125-82 modified with ~2 v % tridecanol
Feed: PCF solution, plus $Fe(NH_2SO_3)_2$ to ~0.1 M
Batch contact, 2 min in Burrell shaker, R.T.
Circled numbers represent volumes, ① = 10 ml.



	U, g/liter		Np, mg/liter		Tc, mg/liter	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Feed	39.8	39.8	43	43	107	107
Raffinate	0.3	0.3	<0.02	<0.02	27.1	25.3
U Product	10.6	-	1.5	1.3	1.0	1.2
Np Product	0.3	0.3	10.9	11.5	<0.01	<0.01
Tc Product	0.01	0.01	≤0.02	0.04	42.6	42.2
% Balance	105	-	111	117	104	103

technetium is stripped with 1 N NH_4OH; this can probably be accomplished in a single stage contactor instead of requiring a column.

This chemical flowsheet was tested in a batch countercurrent system as shown in Fig. 8. The PCF solution (in 250 ml batches) was treated with 12.5 ml of 1.45 M $Fe(NH_2SO_3)_2$ solution and diluted with water to 525 ml. The extractant was 0.3 M TLA (EK) in Amsco 125-82 modified with 5 v % TDA. Eleven stages were carried through 42 cycles (~4 volume changes) for extraction, and 8 stages through 51 cycles (~6 volume changes) for uranium partition, double diamond pattern.*

*The extraction system was initially filled in 8 preliminary cycles without takeoff, starting with feed solution in stages 1-3 and thereafter supplying fresh feed to stage 1 only. The partition system was initially filled in 8 preliminary cycles without takeoff, supplying pregnant organic solution to stage 1 only.

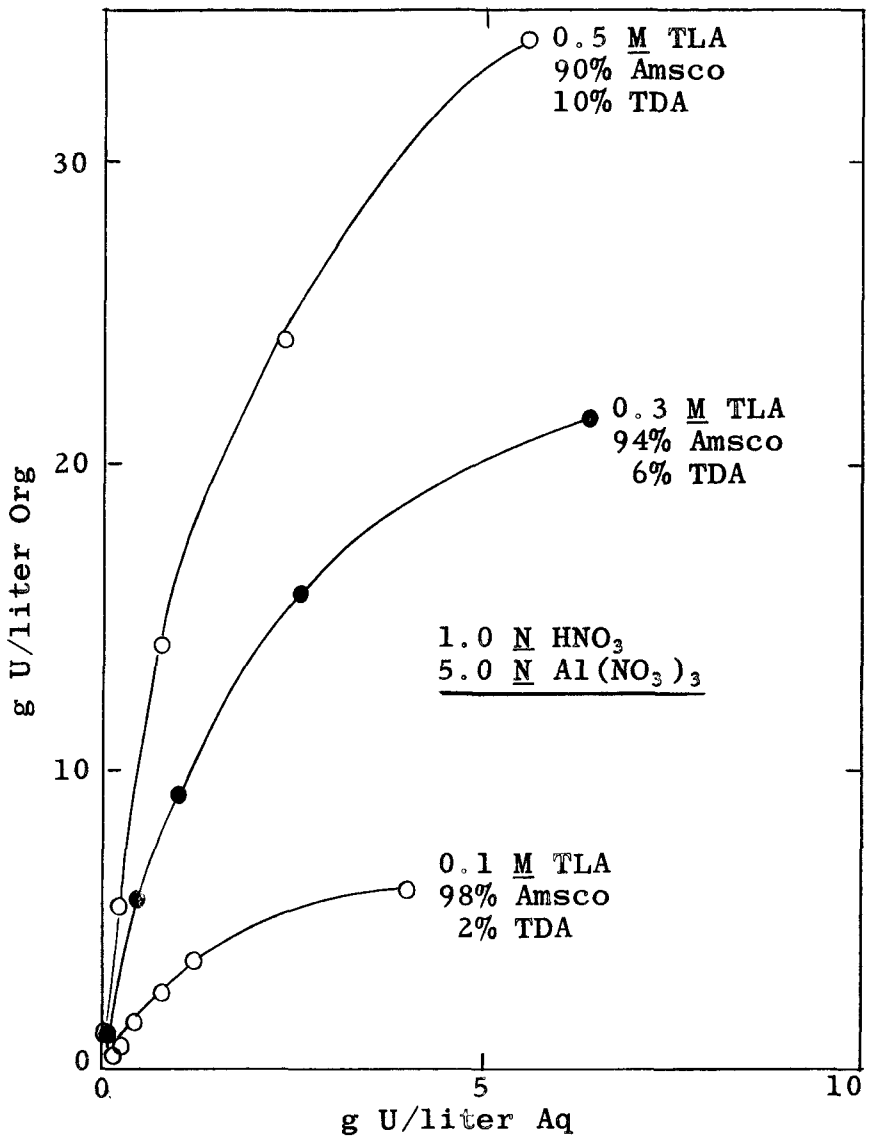


Fig. 3. Uranium Extraction Isotherms with Trilaurylamine in Amsco 125-82-Tridecanol from 1 N HNO_3--5 N $Al(NO_3)_3$ solution.

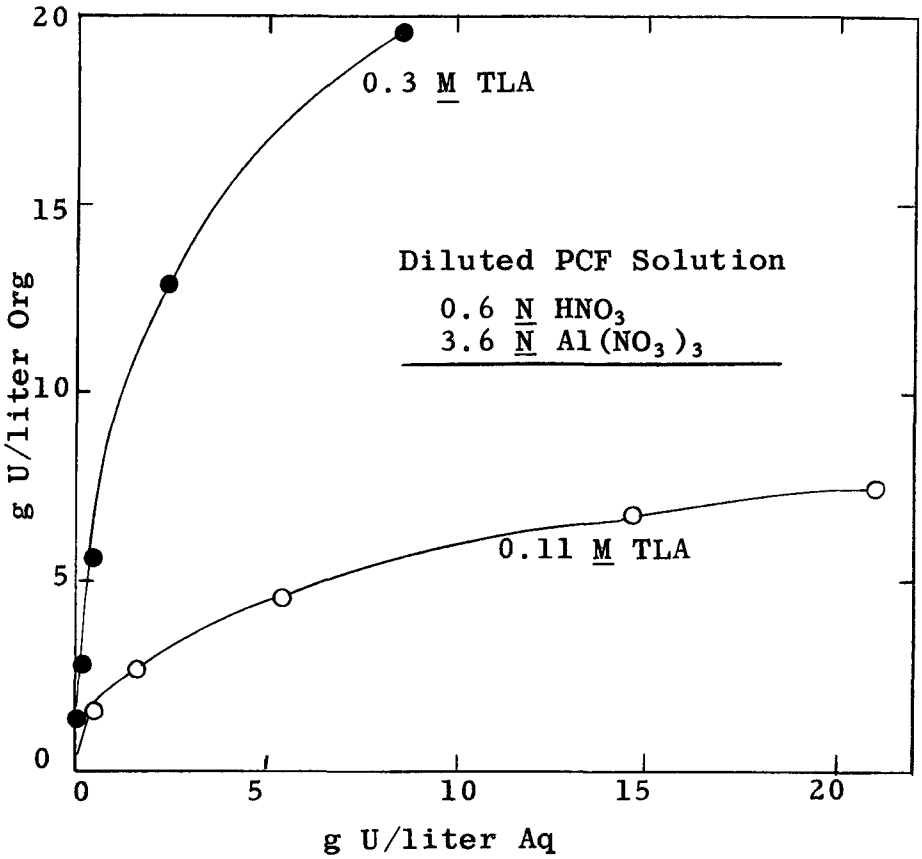


Fig. 4. Uranium Extraction Isotherms with 0.11 M Trilaurylamine and with 0.3 M Trilaurylamine in Amsco 125-82 modified with 5% Tridecanol, from PCF Solution diluted with 1/2 its volume of water.

The volumes used were 30 ml aq/30 ml org per stage in extraction, and 10 ml aq/20 ml org per stage in uranium partition. The neptunium partition and the technetium strip were not countercurrent: For the neptunium partition, the organic contacted three successive aqueous batches, at A/O = 1/1 in each. The technetium strip used a single contact, at A/O = 1/2. The entire amount of organic product from the extraction (less analytical samples) was mixed for feed to the uranium partition, and similarly from that to the neptunium partition, and the technetium strip. The final profile of the extraction system (Figs. 9-10) showed ~0.01% of the uranium remaining in the raffinate. The first 5 stages were running at close to the maximum uranium concentration, so that a little lower uranium loading (lower A/O), a similarly complete extraction could have been accomplished in about 6 stages, or ~99% extraction in about 3 stages. The final profile of the uranium partition system (Figs. 11-12) showed <0.01% of the uranium remaining in the organic at the 8th stage, and only a little over 1% at the 4th stage. Eighth-stage organics analyzed at several cycles between the 10th

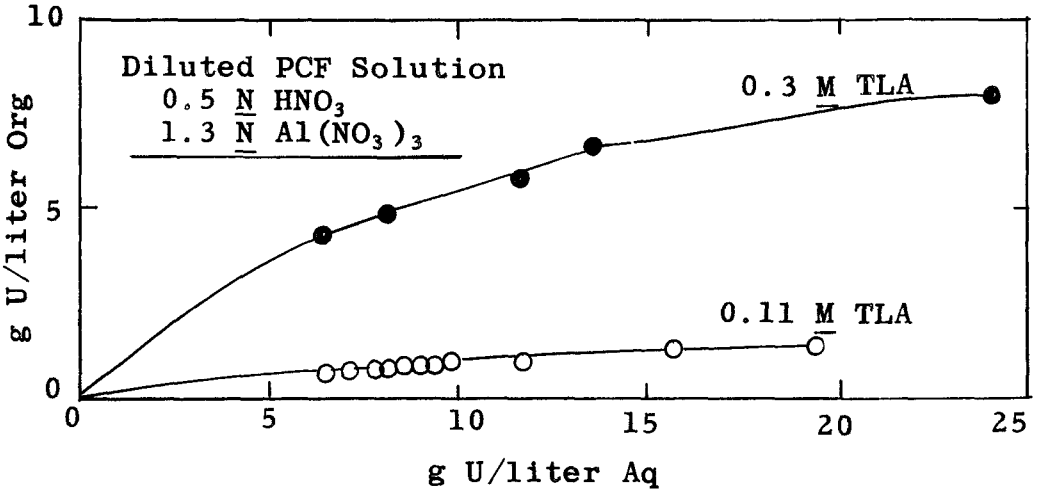


Fig. 5. Uranium Extraction Isotherm with 0.11 M Trilaurylamine and with 0.3 M Trilaurylamine in Amsco 125-82 modified with 5% Tridecanol from diluted PCF Solution, PCF/0.5 N HNO_3/water = 1/2/1.

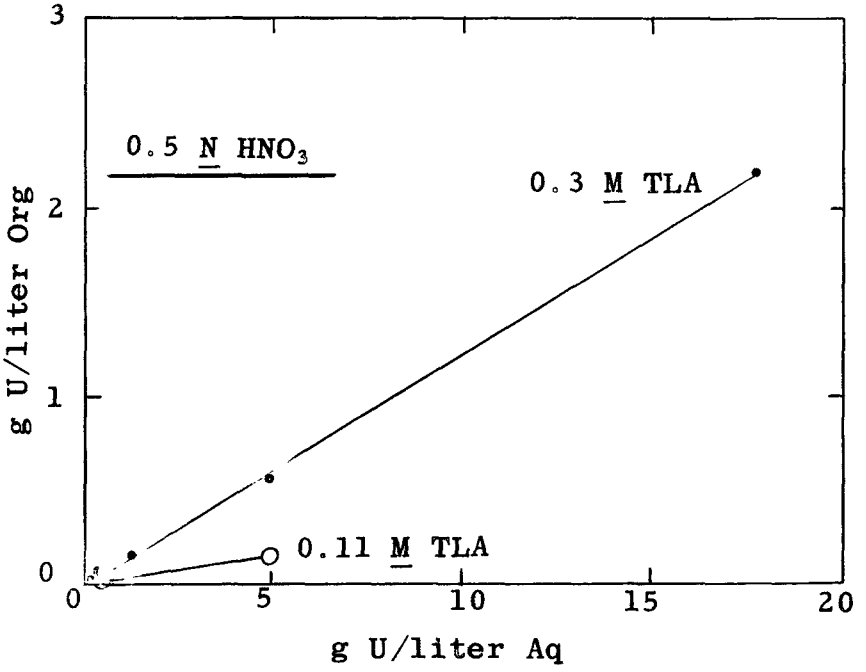


Fig. 6. Uranium Stripping Isotherms with 0.5 N HNO_3 from TLA Solutions loaded from diluted PCF Solution (Fig. 5.).

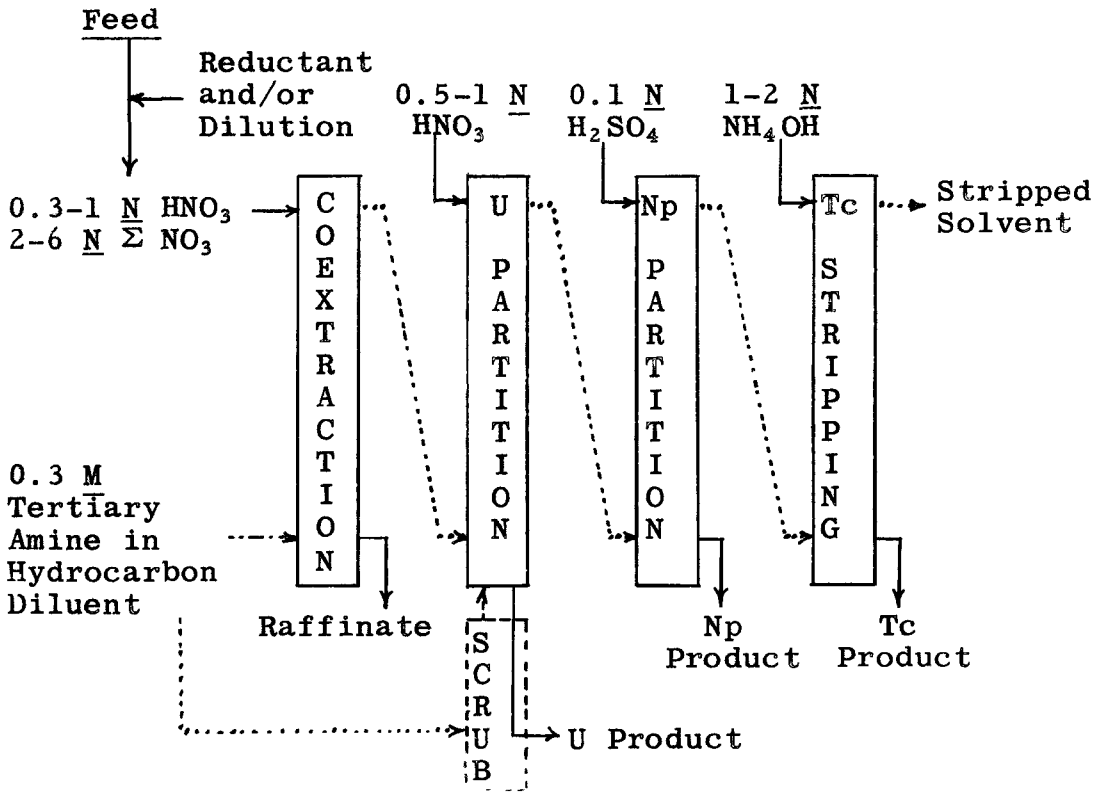


Fig. 7. Schematic Flowsheet for Recovery and Separation of Tc, Np, and U from HNO_3-$Al(NO_3)_3$ Solutions of Fluorinator Plant Residues.

and 50th varied between 0.025 and 0.004% of the initial uranium.

The first neptunium and technetium analyses reported on this run indicated >99.8% of each extracted within the first 5 extraction stages, even though these 5 stages were heavily loaded with uranium. About 1.5% of the technetium was lost with the partitioned uranium, but the neptunium loss was much higher.* Stripping of neptunium and technetium appeared to be essentially complete, and with <0.1% cross contamination.

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*Possibly because of oxidation of Np(IV), which might call for addition of a holding reductant to the nitric acid solution.

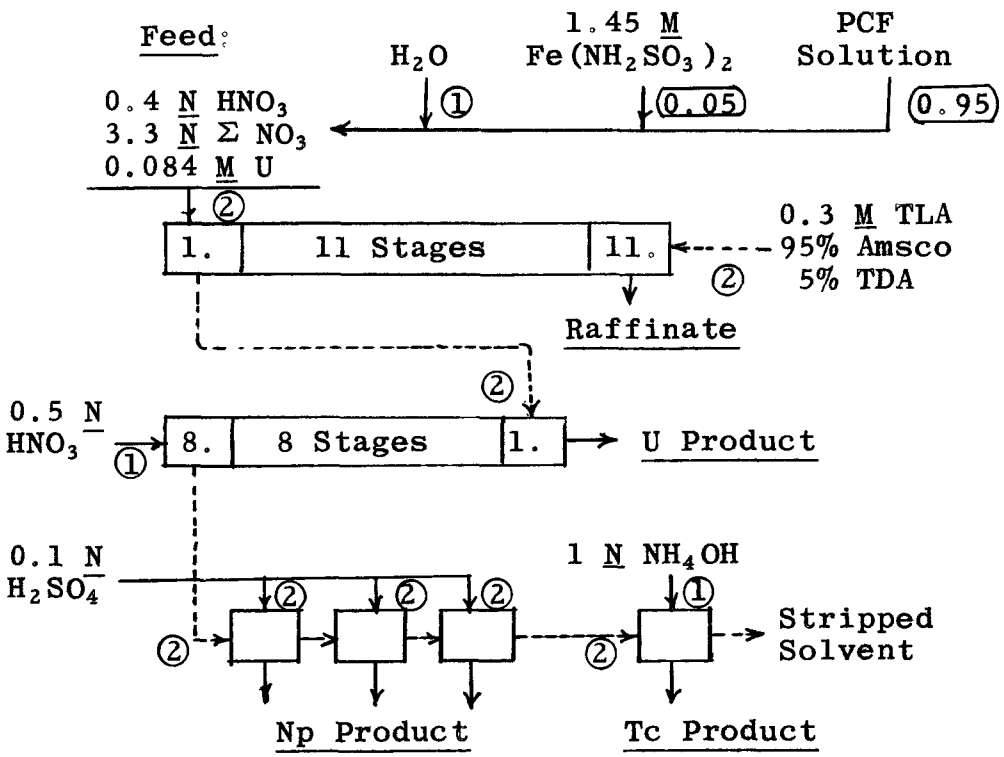

Fig. 8. Test Conditions, Batch countercurrent test of Tc-Np-U recovery. Circled numbers represent relative volumes.

2.2 Extraction of Np(IV) by Quaternary Ammonium Nitrates (Boyd Weaver)

The extraction of Np(IV) from nitric acid solutions by tetraheptyl ammonium nitrate (THA) has been measured and compared with data for extraction by didodecenyl dimethyl ammonium nitrate (B-104),[10] Fig. 13. Xylene solutions of both of these reagents show good phase separation properties and low aqueous solubilities. Extraction by 0.1 M THA is approximately equal to that by 0.2 M B-104 from 4 N HNO_3, but extraction by THA decreases above 1 N HNO_3, while that by B-104 increases with acidity. Extraction by THA decreases below 1 N HNO_3, where the Np(IV) is in a hydrolyzed form, but is still much too high to permit stripping by 0.1 N HNO_3. The neptunium is stripped by dilute H_2SO_4.

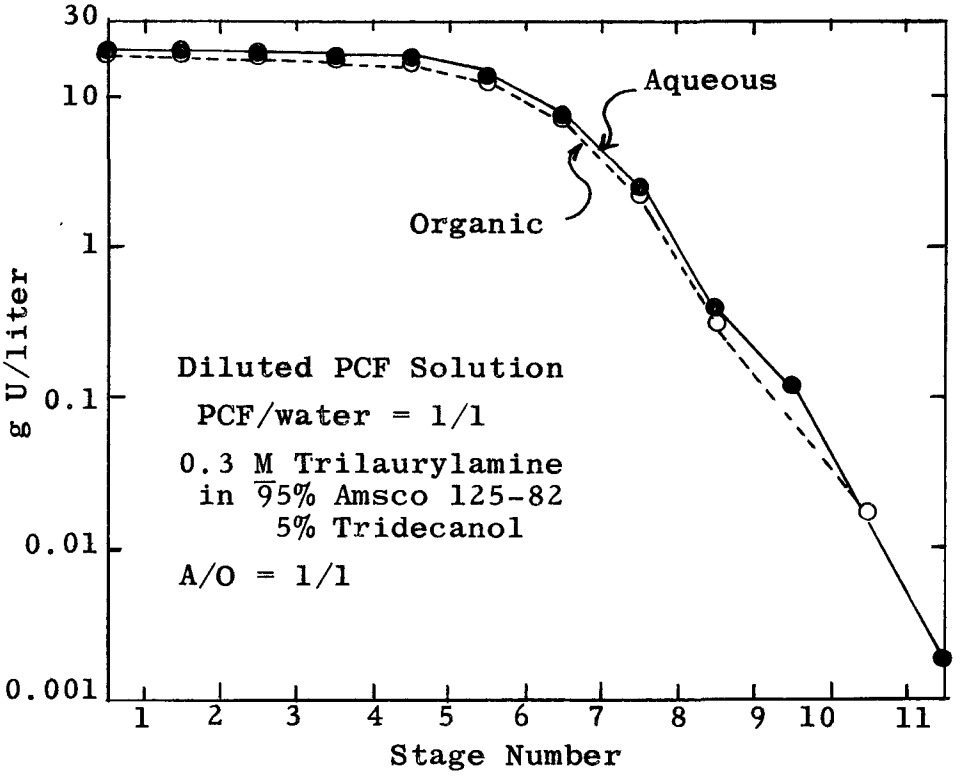

Fig. 9. Final Uranium Profile (42 cycles), Coextraction Batch Countercurrent Tc-Np-U Recovery Test

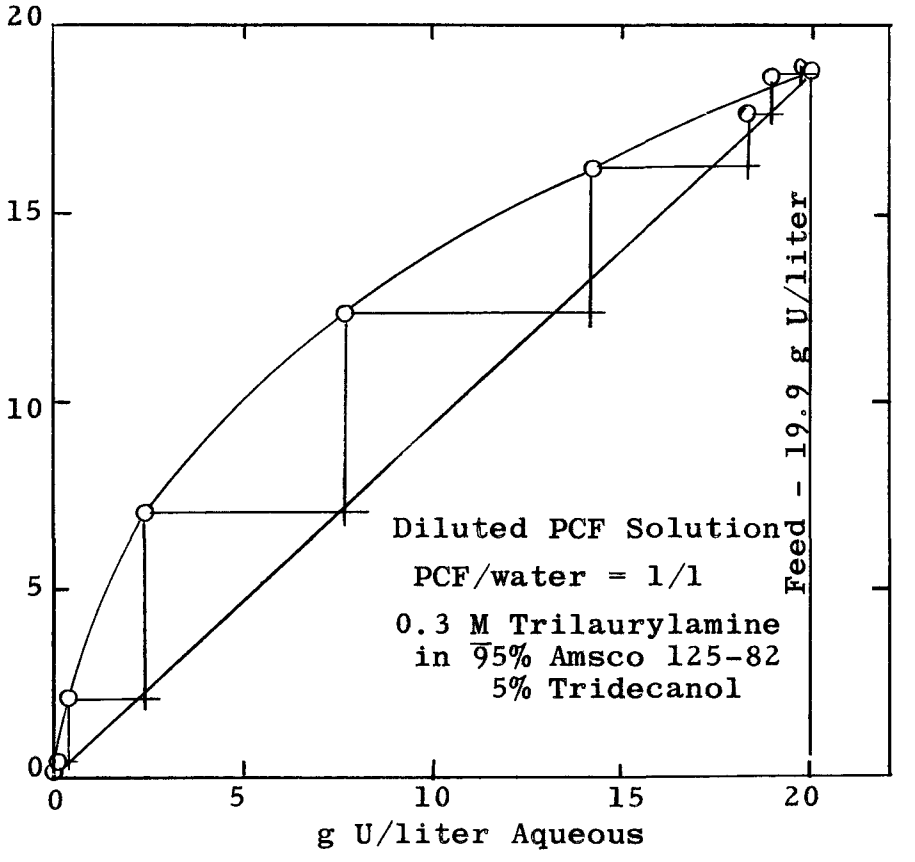

Fig. 10. Uranium Extraction Isotherm, Final Profile (42 cycles), Batch Countercurrent Tc-Np-U Recovery Test.

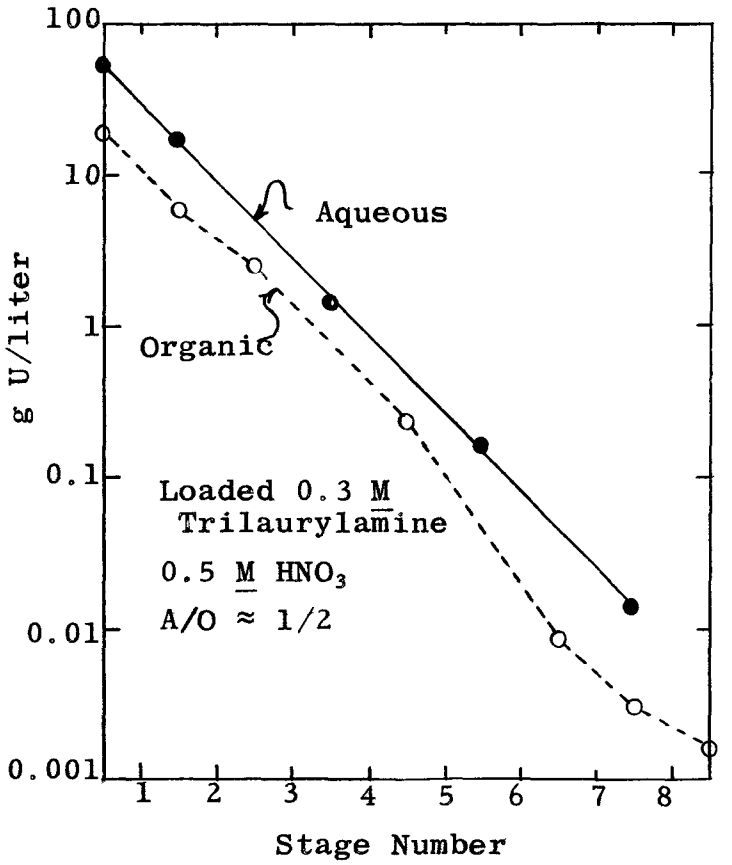

Fig. 11. Final Uranium Profile (51 cycles), Uranium Partition, Batch Countercurrent Tc-Np-U Recovery Test.

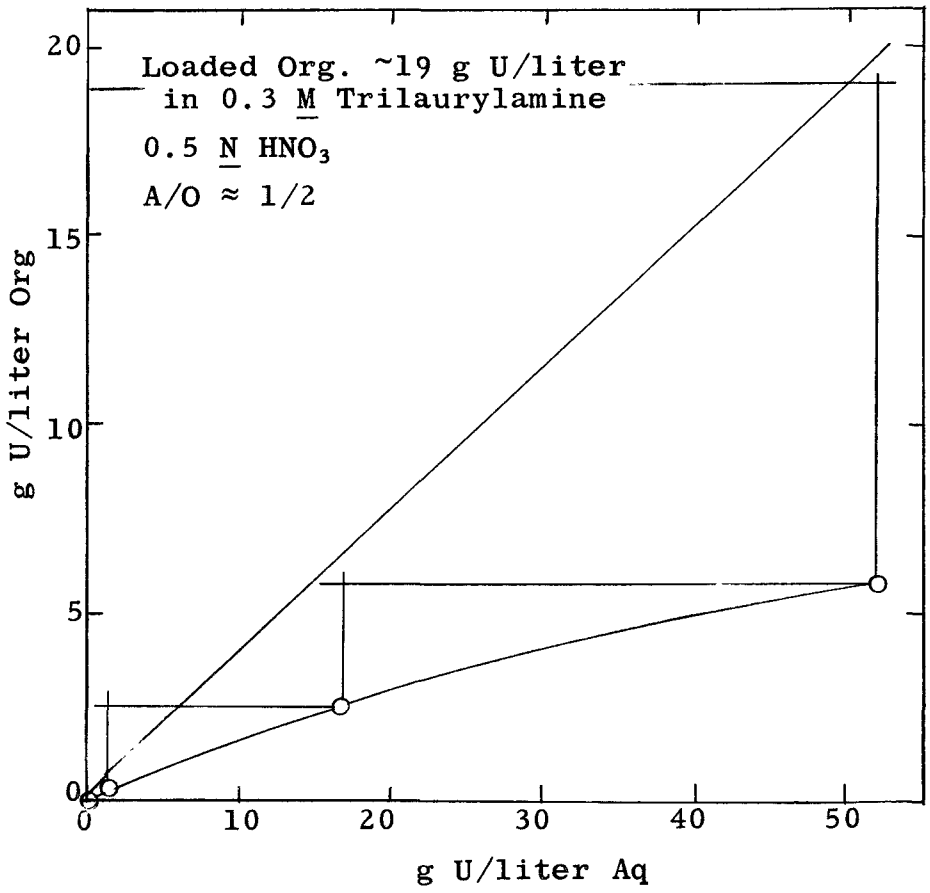

Fig. 12. Uranium Stripping Isotherm, Final Profile (51 cycles), Batch Countercurrent Tc-Np-U Recovery Test.

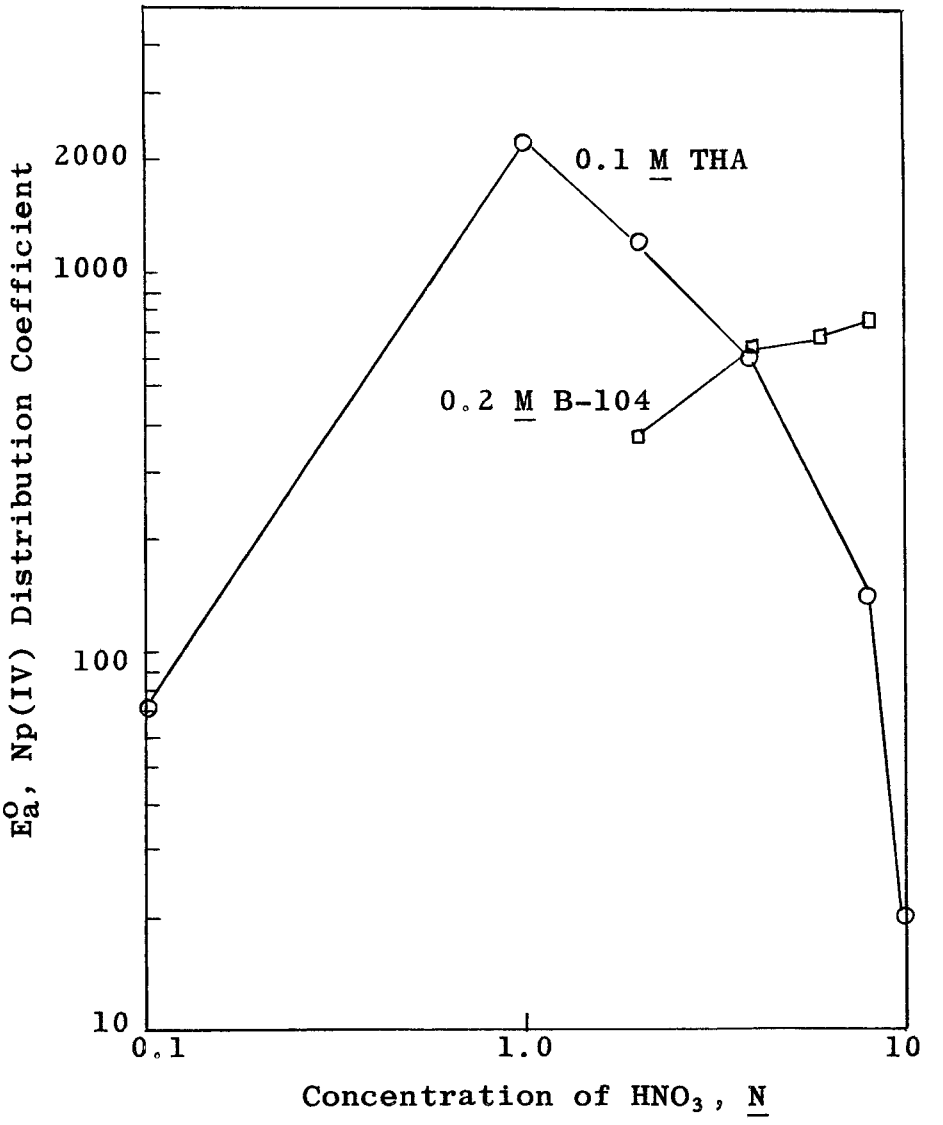

Fig. 13. Extraction of Np(IV) from HNO_3 by Quaternary Ammonium Nitrates in Xylene.

2.3 Sodium Carbonate-Alumina Procedure for Solvent Recovery: Solids Removal Study (A. T. Gresky, R. G. Mansfield)

A solvent recovery procedure involving successive use of Na_2CO_3-washing and alumina-adsorption[12,14] has been demonstrated in the laboratory as a superior method for purifying and decontaminating TBP process solvents. However, the procedure as presently conceived is limited for practical use because of (1) the excessive solids/solvent ratios employed and (2) unknowns regarding physical removal of fine solids by means other than centrifugation or filtration.

In regard to the latter point, results from recent scouting tests indicate that suspended Al_2O_3 fines may be effectively removed from 1 M TBP (in Amsco 125-82) by countercurrent washing with water. Most of the fine solids (probably less than 325 mesh) transfer into the aqueous phase to form a light slurry, while small quantities collect at the interfaces. It seems likely that such a procedure may be a feasible alternate to centrifugation or filtration.

In the scouting tests 1 M TBP (in Amsco 125-82) was first treated by washing twice with an equal volume of 0.2 M Na_2CO_3. The washed solvent was then thoroughly contacted with activated alumina (Fisher chromatographic grade, 2% (-50 +100 mesh), 97% (-100 +200), 0.7% (-200 +325), 0.3% (-325)), employing 100 g of Al_2O_3 per liter of solvent. Greater than 99.9% of the alumina was observed to settle in about 30 seconds, whereas a remaining quantity of very finely divided solids appeared to be permanently suspended. By centrifuging, filtering, and weighing, it was found that these solids amounted to about 50 to 60 mg per liter of solvent. (A secondary observation from this test is that pre-washing of the fines might be of value in a solvent recovery process to minimize problems of the final solids-removal step.)

A total of 1600 ml of the solvent containing the suspended solids was contacted with 80 ml of water in the following manner: 20 ml of water was placed in each of four contactors (Burrell shakers); sixteen (16) 100 ml volumes of the solvent were then successively contacted (at high speed for 2 min) in each stage, so that on completion of the experiment the water in stage 1 had contacted a total of 1600 ml, stage 2 a total of 1500 ml, stage 3 a total of 1400 ml, and stage 4 a total of 1300 ml; in effect simulating a system with an organic/aqueous flow ratio of about 200/1. At the end of the experiment, each stage contained 100 ml of 1 M TBP (in Amsco) and about 20 ml of water. Suspended solids were visible in the aqueous phases in stages 1 and 2. A considerable amount of very fine solids were trapped at the interface in stage 1. The 1200 ml of scrubbed solvent which passed through the system was water-white and contained no filterable solids. Phase separation times in all stages were extremely rapid

(<30 seconds) including stage 1 which contained the bulk of the solids. The organic and aqueous phases in each of the four stages were filtered through a tared medium ground-glass filter and total solid weights were measured, as follows: Stage 1, 60 mg; stage 2, 26 mg; stage 3, about 3 mg; and stage 4, about 1 mg. A total ratio of 90 mg solids/1600 ml of organic solvent (equal to about 56 mg/liter) checks well with the previously measured value of 50 to 60 mg/liter.

Conclusions from this rather crude type of experiment are necessarily qualitative in nature. However, it suggests that removal of fine solids from Al_2O_3-treated process solvents (TBP-Amsco, etc.) is physically feasible by washing with water. The removed solids appear primarily in an aqueous slurry and secondarily as suspensions at the organic-aqueous interfaces. Several stages should be included in such a unit operation (if for no other reason than to limit entrainment difficulties). High organic/aqueous flow ratio (e.g. 50 to 200) appear feasible, assuming the suspended Al_2O_3/organic ratio in the given experiment represents a fairly average condition. If true, low-level waste disposal volumes from such clean up processes can be small in comparison to those experienced already in the Na_2CO_3 procedure.

Additional experiments on the Al_2O_3 method will be performed to establish the effect of particle size on removing radioactive contaminants and on purification with respect to nitration products and polymeric organophosphorus impurities. Such experiments will provide data on Al_2O_3-capacity for such impurities. Also, it will be interesting to determine whether use of very finely-divided alumina, with its high surface-area, will permit reduction in the quantity of alumina needed for effective solvent clean-up to a point acceptable for plant operation.

2.4 Countercurrent Tests with TBP and DSBPP: Effect of Nitrite-Acetone Treatment of Purex Aqueous Feeds on Ru and Zr-Nb Decontamination (A. T. Gresky, R. G. Mansfield)

Zirconium-niobium and ruthenium decontamination of the uranium and plutonium products consistently constitutes the major decontamination problem of the Purex-type processes employing tributylphosphate (TBP). Preliminary batch and laboratory countercurrent extraction tests comparing the TBP and di-sec-butyl phenylphosphonate (DSBPP) reagents have shown that the latter generally permits only a slight advantage in decontamination from these particular fission products. However, one of the previously described countercurrent runs with DSBPP,[15] simulating conditions of the Purex co-decontamination cycle, demonstrated excellent decontamination from both Ru (DF of 1100) and Zr-Nb (DF of 13,000). This particular run was made to afford a simultaneous evaluation of two variables:

(1) a treatment of the organic extractant by an alumina-adsorption technique (100 g Al_2O_3/liter for 1 hr at R.T.) subsequent to the usual washing with 0.2 M Na_2CO_3 for organic acid removal; and (2) a treatment of the aqueous feed by the addition of acetone (1% by volume) and subsequent digestion at 25-100°C, which had been shown in early Purex and Redox developments to suppress Ru extraction and to permit plutonium valence adjustments to Pu^{+4}. Since it was not possible to readily ascertain whether the improved decontamination efficiency resulted from (1) the more elaborate Na_2CO_3-Al_2O_3 clean-up of the organic phase or (2) the acetone treatment of the aqueous feed, a series of six countercurrent runs was made to determine the responsible variable. One (1) M TBP (in Solvesso-100) and 1 M DSBPP (in Solvesso-100) were compared, employing identical F.P.-spiked aqueous feeds, scrubbing solutions, and flow conditions, in tests of three sets of varying conditions: (1) a control, not involving any novel organic or aqueous treatment; (2) alumina treatment of the organic extractant, and $NaNO_2$-acetone treatment of the aqueous feed. As suggested by data previously presented in ORNL CF-59-10-101,[15] regarding procedures for the latter treatment, the simulated dissolver solution (spiked with dissolved irradiated uranium) was adjusted to -0.3 M HNO_3, 0.025 M $NaNO_2$ and about 2 M U, and permitted to stand at R.T. for about 1 hr; after subsequent adjustment to +0.3 M HNO_3, 1.0% acetone (by volume) was added to the feed solution; after about 1 hr the solution was heated to 90-100°C, permitting volatilization of excess acetone; after another hour, the solution was cooled and finally adjusted to feed conditions by HNO_3 addition.

A summary of the results on O/A distribution and overall decontamination factors for Zr-Nb γ is given in Table 7, indicating that the acetone-treatment accounted for major decontamination advantages. The DC's (O/A) and/or EF's at the feed point decreased by factors of 25-30; and the overall Zr-Nb decontamination factors increased by factors of 11 to 40, the largest increase being associated with the DSBPP case.

The summary in Table 8 indicates a similar effect for Ru γ behavior, with DF increases of 20 to 23 being observed in the respective TBP and DSBPP cases. (Some slight DF increase also appeared to result from the Al_2O_3 treatment of the organic extractant.) The DC's (O/A) and/or EF's at the feed point decreased by factors of about 23 to 30. More com- data for the six runs are recorded in Tables 9 through 14.

One of the more surprising aspects of this series of studies was the significant effect of the acetone-treatment on Zr-Nb decontamination. Previous work had demonstrated the beneficial effects on the ruthenium decontamination, but had not been extended to consideration of Zr-Nb. Although the chemical and/or physical mechanisms of the treatment procedure are not defined, its potential advantages to process application would seem to warrant its further study in laboratory tests.

Table 7. Effect of Organic and Aqueous Treatment Procedures on Zr-Nb Extraction and Decontamination

Results of countercurrent tests employing 1 M TBP or 1 M DSBPP in Solvesso-100; aqueous feed: 427 g U/liter, 2 N HNO_3, 0.005 M $NaNO_2$, F.P. spike; aqueous scrub: 2 N HNO_3; F/S/O = 1/0.75/4.75

Countercurrent Stage	Zr-Nb Extraction Factors ($DC_a^o x FR_a^o$)					
	1 M TBP			1 M DSBPP		
	1	2	3	1	2	3
6S	4.3	6.33	1.73	1.2	6.62	0.85
4S	0.77	2.37	0.5	0.32	1.51	1.69
2S	0.12	0.35	0.04	0.092	0.13	0.012
1E	0.012	0.015	0.0005*	0.011	0.009	0.0004*
3E	0.018	0.021	0.0019	0.010	0.009	0.0020
5E	0.018	0.018	0.0019	0.012	0.013	0.0026
Overall DF's	(1130)	(1080)	(11,900)*	(566)	(990)	(23,400)*

Run 1) Control: 0.2 M Na_2CO_3-washed organic extractant; no aqueous treatment

Run 2) Extractant additionally treated by Al_2O_3 (100 g/liter for 1 hr); no aqueous treatment

Run 3)* Extractant additionally treated by Al_2O_3 (100 g/liter for 1 hr); 1% acetone-digestion of aqueous feed

*Note large decrease in extraction factors at feed point, and the large increase in DF's.

2.5 Effect of Nitrated Fractions of Amsco 125-82 on Zr-Nb Extractions by TBP (C. A. Blake, J. M. Schmitt, A. T. Gresky)

Previously reported results (ORNL CF-59-11-132) indicated that nitrated products in diluents such as Amsco 125-82 can, in combination with TBP, play a significant role in the extraction of Zr-Nb from nitrate process liquors. In general, the effect of nitrated products (resulting from high temperature reactions with HNO_3) was found to be (1) quite dependent on the presence of TBP and (2) strongly enhanced by pretreatments of the extractants by $Ca(OH)_2$.

Recently, results of further tests of nitrated products in various distillation fractions of Amsco 125-82 have confirmed the observations drawn previously. These tests were carried out as follows: (1) A volume of Amsco 125-82 was distilled at 15-18 mm of pressure through a temperature range of 66°C to >92°C to obtain seven separate fractions; (2) six of the seven fractions were refluxed separately for 4 hr with

Table 8. Effect of Organic and Aqueous Treatment Procedures on Ru Extraction and Decontamination

Results of countercurrent tests employing 1 M TBP or 1 M DSBPP in Solvesso-100; aqueous feed: 427 g U/liter, 2 N HNO_3, 0.005 M $NaNO_2$, F.P. spike; aqueous scrub: 2 N HNO_3; F/S/O = 1/0.75/4.75

Counter-current Stage	Ru γ Extraction Factors ($DC_a^o x FR_a^o$)					
	1 M TBP			1 M DSBPP		
	1	2	3*	1	2	3*
6S	2.05	2.21	1.48	0.965	2.37	1.18
4S	0.69	1.09	0.35	0.335	1.18	0.434
2S	0.248	0.413	0.047	0.189	0.305	0.032
1E	0.0173	0.020	0.0008*	0.0087	0.019	0.001*
3E	0.01	0.097	0.0017	0.054	0.059	0.0026
5E	0.177	0.18	0.0009	0.125	0.136	0.0074
Overall DF's	(640)	(768)	(13,000)*	(480)	(570)	(11,000)*

Run 1) Control: 0.2 M Na_2CO_3-washed organic extractant; no aqueous treatment
Run 2) Extractant additionally treated by Al_2O_3 (100 g/liter for 1 hr); no aqueous treatment
Run 3)* Extractant additionally treated by Al_2O_3 (100 g/liter for 1 hr); 1% acetone-digestion of aqueous feed

*Note large decrease in extraction factors at feed point and the large increase in DF's.

equal volumes of 2 M HNO_3 to cause nitration and other degradative reactions with susceptible organic components; (3) the nitrated fractions were employed as diluents to prepare six samples of 1 M TBP extractant; (4) these six samples were then washed twice with equal volumes of 0.2 M NaOH to assure removal of low molecular weight organophosphorus acids and other aqueous soluble components of the TBP and the "degraded Amsco" diluent; (5) the NaOH-washed samples were divided into two portions and further treated by alternate methods, employing in one case (a) a single equal volume wash with 2 M HNO_3, and in the other case (b) a 1-hr contact with solid $Ca(OH)_2$, at a ratio of 200 g solid per liter of the organic extractant; (6) the six samples each of portions 5a and 5b were employed in tracer tests in which the extractant was first contacted with an equal volume of a stock 2 M HNO_3 solution containing Zr-Nb γ activity, and then subsequently scrubbed with three successive passes of 2 M HNO_3 solution; (7) the Zr-Nb γ activity in the organic phases from each of the four (1 extraction plus 3 scrub) steps was determined to establish comparisons of Zr-Nb extraction and retention.

Table 9. U and F.P. Extraction in 1 M TBP (Solvesso-100): Countercurrent Test

($NaNO_2$ treatment of aqueous feed; Na_2CO_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml, 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA $\leq$ 0.006%; gross β D.F. = 1240; gross γ D.F. = 1260; Ru γ D.F. = 640; Zr-Nb γ D.F. = 1130; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	77	0.033	0.060	0.024	0.021
-A	-	0.082	0.101	0.074	0.031
(EF_a^o)	-	(2.54)	(3.76)	(2.05)	(4.3)
4S-O	-	0.089	0.12	0.071	0.035
-A	-	0.790	0.97	0.65	0.29
(EF_a^o)	-	(0.72)	(0.79)	(0.69)	(0.77)
2S-O	-	0.150	0.192	0.129	0.052
-A	-	5.7	7.2	3.30	2.7
(EF_a^o)	-	(0.17)	(0.17)	(0.248)	(0.12)
1E-O	80.0	0.36	0.55	0.33	0.29
-A	6.4	140.0	176.0	52.0	65.0
(EF_a^o)	(34.0)	(0.007)	(0.008)	(0.0173)	(0.012)
3E-O	-	3.0	3.3	2.5	0.51
-A	<0.01	169.0	210.0	69.0	76.0
(EF_a^o)	-	(0.048)	(0.043)	(0.01)	(0.018)
5E-O	-	3.3	4.1	3.7	0.47
-A	-	154.0	190.0	57.0	72.0
(EF_a^o)	-	(0.058)	(0.059)	(0.177)	(0.018)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 10. U and F.P. Extraction in 1 M TBP (Solvesso-100): Countercurrent Test

($NaNO_2$ treatment of aqueous feed; Na_2CO_3 + Al_2O_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml; 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA = 0.0013%; gross β D.F. = 674; gross γ D.F. = 1300; Ru γ D.F. = 768; Zr-Nb γ D.F. = 1080; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	76	0.061	0.058	0.020	0.022
-A	-	0.055	0.072	0.057	0.022
(EF_a^o)	-	(6.96)	(5.1)	(2.21)	(6.33)
4S-O	-	0.087	0.097	0.05	0.034
-A	-	0.053	0.36	0.29	0.091
(EF_a^o)	-	(10.4)	(1.71)	(1.09)	(2.37)
2S-O	-	0.133	0.16	0.094	0.049
-A	-	1.51	2.4	1.44	0.89
(EF_a^o)	-	(0.56)	(0.42)	(0.413)	(0.35)
1E-O	77	0.364	0.62	0.35	0.33
-A	6.4	115.0	163.0	48.0	61.0
(EF_a^o)	(32.6)	(0.0086)	(0.0103)	(0.0198)	(0.0147)
3E-O	-	2.1	3.1	2.2	0.48
-A	0.003	134.0	180.0	62.0	61.0
(EF_a^o)	-	(0.0427)	(0.047)	(0.097)	(0.0214)
5E-O	-	3.0	4.4	3.7	0.48
-A	-	144.0	200.0	56.0	73.0
(EF_a^o)	-	(0.0566)	(0.06)	(0.18)	(0.0179)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 11. U and F.P. Extraction in 1 M TBP (Solvesso-100): Countercurrent Test

(Acetone-treated aqueous feed; Na_2CO_3 + Al_2O_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml, 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA = 0.005%; gross β D.F. = 895; gross γ D.F. = 3100; Ru γ D.F. = 13,000; Zr-Nb γ D.F. = 11,900; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	85	0.046	0.024	0.00175	0.002
-A	-	0.027	0.0198	0.0075	0.0073
(EF_a^o)	-	(10.8)	(7.66)	(1.48)	(1.73)
4S-O	-	0.046	0.026	0.0021	0.0026
-A	-	0.085	0.103	0.038	0.033
(EF_a^o)	-	(3.39)	(1.60)	(0.35)	(0.5)
2S-O	-	0.049	0.027	0.0036	0.0030
-A	-	1.11	1.52	0.490	0.49
(EF_a^o)	-	(0.28)	(0.11)	(0.047)	(0.04)
1E-O	102	0.068	0.048	0.0092	0.0116
-A	13.4	137.0	183.0	31.0	59.0
(EF_a^o)	(20.7)	(0.00135)	(0.0007)	(0.00081)	(0.0005)
3E-O	-	0.74	0.054	0.05	0.046
-A	0.008	154.0	210.0	79.0	67.0
(EF_a^o)	-	(0.0131)	(0.0007)	(0.0017)	(0.0019)
5E-O	-	0.97	0.87	0.26	0.057
-A	-	184.0	250.0	75.0	83.0
(EF_a^o)	-	(0.0143)	(0.0095)	(0.00093)	(0.0019)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 12. U and F.P. Extraction in 1 M DSBPP (Solvesso-100): Countercurrent Test

($NaNO_2$ treatment of aqueous feed; Na_2CO_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml, 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA = 0.0013%; gross β D.F. = 1140; gross γ D.F. = 900; Ru γ D.F. = 480; Zr-Nb γ D.F. = 566; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	78.0	0.036	0.084	0.032	0.042
-A	-	0.29	0.44	0.21	0.22
(EF_a^o)	-	(0.79)	(1.21)	(0.965)	(1.2)
4S-O	-	0.061	0.12	0.055	0.059
-A	-	1.85	2.50	1.04	1.16
(EF_a^o)	-	(0.21)	(0.30)	(0.335)	(0.32)
2S-O	-	0.127	0.22	0.128	0.088
-A	-	8.6	13.5	4.30	6.1
(EF_a^o)	-	(0.094)	(0.10)	(0.189)	(0.092)
1E-O	81.0	0.28	0.68	0.22	0.44
-A	7.8	186.0	260.0	69.0	113.0
(EF_a^o)	(28.3)	(0.004)	(0.007)	(0.0087)	(0.011)
3E-O	-	1.9	2.2	1.77	0.37
-A	0.002	130.0	250.0	89.0	103.0
(EF_a^o)	-	(0.038)	(0.024)	(0.054)	(0.010)
5E-O	-	2.9	3.3	3.0	0.53
-A	-	161.0	260.0	65.0	120.0
(EF_a^o)	-	(0.049)	(0.035)	(0.125)	(0.012)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 13. U and F.P. Extraction in 1 M DSBPP (Solvesso-100): Countercurrent Test

($NaNO_2$ treatment of aqueous feed; Na_2CO_3 + Al_2O_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml, 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA = 0.0019%; gross β D.F. = 1415; gross γ D.F. = 1100; Ru γ D.F. = 570; Zr-Nb γ D.F. = 990; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	79.0	0.029	0.072	0.027	0.024
-A	-	0.065	0.089	0.072	0.023
(EF_a^o)	-	(2.82)	(5.12)	(2.37)	(6.62)
4S-O	-	0.068	0.158	0.08	0.043
-A	-	0.42	0.61	0.43	0.18
(EF_a^o)	-	(1.03)	(1.64)	(1.18)	(1.51)
2S-O	-	0.183	0.24	0.154	0.049
-A	-	4.9	7.0	3.2	2.4
(EF_a^o)	-	(0.24)	(0.22)	(0.305)	(0.13)
1E-O	87.0	0.33	0.58	0.40	0.25
-A	8.2	164.0	210.0	56.0	77.0
(EF_a^o)	(28.8)	(0.005)	(0.007)	(0.019)	(0.009)
3E-O	-	1.35	1.56	1.39	0.25
-A	0.003	168.0	210.0	64.0	75.0
(EF_a^o)	-	(0.022)	(0.020)	(0.059)	(0.009)
5E-O	-	2.30	3.3	2.9	0.38
-A	-	176.0	220.0	58.0	79.0
(EF_a^o)	-	(0.036)	(0.041)	(0.136)	(0.013)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 14. U and F.P. Extraction in 1 M DSBPP (Solvesso-100): Countercurrent Test

(Acetone-treated aqueous feed; Na_2CO_3 + Al_2O_3 treatment of organic extractant)

Aqueous feed: 427 g U/liter, 2.0 N HNO_3, 2.6×10^7 gross β c/m/ml, 3.6×10^7 gross γ c/m/ml, 1.06×10^7 Ru γ c/m/ml, 1.13×10^7 Zr-Nb γ c/m/ml, 1.7×10^7 TRE β c/m/ml; aqueous scrub = 2.0 N HNO_3; F/S/O = 1/0.75/4.75; 2.5 volume changes

U loss at 3 EA = 0.007%; gross β D.F. = 1000; gross γ D.F. = 3600; Ru γ D.F. = 11,000; Zr-Nb γ D.F. = 23,000; TRE β D.F. $>3.6 \times 10^4$

Stage	U	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O	83	0.041	0.021	0.00196	0.00102
-A	-	0.021	0.027	0.0105	0.0076
(EF_a^o)	-	(8.96)	(4.92)	(1.18)	(0.85)
4S-O	-	0.055	0.028	0.0052	0.00184
-A	-	0.171	0.021	0.076	0.0069
(EF_a^o)	-	(2.04)	(8.45)	(0.434)	(1.69)
2S-O	-	0.057	0.034	0.0086	0.0031
-A	-	3.6	4.7	1.71	1.59
(EF_a^o)	-	(0.10)	(0.046)	(0.032)	(0.012)
1E-O	103	0.073	0.056	0.028	0.0119
-A	13.7	189.0	250.0	75.0	82.0
(EF_a^o)	(20.5)	(0.001)	(0.0006)	(0.001)	(0.0004)
3E-O	-	0.39	0.38	0.07	0.059
-A	0.011	180.0	240.0	74.0	81.0
(EF_a^o)	-	(0.0059)	(0.0043)	(0.0026)	(0.0020)
5E-O	-	0.60	0.61	0.21	0.077
-A	-	181.0	240.0	77.0	82.0
(EF_a^o)	-	(0.009)	(0.007)	(0.0074)	(0.0026)

Note: U in g/liter; activities in c/m/ml $\times 10^{-5}$; $EF_a^o = DC_a^o \times FR_a^o$.

Table 15 records data from the extraction step and third scrubbing step as obtained for the twelve series of tests. The evidence indicates that (1) the $Ca(OH)_2$-treated samples (with one exception) extracted and retained a significantly greater quantity of Zr-Nb, and (2) the last ~10% fraction of the distilled Amsco diluent, in the case of both the HNO_3 and $Ca(OH)_2$ treatment, yielded significantly greater Zr-Nb extraction and retention than did the other fractions. This suggests that the last or high-temperature fraction contained a higher proportion of the components of virgin Amsco 125-82 that are susceptible to reaction with nitric acid (e.g., unsaturates, tertiary hydrogen atoms). The significant Zr-Nb extraction and retention in fractions 4 and 5 also suggest that portions of the active components can distill throughout a major part of the boiling range.

Table 15. Zr-Nb Tests of 1 M TBP Diluted with Various Nitrated Fractions of Amsco 125-82

(Effects of Extractant Treatment by (a) $NaOH-HNO_3$ and (b) $NaOH-Ca(OH)_2$)

Amsco 125-82 Fraction (No.)	Boiling Range (°C)	Volume (%)	Zr-Nb Activity in 1 M TBP (in γ c/s/ml)			
			(a) $NaOH(2x) + HNO_3(1x)$		(b) $NaOH(2x) + Ca(OH)_2(1x)$	
			Extr'n. Stage	3rd Scrub Stage	Extr'n. Stage	3rd Scrub Stage
1	66-70	10.2	293	7.9	677	38
2	70-74	11.7	298	13.4	91	9
3	74-76	7.6	343	28.3	913	59
4	76-78	19.2	309	10.1	962	114
5	78-80	35.9	220	9.6	2660	388
6	80-84	5.4	-	-	-	-
7	84-92	7.1	497	74.2	4940	2040
8	(residue)	3.1	-	-	-	-
Total	66-92+	100.2				

2.6 Chemical Degradation of TBP-Amsco 125-82 Systems (C. A. Blake, A. T. Gresky, H. Goren, J. M. Schmitt)

Severe degradation of TBP-Amsco 125-82 solutions with nitric acid (refluxing with 2 M HNO_3 at 107°C) was described last month.[12] Diluent reaction products were found to be quite important as contributors to Zr-Nb extraction and as affecting efficiency of clean-up procedures. This section presents the results of studies under milder conditions (treating with 2 M HNO_3 at 60°C for from 1 to 48 hr). In these tests TBP degradation appeared to be the more important

factor. Scrubbing with aqueous sodium carbonate and sodium hydroxide effectively removed the degradation products from solution, and little advantage was gained by further treatment with solid sorbants. (However, diluent degradation might be of much greater significance if there were also important radiation damage, as might be met in radiochemical processing.)

The 60° degradation tests are summarized schematically in Fig. 14, using the same notation as described previously.[12] The series of tests included (1) stepwise degradation for a total of 4 hr, with sodium hydroxide scrubbing after each 1-hr interval, (2) degradation for a total of 8 hr with sodium carbonate and calcium hydroxide treatment after 4 hr, (3) degradation for a total of 32 hr with sodium carbonate and aluminum oxide treatment after 16 hr, and (4) uninterrupted degradation for 4 and 16 (i.e., the first intervals of (2) and (3), respectively) and 48 hr. As previously, the extent of degradation of the various solvent samples was measured by Zr-Nb extraction, nitric acid scrubbing tests. After degradation and prior to the Zr-Nb extraction-retention tests, each solvent sample was analyzed for its apparent TBP content by its ability to extract nitric acid, as determined by the usual titration procedure. Each solvent was then adjusted to 1 M TBP by dilution with Amsco 125-82 that had been degraded separately under identical conditions.

The most significant observations are as follows:

(1) Samples of solvent which had been subjected to uninterrupted degradation of 4, 16, and 48 hr were used without further treatment to extract Zr-Nb activity (the "As-Is" tests in Fig. 14). Extraction was high for all three tests, and a 3-fold increase in extraction was observed when degradation was increased from 4 to 16 hr. The 16 and 48 hr tests showed about the same extraction level, but the difficulty of stripping the activity by nitric acid scrubbing increased with degradation time throughout. The same materials after scrubbing with sodium carbonate extracted ~95% less activity. The high extraction of the "As-Is" materials is due to a large degree, then, to the presence of significant concentrations of low molecular weight acids (e.g., DBP), easily stripped from the organic phase with sodium carbonate, but difficultly stripped with nitric acid. The leveling off of extraction with increased degradation may not indicate a leveling off of the concentrations of these acids, but might instead reflect their interaction with other degradation products.

(2) Four tests were made of direct treatment with solids: $Ca(OH)_2$ after the 4 hr uninterrupted degradation, Al_2O_3 after 16 hr, and both after 48 hr. The $Ca(OH)_2$ had little effect, the results appearing slightly worse than the "As-Is" results in the 4-hr test and slightly better in the 48-hr test. In the previously reported tests after degradation at higher temperature, direct treatment with $Ca(OH)_2$ had considerable

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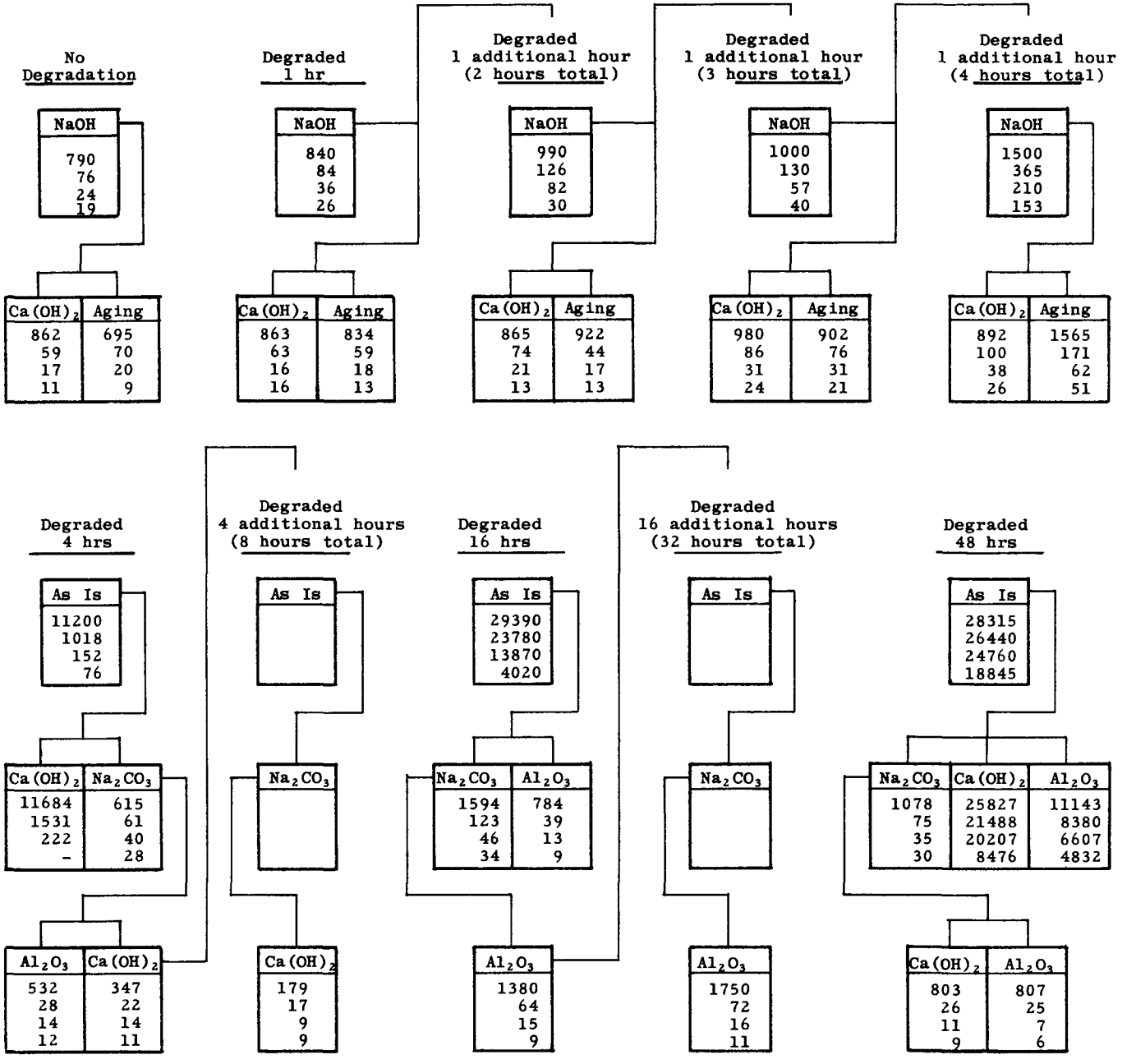

Key - Boxed data show the results of Zr-Nb extraction tests:

Cleanup
Extract
Scrub 1
Scrub 2
Scrub 3

Cleanup: "NaOH" - 10 min scrub with equal volume of 1 M NaOH, followed by 2 additional 10 min scrubs with equal volumes of 0.01 M NaOH
"Na_2CO_3" - 3 successive 10 min scrubs with equal volumes of 0.2 M Na_2CO_3
"$Ca(OH)_2$", "Al_2O_3" - 1 hr contact with 200 g solid reagent per liter organic phase

Extract: Zr-Nb γ (c/s/ml) extracted from equal volume of 2 M HNO_3 (initial), 10 min gross γ in head ~1×10^5 c/s/ml, ~25% counting efficiency

Scrub: Zr-Nb γ (c/s/ml) remaining in organic phase after 10 min scrub with an equal volume of 2 M HNO_3

Fig. 14. Zr-Nb Extraction with 1 M TBP-Amsco 125-82 Solutions Degraded by Nitric Acid (Conditions for degrading - Agitation with equal volume 2 N HNO_3, 60°C, under reflux).

adverse effects on Zr-Nb extraction and retention, which were attributed mainly to some interaction with TBP or diluent nitration products. Thus, it follows that under the milder conditions of degradation (lower temperatures) TBP or diluent nitration had a lesser effect on Zr-Nb extraction behavior than that caused by the degradation of TBP to low-weight acids.

(3) The direct treatment with Al_2O_3 was more effective than the Na_2CO_3 treatment after 16 hr, but much less effective after 48 hr. An attractive interpretation is that the amount of Al_2O_3 used was able to sorb the quantity of low weight acids produced in 16 hr but not that produced in 48 hr. The comparison also suggests that Zr-Nb extractants other than low-weight acids were of a higher level after 16 than after 48 hr, since the Na_2CO_3 was more effective after 48 than after 16 hr, and the Al_2O_3 was more effective than Na_2CO_3 after 16 hr. (However, it is surprising that the Zr-Nb extraction was higher after Na_2CO_3-Al_2O_3 consecutive treatments than after direct Al_2O_3.)

(4) In each of the tests, Al_2O_3 and/or $Ca(OH)_2$ was used after a scrub with Na_2CO_3 or NaOH. Except for the extraction by the control (862 vs 790) and 1 hr-degraded solvent (863 vs 840), each gave slightly lowered Zr-Nb extraction and retention. This appears to support the suggestion that nitration products were minor contaminants in these tests (again noting that the extractions appeared exceptional in the 16-hr test).

(5) After each of the 1-hr degradation intervals, portions of the hydroxide-scrubbed solutions were stored at room temperature for 33 days, and then again scrubbed with sodium hydroxide. No growth of Zr-Nb extractants was found (as has been found in some scrubbing tests); instead, most of the extractions and retentions were slightly lower than after the initial NaOH treatment, and to about the same extent as obtained with the $Ca(OH)_2$ treatment. While the differences are so small that interpretation may not be justified, this suggests that some of the extracting substances may have changed during the 33 days to materials which could be stripped into sodium hydroxide. The similarity of the aging and the calcium hydroxide treatment results suggests further that the extractants which changed with age may be the ones which sorb on the calcium hydroxide.

Ratio of Retention to Extraction. The percent of the initially-extracted Zr-Nb which was retained after 3 nitric acid scrubs (Fig. 15) rose as the degradation time was increased from zero to ~8 hr, then dropped abruptly at 16 hr, and did not change much more at 32 and 48 hr. Throughout, this percent was lower after alkaline scrub-solids treatment than after alkaline scrub only. If these trends are indeed real, the initial increase could reflect the conversion of high molecular weight neutral compounds into high molecular weight acids, the latter compounds being, most probably, stronger extractants. Further degradation of the high molecular weight acids to low weight acids, which are removed during the aqueous alkaline scrub, would account for the decrease beyond the maximum.

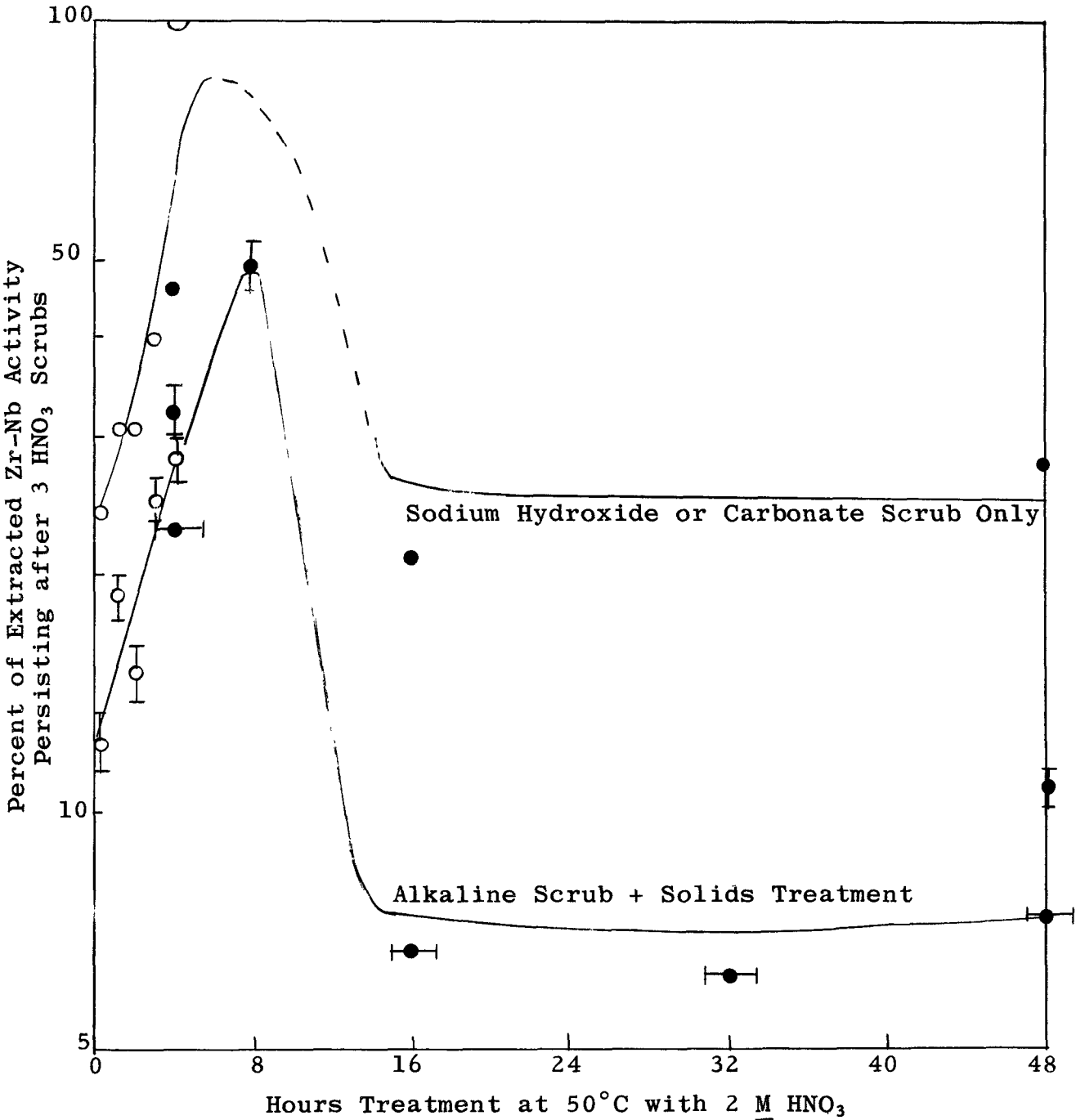

Fig. 15. Variation of Percent Unstripped Activity with Degradation Time.

(Data of Fig. 14. Percent $\equiv \frac{\text{Scrub 3}}{\text{Extract}} \times 100$. ○ NaOH Scrub; ● Na_2CO_3 Scrub; NaOH Scrub, $Ca(OH)_2$ Treatment; Na_2CO_3 Scrub, $Ca(OH)_2$ Treatment; Na_2CO_3 Scrub, Al_2O_3 Treatment)

3.0 FUNDAMENTAL CHEMISTRY

3.1 Interfacial Tensions in Amine Extractant Systems (K. A. Allen, W. J. McDowell, G. N. Case)

Striking differences among the interfacial activities of different salt forms of some amine extractants, in benzene solutions vs aqueous solutions of the corresponding acids, were reported in ORNL CF-59-8-45.[16] Since that time interfacial tensions as a function of concentration have been examined for the extractant systems listed in Table 16. Examples of the γ (interfacial tension, erg cm^{-2})-log concentration relationships for extractants in each group may be seen in Figs. 16 and 17. For comparison, similar curves for some other surfactants are shown.[17,18] Of these, sodium lauryl sulfate and potassium laurate are both strongly surface active. Decanol and benzoyl acetone are examples of intermediately and weakly surface active materials, respectively.

The shapes of the curves may be qualitatively interpreted as follows. At low concentrations the curves should approach the pure solvent value of γ asymptotically. At the steepest portions of the curves (usually inflections) the Gibbs equation (see below) predicts that the interfacial population of solute should reach a maximum. At higher concentrations, decreases in the slopes, followed by asymptotic leveling off at minimum values of γ, indicate that (1) the interface is saturated, (2) the true solute concentration (solute activity) is not increasing as rapidly as the formal solute concentration, or possibly both. The sharp breaks found in the potassium laurate and sodium lauryl sulfate curves were interpreted as critical micelle concentrations (CMC).[18,19] Both papers cited references to similar CMC values obtained by other methods.

Of the extractant systems examined so far only Primene JMT sulfate vs 0.01 N H_2SO_4 (Fig. 16) showed a sharp break plus asymptotic leveling at both high and low concentrations. However, the curves for all the systems grouped under "strongly interface active" suggests that they probably would show asymptotic behavior at the low end if measurements were extended to lower concentrations. The intermediately interface active systems show very slight inflections. The weakly interface active group shows what appears to be the upper asymptotic end of the curve. It is probably not possible to show the break or flattening of the slope at higher concentrations due to solubility limitations.

The reason for the gentle changes in slope shown by the extractant systems in comparison with the abrupt ones shown by the aqueous surfactants is not apparent. A true interface saturation rather than a CMC is a possible explanation. However, since TOAS, which is known from other work[20] to be

Table 16. Systems Examined as Benzene Solutions of the Extractants vs Aqueous Solutions of the Acids

Strongly Interface Active

Di-n-decylamine sulfate (DDAS) vs 0.01 N H_2SO_4
Di-n-decylamine sulfate (DDAS) vs 1 M SO_4 at pH 2
Di-n-decylamine sulfate-bisulfate (DDAS-DDAHS) vs 1 M SO_4 at pH 1.0
Primene JMT vs 0.01 N H_2SO_4
Sodium di(2-ethylhexyl)phosphate (NaD2EHP) vs 1 M SO_4 at pH 10.0

Intermediately Interface Active

Tri-n-octylamine sulfate (TOAS) vs 0.01 N H_2SO_4
Tri-n-octylamine chloride (TOACl) vs 0.01 N HCl

Weakly Interface Active

Tri-n-octylamine vs water
Tri-n-octylamine nitrate vs 0.01 N HNO_3
Tri-n-octylamine perchlorate vs 0.01 N $HClO_4$
Di-n-decylamine vs water
Di-n-decylamine nitrate vs 0.01 N HNO_3
Tri-n-octylphosphine oxide vs 0.01 N H_2SO_4
Tri-n-octylphosphine oxide vs 1 M SO_4 at pH 2.0
Di(2-ethylhexyl)phosphoric acid vs 0.01 N H_2SO_4
Di(2-ethylhexyl)phosphoric acid vs 1 M SO_4 at pH 2.0

monomeric in benzene solution, shows a very small inflection compared to DDAS and Primene JMT sulfate, it is possible that the break observed in these latter curves is associated with micelle formation.

Very approximate estimates of the number, τ, of solute molecules adsorbed per cm^2 interfacial area can be made on the basis of the Gibbs expression, which in rigorous form equates τ to the rate of change of γ with respect to the chemical potential of the solute, μ_2, as follows:

$$\tau = -d\gamma/d\mu_2$$

The approximation $d\mu_2 = kT \, d\ln c$, where k is Boltzmann's constant in erg $molecule^{-1}$ $degree^{-1}$, T is in degrees Kelvin, and c is in any convenient concentration units, then permits estimation of τ from the slopes indicated on plots such as those in Fig. 16 and 17. In order to ascertain whether the

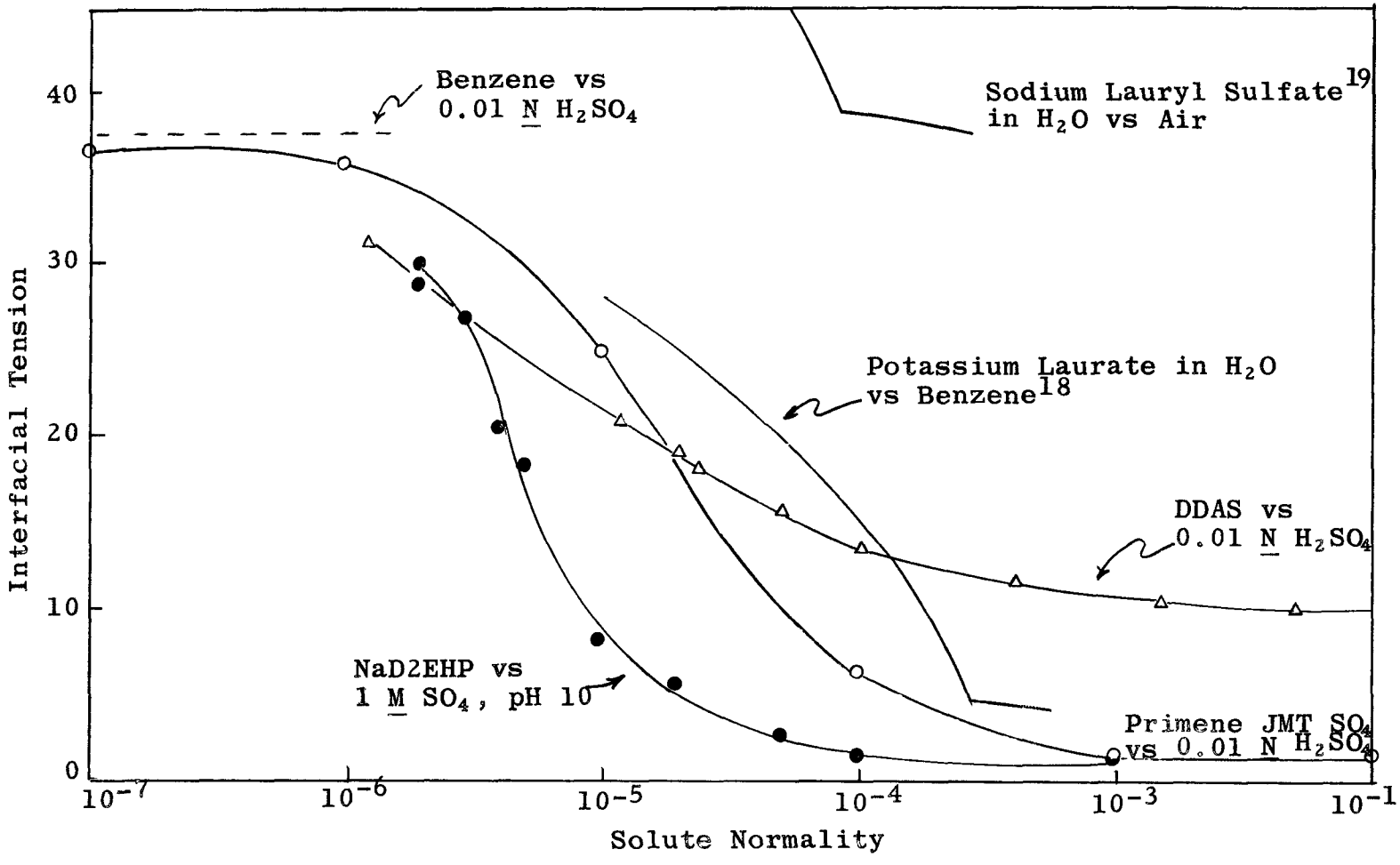

Fig. 16. Interfacial and Surface Tensions of Strong Surfactants.

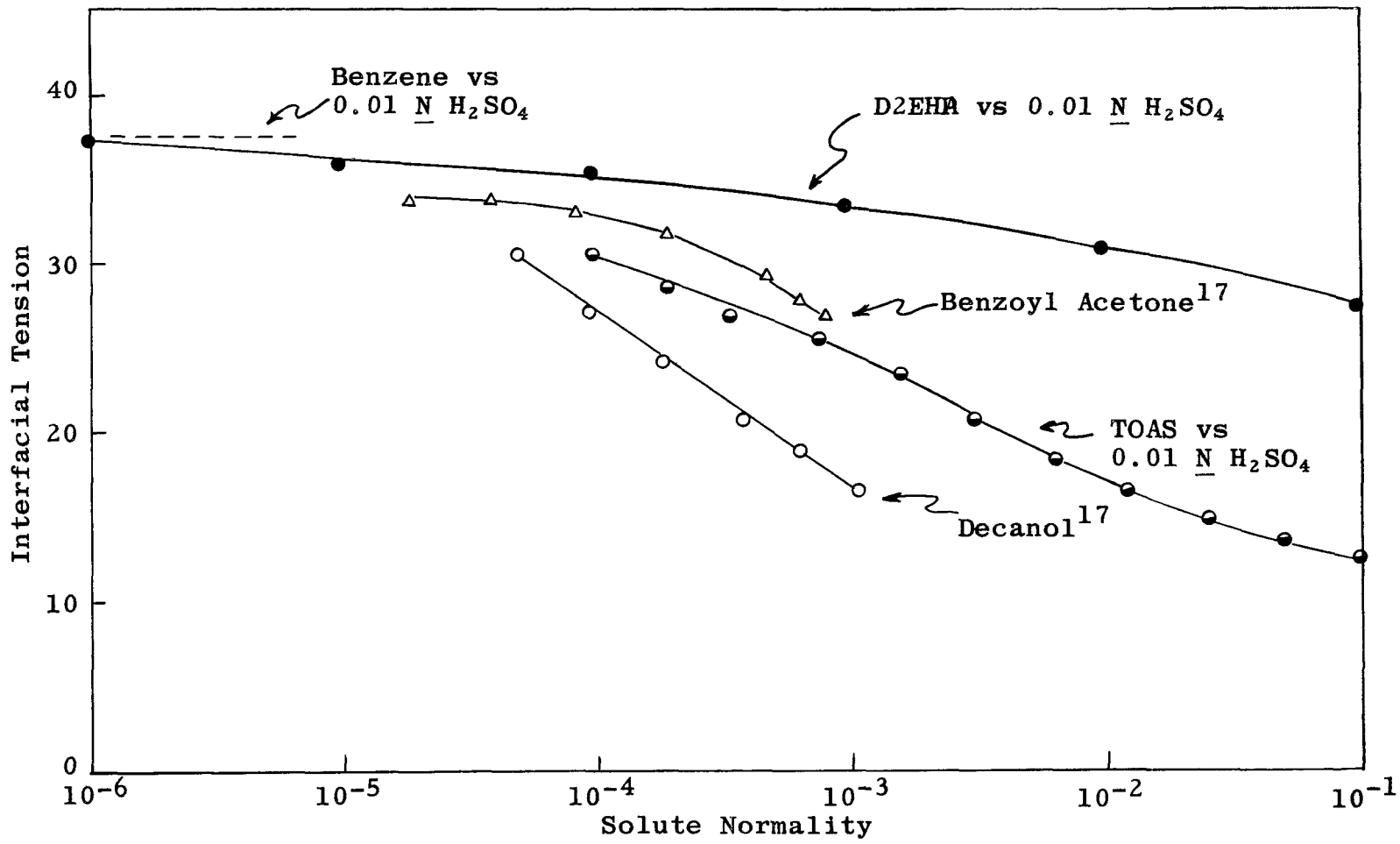

Fig. 17. Interfacial Tensions of Moderate and Weak Surfactants.

maximum values of Γ obtained from these curves would yield reasonable areas per molecule at the interface, the slopes used in Table 17 were taken at the steepest points. The values of Γ and the areas per molecule, A (square Angstroms), shown in Table 17, were computed from the relations

$$\Gamma = -\frac{1}{kT}\,(d\gamma/d\ln c)_{max}$$

and $$A = \frac{10^{16}}{\Gamma}$$

The areas per molecule obtained are in reasonable accord with rough predictions based on 25 A^2 as an approximate cross sectional area requirement for each carbon chain.

Table 17. Estimated Interfacial Areas per Molecule

Solute	$-\left(\frac{d\gamma}{d\ \ln\ c}\right)_{max}\ \frac{erg}{cm^2}$	Γ molecules/cm^2	A $\frac{Angstroms^2}{molecule}$
Primene JMT SO_4	12	2.9×10^{14}	35
DDAS	5.8	1.4×10^{14}	70
TOAS	4.2	1.0×10^{14}	100
TOACl	3.5	0.8×10^{14}	125
NaD2EHP	15	3.6×10^{14}	28
D2EHPA	3.3	0.8×10^{14}	125

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