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CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT SECTION C

PROGRESS REPORT FOR

APRIL-MAY 1960

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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Chemical Development Section C

Progress Report for April-May 1960

K. B. Brown

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

Ammonium Carbonate Stripping of Uranium from Amex Process Solvent

An economical process was successfully demonstrated in bench-scale continuous equipment for stripping uranium from amines with ammonium carbonate solution. By recycling the strip solution to allow build-up of the concentration of ammonium sulfate (formed in the stripping reactions) to 1-2 molar, the solubility of uranium in the aqueous phase was limited to <5 g per liter and ammonium uranyl tricarbonate (AUT) precipitated in the stripping system. The AUT, which settled and filtered rapidly, was readily converted to U_3O_8 by calcination for 2 hr at 500°C yielding a high assay (>98% U_3O_8) product virtually free of sodium, molybdenum, and vanadium.

Technetium and Neptunium Recovery from Fluorination Plant Residues

A continuous countercurrent mixer-settler extraction system has been set up for further testing of the process for recovery of Tc, Np, and U by tertiary amine extraction from uranium hexafluoride transfer cylinder wash solutions. Physical performance was good in startup with a commercial tertiary amine and simulated feed solution. In preparation for the continuous countercurrent testing, the effects of tridecanol addition and of uranium loading on the technetium extraction coefficient were measured. Preliminary tests of neptunium partition from the technetium with very dilute HNO_3 or $HNO_3 + H_2O_2$ were promising, so that the use of sulfate can be avoided if desired. Continuation of a batch countercurrent extraction test to 9+ volume changes confirmed the uranium profiles reported at 4 volume changes.

Effect of Purex Aqueous Feed Adjustment Procedures on Pu Extraction by 1 M Di-sec-butyl Phenylphosphonate (DSBPP) in Solvesso

Batch tests, simulating the feed plate conditions of the Purex codecontamination cycle, indicated that an aqueous feed nitrite concentration in the range of 0.025 and 0.05 M (with digestion at 50°C for 1 hr) was needed to insure complete plutonium (mostly Pu(IV)) extraction by 1 M DSBPP--Solvesso. Other preliminary scouting tests (without nitrite addition) of a similar nature indicated that acetone addition (1% by volume), to either acid-deficient (-0.48 M HNO_3) or acidic (0.3 M HNO_3) aqueous feeds, was effective in con-

verting plutonium to an inextractable state. It is believed that this is due to formation of Pu(III) rather than some inextractable polymeric species.

Solubility of Di-sec-butyl Phenylphosphonate (DSBPP) Complexes of Uranyl and Thorium Nitrates in CCl_4

Scouting tests with 0.7 M DSBPP--CCl_4 have indicated complete solubility of the uranium and thorium complexes with DSBPP, indicating physical feasibility of carbon tetrachloride as a DSBPP diluent in process applications.

Plutonium(IV) Nitrate Extraction with TBP and Phenylphosphonate Esters

Plutonium(IV) extraction coefficients with di-n-butyl phenylphosphonate (DnBPP), di-sec-butyl phenylphosphonate (DsBPP), and tributyl phosphate (TBP) in both direct and back extractions agreed with data previously reported from this laboratory, differing significantly from TBP data in the literature. The discrepancy has not been explained. E_a^o vs $\underline{M}_{HNO_3}$ log plots gave parallel lines for the three reagents, slope ~2.5 from ~2 M down at least to 0.4 M HNO_3 but shifting toward slope ~1 at 4 M HNO_3. The coefficients with DsBPP were close to those with TBP, and those with DnBPP were higher by a factor of ~1.5. At acidities below 0.4 M HNO_3 direct extraction equilibrations continued to decrease with about the same slope, but distribution coefficients from back extractions rose, indicating formation of difficultly-strippable plutonium species in the organic phase.

Ruthenium Extraction by TBP-Amsco 125-82 Solvent

The response of Ru^{106} extraction (as the nitrato nitrosylruthenium complexes) to variations in the treatment of TBP-Amsco 125-82 solvent was tested in a manner similar to that used previously for $Zr\text{-}Nb^{95}$. In contrast to the $Zr\text{-}Nb^{95}$ results, the Ru^{106} extraction properties of a fresh TBP-fresh Amsco solvent were not significantly altered by chemical degradation of the diluent, by simulated degradation of the TBP (i.e., addition of its principal hydrolysis product), or by total solvent irradiation. Only in tests where the Ru^{106} was extracted into a degraded solvent and allowed to age for a period of several days was there evidence that simple scrubbing with acids or alkaline solutions would not effect essentially complete stripping.

Fission Product (Cesium) Recovery

Two solvents, out of a number tested, have shown ability to extract cesium. With sodium tetraphenyl boron in hexone good extractions of cesium were obtained from adjusted Purex 1-WW solutions. Thus far, however, no acceptable way has been found to strip this reagent without converting it to a form which is ineffective for reuse. With dinonyl naphthalene sulfonic acid in Amsco 125-82, the extraction of cesium from the Purex waste liquor was comparatively weak. Process application of this reagent may be possible if future tests show a very high selectivity for cesium over other components of the liquor.

Anomalous Equilibria in Solvent Extraction Systems

Continued examination of solvent extraction systems for anomalous equilibria other than those reported previously for uranium extraction by TOAS and DDAS has resulted in evidence of such behavior in three additional systems (thorium extraction by DDAS and uranium extraction by 1,3-ethylpentyl-4-ethyloctylamine sulfate and Primene JMT sulfate). Several other systems (e.g., TBP, TOPO, D2EHPA, etc.) were examined, but none showed anomalous differences not attributable to experimental uncertainty.

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CONTENTS (Cont'd.)

1.0 RAW MATERIALS PROCESSING

1.1 Ammonium Carbonate Stripping of Uranium from Amines

(D. J. Crouse, F. J. Hurst)

The ammonium carbonate stripping flowsheet previously[1] developed for use with the di(2-ethylhexyl)phosphoric acid extraction (Dapex) process has been applied successfully to the recovery of uranium from Amex solvent. Uranium is precipitated in the stripping system as ammonium uranyl tricarbonate (AUT) by maintaining the ammonium salt (ammonium carbonate plus ammonium sulfate) concentration in the range 1-2 molar and recycling the strip solution. The crystalline AUT settles and filters rapidly and is readily converted to U_3O_8 by calcination at 500°C. Since the product is of high assay (>98% U_3O_8) and virtually free of sodium, molybdenum, and vanadium, it should be highly amenable to the direct reduction-hydrofluorination-fluorination process for producing UF_6.

1.1.1 Solubility of AUT in $(NH_4)_2SO_4$--$(NH_4)_2CO_3$ Solutions. In stripping amines with ammonium carbonate solution, ammonium sulfate is formed (by reaction with amine sulfate-uranyl sulfate) and accumulates in the stripping solution if it is recycled. The solubility of AUT is dependent on the total solute (ammonium carbonate plus ammonium sulfate) concentration and thus effective salting out of AUT can be obtained using relatively low concentrations of ammonium carbonate. In batch solubility studies, wherein the ammonium carbonate concentration was maintained constant at 0.5 molar, the solubility of uranium (Fig. 1) decreased from ~4.5 to ~1 g per liter as the ammonium sulfate concentration was increased from 0.5 to 2 M. The dependence of the solubility on the total solute concentration was essentially identical to that reported previously[1] for the simple ammonium carbonate system. In other tests, in which the total solute concentration was held constant at two molar, the uranium solubility was ~1.4 g per liter and varied <10% as the ammonium carbonate concentration was varied from 0.2 to 0.8 M:

Concentration, molar		Uranium Solubility, g/liter
$(NH_4)_2CO_3$	$(NH_4)_2SO_4$	
0.2	1.8	1.35
0.4	1.6	1.39
0.6	1.4	1.46
0.8	1.2	1.47

These tests were made by shaking an excess of solid AUT with ammonium carbonate-ammonium sulfate solutions. Equilibrium was reached fairly rapidly since analyses after 1, 7, and 10 days were nearly identical. These solubility values are slightly lower than those obtained in continuous runs (Sec. 1.1.2) indicating that equilibrium was not reached in the relatively short contact periods of the continuous tests.

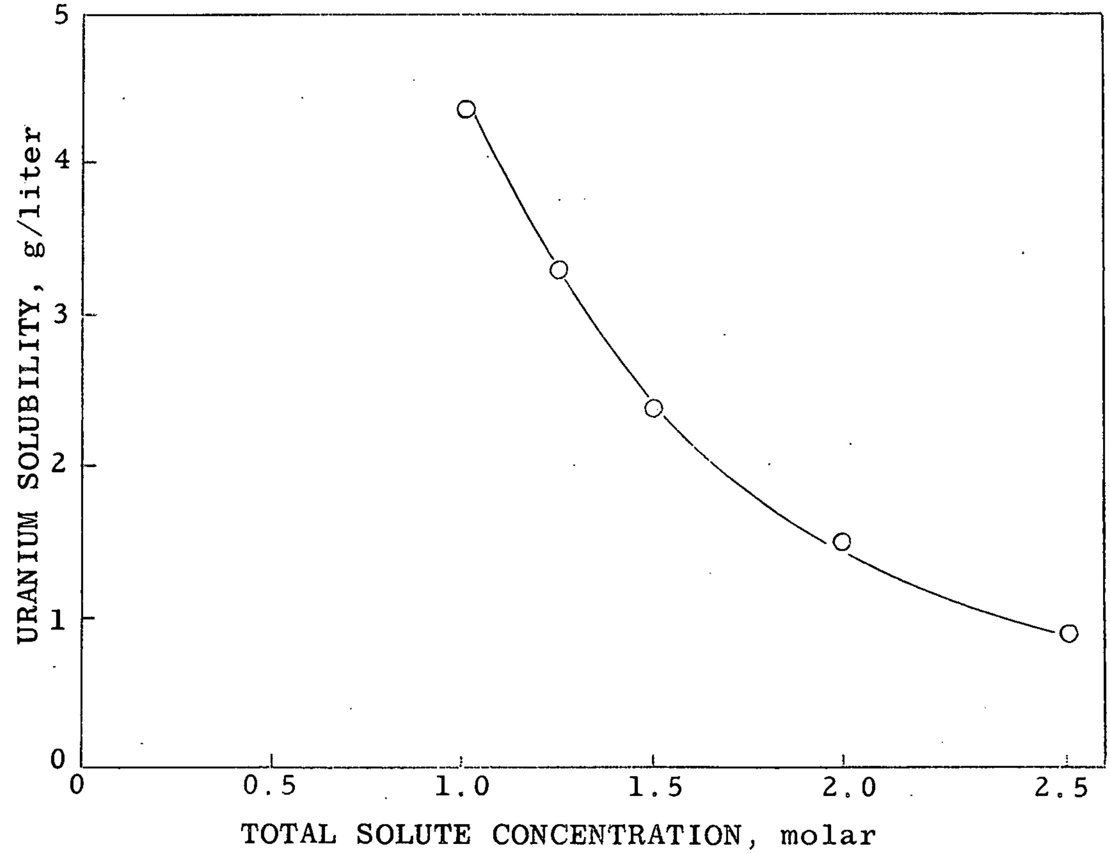

Fig. 1. Solubility of AUT in $(NH_4)_2CO_3$--$(NH_4)_2SO_4$ solutions. $(NH_4)_2CO_3$ concentration held constant at 0.5 M and $(NH_4)_2SO_4$ concentration varied from 0.5 to 2 M.

1.1.2 Continuous Tests. A series of continuous tests were made in a mixer-settler test array using 0.06 M Alamine 336 in 98% kerosene--2% tridecanol to study operational feasibility of the process and to establish reagent costs. The circuit (Fig. 2) included three extraction stages, one water scrub stage, two stripping stages, and a reservoir for decanting the recycle solution from the AUT product. Both the reservoir and the settler of the first stripping stage had conical bottoms to ensure proper discharge of solids. The bulk of the makeup stripping reagent was added by continuously dissolving ammonia and carbon dioxide in the solution contained in the reservoir. Approximately 0.5 M $(NH_4)_2CO_3$ was fed to the second stripping stage, the flow rate of this solution being adjusted to approximately balance aqueous losses from the stripping system. There was a small bleed (2-4% of the organic flow) to prevent excessive accumulation of molybdenum and ammonium sulfate in the recycle solution.

The ammonium sulfate concentration in the recycle solution was controlled at the desired level by adjusting the

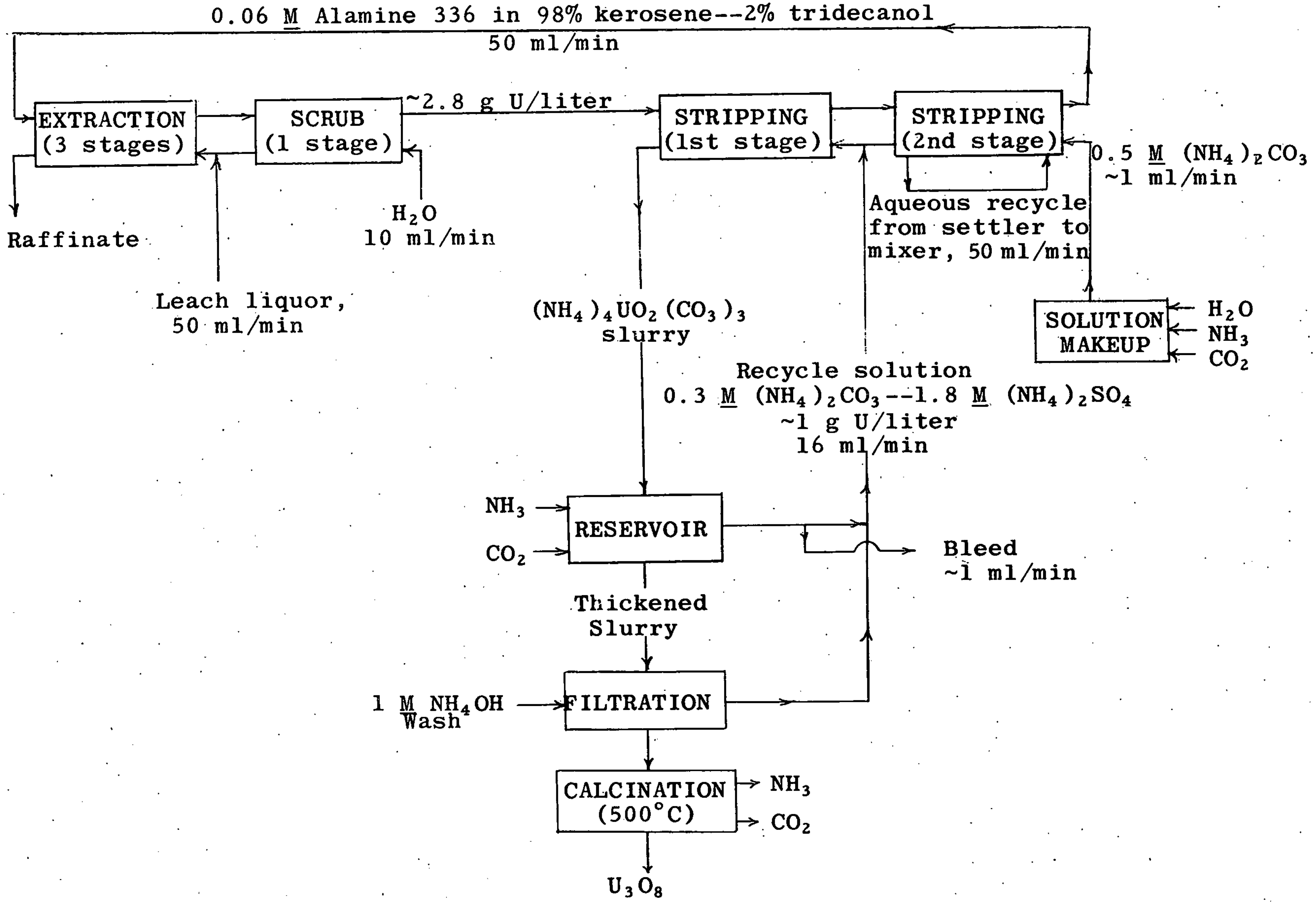

Fig. 2. Ammonium Carbonate Stripping Process

amount of bleed. Stoichiometric chemical requirements for stripping and precipitation are one mole of ammonia per mole of amine plus 6 moles of ammonia and 3 moles of carbon dioxide per mole of uranium recovered. For 0.06 M amine loaded to 2.8 g U per liter, this amounts to 0.67 pound of ammonia and 0.47 pound of carbon dioxide per pound of U_3O_8. In practice, requirements are ~10% higher than stoichiometric to compensate for losses to the bleed solution and by entrainment of strip solution in the solvent.

Extended runs with a synthetic leach liquor (pH 1) containing in grams per liter, 2.8 U, 1.0 V(IV), 0.1 Mo, 1 Fe(II), 1.5 Fe(III), 3 Al, 1 PO_4, and 30 SO_4 showed that the composition of the recycle solution was not critical. Essentially complete stripping of uranium and molybdenum and favorable physical operation were obtained when the $(NH_4)_2CO_3$ + $(NH_4)_2SO_4$ concentration ranged 1-2 molar and the $(NH_4)_2CO_3$ concentration ranged 0.3-1.5 molar. Most of the time the $(NH_4)_2CO_3$ concentration was maintained at a relatively low level (~0.3 M) since this had advantage from the standpoint of reagent economy. With 0.3 M $(NH_4)_2CO_3$, the concentration of uranium in the recycle solution was 1-1.5 g per liter with the $(NH_4)_2SO_4$ concentration controlled at ~2 molar and 2-3 g per liter with $(NH_4)_2SO_4$ concentration controlled at ~1 molar.

In the early tests, one annoying problem was encountered. A small fraction (5-10%) of the uranium precipitate, unlike the normal rapid-settling AUT, was of extremely fine particle size and dispersed fairly uniformly in the organic phase. Analysis showed this precipitate contained uranium, ammonia, and sulfate, but <1% carbonate. Most of the precipitate dissolved in the aqueous phase in the second stripping stage but a portion of it accumulated in the solvent recycle line or was carried back into the extraction system. Although this did not adversely affect physical operation of the stripping system or recoveries in the extraction system, it was considered undesirable and studies were made to eliminate the condition. It was found that essentially all of the precipitate could be redissolved by increasing the residence time in the second stage mixer from its original value of ~10 min to ~45 min but there was still a small accumulation of precipitate in the solvent recycle line. The problem was completely eliminated by changing the design of the first stripping stage mixer. Originally the line connecting the mixer and settler was close to the bottom of the mixer, allowing considerable recycle of organic (the interface in the settler was below the connecting line) from the settler to the mixer which decreased the aqueous/organic phase ratio and the aqueous residence time in the mixer. Change to an overflow type mixer, of approximately equivalent volume (~1200 ml), provided a residence time for both phases of ~18 min and eliminated formation of the troublesome precipitate.

Unlike the Dapex system, where slow accumulation of AUT as a tenacious scale on glass (but not Plexiglas) equipment was a problem, the AUT formed in the Amex system showed no tendency to adhere to either glass or plastic equipment.

The crystalline AUT precipitate settled and filtered rapidly. After being washed on the filter with a small volume of 1 M NH_4OH, it was calcined for 2 hr at 500°C. Typical products (Table 1) analyzed >98% U_3O_8, <0.04% Mo, <0.005% V, <0.01% Fe, <0.3% NH_3, <1.2% SO_4, and <1.5% CO_3.

Table 1. Analysis of Uranium Products from Continuous Runs

Constituent	Product Analysis, % 1	2	3
U_3O_8	98.5	98.7	98.0
Mo	0.033	0.002	0.005
V	0.003	0.003	0.002
Fe	0.002	0.004	0.007
Al	0.01	<0.01	0.06
NH_3	<0.01	0.08	0.22
CO_3	0.25	1.4	0.35
SO_4	1.1	0.08	0.03
PO_4	0.034	0.033	0.023
HNO_3--insoluble uranium	0.00084	0.00019	0.0016
Loss on ignition (1000°C)	-	1.2	-

1.1.3 Recovery of Uranium from the Bleed Solution. The uranium in the bleed solution, which usually is 1-2% of the total uranium processed, must be recovered and separated from molybdenum. Boiling the bleed solution (1.05 g U and 8.1 g Mo per liter, pH 9.5) for 30 min (final pH = 6.3) precipitated >99% of the uranium and only 15% of the molybdenum. This precipitate, which settled and filtered rapidly, can be dissolved in the leach liquor and returned to the extraction circuit.

Effective recovery of uranium and separation from molybdenum was also obtained by acidifying (pH 1.5) the bleed solution with H_2SO_4 and passing it through a column containing an 11 in. bed of 20x50 mesh Type OL activated carbon (Pittsburgh Coke and Chemical Co.). About 14 column volumes of acidified bleed solution (0.9 g U and 8.2 g Mo per liter) were passed through the column. The molybdenum concentration in the effluent, which was less than 0.6 g per liter for the first 8 column volumes, increased to 1.3 and 3.9 g per liter after passage of 10 and 14 column volumes, respectively.

The column, loaded to ~270 g Mo per kilogram of carbon, was washed with 2 column volumes of water. The total effluent (including the wash), which contained >96% of the uranium and only ~20% of the molybdenum, can be recycled to the extraction circuit. Molybdenum was eluted effectively from the column with 2 M NH_4OH. High-purity molybdic oxide can be recovered from this solution by evaporation and calcination of the residue.

1.1.4 Estimated Reagent Costs. Based on data from the continuous runs, total reagent costs for the extraction, stripping, and precipitation steps are estimated at 9.5¢/lb U_3O_8 (Table 2). This estimate assumes use of commercial carbon dioxide (5¢/lb). Use of flue gas as a source of carbon dioxide offers a potential cost saving of ~2¢/lb U_3O_8. Recovery of the stripping reagent from the calciner off-gases offers further potential for reducing reagent costs.

Table 2. Estimated Reagent Costs for Ammonium Carbonate Stripping

(Assumes treatment of a liquor containing 1.2 g U_3O_8 per liter)

Chemical	Consumption	Consumption, lb/lb U_3O_8	Unit Cost, ¢/lb	Cost, ¢/lb U_3O_8
NH_3	Stripping	0.74	5.9	4.4
CO_2	Stripping	0.52	5	2.6
Alamine 336	Distribution to raffinate (<5 ppm)	<0.004	125	<0.5
Organic phase	Entrainment and spillage[a]	0.05 gal	39¢/gal	2.0
			Total	9.5

[a] Entrainment and spillage estimated at 0.05% of raffinate volume.

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. Studies leading to a tentative chemical flowsheet for recovery and separation of Tc, Np, and U by tertiary amine extraction were reported previously, including a batch countercurrent test of the extraction and partition steps.[2,3] A continuous countercurrent mixer-settler system has been set up for further testing of this process, and is in shake-down operation with simulated feed solution and a commercial amine. In preparation for the continuous countercurrent tests, further measurements were made of the behavior of different amines, on the effects of tridecanol (diluent modifier) and uranium loading on technetium extraction, and on dilute HNO_3 and HNO_3-H_2O_2 as alternative neptunium stripping agents to avoid the use of sulfate.

2.1.1 Continuous Extraction System. A series of 21 small glass mixer-settlers were set up so as to be divisible into any combination of coextraction, partition, and stripping banks. The mixer-settlers have been described by Weaver and Kappelmann.[4] Their holdup each is about 250 ml organic + aqueous. All feeds are metered by bellows pumps which are calibrated and continuously checked by using tubulated graduated cylinders for the feed reservoirs. The first system to be checked is as follows:

Bank	Stages	Aq. Solution	ml Aq/hr	A/O
Coextraction	6	Simulated feed	257	0.85/1
U partition	6	1 N HNO_3	150	1/2
Np partition	7	0.05 N HNO_3	50	1/6
Tc stripping	2	1 N NH_4OH	150	1/2

The extractant is 0.3 M Alamine 336* (free base form) in 90% Amsco 125-82--10% tridecanol, at a flow rate of 300 ml/hr. The head solution contains (g/liter) 40 U, 2.5 Th, 45 Al, 4 Fe, 2 Cr, 2 Ni, 0.25 Mn, 0.5 Cu; 0.5 M F^-, 1 M H^+, and 6.8 M total nitrate. These are approximately the concentrations of the major constituents in the plant solution PCF (ORNL CF-60-1-119, Table 4). The feed solution is prepared by adding ferrous sulfamate to 0.1 M and then diluting to twice the original volume. No distribution analyses have yet been obtained from the startup of the system. Physical operation has been good, with sharp phase separation, clear aqueous phases, and cloudy to clear organic phases.

After the uranium distribution has been checked, neptunium and technetium tracers are to be added in separate runs with the simulated feed, before actual plant solution is tested.

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*Alamine 336 is a commercial tertiary amine with a random mixture of principally C_8 and C_{10} straight-chain alkyls.

2.1.2 Batch Countercurrent Extraction. A batch countercurrent test of the Tc-Np-U extraction was previously reported, in which 11 extraction stages were carried through 42 cycles, or ~4 volume changes (ORNL CF-60-1-119, p. 16 ff, Figs. 8-10). The same extraction bank was subsequently carried through 60 more cycles, primarily to furnish fresh solvent for uranium-neptunium partition tests.[3] The uranium profiles across the extraction system after the 102nd cycle were in good agreement with those after the 42nd cycle (Figs. 3 and 4). The first six stages reached close to saturation, with the aqueous uranium concentrations almost exactly as before and the organic uranium concentrations slightly higher. Stages 7-11 showed increased uranium concentrations in both phases, falling along the same extraction isotherm as before. The raffinate was higher than at the 42nd cycle, but still <0.1% of the feed uranium concentrate.

2.1.3 Effect of Tridecanol on E_a^o(Tc). The addition of 5 v % tridecanol (TDA) to trilaurylamine (TLA) was previously observed to decrease the technetium extraction coefficient by about 1/2. In preparation for continuous countercurrent tests with Alamine 336, the effect of TDA on extraction with this amine was measured, and the effect on extraction with

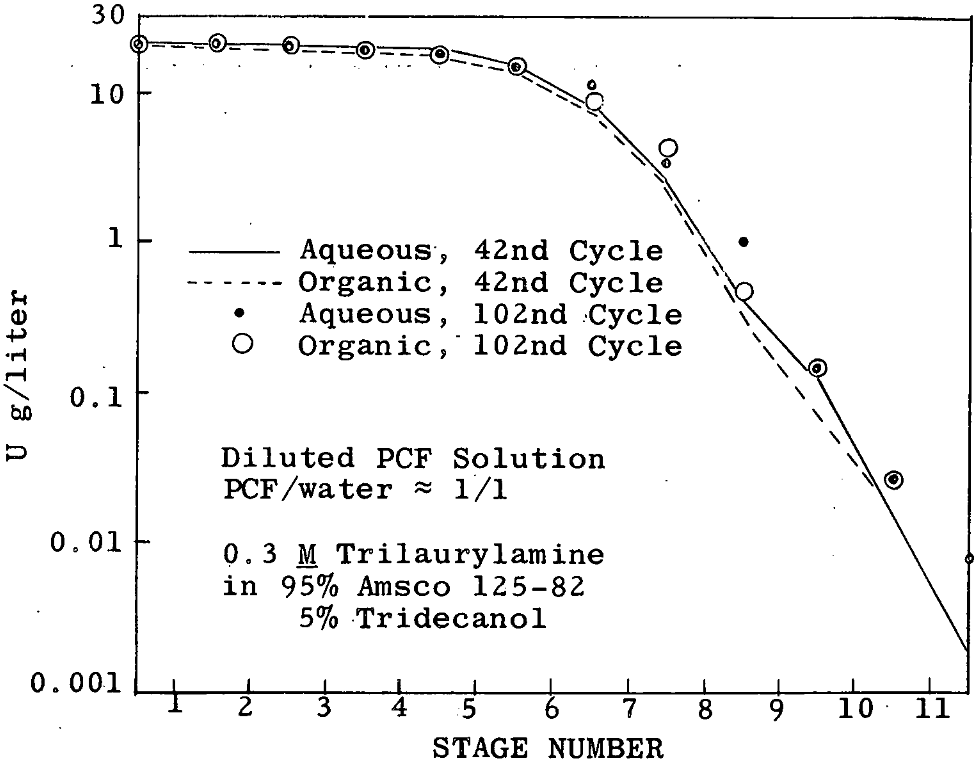

Fig. 3. Uranium Profiles (42 and 102 cycles), Coextraction Batch Countercurrent Tc-Np-U Recovery Test

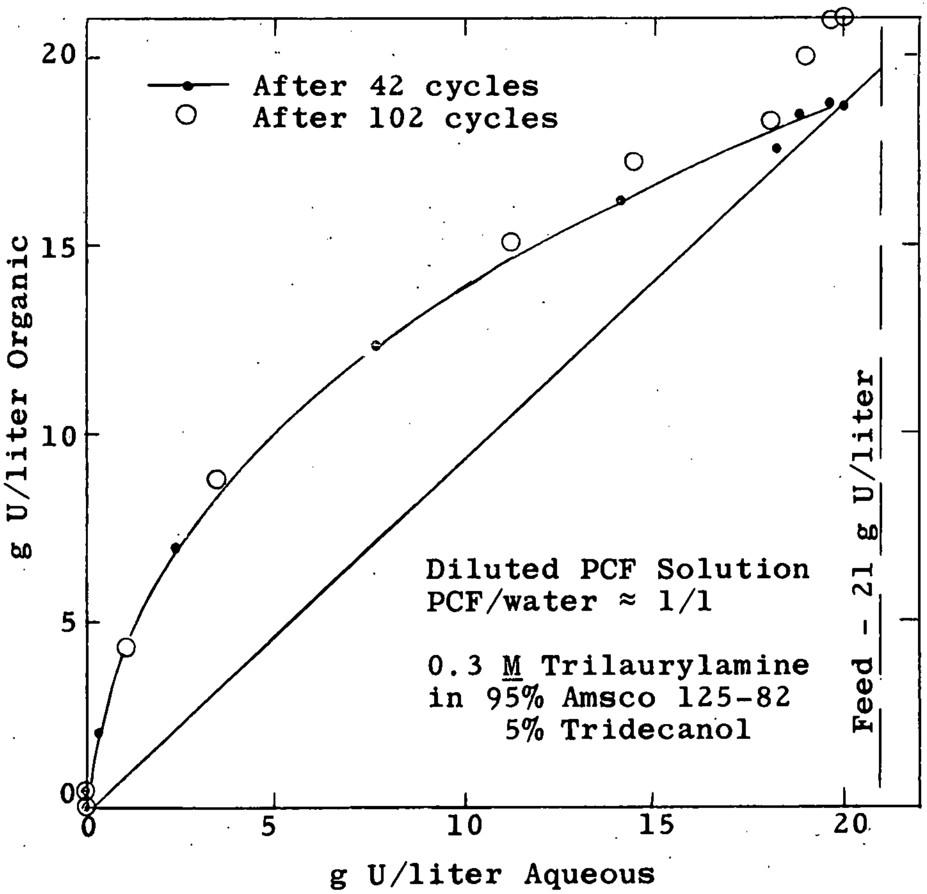

Fig. 4. Uranium Extraction Isotherm from Profiles (42 and 102 cycles), Batch Countercurrent Tc-Np-U Recovery Test.

TLA was rechecked (Fig. 5). E_a^o(Tc) with 0.3 M TLA in Amsco 125-82 decreased by 40-45% on addition of 5 v % TDA in extraction from 1 N and 0.5 N HNO_3. Alamine 336 could not be checked without TDA because of third-phase formation. The decrease in E_a^o(Tc) in extraction from 1 N HNO_3 on increase of the TDA concentration from 5 to 12.5 v % was only ~20%. These extractions used carrier-free Tc-195m tracer. The agreement was good between direct extractions and back extractions with barren 1 N HNO_3, showing that the distribution coefficients were not affected by non-extractable or highly-extractable contaminant activities.

2.1.4 Effect of Uranium Loading on E_a^o(Tc). The effect of uranium loading on the technetium extraction coefficient was checked with 0.3 M TLA in 95% Amsco 125-82--5% TDA in extraction from 1 N HNO_3 (Fig. 6). The aqueous phases contained uranium initially at 25, 50, 75, 100, and 125 g/liter, which decreased to 24, 46, 68, 93, and 113 g/liter at equilibrium. E_a^o(Tc) at the highest uranium (17 g/liter, 0.07 M in the organic phase) was 20% of its value at the lowest

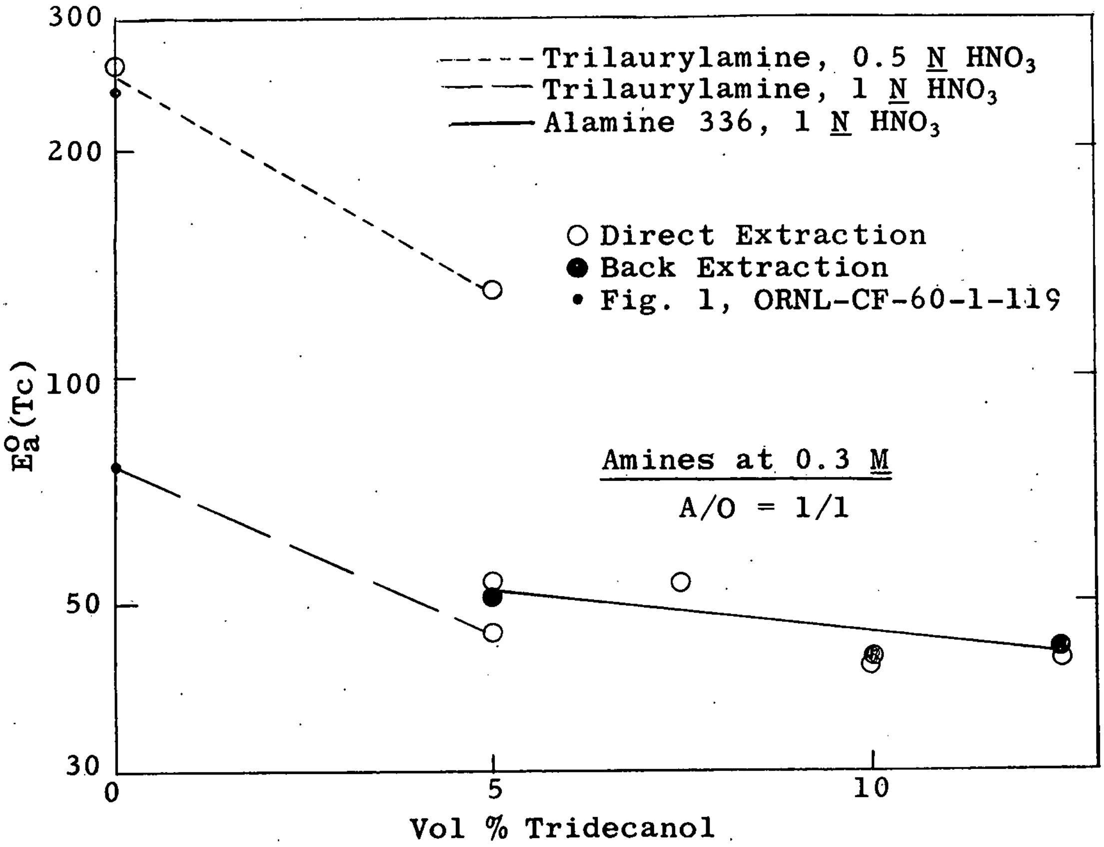

Fig. 5. Decrease of Technetium Extraction Coefficient with Increasing Concentration of Tridecanol in Amsco 125-82.

uranium tested (4 g/liter, 0.017 M), and 16% of its value in the absence of uranium (Fig. 5). In contrast to this sharp decrease in E_a^o(Tc), E_a^o(U) was nearly constant. Although both E_a^o(Tc) and E_a^o(U) vary with the first power of the available amine concentration, the depression of E_a^o(U) by increased loading was partly compensated by increased uranyl nitrate self-salting, while the dropping E_a^o(Tc) was further depressed by increased nitrate competition.

2.1.5 Neptunium Partitioning. In all the test work previously reported, neptunium was partitioned from the technetium with 0.1 N H_2SO_4, which is a highly effective stripping agent for the neptunium and also is about optimum for the retention of technetium in the extract. However, the presence of sulfate might be objectionable in subsequent further concentration or purification of the neptunium. Other possibilities suggested for neptunium stripping include oxalic acid,[5] very dilute nitric acid,[5] and nitric acid with hydrogen peroxide.[6] The latter two were tested in batch equilibrations with 0.3 M Alamine 336 in 90% Amsco 125-82--

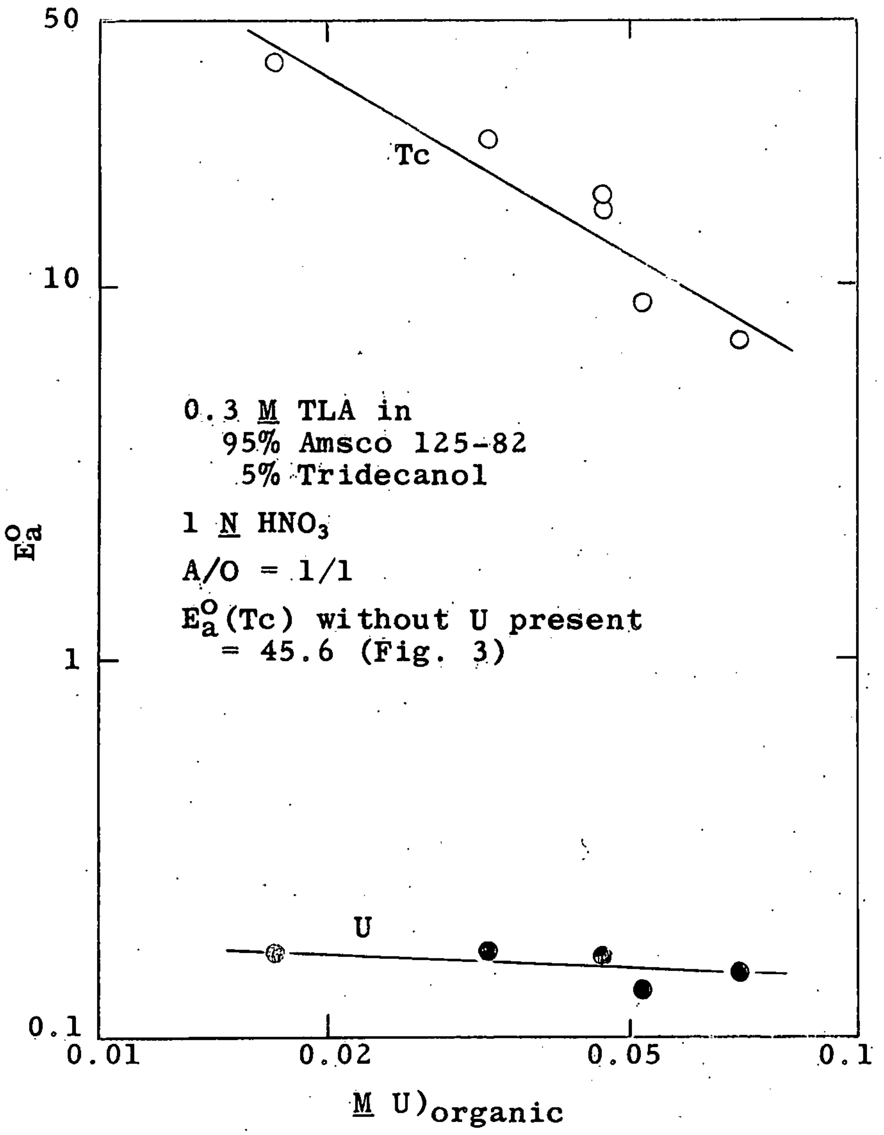

Fig. 6. Effect of Uranium Loading on Uranium and Technetium extraction coefficients.

10% TDA, containing Np-238 tracer extracted from and scrubbed with 1 N HNO_3. The stripping coefficient S_o^a(Np) with 0.05 M HNO_3 were 6 at A/O = 1/1 and 15 at A/O = 2/1. With 1% and 10% H_2O_2 in 0.05 N HNO_3, A/O = 1/1, the tracer Np left in the organic phase was indistinguishable from background, S_o^a(Np) $\geq$50.

These results suggest that neptunium stripping with 0.05 N HNO_3 alone may be operable and, if not, effective stripping can be assured by the addition of some peroxide to oxidize the Np(IV) to non-extractable Np(V). Neither 0.05 N HNO_3 alone nor with H_2O_2 should strip technetium significantly. The neptunium partitioning with dilute nitric acid alone is still in question, in spite of the foregoing results, because previous experience has shown that trouble may be encountered from hydrolysis of the neptunium.[5]

2.2 Effect of Purex Aqueous Feed Adjustment Procedures on Pu Extraction by 1 M Di-sec-butyl Phenylphosphonate (DSBPP) in Solvesso (A. T. Gresky, R. G. Mansfield)

Studies of the Purex codecontamination cycle have been made previously to evaluate the use of DSBPP as the extracting agent, the behavior of various diluents, and the possible benefits that might be derived from pretreating the feed with acetone. During the course of this work unexplained difficulties have been experienced with Pu extraction. Consequently, further tests have been made to determine whether the erratic behavior of Pu might be due to such causes as (1) inadvertent addition of insufficient nitrite for complete conversion to Pu(IV), (2) insufficient digestion periods or temperature for complete oxidation to Pu(IV), or (3) the production of stable polymeric species during certain feed adjustment steps involving acid-deficient conditions.

To test the nitrite requirements, a plutonium spike (which had been stored in 2 N HNO_3) was added to an acidic feed solution which was adjusted to concentrations of 430 g U/liter, 2.03 N HNO_3, and 1.02×10^5 Pu α c/m/ml. The solution was divided into five portions, to four of which solid $NaNO_2$ was added for adjustment to nitrite concentrations of 0.005, 0.01, 0.025, and 0.05 M, and one of which was employed as a control or blank (no nitrite addition). The five solutions were then digested at 50°C for 1 hr, after which they were cooled to room temperature for the batch extraction tests. An aqueous scrub solution of 2 M HNO_3 and an organic extractant of 1 M di-sec-butyl phenylphosphonate (DSBPP) in Solvesso-100 were prepared. The latter was treated by washing twice with 0.2 M Na_2CO_3 and by subsequent contact with chromatographic-grade alumina (100 g Al_2O_3/liter of solvent). In the batch extraction tests one volume of each of the five prepared feeds was combined with a 0.75 volume of the aqueous scrub solution and then contacted once with 4.75 volumes of the organic extractant. Plutonium α analyses were obtained for determination of distribution coefficients. The aqueous solutions from the first test were then contacted with a second pass of the extractant, and Pu distribution coefficients were again determined. Data from the two series of tests were recorded in Tables 3 and 4.

The total % Pu extracted in the 0.025 and 0.05 M $NaNO_2$ cases appeared to be nearly equal at about 95.4%, suggesting that this range of nitrite concentrations should provide nearly complete conversion of plutonium to the Pu(IV) state.

Table 3. Pu Distribution Coefficients and Extraction Factors as Functions of Nitrite Addition to Aqueous Feed

Batch test conditions: Organic extractant: 1 M DSBPP in Solvesso-100; Aqueous feed: 430 g U/liter, 2.03 N HNO_3, 1.02×10^5 Pu α c/m/ml; ($NaNO_2$ as indicated was added to aqueous feeds, which were subsequently heated to 50°C for 1 hr); Aqueous scrub: 2 N HNO_3; F/S/O = 1.0/0.75/4.75; A/O ratio after contact ≅ 3.6; aqueous phase was contacted with two successive passes of organic extractant.

	Pu (α c/m/ml x 10^{-4}) After Extraction ($\underline{M}$ $NaNO_2$ Added to Aqueous Feed)				
Pass	0.0	0.005	0.01	0.025	0.05
1E-O	0.51	0.79	1.53	1.76	1.83
-A	5.2	4.4	1.78	1.17	1.05
(DC$_a^o$)	(0.1)	(0.18)	(0.86)	(1.51)	(1.74)
(EF$_a^o$)	(0.35)	(0.65)	(3.1)	(5.42)	(6.27)
2E-O	0.57	0.38	0.35	0.29	0.22
-A	4.2	3.8	1.42	0.42	0.38
(DC$_a^o$)	(0.14)	(0.10)	(0.25)	(0.69)	(0.58)
(EF$_a^o$)	(0.49)	(0.36)	(0.89)	(2.49)	(2.09)

Table 4. Calculated Percent of Aqueous Feed Pu in Organic Extracts and Aqueous Raffinates

(See data and conditions in Table 3)

	% Pu in Organic Extracts and Aqueous Raffinate (M $NaNO_2$ Added to Aqueous Feed)				
Stage	0.0	0.005	0.01	0.025	0.05
1E-O	23.7	36.8	71.0	81.8	85.1
2E-O	26.5	17.7	16.3	13.5	10.3
2E-A	50.3	45.5	16.9	5.0	4.5
(Total)	(100.5)	(100.0)[a]	(104.2)	(100.3)	(99.9)

[a] Material balances normalized on the basis of this test.

The empirical tests were not extensive enough to permit determination of 100% Pu extractability. The observed extraction factors in the second passes of the two cases suggest that additional Pu extraction could have been expected on a third pass; however, the lower Pu distribution coefficient may indicate the presence of some Pu(VI). A plot of the data is shown in Fig. 7.

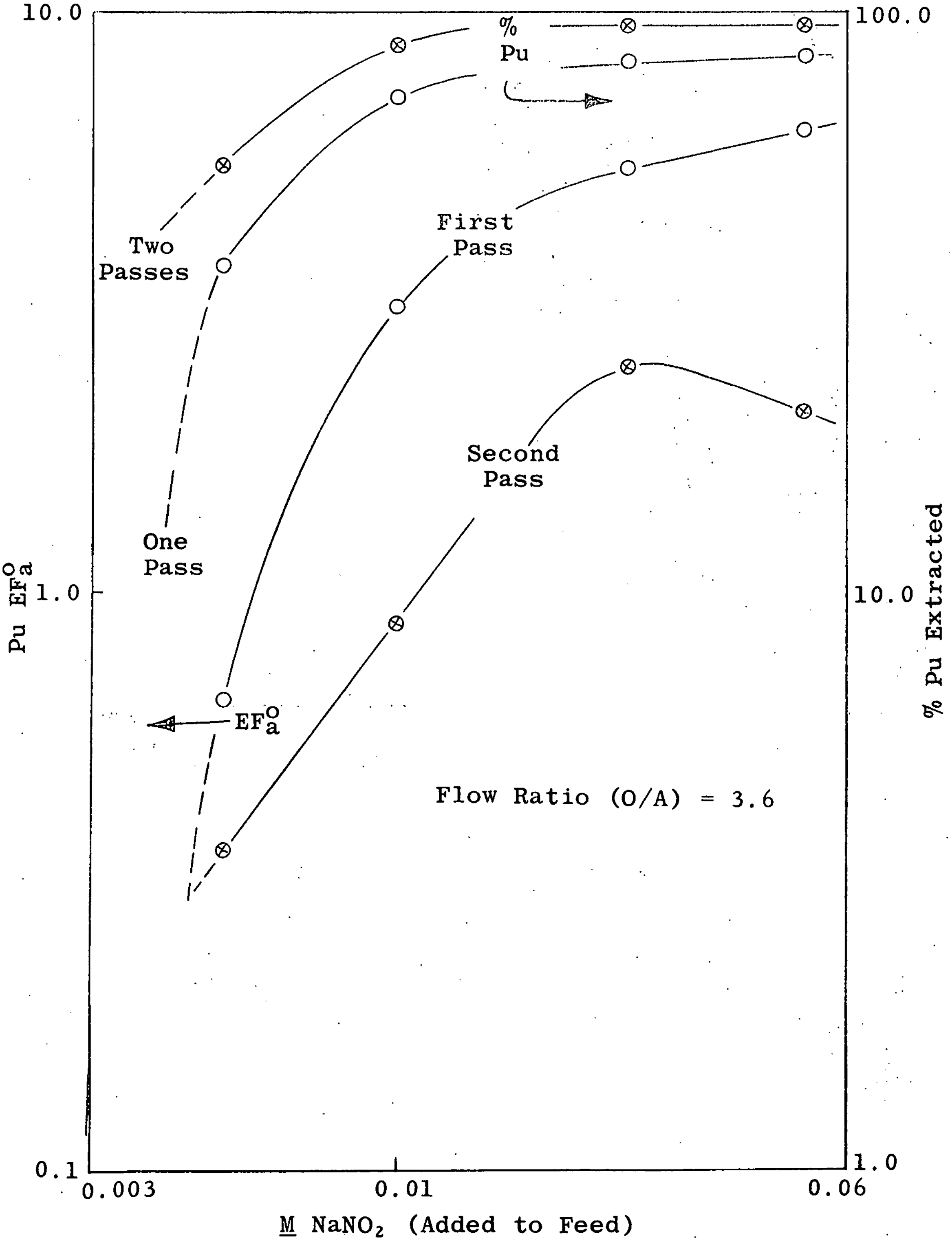

Fig. 7. Pu EF's (O/A) and % Pu Extracted as Functions of Nitrate Addition to Aqueous Feed.

Two additional batch scouting tests (without nitrite additions) were performed to ascertain the magnitude of the effects on plutonium extractability of (1) ageing the plutonium tracer in acid-deficient uranyl nitrate solutions, and (2) treating the feed with acetone. In one test an acid-deficient aqueous nitrate solution containing 470 g U/liter, 1.1×10^5 Pu α c/m/ml, and adjusted (by UO_3 addition) to -0.48 $\underline{N}$ HNO_3, was permitted to stand for two weeks at room temperature. After subsequent adjustment to +0.37 $\underline{M}$ HNO_3, 1% (by volume) acetone was added and the solution was heated at 90°C for 1 hr. Subsequently this feed solution was employed in batch extraction tests similar to those described above. Low Pu DC_a^o's of 0.027 and 0.007, and Pu extractions of 7.9 and 2.3%, were observed in the two successive steps of the batch tests. The Pu DC's were observed to be about 3.7 and 20 times less than observed in the abovementioned control test where no nitrite addition was made. In another test, an acidic aqueous nitrate solution containing 580 g U/liter, 0.3 $\underline{N}$ HNO_3, 1.28×10^5 Pu α c/m/ml was adjusted (without ageing) to 1% by volume acetone then heated for 1 hr at 90°C. Subsequent extraction tests similar to those described above revealed low Pu DC_a^o's of 0.039 and 0.009, and Pu extractions of 12 and 3%, in the two successive extraction steps. The Pu DC's were about 2.6 and 15.6 times less than observed in the above control test where no nitrite addition was made. These two tests permit the qualitative conclusions that the acetone converts most of the plutonium either to the less extractable Pu(III) or to a less extractable polymeric state, the effect being more marked in the HNO_3-deficient feed solutions. Of these two possibilities, it is believed that reduction to Pu(III) is more likely than the formation of highly significant quantities of stable Pu polymers. For instance, some earlier tests have indicated that subsequent addition of nitrite ion will readily convert greater than 99% of the plutonium to the extractable Pu(IV) state. Since previous studies of the acetone pretreatment method have demonstrated marked advantages in Pu and Zr-Nb decontamination in the Purex codecontamination cycle, further studies are planned to afford assurance that deleterious effects on plutonium extraction are not created.

2.3 Solubility of Di-*sec*-butyl Phenylphosphonate (DSBPP) Complexes of Uranyl and Thorium Nitrates in CCl_4

(A. T. Gresky, R. G. Mansfield)

Organic phases of 0.7 $\underline{M}$ DSBPP-CCl_4 were contacted and equilibrated with crystalline (1) $UO_2(NO_3)_2 \cdot 6H_2O$ in one case, and (2) $Th(NO_3)_4 \cdot 4H_2O$ 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 0.314 $\underline{M}$ $UO_2(NO_3)_2$ and 0.288 $\underline{M}$ $Th(NO_3)_4$, respectively. Assuming an organic volume increase of 11.3%, the values correspond to complexes of $2DSBPP \cdot UO_2(NO_3)_2$ and 2.18 $DSBPP \cdot Th(NO_3)_4$. There was no evidence of precipitation, crystallization or two-phase formation in either of the saturated reagent solutions.

These brief scouting tests indicate that carbon tetrachloride is a feasible DSBPP diluent for uranium and thorium process applications insofar as the complex solubility and stability are concerned. The tests also suggest the probability that $DSBPP \cdot Pu(NO_3)_4$ complexes are soluble in CCl_4 and that the DSBPP-CCl_4 system is worthy of investigation as a substitute for the TBP-CCl_4 systems presently employed in plutonium purification cycles.

2.4 Plutonium(IV) Nitrate Extraction with TBP and Phenylphosphonate Esters (C. F. Coleman, D. E. Horner)

Plutonium(IV) extraction coefficients with di-n-butyl phenylphosphonate (DnBPP), di-sec-butyl phenylphosphonate (DsBPP), and tributyl phosphate (TBP) were previously reported[7] for which the E_a^o vs $\underline{M}_{HNO_3}$ curves were closely parallel for all three reagents, but were steeper and reached lower values of E_a^o than was shown by TBP data from the literature.[8] Continued measurements in these systems corroborated the steep slopes at least down to ~0.4 $\underline{M}$ HNO_3, leaving unexplained the discrepancy between these and the literature data.

Between 0.4 and 2 $\underline{M}$ HNO_3 the slopes log E_a^o vs log $\underline{M}_{HNO_3}$ were close to 2.5 (Fig. 8, from Fig. 9, A-C). The coefficients with DsBPP were close to those with TBP, while those with DnBPP were higher by a factor of about 1.5. More extensive equilibrations are shown separately for each of the three reagents in Fig. 9. Here the solid black points all represent independent direct extraction equilibrations at the equilibrium aqueous nitric acid concentrations shown.* While there was noticeable scatter, especially with TBP, these data definitely show parallel nearly-straight lines of slope ~2.5 from ~0.1 to ~2 $\underline{M}$ HNO_3, shifting toward slope ~1 at ~4 $\underline{M}$ HNO_3. For TBP, these extraction coefficients agree fairly well with those of Best et al.[8] at 4 $\underline{M}$ HNO_3, but not at concentrations below 1 $\underline{M}$ HNO_3. (For this comparison, Best's coefficients were normalized from 19% TBP to 1 $\underline{M}$ TBP using $E_a^o \propto \underline{M}_{TBP}^2$, Fig. 9D.) The slope of a smooth curve through Best's data shifts from ~1.7 above 2.5 $\underline{M}$ toward ~1.0 at 0.2 $\underline{M}$ HNO_3.

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*For some of the equilibrations in Fig. 9 (marked ▲, △, ■) the equilibrium aqueous nitric acid was calculated from the initial concentration by means of independently-measured acid extraction coefficients.[10] For the others the reagent was pre-equilibrated to avoid acid extraction, or the final acidity was measured by titration.

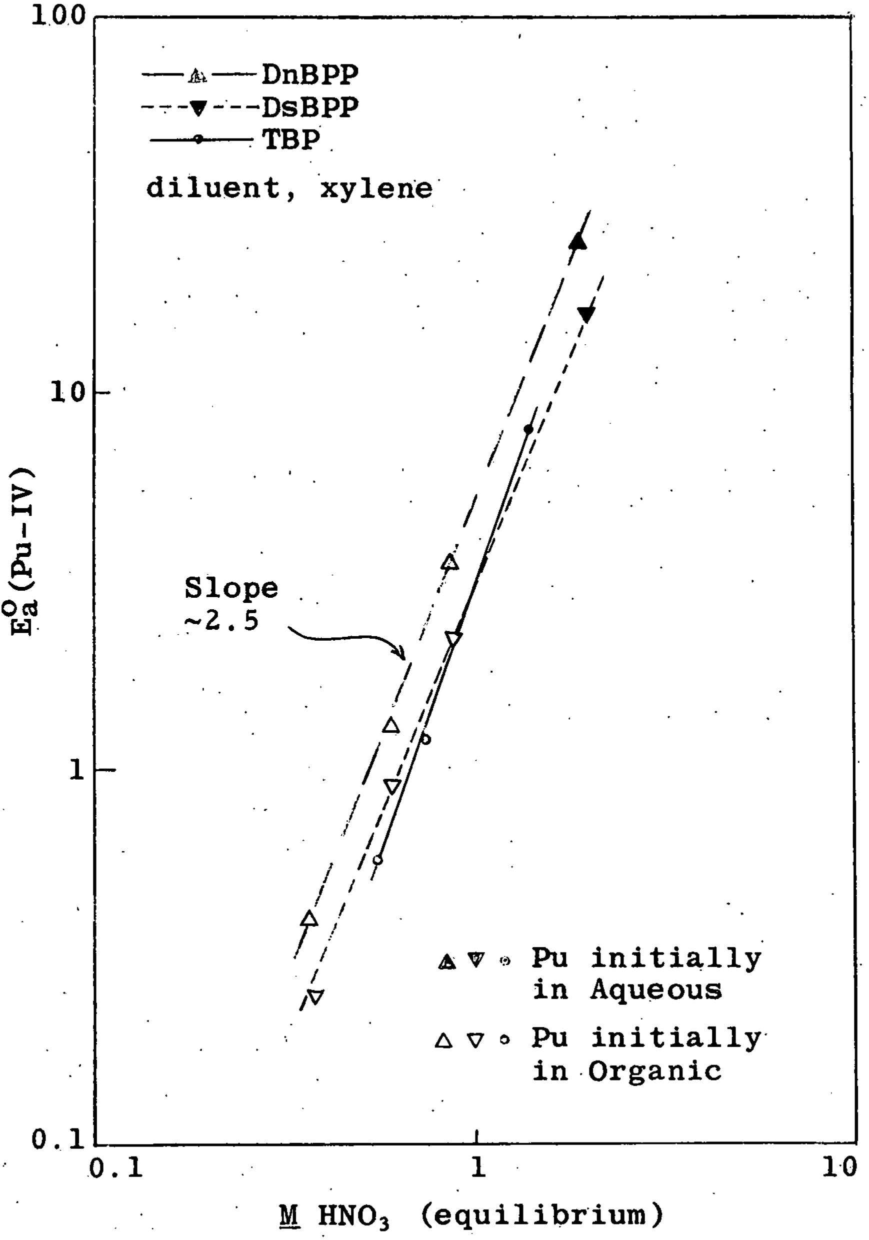

Fig. 8. Plutonium(IV) Extraction from Nitric Acid Solutions by 1 $\underline{M}$ Di-n-butyl phenylphosphonate, Di-sec-butyl phenylphosphonate, and Tributyl phosphate.

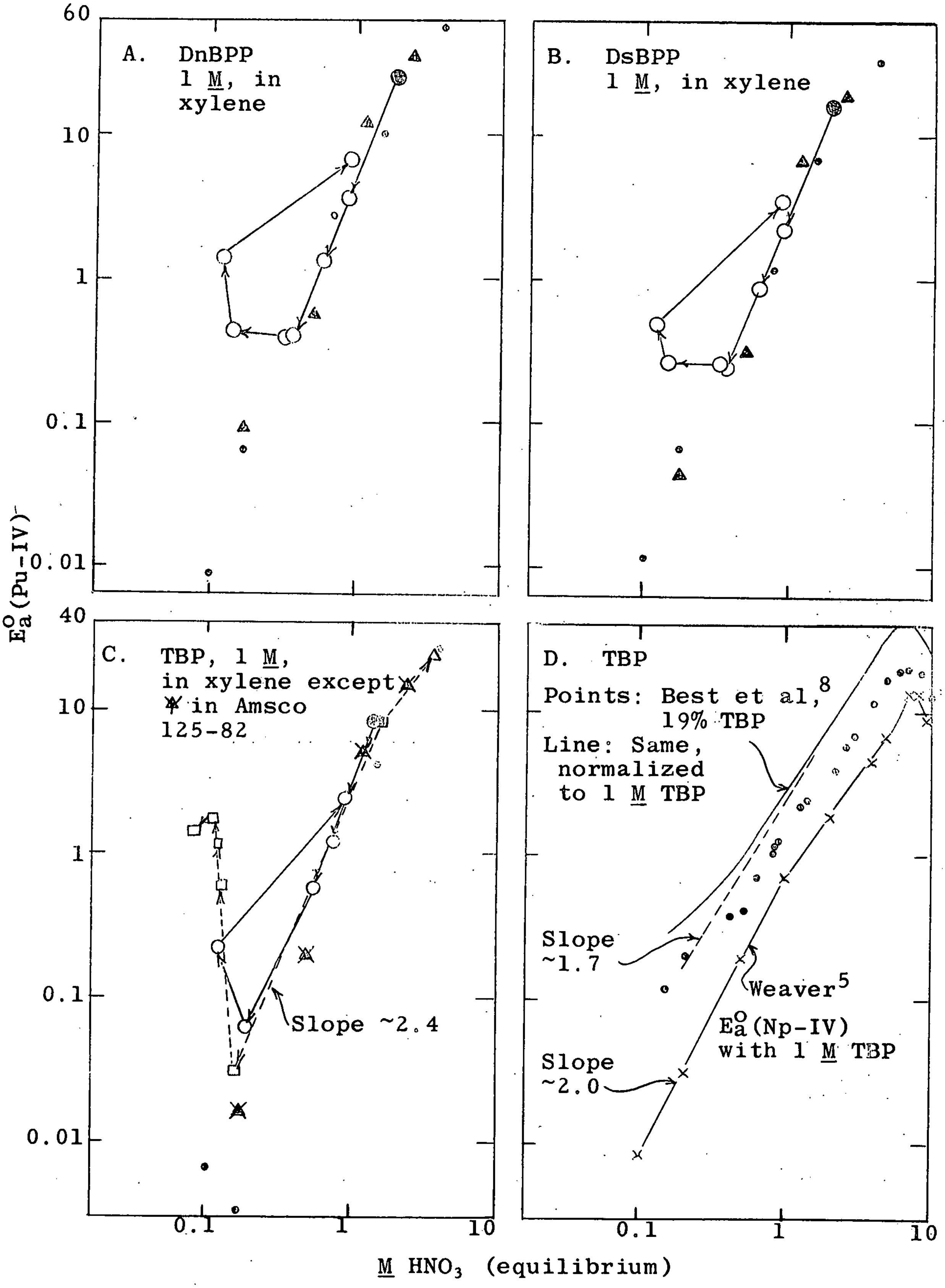

Fig. 9. Anomalous Stripping of Plutonium(IV)
● ■ Direct extraction of Pu initially in aqueous phase
○ □ △ Stripping of extracted Pu; arrows show successive equilibrations.
Reagents scrubbed with (▲) 2% NaOH or (□,○) 2% Na_1CO_3 and alumina, 2 M HNO_3, and water.

One possibility considered in attempting to resolve this discrepancy was that the extraction coefficients in the present work might be erroneously low at the low acidities because of polymerization or other hydrolysis reaction rendering a large fraction of the plutonium inextractable.* If that explanation were correct, back extractions by barren nitric acid solutions should involve less or none of the inextractable species, and hence should show higher distribution coefficients. Instead, the back extractions corroborated the direct extractions down to 0.4 $\underline{M}$ HNO_3 (Figs. 9A-9C). At lower acidities the back extractions neither confirmed nor contradicted the direct extractions (see below).

At the same time, it is difficult to suggest that Best's extraction coefficients might be high by more than a small amount, i.e., by a factor of ~2 at the lowest acidity and less at the higher acidities. The basis for this statement is that the most likely cause for erroneously high extraction coefficients in the direct extraction of trace plutonium would be the presence of a trace contaminant of much higher extraction power than TBP, whose effect would be swamped out in extraction of plutonium at macro concentrations. Best's macro extractions are in fairly good agreement** with the dashed line in Fig. 9D, which is the extension of the upper portion of the trace extraction curve, slope 1.7, and is only a little closer than that curve to the slope 2.5 line found in the present measurements. This internal evidence does not exclude the possibility of high coefficients due to a large amount of contaminant of only moderately higher extraction power than TBP, but this seems considerably less likely than trace contamination. Thus, as stated above, the discrepancy between this and the present work remains unresolved.

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*From measurements at macro plutonium concentrations,[9] the plutonium at these low concentrations would not be expected to polymerize at acidities above 0.1 $\underline{M}$. However, the possibility was still considered that hydrolysis short of actual polymerization might impair extraction at acidities somewhat higher than was indicated by the polymerization studies.

**The macro extraction coefficients actually measured were somewhat higher than the trace extraction coefficients, which Best et al. attributed to the significant contributions of plutonium nitrate to the total nitrate salting concentration. They state that normalization using $E_a^o \propto \underline{M}_{NO_3}^3$ makes the macro extraction coefficients agree with the trace extraction coefficients. However, a plot of all of their reported macro extractions (Fig. 10) shows that normalization using either $E_a^o \propto \underline{M}_{NO_3}^4$ or $E_a^o \propto \underline{M}_{NO_3}^3$ makes the macro data, within considerable scatter, agree better with the extended slope 1.7 line than with the trace extraction curve.

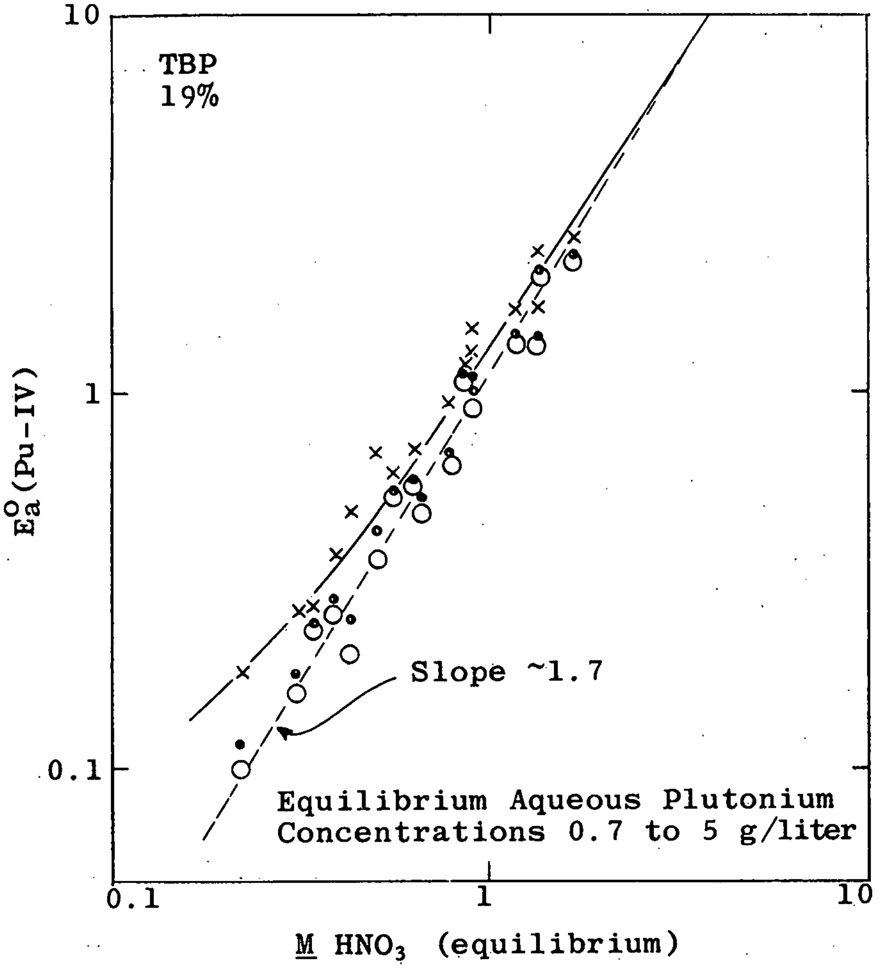

Fig. 10. Extraction of Macro Plutonium with 19% TBP, Best et al.[8] Points X normalized to $[\Sigma NO_3] = [HNO_3]$ using -

•, $E \propto [NO_3]^3$
○, $E \propto [NO_3]^4$

The solid line is the smoothed curve fitted to the trace plutonium extractions of Best et al., cf. Fig. 9-D.

Extraction coefficients for trace neptunium(IV) with 1 M TBP in xylene[5] are also included in Fig. 9D. Neptunium(IV) extractions generally parallel plutonium(IV) extractions closely. Here the slope between 0.1 and 1 M HNO_3 is ~2.0, in between the slopes from the two plutonium studies.

Returning now to the back-extraction series in Figs. 9A-9C, their behavior changed abruptly when the acidity fell much below 0.4 M. Instead of continuing to decrease with decreasing acidity, the distribution coefficients leveled off and then rose, eventually exceeding unity in the one case of five successive scrubs with 0.1 M HNO_3 (Fig. 9C, □). In each of the other three series the last scrub was with 1 M HNO_3, which gave coefficients almost back in line with the other high-acid equilibrations. The tentative explanation offered for this behavior is that significant hydrolysis did indeed occur at acidities not much below 0.4 M, at least in the organic phase, to produce a difficultly-stripped plutonium species that was probably non-transferable rather than highly-extractable. It is tempting to suggest that it was non-transferable because it had polymerized. However, if polymer were involved it differed from that studied in the aqueous phase[9] in at least two respects: in being formed at acidities above 0.3 M, and in rather readily reverting to transferable species at acidity <1 M.* The initial scrub acidities, equilibrium acidities, and initial plutonium concentrations for these series are summarized with the distribution coefficients in Table 5. Both phases were analyzed after each equilibration, with good material balances.

The plutonium(IV) was prepared at ~1 g/liter in 2 M HNO_3 solution by reduction with hydroxylamine nitrate (0.1 M, >2 hr at room temperature) followed by oxidation with sodium nitrite (0.5 M, 10 min at 50°C). Aliquots of this solution were pipetted into solutions of the required initial acidity to give the indicated plutonium concentrations (86 to 170 mg Pu/liter) for the extractions listed in Table 5, and to give 5-15 mg Pu/liter for all the other extractions.

2.5 Ruthenium Extraction by TBP-Amsco 125-82 Solvent: Extraction Properties of the Nitrosylruthenium Nitrate Complexes by Degraded Solvent and Response to Solvent Cleanup Procedures (C. A. Blake, J. M. Schmitt)

Extraction of ruthenium, zirconium and niobium can contribute to poor decontamination in chemical processing of reactor fuel solutions. Zirconium-niobium extraction by chemically and radiation degraded TBP-Amsco 125-82 solvents and the effectiveness of certain solvent cleanup methods were studied previously.[1,2] Recently similar studies have been made of the extraction of Ru^{106}.

As might be expected from known differences in chemistry, the test results with ruthenium were considerably different from those obtained previously with zirconium-niobium. Thus, the ruthenium extraction properties of a fresh TBP-fresh Amsco mixture were not significantly altered

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*The extraction coefficients after the 1 M HNO_3 scrubs are higher than the indicated straight lines by factors of 1.1 to 1.5, suggesting 10 to 30% unstrippable plutonium still present.

Table 5. Acid and Plutonium Concentrations in Extraction and Stripping Equilibrations

1 M Extractants in xylene
Phase ratio A/O = 1/1

Extractant	Nitric Acid, M		Initial Pu	
	Initial	Equilibrium	mg/liter	D_a^o(Pu)
DnBPP	2.0	1.9	170	25
	0.5	0.87		3.5
	0.5	0.60		1.3
	0.3	0.37		0.40
	0.3	0.33		0.39
	0.1	0.14		0.43
	0.1	0.12		1.4
	1.0	0.90		6.6
DSBPP	2.0	2.0	170	16
	0.5	0.88		2.2
	0.5	0.61		0.90
	0.3	0.38		0.25
	0.3	0.33		0.27
	0.1	0.14		0.27
	0.1	0.12		0.51
	1.0	0.88		3.6
TBP	1.7	1.4	100	8.0
	0.50	0.73		1.2
	0.50	0.55		0.59
	0.10	0.19		0.06
	0.10	0.12		0.22
	1.0	0.88		2.4
	2.0	(1.6)[b]	86	8.3
	4.0[a]	(3.6)[b]		24
	H_2O[a,c]	0.16		0.03
	0.1	0.13		0.58
	0.1	0.12		1.1
	0.1	0.11		1.6
	0.1	0.11		1.7
	0.1	0.08		1.4

[a] Organic from initial extraction split: one portion scrubbed with 4 M HNO_3 only, the other scrubbed with water and then 0.1 M HNO_3.

[b] Equilibrium acidity calculated from independently measured nitric acid extraction coefficients.[10]

[c] Phase ratio A/O = 2/1 instead of 1/1.

by severe chemical degradation of the diluent, by simulated degradation of the TBP (addition of its principal hydrolysis product), or by irradiation of the TBP-Amsco mixture. Only in tests where the ruthenium was extracted into a degraded solvent and allowed to age for a period of several days was there evidence that normal scrubbing with acids or alkaline solutions would not effect essentially complete stripping.

2.5.1 Preparation of Aqueous Ruthenium Solutions. The nitrate complexes of nitrosylruthenium [$Ru(NO)^{+3}$] were selected for study utilizing the work of J. M. Fletcher et al.,[11,12] which describes methods for preparing reproducible solutions and identifies and discusses the properties of a series of complexes, cationic, anionic, and neutral, containing from 1 to 5 nitrate groups. In their work it is recognized that other species can be formed, but it is stated that "it is likely that batch or continuous dissolution (of irradiated fuels) in boiling nitric acid will produce feed solutions containing a substantial fraction of the ruthenium in the form of nitrato nitrosylruthenium complexes." Following the suggested method,[12] the Ru^{106} stock solution used in the current ORNL tests was prepared by adding concentrated nitric acid to $Ru^{106}Cl_3$ in 6 M HCl, evaporating to near dryness and repeating twice. The nitrate was then refluxed for 2 hr in 10 M nitric acid and stored in a dark bottle.

The calculated relative amounts of the individual complexes which should exist at equilibrium in nitric acid systems are shown in Fig. 11.[11] At 2 M nitric acid the mono, di, tri, and higher complexes constitute 47%, 28%, 20%, and 5% of the total, respectively. Equilibrium is reached rather slowly (e.g., 1/2 time for disappearance of the tetra and pentanitrato species is 30 min in 3 M nitric acid), so that the solutions prepared by dilution of the 10 M stock solution were aged for several days before use.

A few extraction tests with TBP were sufficient to establish that the aqueous ruthenium solutions used in the present work were equivalent to those used in the work of Fletcher and Brown, et al.[11,12] Their experiments were made with TBP dissolved in "odorless kerosene." The present tests used Amsco 125-82 (primarily saturated aliphatic hydrocarbon), and Solvesso-100 (primarily aromatic hydrocarbons). The 1.1 M TBP odorless kerosene data coincide with the 1.0 M TBP-Amsco 125-82 data in the 2-4 M nitric acid range (Fig. 12), with only a slight deviation below 2 M. Extraction coefficients with TBP in Solvesso-100 are lower by factors of 2-3.

The tetranitrato and pentanitrato complexes, $H[RuNO(NO_3)_4]$ and $H_2[RuNO(NO_3)_5]$, are preferentially extracted by TBP. The extraction of these acids depends

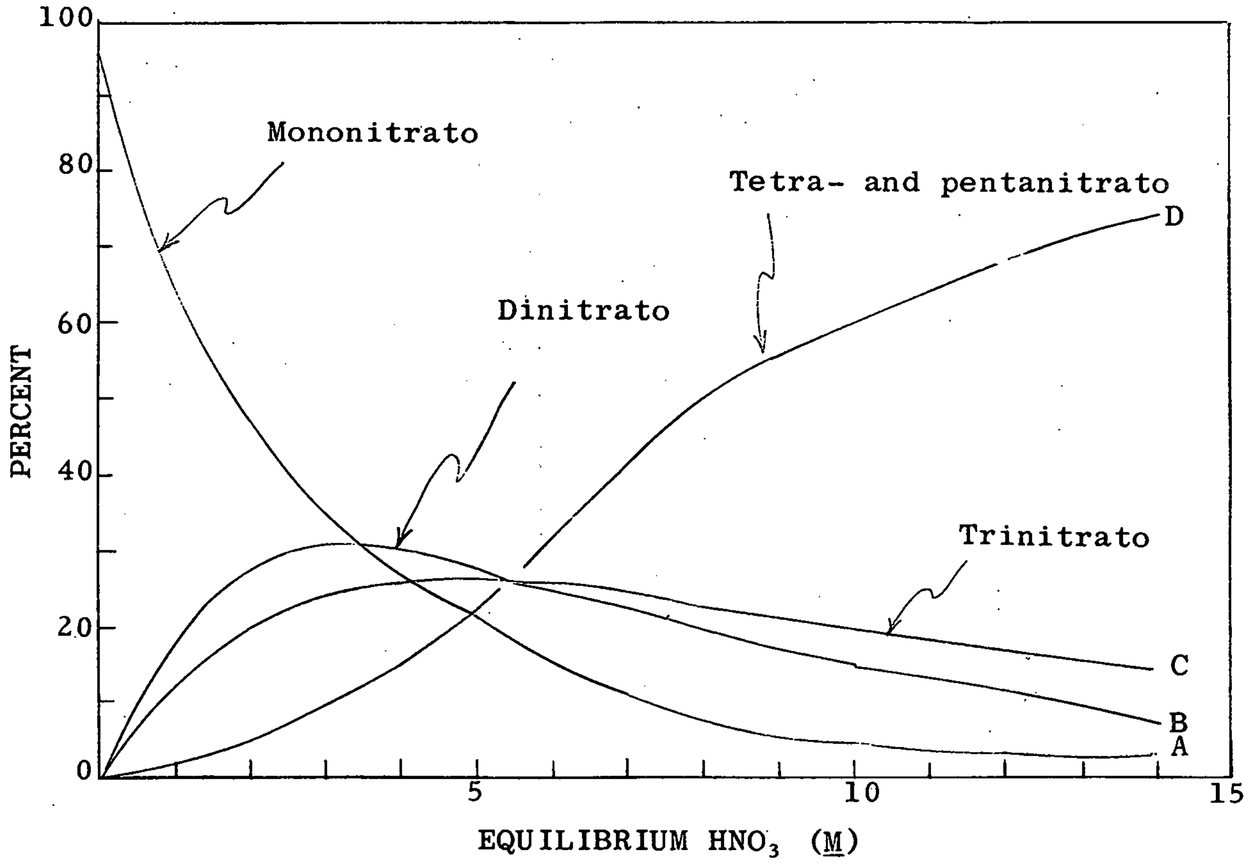


Fig. 11. Composition of Solutions of Nitrosylruthenium nitrato Complexes at Equilibrium in Nitric Acid.[11]

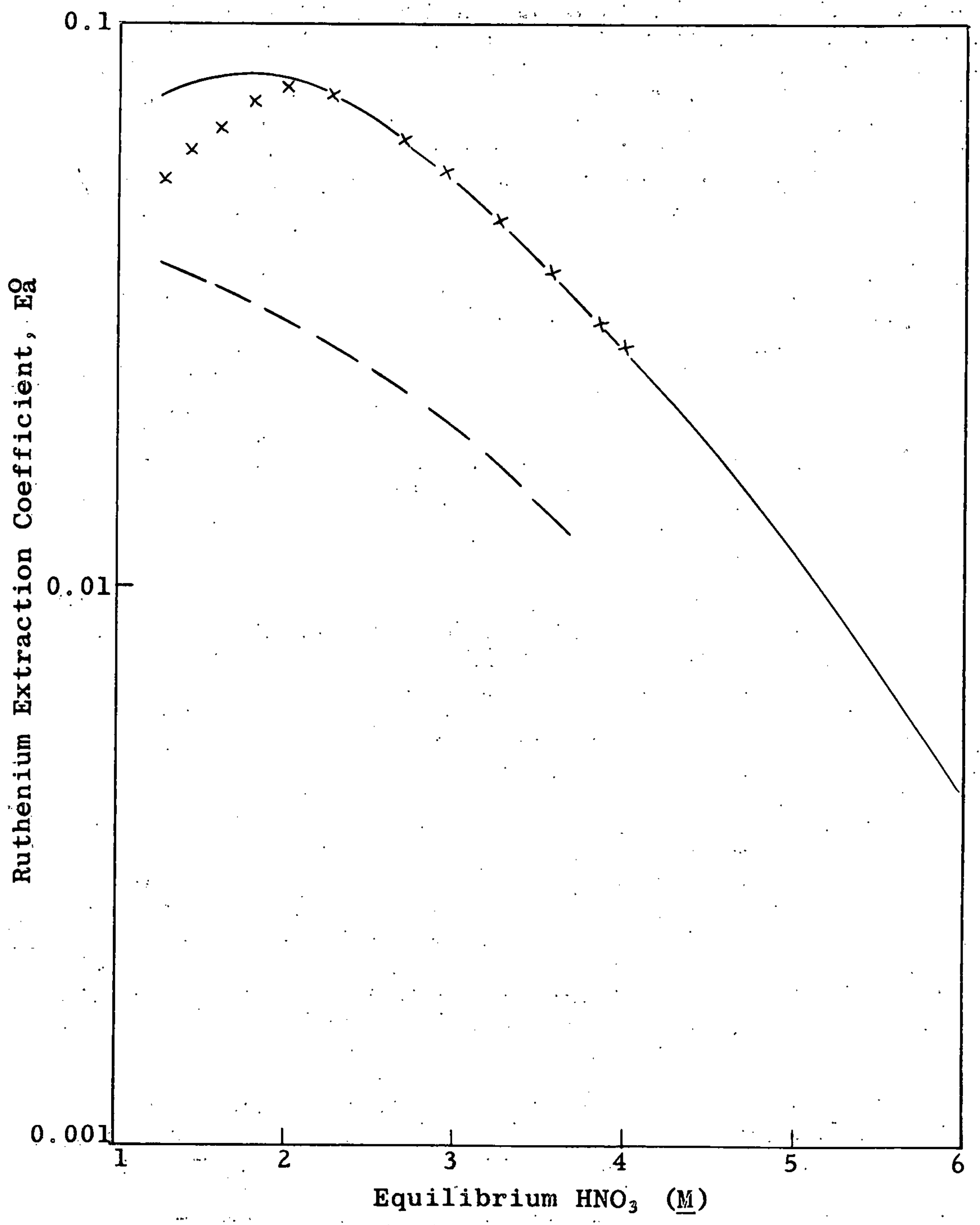


Fig. 12. Extraction of Nitrosylruthenium Complexes by ~1 M TBP at Room Temperature.

Amsco 125-82 ———
Solvesso 100 — —
Odorless Kerosene[12] × × × ×

first on the coordination of TBP to hydrogen atoms in the undissociated acids, the same mechanism as that which determines the extraction by TBP of nitric acid itself. The ruthenium extraction coefficient is very low at high acidities because the extractable species, though predominant, are in competition with nitric acid for the TBP. The coefficient increases as acidity decreases, but then falls away as the other, less extractable, species begin to predominate and finally, at 1.5-2.0 M nitric acid, goes through a maximum.

Equilibrium extraction coefficients for the individual tetra- and pentanitrato species would, of course, be higher than the ones shown which were calculated from the final organic and aqueous total ruthenium concentrations, making no allowance for the large quantity of relatively inextractable ruthenium involved in the lower nitrato complexes. Previous[12] estimates of the distribution coefficient of the most extractable species were approximately 50x greater (E_a^o ~5) than the observed gross coefficient from 2 M nitric acid.

2.5.2 Comparison of Ru, Zr-Nb and Eu Extraction. The decrease with increasing nitric acid concentration of the extraction coefficient of the nitrosylruthenium complexes contrasts with the increases shown by zirconium and niobium (Fig. 13). This behavior can be a factor in limiting decontamination of solutions containing fission products and in reagent cleanup. For example, at about 2 M nitric acid, the gross extraction coefficients for ruthenium and zirconium are about equal. However, as noted above, the coefficient for the particular species of ruthenium that are extracted can be considerably higher and this effect will be evident during scrubbing. Conversely, a more concentrated nitric acid solution, effective for scrubbing ruthenium, becomes less so for zirconium and niobium. From previous work[7] it is known that the extraction coefficients of europium, typifying the rare earths, are low and are not nearly as sensitive to nitric acid concentration.

2.5.3 Extraction by Degraded Solvents. Ruthenium (solutions prepared as described above) was extracted from 2 M nitric acid by solvents comprised of 1 M TBP in Amsco 125-82 which were initially (1) untreated, (2) prepared from Amsco which had been severely degraded by refluxing for 4 hr at 107°C with 2 M nitric acid, (3) irradiated to 318 watt hr/liter (cobalt^{60} source), or (4) spiked with 0.1 M dibutylphosphoric acid, a hydrolysis product of TBP. In addition, the reagents of tests 1 and 2 were subjected in parallel testing to cleanup treatment before ruthenium extraction. All of the organic extracts were scrubbed 3 times with 2 M nitric acid. The data from the 4 test sequences are summarized in Fig. 14, following the conventions used

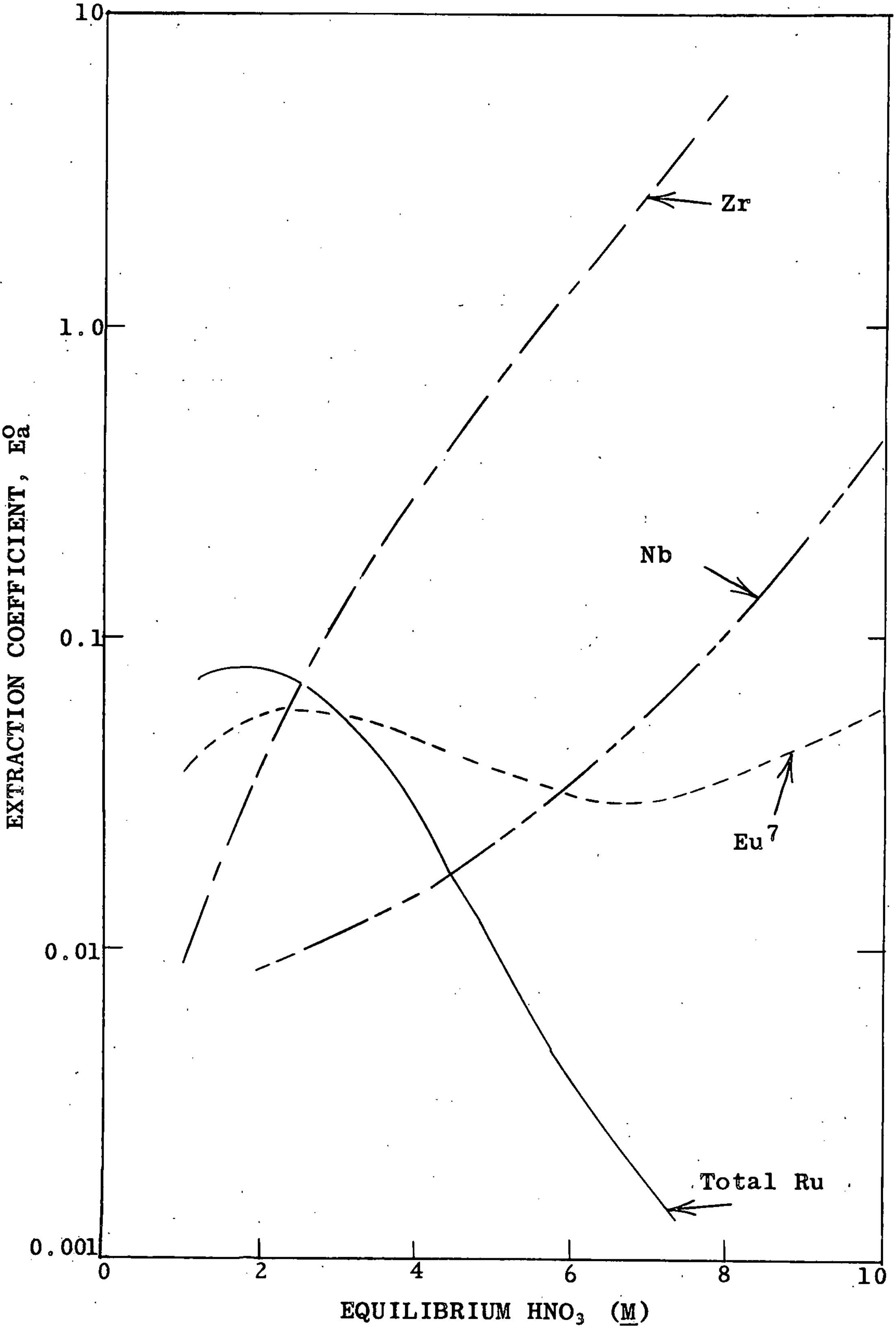
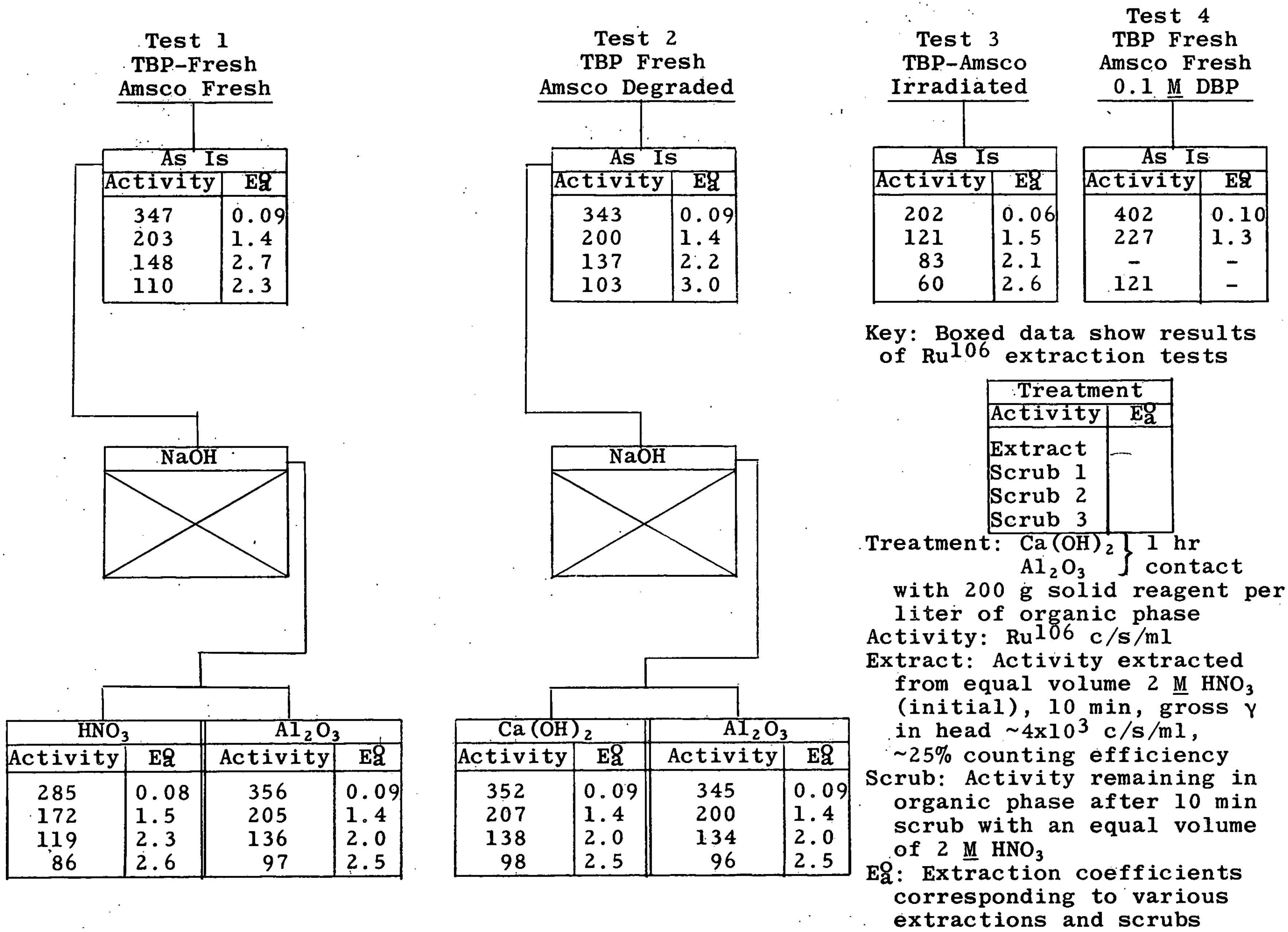


Fig. 13. Extraction of Several Fission Products with 1.0 M TBP in Amsco 125-82.



Test 1
TBP-Fresh
Amsco Fresh

As Is	
Activity	E_a^o
347	0.09
203	1.4
148	2.7
110	2.3

NaOH

HNO_3		Al_2O_3	
Activity	E_a^o	Activity	E_a^o
285	0.08	356	0.09
172	1.5	205	1.4
119	2.3	136	2.0
86	2.6	97	2.5

Test 2
TBP Fresh
Amsco Degraded

As Is	
Activity	E_a^o
343	0.09
200	1.4
137	2.2
103	3.0

NaOH

$Ca(OH)_2$		Al_2O_3	
Activity	E_a^o	Activity	E_a^o
352	0.09	345	0.09
207	1.4	200	1.4
138	2.0	134	2.0
98	2.5	96	2.5

Test 3
TBP-Amsco
Irradiated

As Is	
Activity	E_a^o
202	0.06
121	1.5
83	2.1
60	2.6

Test 4
TBP Fresh
Amsco Fresh
0.1 M DBP

As Is	
Activity	E_a^o
402	0.10
227	1.3
-	-
121	-

Key: Boxed data show results of Ru^{106} extraction tests

Treatment	
Activity	E_a^o
Extract	—
Scrub 1	
Scrub 2	
Scrub 3	

Treatment: $Ca(OH)_2$ } 1 hr
Al_2O_3 } contact
with 200 g solid reagent per liter of organic phase

Activity: Ru^{106} c/s/ml

Extract: Activity extracted from equal volume 2 M HNO_3 (initial), 10 min, gross γ in head ~4x10^3 c/s/ml, ~25% counting efficiency

Scrub: Activity remaining in organic phase after 10 min scrub with an equal volume of 2 M HNO_3

E_a^o: Extraction coefficients corresponding to various extractions and scrubs

Fig. 14. Ru^{106} Extraction with 1 M TBP--Amsco 125-82 Solutions.

previously.[1,2] Thus, the numbers in the "Activity" column of each block in Fig. 14 represent (see key), first, the total activity extracted and, then, the activity remaining in the organic phase after each of the 3 successive scrubs. Also included are the corresponding extraction coefficients.

The data show nearly identical behavior in fresh and degraded Amsco 125-82 (tests 1 and 2), which is in sharp contrast with similar tests with Zr-Nb Y tracer.[1,2] Degradation products which were strong Zr-Nb extractants, which resisted scrubbing with sodium hydroxide or carbonate solutions, which sorbed on activated alumina, or which responded to calcium hydroxide treatment by becoming even stronger extractants are apparently very weak ruthenium extractants in the present aqueous tracer solution.

The irradiated solvent of test 3 (318 watt hr/liter, cobalt^{60} source, no aqueous phase present) had, if anything, less tendency to extract ruthenium.

Although TBP was not degraded in these tests, 0.1 M dibutylphosphoric acid was added in the 4th test to simulate a degraded TBP. The extraction and scrubbing data deviate only slightly from the fresh TBP-fresh Amsco data, denying, at least under these conditions, synergistic extraction of ruthenium or appreciable extraction of cationic ruthenium species.

In another test series, Ru was extracted from 2 M nitric acid into the fresh and degraded Amsco - 1 M TBP solvents and allowed to age. At elapsed times up to 54 days essentially no change was observed in the fresh Amsco solution when scrubbed with 2 M nitric acid (Table 6). The activity became more difficult to strip from the degraded solution, however, possibly going through a maximum. Use of 4 M and 8 M acid led to more efficient scrubbing, as expected, but the effect of aging was still apparent. Scrubbing with sodium carbonate (0.2 M) removed essentially all of the activity from the fresh Amsco solution, and was effective on the freshly degraded sample, but again significant activity remained in the aged samples.

3.0 FISSION PRODUCT RECOVERY

3.1 Solvent Extraction of Cesium (R. P. Wischow, D. E. Horner, M. J. Debnam, W. B. Howerton)

Studies on the solvent extraction of cesium with mono-[13,14] and dialkylphosphoric acids[15-17] were reported previously. Recently these studies have been extended to a number of other possible extractants. In preliminary

Table 6. Ru^{106} γ Activity (c/s/ml) Remaining in TBP-Amsco 125-82 Extracts After Aging and Scrubbing

Scrub[c]		1 $\underline{M}$ TBP[a] in					
		Fresh Amsco			Degraded Amsco[b]		
	Concentration	Days Aged			Days Aged		
Reagent	($\underline{M}$)	0	11	~50	0	11	~50
HNO_3	2	200	134	126	200	220	185
HNO_3	2	145	71	100	137	170	156
HNO_3	2	108	56	88	100	143	126
Na_2CO_3	0.2			3			8
HNO_3	3.7		46	55		130	117
HNO_3	4		15	15		95	77
HNO_3	4		8	8		85	66
Na_2CO_3	0.2		2	1		27	11
HNO_3	7.4			17			76
HNO_3	8			8			55
HNO_3	8			7			44
Na_2CO_3	0.2			2			12

[a] Initially containing 340 c/s/ml, extracted at phase ratio A/O = 1 from 2 $\underline{M}$ nitric acid containing 4000 c/s/ml Ru^{106}.

[b] Amsco 125-82 degraded by refluxing (at 107°C) with 2 $\underline{M}$ nitric acid for 4 hr.

[c] HNO_3 - 3 successive 10-min contacts at phase ratio A/O = 1; Na_2CO_3 - 1 10-min contact at phase ratio A/O = 1.

screening tests (Table 7) it was found that significant extractions of cesium from sodium nitrate solution could be obtained with dinonyl naphthalene sulfonic acid (DNNSA) in Amsco 125-82 or with sodium tetraphenyl boron ($Na\phi_4B$) in hexone. Insignificant extractions were obtained with a variety of amines, phenols, fatty acids, organophosphorus acids or dodecyl boric acid.

The preliminary results with DNNSA and $Na\phi_4B$ encouraged further studies of these extractants for possible process application. In tests described below, it was found that effective cesium extractions could be obtained with $Na\phi_4B$ from simulated Purex 1-WW liquor. Thus far, however, no acceptable way has been found to strip this reagent without converting it to a form which is ineffective for reuse. With DNNSA the extractions of cesium from the Purex waste liquor were comparatively weak. Process application of this

Table 7. Reagent Screening for Cesium Extraction

Organic phase: 0.1 M reagent in diluent
Aqueous phase: 0.5 M $NaNO_3$; 0.5 M NaCl, or 0.25 M Na_2SO_4, Cs-134 tracer
Phase ratio, O/A: 1.0

Reagent	Diluent	Equil. Aqueous pH	Cs E_a^o		
			0.5 M $NaNO_3$	0.5 M NaCl	0.5 M Na_2SO_4
Sodium tetraphenyl boron	Hexone	4	2.3	-	-
Dinonyl naphthalene sulfonic acid	Amsco 125-82	0-11	0.5	-	-
Amines					
Primene JMT	Xylene	7-8	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
(S-24); Bis(1-isobutyl-3,5-dimethylhexyl)amine	Xylene	5-6	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
N-Benzylheptadecylamine	Xylene	4-6	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Trilaurylamine	Amsco 125-82	4-6	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Phenols					
p-Benzylaminophenol	Butylacetate	12	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
2,4,6-Tris(dimethylaminoethyl)phenol	Amsco 125-82	10-11	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Dinonyl phenol	Amsco 125-82	11	0.057	-	-
Acids					
Di(2-ethylhexyl)phosphoric acid		6	0.03	-	-
Di(n-hexyl)phosphinic acid	Amsco 125-82	3	$<10^{-2}$	-	-
Hexamethylene diphosphonic acid	Amsco 125-82	2	$<10^{-2}$	-	-
Di(2-ethylhexyl)dithio phosphoric acid	Amsco 125-82	3	$<10^{-2}$	-	-
Dodecyl boric acid[a]	Amsco 125-82	3	$<10^{-2}$	-	-
Palmitic acid	Amsco 125-82	3	$<10^{-2}$	-	-
Oleic acid	Amsco 125-82	3	$<10^{-2}$	-	-
Stearic acid	Amsco 125-82	3	$<10^{-2}$	-	-

[a] 0.4 M reagent.

reagent would be possible only if future tests show a very high selectivity for cesium over other components of the liquor.

3.1.1 Cesium Extraction from $NaNO_3$ Solution with Sodium Tetraphenyl Boron ($Na\phi_4B$). Cesium extractions by $Na\phi_4B$ from solutions of different $NaNO_3$ concentrations and pH are shown in Tables 8, 9, and 10. Little influence on the extraction was noted by pH variation between 3 and 12. At a low pH (0.1), the extraction was severely depressed (Table 8). Increased $NaNO_3$ concentration also inhibited the extractions. However, useful coefficients were obtained even from 3 M $NaNO_3$ when the $Na\phi_4B$ concentration was 0.2 M or above (Table 9). Increasing the $Na\phi_4B$ concentration increased the cesium extraction coefficient according to the approximate relationship $E^o_a \propto [Na\phi_4B]^{2.9-3.5}$. Thus, an extraction coefficient of 29 was obtained from 3 M $NaNO_3$ with 0.5 M $Na\phi_4B$ in hexone (Table 10 and Fig. 15).

Table 8. Cesium Extraction with $Na\phi_4B$-Hexone from 2 M $NaNO_3$

Organic: 0.1 M $Na\phi_4B$-hexone
Aqueous: 2 M $NaNO_3$, 0.13 g Cs^+/liter, Cs-134, pH varied with NaOH
Phase ratio, O/A = 1

Aqueous Equilibrium pH	Cs E^o_a
0.1	0.003
3.1	0.50
3.2	0.47
3.3	0.46
3.5	0.63
12	0.49
13	0.47
13	0.44

Table 9. Effect of Na^+ upon Cesium Extraction with $Na\phi_4B$

Organic: 0.1 M $Na\phi_4B$ in hexone
Aqueous: 0.5 M, 2 M, and 3 M $NaNO_3$, Cs-134, pH 3.5-4.0
Phase ratio, O/A = 1

$NaNO_3$, M	Cs E^o_a	Aqueous Equilibrium pH
0.5	2.3	4.0
2.0	0.63	3.5
3.0	0.25	4.0

Table 10. Cesium Extraction from 0.5 M and 3 M $NaNO_3$
as a Function of Naϕ_4B Concentration

Organic: 0.1-0.5 M Naϕ_4B in hexone
Aqueous: 0.5 M $NaNO_3$ and 3 M $NaNO_3$, Cs-134, pH adjusted with NaOH
Phase ratio, O/A = 1

Naϕ_4B, M	Aqueous Equil. pH	0.5 M $NaNO_3$	3 M $NaNO_3$
0.1	4	2.3	-
0.2	4	7.1	1.2
0.3	4	26	3.2
0.4	4	54	9.4
0.5	4	220	29

3.1.2 Cesium Extraction with Naϕ_4B from Simulated Purex Waste. Extractions of cesium from simulated Purex wastes as compared to those from 3 M $NaNO_3$ solutions are shown in Table 11. In these tests the 1-WW (composition given in Table 11) was adjusted initially to 1 M tartrate and then to pH 6 with NaOH. The overall dilution factor was 3 and the final sodium ion concentration was 2.8 M. It may be noted from the table that cesium was extracted as effectively from the adjusted 1-WW solution as from the pure 3 M $NaNO_3$. Evidently, the presence of iron, sulfate, phosphate, etc. in the waste liquor had little effect on the extraction process.

In other tests (not shown) it was found that neither zirconium-niobium nor europium is extracted by Naϕ_4B from the adjusted Purex 1-WW. For example, with 0.5 M Naϕ_4B in hexone (phase ratio, O/A = 1) the zirconium-niobium and europium extraction coefficients were $<10^{-4}$ and $<10^{-5}$, respectively.

3.1.3 Stability of Naϕ_4B-Hexone Solvent. Aqueous solutions of Naϕ_4B are reported to decompose upon standing.[18] As a cursory check on stability of Naϕ_4B in hexone tests were made in which cesium was extracted from adjusted Purex 1-WW by 0.5 M Naϕ_4B in hexone, which had been aged for periods of one and two weeks. Cesium extraction coefficients of 36, 38, and 36 were obtained with fresh solvent, solvent aged for one week, and solvent aged for two weeks, respectively. The Naϕ_4B-hexone solutions obviously had not decomposed appreciably within the time period studied.

3.1.4 Cesium Stripping from Naϕ_4B-Hexone. A number of reagents have been tested for their ability to strip cesium from the Naϕ_4B-hexone solvent (Table 12). Attempts to re-

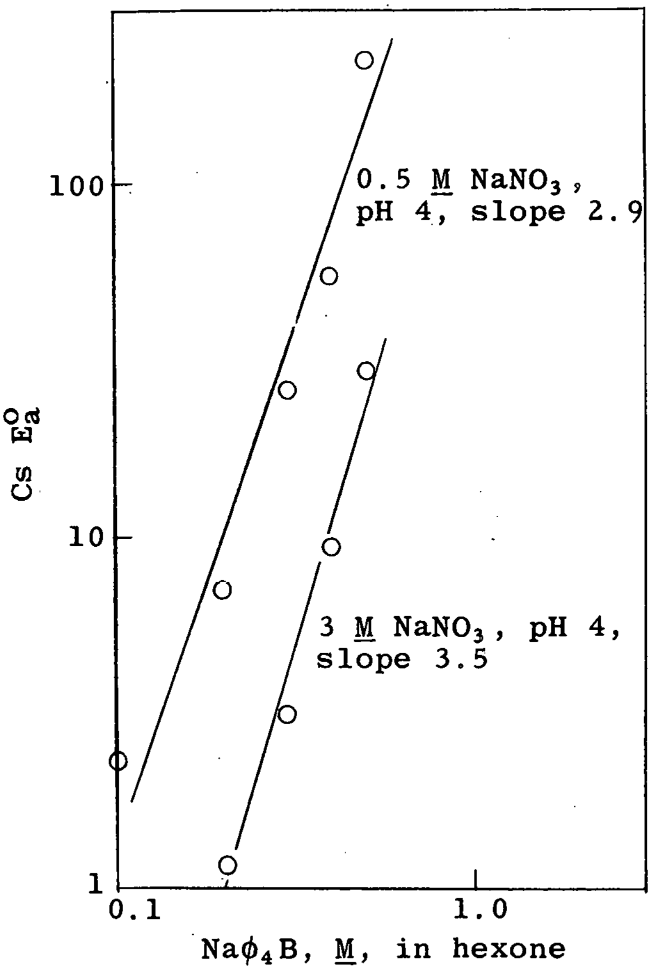


Fig. 15. Cesium Extraction from $NaNO_3$ as a Function of Naϕ_4B Concentration.

place cesium in the organic phase by Na^+, Li^+, NH_4^+ or Al^{+3} were not successful. Precipitates formed with NH_4^+ salts were probably due to insolubility of $NH_4\phi_4B$ in hexone. The type of anion had little effect on the stripping results.

Effective stripping was obtained by dilute solutions of mineral acids. Unfortunately, however, the Naϕ_4B was converted by the acids to a form (possibly tetraphenyl boron) which upon recycle was an ineffective cesium extract. It was found impossible to regenerate the stripped solvent to its original form by treating with caustic.

3.1.5 Cesium Extraction by DNNSA in Amsco 125-82 from $NaNO_3$, $Na_2C_4H_4O_6$ and Purex 1-WW Solutions. Lindenbaum and Boyd[19] have noted that dinonyl naphthalene sulfonic acid

Table 11. $Na\phi_4B$ Extraction of Cesium from Adjusted Synthetic Purex 1-WW and 3 M $NaNO_3$

Organic: $Na\phi_4B$ in hexone
Aqueous: (1) 3 M $NaNO_3$, Cs-134
(2) Synthetic Purex 1-WW, 4 M H^+, 0.5 M Fe^{+3}, 0.6 M Na^+, 0.1 M Al^{+3}, 0.01 M Cr^{+3}, Ni^{+2}, UO_2^{++}, $PO_4^{\equiv}$, 0.02 M Si, 1 M $SO_4^{=}$, 0.17 g Sr^{+2}/liter, 0.47 g Ce^{+3}/liter, 0.83 g RE^{+3}/liter, 0.37 g Cs^+/liter, 0.29 g Ru^{+4}/liter, 0.6 g Zr/liter, Cs-134, initially 1 M tartrate, adjusted to pH 6 with NaOH; dilution factor 3, Na^+ = 2.8 M
Phase ratio: 1

	3 M $NaNO_3$		Adjusted 1-WW 2.8 M Na^+	
$Na\phi_4B$, M	Equilibrium pH	Cs E_a^o	Equilibrium pH	Cs E_a^o
0.2	4	1.2	5	1.9
0.3	4	3.2	5	5.9
0.4	4	9.4	5	-
0.5	4	29	5	36

Table 12. Stripping of Cesium from $Na\phi_4B$ in Hexone

Organic: $Na\phi_4B$ in hexone, Cs-134 tracer
Aqueous: Stripping solutions as tabulated
Phase ratio, O/A = 1

$Na\phi_4B$, M in hexone	Aqueous Phase, M Reagent	Stripping Coefficient, E_a^o	Remarks
0.3	0.1 HNO_3	0.014	
0.3	0.2 HNO_3	0.11	
0.5	2.0 HNO_3	420	
0.3	0.2 HCl	0.12	
0.5	3.0 HCl	1300	
0.3	3.0 HCl	1000	
0.3	0.1 H_2SO_4	0.12	
0.3	0.2 HF	0.02	
0.3	H_2O	-	Emulsion
0.3	1.0 $(NH_4)_2SO_4$	-	Precipitated
0.3	2.0 NH_4NO_3	-	Precipitated
0.3	2.0 NH_4Cl	-	Precipitated
0.3	0.25 NaOH	0.01	
0.3	0.2 $LiNO_3$	0.016	
0.3	0.2 HCl + 0.2 NaCl	0.23	
0.3	0.2 NaF	0.012	
0.3	0.2 NaF + 0.2 HF	0.02	
0.3	1.0 $Al_2(SO_4)_3$	0.65	

(DNNSA) in benzene extracts Zn(II), Cs, Fe(III), and Ce(III) from HCl and $HClO_4$. Further studies reported here were made to test the performance of this reagent under conditions more closely allied with those expected in process application. As shown in Tables 13-16 and Fig. 16, most effective extractions of cesium from sodium nitrate solutions were obtained when the DNNSA concentration was relatively high and the sodium nitrate concentration was low. From adjusted Purex 1-WW solutions, the extraction coefficient was only ~0.4 when the DNNSA concentration in the organic phase was 0.5 M. Changing the diluent failed to improve the cesium extractability.

The low cesium extraction power of the DNNSA detracts from the potential utility of this reagent as a process extractant. On the other hand, application may still be possible if the extraction of cesium is sizeably greater than that of other components of the Purex waste. Further studies of the selectivity of DNNSA for cesium are being made.

Table 13. DNNSA Extraction of Cesium from 0.5 M $NaNO_3$ as a Function of pH

Organic: 0.1 M DNNSA in Amsco 125-82
Aqueous: 0.5 M $NaNO_3$, Cs-134 tracer, pH varied with NaOH
Phase ratio, O/A = 1

Aqueous Equilibrium pH	Cs E_a^o
<0	0.45
0	0.52
0.5	0.46
1.1	0.45
1.3	0.48
10.0	0.50
10.3	0.50
10.6	0.49
10.8	0.49
11.1	0.48

4.0 FUNDAMENTAL CHEMISTRY

4.1 Anomalous Equilibria in Solvent Extraction Systems

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

In continued search for anomalous equilibria in systems other than those already reported,[20] the extraction coefficient dependences on reagent concentration by vigorous and

Table 14. DNNSA Extraction of Cesium from $Na_2C_4H_4O_6$

Organic: 0.5 M DNNSA--Amsco 125-82
Aqueous: 0.4 M $Na_2C_4H_4O_6$, Cs-134, pH varied with NaOH
Phase ratio, O/A = 1

Aqueous Equilibrium pH	Cs E$_a^o$
1.0	1.3
3.0	3.4
3.5	3.6
3.9	2.5
13	0.70

Table 15. DNNSA Extraction of Cesium from Tartrate-Complexed, Synthetic Purex 1-WW

Organic: 0.5 M DNNSA - diluent
Aqueous: Synthetic Purex 1-WW, initially 1 M tartrate, adjusted to pH 6 with NaOH, dilution factor = 3
Phase ratio, O/A = 1

Organic Phase Diluent	Aqueous Equilibrium pH	Cs E$_a^o$
Amsco 125-82	2.2	0.37
Xylene	2.2	0.44
Hexone	2.2	0.26
Carbon tetrachloride	2.2	0.39
Butyl acetate	2.2	0.24

Table 16. Variation of Cs E$_a^o$ as a Function of $NaNO_3$

Organic: 0.5 M DNNSA--Amsco 125-82
Aqueous: 0.2-3.0 M $NaNO_3$, Cs-134, pH varied with NaOH
Phase ratio, O/A = 1

	Aqueous Phase	
M $NaNO_3$	Equilibrium pH	Cs E$_a^o$
0.2	1.2	2.7
0.2	13	2.0
0.5	13	1.4
1.0	13	0.74
3.0	0.6	0.22
3.0	2.5	0.37

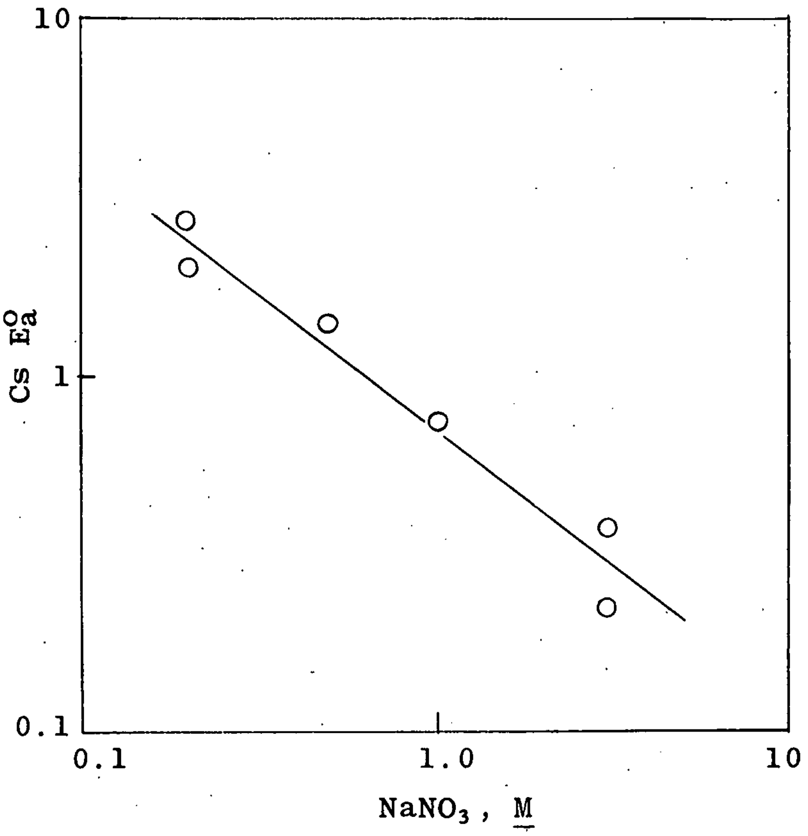


Fig. 16. Cesium Extraction with 0.5 M DNNSA--Amsco 125-82 as a Function of $NaNO_3$ Concentration.

by gentle equilibration have been determined for the systems shown in Table 17. Thorium extraction by di-n-decylamine sulfate (DDAS) and uranium extraction by 1,3-ethylpentyl-4-ethyloctylamine sulfate (EPOS) both showed definite evidence of anomalous behavior. In the former, severe scatter of the experimental points precluded interpretation of the slopes per se; nevertheless, the differences between the two modes of equilibration were consistent and reproducible. The latter system was the first so far examined which has shown anomalous behavior over the entire concentration range of interest. Whereas in the case of TOAS the results from the two equilibrations coincided at low concentrations, while with DDAS there was agreement at high concentrations, it is apparent from Fig. 17 that in the case of EPOS, since the lines cross, the disparities between the two methods continue to become even more pronounced at both ends of the concentration range.

In summary, it is to be pointed out that while anomalous solvent extraction equilibria due to vigorous agitation during equilibration still are apparently not widespread, it has been definitely established in a sufficient number of cases so that its presence in any extractant system must be considered a real possibility until proven otherwise.

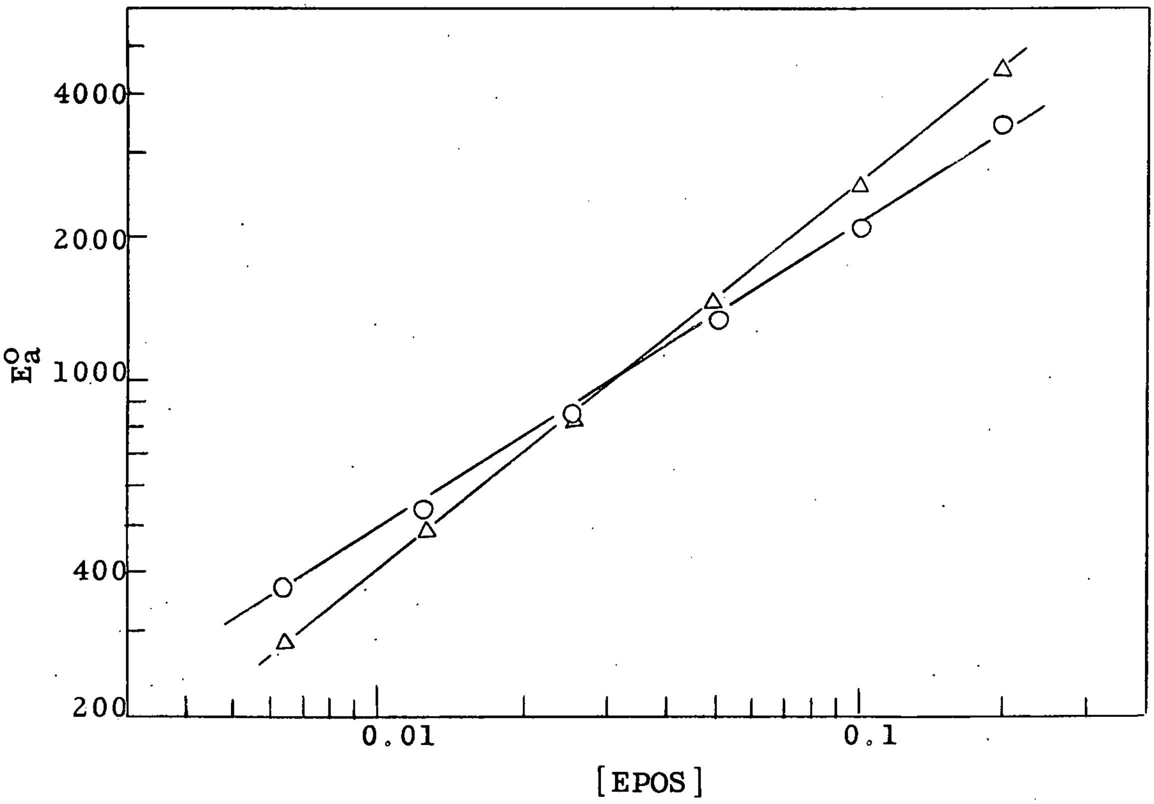


Fig. 17. Extraction of Uranium from 0.01 N H_2SO_4 by EPOS in Benzene: Reagent dependence, comparison of vigorous, , and gentle, , equilibration.

Table 17. Comparison of Reagent Dependence of Extraction Coefficient by Vigorous and Gentle Equilibration for Various Systems

Metal	Extractant	Aqueous Systems	Power Dependence E_a^o on R		Degree of Difference
			Vigorous	Gentle	
U	TOAS	0.01 N H_2SO_4	3 to 1	3 to 2	Marked.
U	DDAS	0.01 N H_2SO_4	1 to 1/2	~0	Marked.
Th	DDAS	0.01 N H_2SO_4	ca. 1/2	<1/2	Definite difference, but scatter makes it impossible to make positive statement about slope.
U	EPOS[a]	0.01 N H_2SO_4	0.28	0.61	Marked.
U	Primene JMT	0.01 N H_2SO_4	0.5	0.5	No difference in initial equilibration but large differences on re-extracting the final aqueous phases with chloroform.
U	TOPO[b]	0.01 N H_2SO_4	2+	2-	Differences were within experimental error but all points by gentle equilibration were higher.
U	D2EHPA[c]	0.01 N H_2SO_4	1.85	1.78	Differences were within experimental error; however, all but one of the points by vigorous equilibration were higher
U	DDAS	0.995 M Na_2SO_4, 0.005 M H_2SO_4	0.2	0.2	No difference.
U	DDAS-HS[d]	0.75 M Na_2SO_4, 0.25 M H_2SO_4	1/2 to 2/3	1/2 to 2/3	No difference in slope but difference in absolute value.

Table 17 (Cont'd.)

Metal	Extractant	Aqueous Systems	Power Dependence E_a^o on R		Degree of Difference
			Vigorous	Gentle	
U	TOAHS-HS[e]	1.0 M H_2SO_4	1.0	1.0	No difference except possibly at very low concentrations.
U	TBP	0.1 N HNO_3	2.7 to 3.0	2.7 to 3.0	None outside experimental error.
U	TBP	4 M HNO_3	1.8	1.8	None outside experimental error.
Th	TOAS	0.01 N H_2SO_4	3 + to 1.5	3+ to 1.8	None outside experimental error.
Th	TOAS	0.995 M Na_2SO_4; 0.005 M H_2SO_4	2.35	2.35	None outside experimental error.
Th	DDAS	0.995 M Na_2SO_4; 0.005 M H_2SO_4	ca. 1/2	ca. 1/2	None outside experimental error.
Sr	NaD2EHP[f]	1 M Na_2SO_4 at pH 10.0	1	1	None outside experimental error.
Sr	NaD2EHP	1 M Na_2SO_4 at pH 5.0	1	1	None outside experimental error.

---

[a] 1,3-Ethylpentyl-4-ethyloctylamine sulfate.
[b] Tri-n-octyl phosphine oxide.
[c] Di(2-ethylhexyl)phosphoric acid.
[d] Di-n-decylamine sulfate + bisulfate.
[e] Tri-n-octylamine sulfate + bisulfate.
[f] Sodium di(2-ethylhexyl)phosphate.

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