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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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ABSTRACT

A flowsheet for the recovery of actinides from TBP-Na_2CO_3 scrub-waste solutions has been developed, based on batch extraction data, and tested, using laboratory-scale countercurrent extraction techniques. The process, called the ARALEX process, uses 2-ethyl-1-hexanol (2-EHOH) to extract the TBP degradation products (HDBP and H_2MBP) from acidified Na_2CO_3 scrub waste leaving the actinides in the aqueous phase. Dibutyl and monobutyl phosphoric acids are attached to the 2-EHOH molecules through hydrogen bonds, which also diminish the ability of the HDBP and H_2MBP to complex actinides. Thus all actinides remain in the aqueous raffinate. Dilute sodium hydroxide solutions can be used to back-extract the dibutyl and monobutyl phosphoric acid esters as their sodium salts. The 2-EHOH can then be recycled.

After extraction of the acidified carbonate waste with 2-EHOH, the actinides may be readily extracted from the raffinate with DHDECMP or, in the case of tetra- and hexavalent actinides, with TBP.

The ARALEX process can also be applied to other actinide waste streams which contain appreciable concentrations of polar organic compounds (e.g., detergents) that interfere with conventional actinide ion exchange and liquid-liquid extraction procedures.

I. INTRODUCTION

Significant amounts of actinides are present in nuclear wastes other than high-level liquid waste produced in spent-nuclear-fuel reprocessing.[1] One such waste stream is produced by scrubbing the radiolytic and hydrolytic degradation products from extractant solutions with Na_2CO_3. Actinide concentrations in the range 0.5-5 kg of actinides may be present in the Na_2CO_3 scrub solutions used to "clean up" TBP-nDD solutions from the reprocessing

of one metric ton of spent nuclear fuel.[1,2] In addition, Na_2CO_3 scrub waste will be generated in the cleanup of the dihexyl-N,N-diethyl carbamoylmethylene phosphonate (DHDECMP) extractant, which is to be used to extract all the actinides from high-level liquid waste (HLLW) in the proposed waste-treatment facility described by Tedder and Blomeke.[3]

Neutral organo-phosphorus-based esters such as TBP and DHDECMP produce acidic compounds as hydrolytic and radiolytic decomposition products.[4,5] These acidic degradation products are themselves good extractants, especially for hexa- and tetravalent actinides and certain fission products such as zirconium. The acidic extractants have especially high distribution ratios at the low acid concentrations used to back extract U(VI) and Pu(IV) from TBP and U(VI), Np(IV), Pu(IV), and Am(III) from DHDECMP. Thus, extractable complexes of actinides and zirconium are present during stripping operations. At high concentrations of degradation products, such as dibutylphosphoric acid (HDBP) and monobutylphosphoric acid (H_2MBP), the extractable complexes may precipitate, sometimes in sufficient quantities to interfere with liquid-liquid extraction operations.

Sodium carbonate is generally used in solvent cleanup operations because it forms the sodium salts of the acidic extractants, which, in the case of the DBP and MBP, have distribution ratios between 30% TBP-nDD and 0.25 M Na_2CO_3 of $<10^{-2}$. In addition, the Na_2CO_3 scrub also forms the carbonato-complexes of the actinides and zirconium, which are fairly soluble in excess carbonate. Diluent degradation products and higher-molecular-weight dialkylphosphoric acids, e.g., butyl lauryl phosphoric acid, are not scrubbed out of the TBP by Na_2CO_3. Thus, better methods for TBP cleanup are still sought.[6] Thus, the resultant Na_2CO_3 scrub solution from TBP-nDD consists essentially of a $NaHCO_3$-$NaNO_3$ solution containing varying amounts of NaDBP, Na_2MDP, carbonato-actinide, and carbonato-zirconium complexes all in concentrations that depend on the extent of hydrolysis and radiolysis. Analogous waste from DHDECMP-DIPB processing would be similar in composition but would contain mono- and diacidic salts of phosphoric acid degradation products of DHDECMP.[5]

The efficient removal of actinides and fission products from Na_2CO_3 scrub solutions presents several problems. Neutralization of the carbonate solutions with HNO_3 and adjustment to a hydrogen ion concentration of ~0.1 M followed by cation exchange would result in poor metal ion absorption on the resin, in precipitate formation of at least a portion of the metal ions as complexes of the degradation products, and in extensive column plugging. Acidification of the carbonate solutions with excess HNO_3 followed by extraction with TBP or preferably DEHDECMP would result in the rapid buildup of intolerable concentrations of acidic degradation products, which prevent efficient back extraction. In addition, precipitate and interfacial crud formation would be extensive. Extraction of the carbonato-actinide complexes with, for example, a quaternary ammonium carbonate extractant in diethylbenzene

results in low recovery of actinides. Emulsion formation also takes place because of interaction between the DBP and MBP salts and the quaternary ammonium ion. Thus, any method for processing the Na_2CO_3 scrub waste must address the problem of the interaction and partitioning of the hydrolytic and radiolytic degradation products that are present, as well as the recovery of the actinides.

Two processes were developed to recover actinides from Na_2CO_3 scrub solutions. The first process involves the use of 0.1 M dihexoxyethylphosphoric acid (HDHoEP) in 2-ethyl-1-hexanoic acid (2-EHA) to extract uranium, neptunium, and plutonium from acidified (to 1 M in HNO_3) Na_2CO_3 scrub solutions, followed by extraction of americium and curium from the raffinate by 0.5 M HDHoEP in DEB. The uranium, neptunium, and plutonium are efficiently stripped from the 0.1 M HDHoEP in 2-EHA with 0.5 M trimethylammonium hydrogenoxalate, and the americium and curium are efficiently stripped from the 0.5 M HDHoEP in DEB with 8 M HNO_3. DBP and MBP in concentrations up to 0.1 M in the Na_2CO_3 solution do not interfere with the extraction or stripping operations. Precipitates such as U(VI) and Pu(IV)-DBP and -MBP complexes readily dissolve in the HDHoEP-2-EHA solvent system and thus present no problems.

The second process involves the extraction of HDBP and H_2MBP (and DHDECMP degradation products) from acidified Na_2CO_3 scrub solutions (3-4 M in HNO_3) using 2-ethyl-1-hexanol (2-EHOH) leaving all actinides and zirconium in the aqueous phase. The raffinate, which is now free of acidic TBP and DHDECMP degradation products, can be either processed using the HLLW process of McIsaac et al.[3] or recycled into the HA column feed. Degradation products extracted into the 2-EHOH are readily stripped with Na_2CO_3 or NaOH using high O/A phase ratios. The 2-EHOH can then be recycled. We refer to this second process as the ARALEX (ARgonne ALcohol EXtraction) process.

Since the ARALEX method is by far the simpler of the two processes, only this process will be described in this report. Extensive extraction equilibria data have been obtained for H_3PO_4, H_2MBP, HDBP, and TBP as a function of nitric acid concentration using 2-EHOH and for H_2MBP and HDBP using 2-ethyl-1-hexanoic acid (2-EHA). Extraction equilibria data have also been obtained for U(VI), Pu(IV), and Am(III) using HDBP- and H_2MBP-EHOH and HDBP-EHA solutions. A conceptual flowsheet based on the use of 2-EHOH has been prepared and tested by continuous and batch countercurrent extractions.

II. EXPERIMENTAL PROCEDURE

A. Solvents and Reagents

The solvents used in this study were obtained from the following sources:

2-ethyl-1-hexanol (99% min)	Union Carbide Corp. Chemicals Division, New York, New York;
1-octanol (distilled in glass)	Burdick & Jackson Laboratories, Muskegon, Michigan;
2-ethyl-1-hexanoic acid (Prac.) 1-octanoic acid (99% min) 1-decanol (99% min)	Eastman Organic Chemicals, Distillation Products Industries, Rochester, New York;
p-diisopropylbenzene	Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

The 2-ethyl-1-hexanol (2-EHOH) and 2-ethyl-1-hexanoic acid (2-EHA) were distilled before being used, whereas the 1-octanol, 1-octanoic acid, and p-diisopropylbenzene (DIPB) were used as received. The n-butanol used to synthesize the DBP and MBP was reagent grade and was distilled from dry molecular sieves before using.

A mixture of dibutyl and monobutyl phosphoric acid, 55 and 45 wt %, respectively, was obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester, New York. All acid solutions were prepared from water purified by a Milli-Q2 system (Millipore Corp., Bedford, MA) and Ultrex ultrapure acids (J. T. Baker, Phillipsburg, NJ). All other reagents were analytical grade.

B. Labeled Compounds

The ^{32}P-labeled butyl esters of phosphoric acid were prepared from neutron-activated P_2O_5. The ^{35}S-labeled dodecyl sulfuric acid (DSA), ^{3}H-labeled diethylenetriaminepentacetic acid (H_5DTPA), ^{3}H-labeled 2-ethyl-1-hexanol (2-EHOH), and ^{32}P-labeled phosphoric acid were obtained from the Amersham Corporation, Arlington Heights, IL. The alpha-active nuclides $^{238}_{92}U$ (4.5×10^9 y), $^{239}_{94}Pu$ (2.4×10^4 y), and $^{241}_{95}Am$ (433 y) were obtained from ANL stocks and purified by standard radiochemical procedures.

C. Preparation of ^{32}P-labeled TBP, DBP, and MBP

A mixture of the butyl esters of phosphoric acid labeled with ^{32}P was prepared by reacting neutron-activated P_2O_5 with butanol in a CCl_4 medium. (Heptane was used when labeled TBP was desired.) The following procedures were used:

About 0.6 g of P_2O_5 was sublimed in a vacuum at 200-250°C into a quartz ampule, ~7.5 cm long and 2-cm OD with a neck 5 cm long and 1-cm OD. After sealing off the ampule on a vacuum line, the P_2O_5 was activated by neutron irradiation at a flux of 6 x 10^{12} n/cm^2·s for 72 h. The reaction with butanol was carried out in the quartz ampule by breaking the ampule open at the neck, introducing a small stirring bar, and then sealing the opening with a silicon rubber sleeve. A solution of 2 mL of butanol in 10 mL of CCl_4 or heptane was injected into the ampule through the rubber sleeve using a hypodermic needle and syringe. The ampule was then placed in a water bath, and the mixture of P_2O_5 plus butanol-CCl_4 or -heptane was stirred for 3 h at 30°C and finally for one-half hour at 70°C. Approximately 1 h was required for the P_2O_5 to completely dissolve in the butanol-CCl_4.

After cooling to room temperature, the solution in the ampule was transferred to a centrifuge tube and equilibrated with an equal volume of aqueous phase containing sufficient NaOH to form the sodium salts of DBP and MBP. The CCl_4 (or heptane) phase, which contained the TBP, was equilibrated a second time with sufficient 0.1 M NaOH to give an aqueous phase having a pH in the range of 11-13.

The combined aqueous phases, which contain the ^{32}P-labeled DBP, MBP, plus any phosphate ion, were scrubbed two more times with an equal volume of CCl_4 to remove traces of TBP and three times with an equal volume of diethyl ether to remove traces of CCl_4. The labeled TBP was recovered from the NaOH-scrubbed heptane phase by first scrubbing the heptane solution with H_2O to remove any base, and then evaporating the heptane at 50-90°C under a stream of nitrogen.

D. Separation and Purification of Labeled DBP and MBP

DBP was separated from MBP using diethyl ether. Under acidic or neutral pH, the DBP reports largely to the ether phase, whereas the MBP remains in the aqueous phase. The aqueous phase from above containing NaDBP and Na_2MBP was acidified to ~1 M H^+ using HCl, and extracted with an equal volume of diethyl ether. The ether phase was then scrubbed 12 times with H_2O using an organic-to-aqueous phase ratio (O/A) of 5.

After scrubbing, the ether phase, which now contained only HDBP, was carefully evaporated to dryness and weighed. The pure undiluted labeled HDBP was then redissolved quantitatively in 2 mL of diethyl ether and back-extracted into an aqueous phase containing the stoichiometric amount of NaOH. Using this procedure, stock solutions that were 0.6-0.7 M in NaDBP were prepared. The specific activity was ~2 x 10^{10} d/m·mmol.

The MBP was purified by first extracting any remaining DBP using 2-ethylhexanoic acid (2-EHA), and then extracting H_2MBP from the aqueous phase using 2-ethylhexanol (2-EHOH). This procedure was developed from

preliminary distribution ratio measurements on crude $DB^{32}P$ and $MB^{32}P$ fractions. The aqueous phases obtained from the ether extraction and scrubbings were combined and extracted three times with 2-EHA using an O/A = 0.5. The raffinate was then acidified to 3-4 M in HNO_3 and extracted with an equal volume of 2-EHOH. After scrubbing the MBP-loaded 2-EHOH two times with 1 M HNO_3 using an O/A = 3, an aliquot of the organic phase was titrated with 0.1 M NaOH to determine the concentration of H_2MBP. The MBP was then back-extracted using the stoichiometric amount of NaOH to give Na_2MBP. Using this procedure, stock solutions containing 0.07 M Na_2MBP were prepared. The specific activity was the same as DBP; namely $\sim 2 \times 10^{10}$ d/m·mmol.

The separated DBP and MBP solutions were analyzed by pH titration using 0.1 M NaOH and found to be >99.5% pure.

E. Separation and Purification of Inactive DBP and MBP

Inactive DBP and MBP were separated using the same procedure as described for the ^{32}P-labeled esters. The starting material was a mixture of DBP (55%) and MBP (45%). After the separated HDBP product was weighed, a final ether extraction was carried out on the NaDBP salt solution to remove traces of TBP. Purity of the separated DBP and MBP was determined by pH titration as previously described. Greater than 99.5% purity was found for each ester.

F. Separation of DBP and MBP by Liquid-Liquid Chromatography

During these investigations, a liquid-liquid chromatographic (LLC) system was developed for separating ^{32}P-labeled HDBP and H_2MBP. This system is based on the use of 1-decanol as the stationary phase and HNO_3 and NH_4OH as the mobile phases. Porasil® (Waters Associates, Milford, MA) was used as the inert support for preparing the LLC columns. Porasil consists of spherical porous silica beads 37-75 μm in diameter. The material was hydraulically graded into two particle-size fractions: 37-60 and >60 μm.[7] The 37-60-μm-dia fraction was used to prepare the LLC columns. Porasil is available in four pore size ranges from <100 to <1500 Å in diameter. Porasil B, which has a pore diameter in the range of 100-200 Å, was used for this separation.

The Porasil B was made hydrophobic by refluxing 24 h in hexamethyldisilazane. The stationary phase (1-decanol) was applied to the Porasil B using conventional solvent-evaporation techniques.[8] Optimum loading of the support was found to be 43 wt %. The equipment used in the chromatographic separations and the general column run procedures are described in Refs. 7 and 8.

Mixtures of H_2MBP and HDBP were loaded onto the 1-decanol columns from 9 M HNO_3. After loading, elution was continued with 8 M HNO_3. The H_2MBP fraction came off the column between 4 and 12 free column volumes (FCV's). Elution was continued for a total of 15 FCV, after which the HDBP

was eluted from the column with 0.02 M NH_4OH. HDBP eluted sharply between 1 and 4 FCV's. A typical elution curve is shown in the Results and Discussion section.

G. Measurements of D

Distribution ratios, D, were made at 25 and 50°C by placing 7-mL culture tubes containing the two phases in a constant-temperature water bath. After 5 min, the tubes were removed from the bath and the phases agitated for 15 s by means of a vortex mixer. The culture tubes were returned to the bath for 1- to 2- min intervals or until the phases disengaged before withdrawing and remixing for 15 s. Four 15-s equilibrations were used for the D measurements.

The distribution ratios for TBP, HDBP, and DSA were measured by reverse or back extraction to minimize the influence of traces of H_2MBP and H_2SO_4, respectively. On the other hand, distribution ratios for H_2MBP, H_3PO_4, and H_5DTPA were measured by forward extraction, after a preliminary extraction with a separate portion of organic phase to minimize the effects of traces of HDBP in H_2MBP and $HC_2H_3O_2$ in H_5DTPA.

In most cases, distribution ratios for the actinide elements were measured by forward extraction because of the low values of D. When convenient, reverse D's were measured to check reversibility.

All radiometric assaying was performed by conventional liquid-scintillation counting techniques using a Beckman LS-100 automatic scintillation counter and Ready-Solv™ GP scintillation solution.

The solubilities of HNO_3 in 2-EHOH or 2-EHA phases that are in equilibrium with fixed concentrations of HNO_3 in the aqueous phase were measured by pH titration. Small volumes of 2-EHOH and 2-EHA were equilibrated three times with titrated HNO_3 solutions at 25 and 50°C using the method described above for D measurements. Organic to aqueous phase ratios (O/A) were two. Aliquots of the equilibrated organic phases were titrated using a Beckman Model 4500 Digital pH meter to determine the concentration of HNO_3.

H. Measurement of 2-EHOH Solubility

The solubility of 2-EHOH in H_2O, in different HNO_3 concentrations, and in Na_2CO_3 at 25 and 50°C was measured using 2-ethyl(2, 3[n]-^{3}H) hexanol. The labeled 2-EHOH as received from Amersham (10 mCi/mL) was diluted to 10 mL with distilled 2-EHOH. Using a calibrated 10-μL glass pipet and scintillation counting, the specific activity of the 10-mL stock solution was measured and found to be 9.31×10^8 c/m·mL or 1.12×10^9 c/m·g. (The density of 2-EHOH = 0.833 g/mL at 20°C.)

Three milliliters of the labeled 2-EHOH stock solution were preconditioned twice with an equal volume of the aqueous phase being investigated. After preconditioning, the labeled organic phase, together with a fresh portion of the aqueous phase being studied, was equilibrated at a given temperature for 5 min with successive 15-s vortexings as described for the D measurements. Preliminary experiments showed that longer equilibration times were unnecessary. Following the equilibration, the two phases were allowed to completely disengage, and then the aqueous phase was withdrawn, centrifuged, and assayed radiometrically. The organic phase was recycled for the next solubility measurement, which usually involved an aqueous phase having a higher HNO_3 concentration.

I. Countercurrent Liquid-Liquid Extractions

Two experimental arrangements were used to carry out countercurrent liquid-liquid extractions. One system consisted of seven jacketed glass separatory vessels equipped with stainless steel centrifugal stirrers. The vessels were maintained at 50°C by means of a constant-temperature bath. The countercurrent transfer of phases was performed manually.

The other system consisted of an eight-stage countercurrent minicentrifugal contactor.[9] The eight-stage minicontactor has a continuous throughput and short-phase contact times (~10 s). Carbonate feed solution, 8 M HNO_3, scrub solution, and organic phase (2-EHOH) were all introduced into stage 4. Since there is only one aqueous and one organic-phase entry port on each contactor, the inlet tubes were modified to accommodate the extra solution. The scrub and 8 M HNO_3 were introduced into the aqueous inlet using a tee joint in the inlet line. The organic phase and carbonate feed solution were introduced into the organic inlet. To prevent these two phases, i.e., the organic and carbonate solutions, from mixing, the carbonate feed entered the mixing chamber through a capillary tube contained within the inlet line feeding in the organic phase.

No provision was available for operating the centrifugal contactors at elevated temperatures; therefore, room-temperature conditions were used for all countercurrent extraction runs using the contactors.

J. Flowsheet Testing

Two procedures were used to prepare Na_2CO_3 scrub-waste solutions. The first procedure, used when U(VI) was the only actinide present, involved direct dissolutions of all salts and metal ions in the Na_2CO_3-$NaHCO_3$ solution. The second procedure involved the preparation of a dodecane solution containing 0.02-0.04 M HDBP and 0.0067-0.0134 M H_2MBP. This solution was used to extract measured amounts of U(VI) and Pu(IV). The resultant organic phase plus precipitates was then slurried with the required amount of Na_2CO_3 until all the DBP, MBP, U(VI), and Pu(IV) stripped into the aqueous phase.

All uranium and plutonium analyses were performed by isotopic dilution and radiometric techniques, respectively. DBP and MBP were analyzed by ion chromatography.[10] Individual countercurrent extraction experiments were performed using ^{32}P-labeled esters to more accurately measure the partitioning of DBP and MBP in each stage.

III. THEORY

Several investigations performed a number of years ago showed that dialkyl and monoalkyl phosphoric acids are dimeric and polymeric, respectively, in solvents of low polarity, such as heptane and benzene.[11-13] It has also been shown that the more polar solvents such as ketones, alcohols, and carboxylic acids tend to depolymerize and complex dialkyl and monoalkyl phosphoric acids.[12,14-20] The polar solvents reduce the polymerization of di- and mono-alkylphosphoric acids because they form hydrogen bonds between the phosphoryl and acidic groups of the extractant and the polar groups of the solvents.

In addition to depolymerizing acidic organophosphorus-based extractants, polar solvents dramatically reduce the distribution ratios of metal ions.[15-20] Dyrssen and Ekberg[15] found that the distribution ratio, D, of Y(III) between a solution of 0.1 M HDBP in chloroform and 0.1 M HNO_3 could be reduced by four orders of magnitude by the addition of methylisobutyl carbinol (hexol) up to 2 M in concentration. Mason et al.[17,19] reported similar effects on the D's of certain actinides and lanthanides using HDEHP in decyl alcohol and in 2-ethyl-1-hexanoic acid.

A solvent suitable for processing the Na_2CO_3 scrub solution should have a distribution ratio, D, for both HDBP and H_2MBP of 5 or greater and a D for actinides (IV) and (VI) of <0.1 at the desired HNO_3 concentration. To assess the suitability of different solvent systems, comparisons were made of the partitioning, dimerization, and complex formation constants of HDBP in solvents of widely differing polarity. The partitioning and dimerization constants, K_p and K_2, respectively, are defined by the following equations:

$$K_p = \frac{[HA]_{org}}{[HA]_{aq}}, \tag{1}$$

$$2HA_{org} \rightleftarrows H_2A_{2org}, \tag{2}$$

and

$$K_2 = \frac{[H_2A_2]_{org}}{[HA]^2_{org}}, \tag{3}$$

where [HA] and $[H_2A_2]$ are the equilibrium concentrations of the monomeric and dimeric forms of HDBP, and K_p and K_2 were calculated from the following equation derived by Dyrssen[12] and Hardy and Scargill:[14]

$$D = \frac{K_p}{\varphi} + \frac{2K_2K_p^2C_{aq}}{\varphi^2}, \tag{4}$$

where D is the distribution ratio, C_{aq} is the total formula weight concentration of HDBP in equilibrium with the organic phase, and φ equals $(1 + K_a[H^+]^{-1})$; K_a is the acidity constant for HDBP, which has a value of 10^{-1} at 25°C and $\mu = 0.1$.[12] Plots of D versus C_{aq} for HDBP using 2-ethyl-1-hexanol (2-EHOH), 2-ethyl-1-hexanoic acid (2-EHA), and p-diisopropylbenzene (p-DIPB) versus 0.1 M HNO_3 at 25°C are shown in Fig. 1. At low concentrations of C_{aq}, the horizontal asymptote gives

$$\log D = \log K_p\varphi^{-1}. \tag{5}$$

The point of intersection of the two asymptotes gives the value for $\log 2K_pK_2/\varphi$.

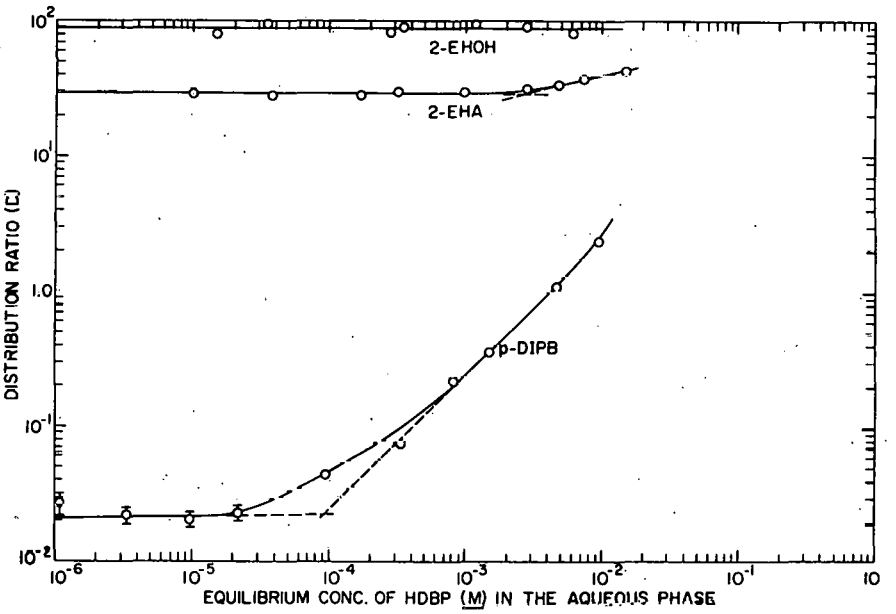

Fig. 1. Distribution Ratios of HDBP vs Equilibrium Aqueous Concentration of HDBP Using 2-ethyl-1-hexanol (2-EHOH), 2-ethyl-1-hexanoic Acid (2-EHA), and p-diisopropylbenzene (p-DIPB). Aqueous phase = 0.1 M HNO_3. T = 25°C.

Values for K_p and K_2 for a variety of solvents are shown in Table I. Data obtained by Dyrssen and Hay[16] and Hardy and Scargill[14] were included for comparison. The data in Table I show that, as the partitioning constant increases, the dimerization constant decreases. Thus, those solvents having the greatest ability to break the very stable HDBP dimer have the greatest tendency to extract the HDBP. Aliphatic alcohols show this property to the

greatest extent. In aliphatic alcohols, the interaction between the solvent and HDBP is sufficiently strong so that the D is independent of C_{aq} (see Fig. 1). Thus, K_p divided by two gives D. The high K_p and low K_2 obtained with aliphatic alcohols as solvents is due to the strong hydrogen bonds that form between the hydroxyl group of the alcohol and the phosphoryl and acidic hydrogen groups of HDBP. The probable structure of the alcohol-HDBP complex is shown in Fig. 2.

TABLE I. Partition and Dimerization Constants for HDBP in Various Systems, 25°C

System	log K_p (2σ)	log K_2	Reference
2-ethyl-1-hexanol/0.1 M HNO_3	2.25 ± 0.03	<-0.2	This work
4-methyl-2-pentanol/0.1 M HNO_3	2.21 ± 0.05	<1	16
1-octanol/0.1 M HNO_3	2.16 ± 0.02	<1	This work
1-decanol/0.1 M HNO_3	2.15 ± 0.02	<1	This work
1-octanoic acid/0.1 M HNO_3	1.80 ± 0.02	N.D.[a]	This work
2-ethyl-1-hexanoic acid/0.1 M HNO_3	1.76 ± 0.02	0.54	This work
methyl isobutylketone/0.1 M HNO_3	1.36	1.19	16
isopropyl ether/0.1 M HNO_3	0.52	2.29	16
benzene/1 M HNO_3	-0.42	4.88	14
p-diisopropylbenzene/0.1 M HNO_3	-1.36	5.38	This work
kerosene/1 M HNO_3	-1.96	5.78	14
carbon tetrachloride/0.1 M HNO_3	-1.44	6.49	16

[a]N.D. = Not Determined.

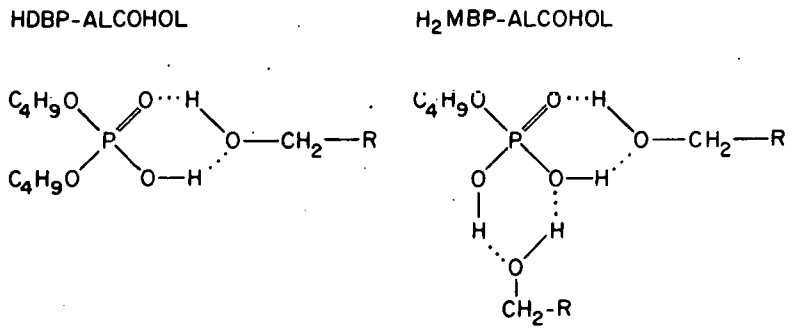

Fig. 2
Structure of Hydrogen-bonded Complexes between an Aliphatic Alcohol and HDBP and H_2MBP

The data in Fig. 1 and Table I show that alcohols are better extractants for HDBP than are carboxylic acids. One might expect the reverse to be true because carboxylic acids probably form hydrogen-bonded complexes with HDBP that are similar in structure to the very stable HDBP dimer (see Fig. 3). Such structures have resonance stabilization and favorable hydrogen-bond angles.

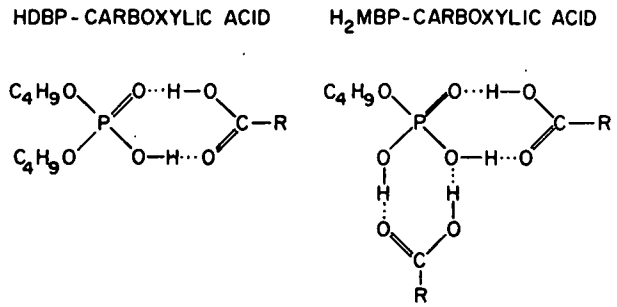

Fig. 3. Structure of Hydrogen-bonded Complexes between an Aliphatic Carboxylic Acid and HDBP and H_2MBP

However, one must consider the energy of association between the solvent molecules themselves. Association between solvent molecules must be broken in order for complexing with HDBP to take place. Carboxylic acids are much more strongly associated than alcohols (as indicated by differences in boiling points) because they form stable dimers analogous to dialkyl phosphoric acids.[12] Thus, the difference in K_p and K_2 between alcohols and carboxylic acids may be explained, at least qualitatively, by the larger energy required to dissociate the carboxylic acids before the formation of the HDBP complex.

There also might be some difference in the stabilities of the hydrogen-bonded HDBP-alcohol and HDBP-carboxylic acid complexes, which would either augment (alcohol more stable than carboxylic acid complex) or diminish (carboxylic acid more stable than alcohol complex) the difference between the two solvents.

A comparison of the constants in Table I for the 2-ethylhexyl and n-octyl isomers of the alcohol and carboxylic acid shows a small but measurable difference in K_p. These results are difficult to explain from the standpoint of the relative contributions of steric and inductive effects. The branched chain isomers are less associated due to steric effects (as indicated by differences in boiling points) and form weaker acids due to inductive effects. Both of these effects would enhance the stability of the 2-ethylhexyl alcohol and carboxylic complexes with HDBP.

However, space-filling (Leybold-Hereaus) atom models show that steric effects also interfere to some degree with rotation around the hydroxyl and carboxyl groups. In addition, the enhanced electron density on the oxygens of the hydroxyl and carboxyl groups (due to inductive effects from branching in the alkyl chain) may not always increase hydrogen-bond strength because the -OH and -COOH groups have both donor and acceptor properties. Thus, it is difficult to explain the difference in the n-octyl and 2-ethylhexyl isomers even qualitatively. However, the constants in Table I do not differ greatly for the two isomers; therefore selection of solvents would be based on other considerations.

Of the solvents listed in Table I, 2-ethyl-1-hexanol appears to be the best choice for processing the Na_2CO_3 scrub solutions; 2-EHOH has the highest K_p, is commercially available, is less expensive than the straight-chain alcohols, and has an acceptable flash point of 85°C.[21] In addition, the D for H_2MBP using 2-EHOH is greater than one; all other nonalcoholic solvents have D's for H_2MBP much less than one.

IV. RESULTS AND DISCUSSION

A. Extraction of TBP, HDBP, H_2MBP, and H_3PO_4 by 2-EHOH

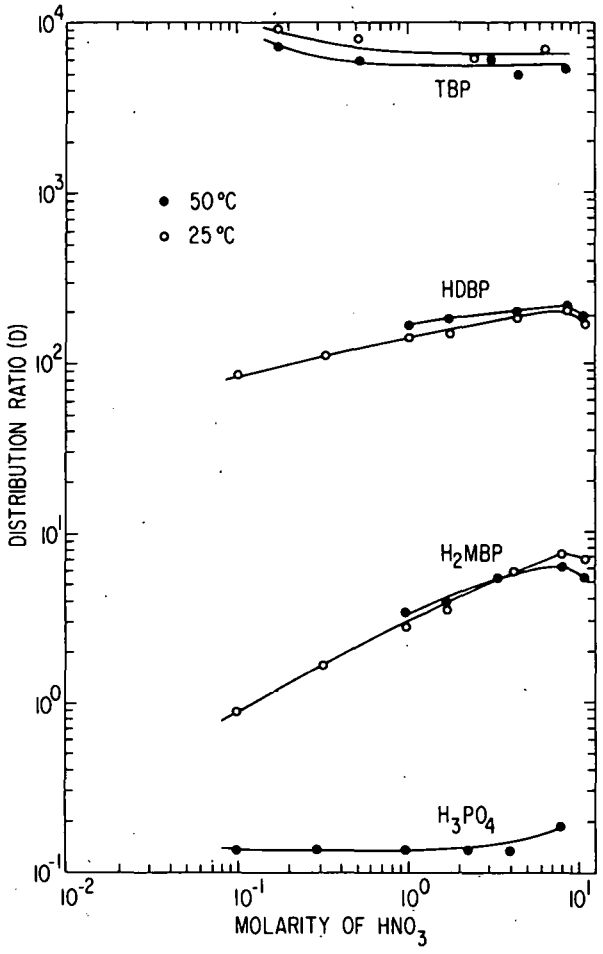

Fig. 4. Distribution Ratios of Tri-n-butyl Phosphate (TBP), Dibutyl Phosphoric Acid (HDBP), Monobutyl Phosphoric Acid (H_2MBP), and Phosphoric Acid (H_3PO_4) vs Aqueous HNO_3 Concentration. Organic phase = 2-ethyl-1-hexanol. T = 25 and 50°C.

Figure 4 shows the D's for the extraction of HDBP, H_2MBP, and H_3PO_4 as a function of HNO_3 concentration in the aqueous phase using 2-EHOH. The order of extractability for the three compounds shown in Fig. 4 is expected, since increasing the number of butyl groups and decreasing the number of hydrophilic groups decreases compatibility with the water structure and increases compatibility with the organic phase. The approximate D at 2 M HNO_3 for any of the three esters and phosphoric acid is given by the equation

$$D = 0.14(30)^n, \qquad (6)$$

where n equals the number of butyl groups. It is important to note the D's achieved for the extraction of H_2MBP using 2-EHOH; H_2MBP is miscible with H_2O in all proportions and therefore difficult to extract into a water-immiscible solvent[14] unless a polar compound such as TBP is present in the organic phase. The probable structure of the H_2MBP-alcohol complex is shown in Fig. 2.

Initial increases in D's for both HDBP and H_2MBP in the range of 0.1 M to 8 M HNO_3 are probably due to a combination of the diminution in the concentration of DBP^{-1} and $HMBP^{-1}$ in the aqueous phase and to "salting-out" effects from the HNO_3. Eventually, the D's for both HDBP and H_2MBP decrease with increasing HNO_3 due to the competition with extractable HNO_3 for donor oxygens in the 2-EHOH and phosphorus compounds. Figure 5 shows the extraction of HNO_3 by 2-EHOH and 2-EHA.

From a practical standpoint, the effect of temperature on the D -versus-HNO_3 curves is, in general, insignificant. Increases in temperature would decrease the association of highly polar solvents, which may explain the

higher D's at 50°C and low acidities. The extraction of HNO_3 by 2-EHOH is about 5% higher at 50 than 25°C, which probably accounts for the lower D's at the higher temperature and acidities. The effect of macro concentrations (up to stoichiometric) of UO_2^{2+} on the D's of HDBP and H_2MBP from 3.5 M HNO_3 at 50°C was also found to be insignificant.

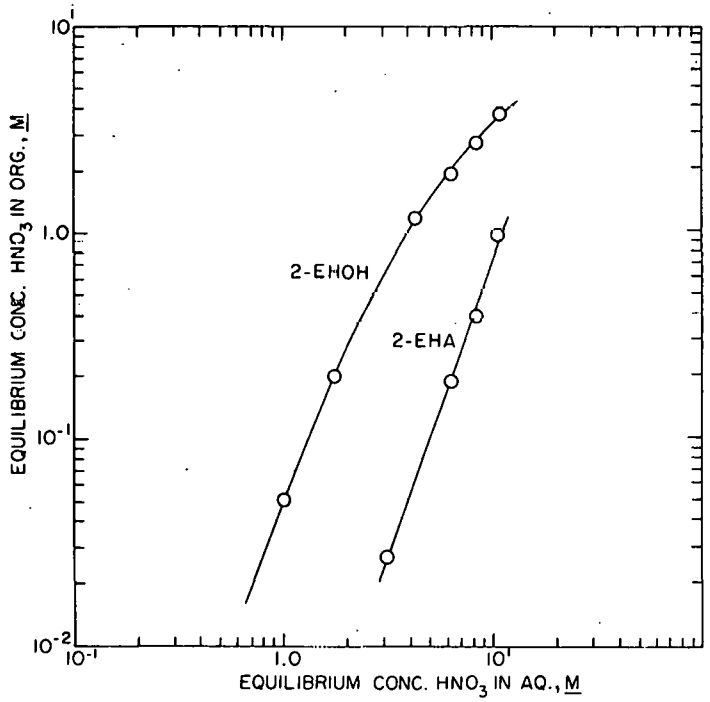

Fig. 5

Equilibrium Curve for the Extraction of Nitric Acid Using 2-ethyl-1-hexanol (2-EHOH) and 2-ethyl-1-hexanoic Acid (2-EHA). T = 25°C.

From a practical standpoint, extraction of a mixture of HDBP and H_2MBP from HNO_3 would be determined by the D's for H_2MBP. Nitric acid solutions in the 2 M to 6 M range are practical conditions from the standpoint of D's and nitric acid economy.

The D's for TBP and H_3PO_4 measured at different HNO_3 concentrations show only slight changes. In the case of TBP, the decrease in D at high acidity may be due to hydrogen bonding between extractable HNO_3 and the donor oxygen in 2-EHOH and TBP. However, reproducibility in the D measurements for TBP was not very good (within 20%), probably because of hydrolysis of the TBP to acidic esters, which have lower D's. Thus, one should not place too much significance in the shape of the TBP-versus-HNO_3 curve. Reproducibility was also poor for the measurements of D's for H_3PO_4. The ^{32}P-labeled H_3PO_4 tended to adsorb on the walls of container vessels, which made accurate measurements difficult, especially at 25°C.

B. Extraction of HDBP and H_2MBP with 2-EHA

Figure 6 shows the extraction of HDBP and H_2MBP as a function of HNO_3 concentration in the aqueous phase using 2-EHA. The curve for HDBP in Fig. 6 is somewhat analogous to the corresponding data using 2-EHOH;

thus a similar explanation can be given to account for these variations. However, in the case of H_2MBP, the D-versus-HNO_3 curve is significantly different from the corresponding curve using 2-EHOH. It is not possible to explain the D-versus-HNO_3 data for H_2MBP in Fig. 6 from the available data. However, the extraction of large amounts of HNO_3 by 2-EHA at high aqueous HNO_3 concentrations is probably significant (see Fig. 5). This extractable HNO_3 bonds to the carbonyl and oxygen groups of 2-EHA, weakening the dimer structure. The resultant 2-EHA·$(HNO_3)_n$ complex is probably involved in the extraction of both HDBP and H_2MBP at high aqueous HNO_3 concentrations. Possible HDBP- and H_2MBP-EHA structures are shown in Fig. 7.

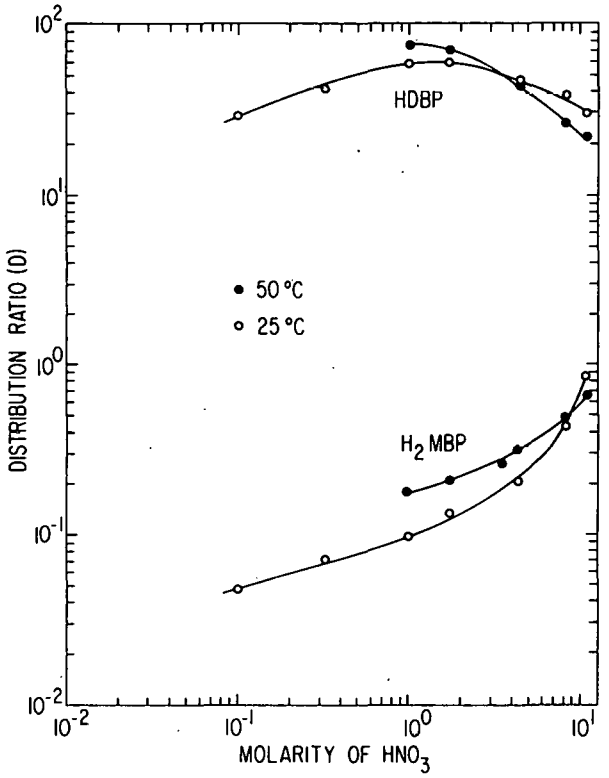

Fig. 6. Distribution Ratios of Dibutyl Phosphoric Acid (HDBP) and Monobutyl Phosphoric Acid (H_2MBP) vs Aqueous HNO_3 Concentration. Organic phase = 2-ethyl-1-hexanoic acid. T = 25 and 50°C.

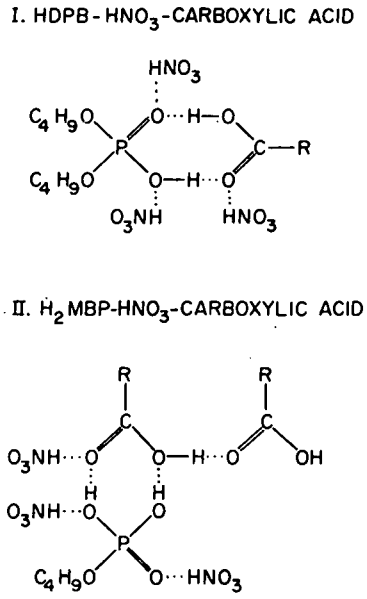

Fig. 7. Structure of Hydrogen-bonded Complexes between Carboxylic Acid-HDBP-HNO_3 and Carboxylic Acid-H_2MBP-HNO_3

The data in Fig. 6 show that 2-EHA is an unsatisfactory solvent for removing both HDBP and H_2MBP from HNO_3, since the D's for H_2MBP are less than 1.0. Increasing the temperature brings about only a small increase in D's, as was the case for 2-EHOH.

C. Extraction of DSA and H_5DTPA

Figure 8 shows the D's for dodecyl sulfuric acid (DSA) (the acidic form of the commonly used detergent, sodium dodecyl sulfate) and diethylenetriamine-pentacetic acid (H_5DTPA). Both of these compounds could be constituents in a

salt waste-treatment facility of a fuel-reprocessing plant[1,3] and therefore were included in the study. As expected, DSA behaves similar to HDBP. Hydrogen-bonded complexes analogous to those shown in Fig. 2 can be formed between the -OH group of the alcohol and the $-OSO_3H$ radical of DSA. Cationic (quaternary ammonium salts) and neutral detergents are also strongly extracted by 2-EHOH. On the other hand, H_5DTPA is very poorly extracted because of the large number of hydrophilic groups and the absence of a long hydrocarbon group. In this respect, it is analogous to H_3PO_4, which has similar D's.

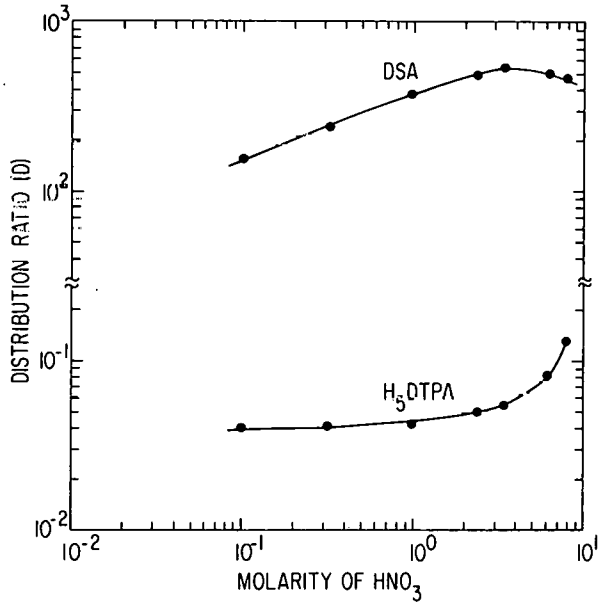

Fig. 8

Distribution Ratios of Dodecyl Sulfuric Acid (DSA) and Diethylenetriaminepentacetic Acid (H_5DTPA) vs Aqueous HNO_3 Concentration. Organic phase = 2-ethyl-1-hexanol. T = 50°C.

D. Interaction Effects of H_2MBP and HDBP

Hardy and Scargill[14] have shown that the presence of HDBP in kerosene has a pronounced effect on the extraction of H_2MBP. This behavior is due to hydrogen bonding of the two esters to each other in a manner analogous to structures shown in Figs. 2 and 3. However, one would not expect interaction between HDBP and H_2MBP in a highly polar solvent, such as 2-EHOH or 2-EHA, unless the concentration of one of the esters was above 0.1 M. The extraction of ^{32}P-labeled H_2MBP was measured in 2-EHOH and in 2-EHA, both of which contained unlabeled HDBP, 2×10^{-2} M in concentration. No difference in the D for H_2MBP was found in the absence or presence of HDBP.

E. Extraction of NaDBP and Na_2MBP

The distribution ratios, D, of the sodium salts of DBP and MBP were measured between 0.25 M Na_2CO_3 and 2-EHOH and between Na_2CO_3 and 2-EHA. The data are shown in Table II. The low D's for the NaDBP and Na_2MBP from 2-EHOH affords a convenient method for scrubbing these compounds from the solvent. DBP was not effectively scrubbed from the 2-EHA because the Na_2CO_3 is largely consumed by the carboxylic acid. Although the equilibrium constant for the equation

$$C_7H_{15}COONa + (C_4H_9O)_2POOH \rightleftarrows C_7H_{15}COOH + (C_4H_9O)_2POONa \quad (7)$$

lies to the right because 2-EHA is a weaker acid than HDBP, a large fraction of the 2-EHA would have to be neutralized before DBP would be converted entirely to sodium salt. Therefore, the ability to remove DBP and MBP by back-extracting DBP and MBP from the alcohol solvent is another advantage of the 2-EHOH over 2-EHA.

TABLE II. Distribution Ratios, D, of NaDBP and Na_2MBP
Aqueous Phase = 0.25 M Na_2CO_3
Temperature = 50°C

	2-EHOH		2-EHA	
	1st Ext.	2nd Ext.	1st Ext.	2nd Ext.
NaDBP	1.5×10^{-2}	1.9×10^{-2}	1.1	1.1
Na_2MBP	3.5×10^{-4}	2.2×10^{-4}	9.4×10^{-3}	6.9×10^{-3}

Stripping experiments using 0.25 M Na_2CO_3 performed on 2-EHOH containing macro concentrations of DBP revealed serious emulsion problems in the first contactor where the bulk of the DBP is converted to its sodium salt. Additional stripping experiments showed that 0.1 M NaOH gave more favorable results, although phase disengagement was still relatively slow. For example, equilibration of 2-EHOH + 0.016 M HDBP + 0.0053 M H_2MBP with 0.1 M NaOH using an organic-to-aqueous phase ratio of 3.0 ($\overline{R}$ = 3.0) gave a combined DBP + MBP distribution ratio of 2×10^{-3}. The phases disengaged completely in 1 min and 40 s, as compared to ~30 s when nitric acid is the aqueous phase. No emulsion was present. Thus, NaOH appears to be just as efficient as Na_2CO_3 in back-extracting DBP and MBP from 2-EHOH and at the same time does not produce any serious emulsion problems.

F. Extraction of Actinides by HDBP and H_2MBP in 2-EHOH

The second objective in the development of a process for removing TBP and DHDECMP degradation products from acidified Na_2CO_3 scrub solutions was to effectively retain the actinides in the aqueous phase during the extraction of DBP and MBP. To achieve this objective, the DBP- and MBP-actinide complexes have to be effectively dissociated by bonding of solvent molecules to the coordinating groups of the HDBP and H_2MBP. Figure 9 shows the extraction of U(VI), Pu(IV), and Am(III) as a function of the concentration of HDBP and H_2MBP in 2-EHOH, at a constant HNO_3 concentration of 3.5 M. It can be seen that neither DBP nor MBP is an effective extractant in 2-EHOH, even for Pu(IV), although ester concentrations above 0.05 M give D's that are greater than one. For comparison, the D for Pu(IV) using 0.02 M HDBP in p-diisopropylbenzene is approximately two orders of magnitude greater than when 2-EHOH is used as the diluent. The differences in D's is even greater when aliphatic diluents, e.g., dodecane,

are compared with 2-EHOH. As the concentrations of HDBP and H_2MBP decrease, the D's for U(VI) and Pu(IV) gradually approach that of the pure 2-EHOH in equilibrium with 3.5 M HNO_3.

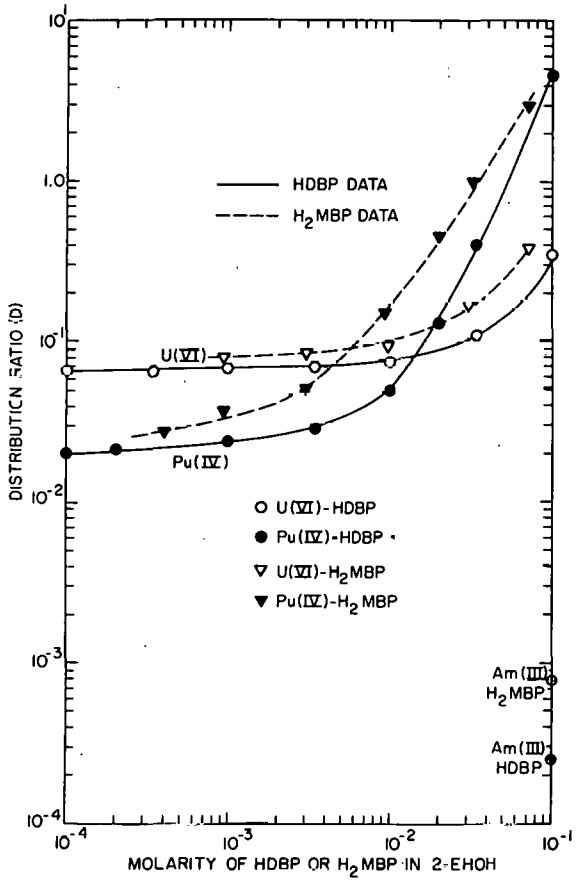

Fig. 9

Distribution Ratios of U(VI), Pu(IV), and Am(III) for HDBP and H_2MBP in 2-EHOH. Aqueous phase = 3.5 M HNO_3. T = 50°C.

Note that the D's for U(VI), Pu(IV), and Am(III) are higher for H_2MBP than HDBP. However, since the H_2MBP concentration produced by radiolysis and hydrolysis of TBP is always significantly less than HDBP, the net effect of the two esters is approximately the same. The data in Fig. 9 also show that Pu(IV) is more strongly extracted by DBP and MBP than U(VI), which is expected.[11-13] However, the reverse order of extraction is found for the pure alcohol. The actual compound (or compounds) involved in the extraction of U(VI) or Pu(IV) is not certain. Since the calculated concentration of uncomplexed DBP in 0.1 M DBP in 2-EHOH solution is only 2×10^{-5} M, the HDBP-alcohol complex is probably directly involved in the extraction. Studies by Mason et al.[17] support this contention.

Figures 10 and 11 show the D's for U(VI) and Pu(IV), respectively, as a function of HNO_3 concentration using 0.02 M HDBP and H_2MBP in 2-EHOH and using pure 2-EHOH. Americum(III) was not studied because its D was too low to be of significance. An ester concentration of 0.02 M was chosen because it was felt that this would be approximately two times the highest concentration of either compound that would be present in the acidified

Na_2CO_3 scrub solutions. Although the minima in the D-versus-HNO_3 curves for U(VI) and Pu(IV) occur at different acidities, all the D's are sufficiently low in the 3-4 M HNO_3 range so that they can be scrubbed out of the 2-EHOH phase using, for example, 3.5 M HNO_3.

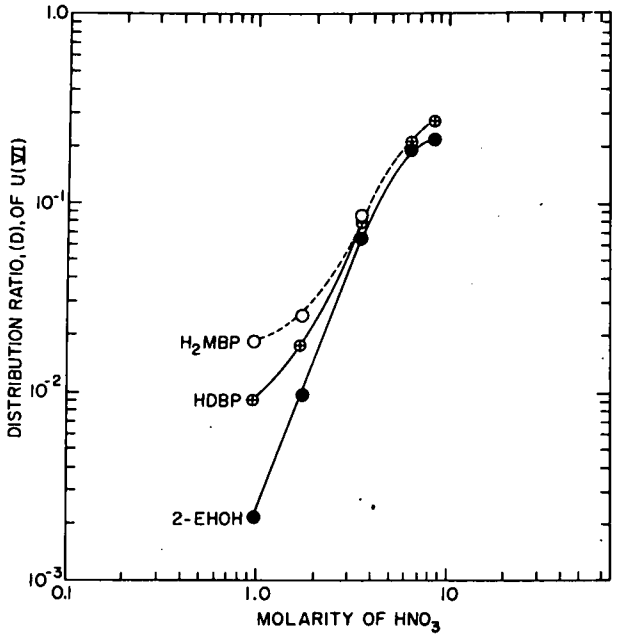

Fig. 10. Distribution Ratios of U(VI) for 0.02 M HDBP in 2-EHOH, for 0.02 M H_2MBP in 2-EHOH, and for Pure 2-EHOH as Functions of HNO_3 Concentration. T = 50°C.

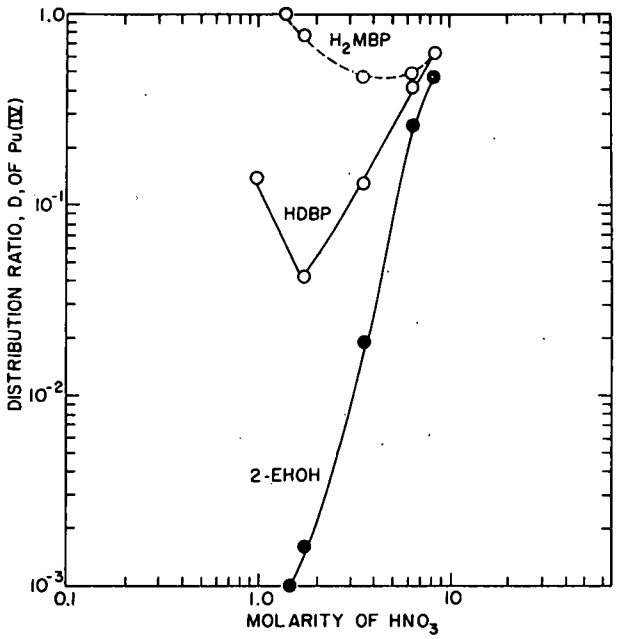

Fig. 11. Distribution Ratios of Pu(IV) for 0.02 M HDBP in 2-EHOH, for 0.02 M H_2MBP in 2-EHOH, and for Pure 2-EHOH as Functions of HNO_3 Concentration. T = 50°C.

Additional distribution-ratio measurements of Pu(IV) from nitric acid-oxalic acid mixtures using 0.02 M H_2MBP and 0.02 M HDBP showed some advantages over pure nitric acid solutions for decontaminating the organic phase. For example, a scrub contact with 1 M HNO_3 - 0.05 M $H_2C_2O_4$ reduced the D for Pu(IV) to less than 0.1 when the organic phase was 0.02 M H_2MBP in 2-EHOH. The influence of oxalic concentration on the D of H_2MBP from 1 M HNO_3 was relatively small. The distribution ratio of H_2MBP from 1 M HNO_3 at 50°C varied from 3.6 to 3.3 when $H_2C_2O_4$ was increased from 0.01 M to 0.10 M.

In addition to reducing the D's for Pu(IV), oxalic acid also reduces the D's for Zr(IV). Zirconium(IV) forms an insoluble compound with MBP, which appears at the interface as a white scum. The presence of oxalic acid in the scrub solution helps but does not completely prevent the formation of this precipitate when Zr(IV) is present in solution in macro concentrations.

G. Extraction of Actinides by HDBP in 2-EHA

Figure 12 shows the extraction of U(VI), Pu(IV), and Am(III) as a function of HDBP in 2-EHA, at a constant HNO_3 concentration of 3.5 M.

Monobutylphosphoric acid was not studied because the D for H_2MBP between 2-EHA and 3.5 M HNO_3 is only 0.28. The data in Fig. 12 show that HDBP is also a very poor extractant in the carboxylic acid solvent. In addition, the pure 2-EHA is a much poorer extractant for U(VI) and Pu(IV) than 2-EHOH, as can be seen at the low HDBP concentrations.

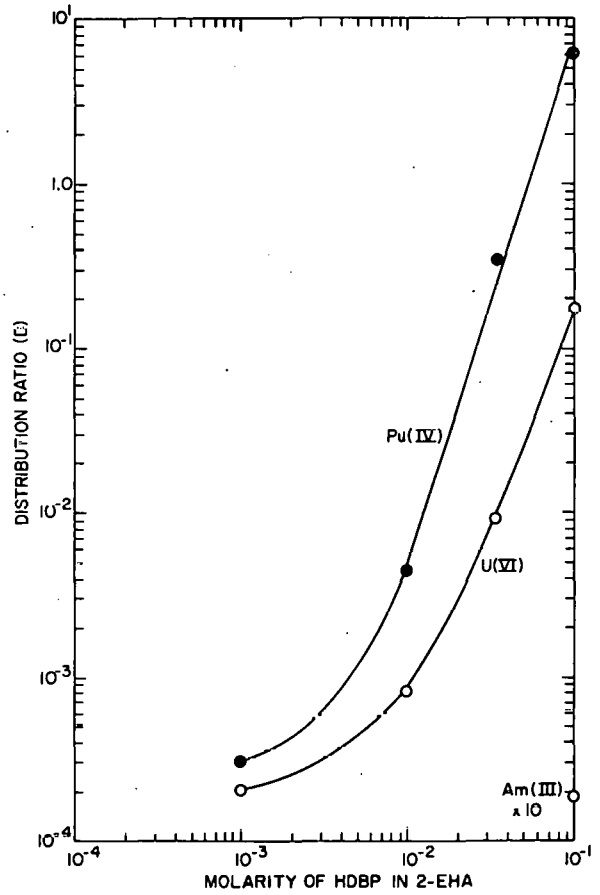

Fig. 12

Distribution Ratios of U(VI), Pu(IV) and Am(III) for HDBP in 2-EHA. Aqueous phase = 3.5 M HNO_3. T = 50°C.

At 0.02 M HDBP in 2-EHA, the D's are so low that no HNO_3 dependency was measured. From the standpoint of actinide extraction alone, 2-EHA is superior to 2-EHOH in keeping the actinides in the aqueous phase. However, the facts that 2-EHA does not extract H_3MBP sufficiently well and that it is difficult to back-extract the sodium salt of DBP are major disadvantages of the 2-EHA solvent.

H. Extractant Dependency of HDBP Using 2-EHOH

The variation in the D of HDBP-versus-the 2-EHOH concentration in benzene is shown in Fig. 13. At low concentrations, e.g., $<10^{-1}$ M EHOH, the D of HDBP is essentially that of pure benzene, whereas at higher EHOH concentrations, the alcohol is the dominant extractant. If one corrects for the influence of benzene, assuming negligible interaction between the EHOH-HDBP complex and the benzene, then the slope of the D-versus-2-EHOH curve is second power at low alcohol concentrations and close to first power at

intermediate alcohol concentrations. Since it is well known that HDBP is a dimer in benzene,[12] the second-power dependency may be explained by the following reaction taking place at low alcohol concentrations:

$$(HDBP)_{2_{org}} + 2(EHOH)_{org} \rightleftarrows 2(EHOH \cdot HDBP)_{org}, \quad (8)$$

where (EHOH) is 2-ethyl-1-hexanol. At higher alcohol concentrations, the HDBP dimer concentration is very low and the following reaction prevails:

$$(HDBP)_{aq} + (EHOH)_{org} \rightleftarrows (EHOH \cdot HDBP)_{org}. \quad (9)$$

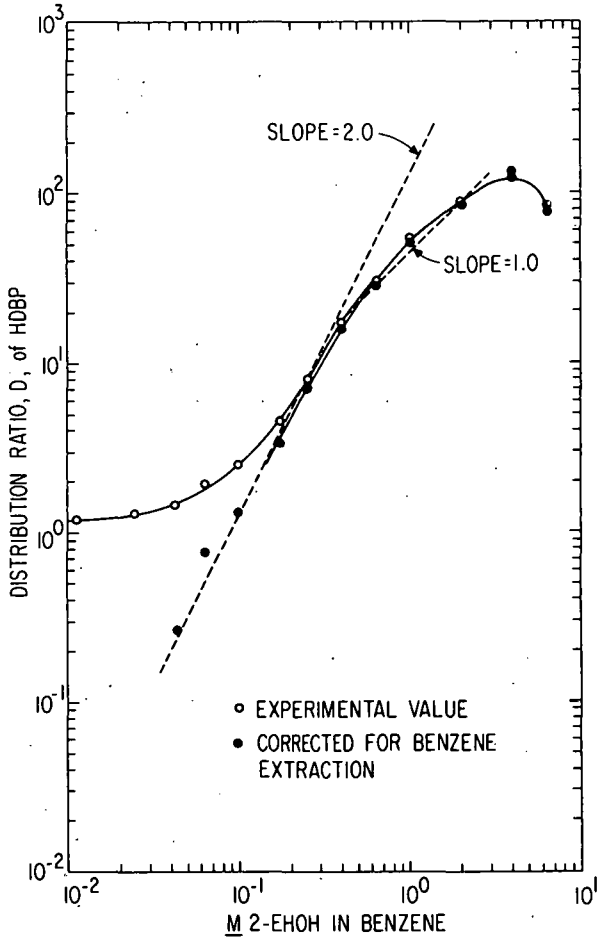

Fig. 13

Distribution Ratios, D, of HDBP vs EHOH Concentration in Benzene. Aqueous phase = 0.1 M HNO_3. T = 25°C.

The data in Fig. 13 show a small decrease in D from 4 M to undiluted (6.4 M) 2-EHOH. No explanation for this decrease can be given at this time. Note that ~17% 2-EHOH (1.0 M) in an aromatic diluent would also be an efficient extractant for HDBP, and of course TBP. Under some circumstances, a more dilute alcohol solvent may be desirable. However, for the present study, undiluted 2-EHOH was chosen for flowsheet testing.

I. Solubility of 2-EHOH in the H_2O-HNO_3 System and in Na_2CO_3

The solubility of 2-EHOH in H_2O, in different HNO_3 solutions, and in 0.25 M Na_2CO_3 at 25 and 50°C is shown in Table III. Minimum solubility of 2-EHOH in the H_2O-HNO_3 system occurs around 0.3 M HNO_3 and then steadily increases with increasing HNO_3 concentration. High HNO_3 concentration probably enhances solubility because of the lowering of the free H_2O concentration and hydrogen bonding to the alcohol. Both effects would make the alcohol more compatible with the aqueous phase.

The D's for 2-EHOH between 3.5 M HNO_3 and dodecane and diisopropylbenzene are 12 and 23 at 25°C, respectively. (The concentration of 2-EHOH in dodecane and diisopropylbenzene was 10^{-2} M.) Therefore, both of these solvents could be used to scrub dissolved 2-EHOH from nitric acid solutions.

TABLE III. Solubility of 2-ethyl-1-hexanol in H_2O, in HNO_3 Solution, and in Na_2CO_3 Solution

Solution	Solubility (Molarity) 25°C	50°C
H_2O	1.3×10^{-2}	1.1×10^{-2}
0.103 M HNO_3	9.3×10^{-3}	9.5×10^{-3}
0.318 M HNO_3	9.7×10^{-3}	8.9×10^{-3}
0.983 M HNO_3	1.1×10^{-2}	1.1×10^{-2}
2.39 M HNO_3	1.4×10^{-2}	1.4×10^{-2}
3.52 M HNO_3	2.0×10^{-2}	2.0×10^{-2}
6.32 M HNO_3	2.3×10^{-2}	2.6×10^{-2}
8.42 M HNO_3	2.7×10^{-2}	3.0×10^{-2}
0.25 M Na_2CO_3	5.3×10^{-3}	5.3×10^{-3}

J. Chromatographic Separation of H_2MBP and HDBP

Figure 14 shows a typical LLC separation of H_2MBP and HDBP using 1-decanol as the stationary phase. This mode of separation is very efficient on a laboratory scale and was used frequently, not only to separate mixtures of labeled HDBP and H_2MBP, but also to check the purity of HDBP and H_2MBP stock solutions. Unfortunately, the LLC columns were not very stable due to the lack of retention of the alcohol on the Porasil B support. It was found that 1-decanol was superior to the octanol isomers with respect to stationary phase retention. The average column lifetime was found to be only about five runs. Consequently, industrial-scale applications of this technique are impractical.

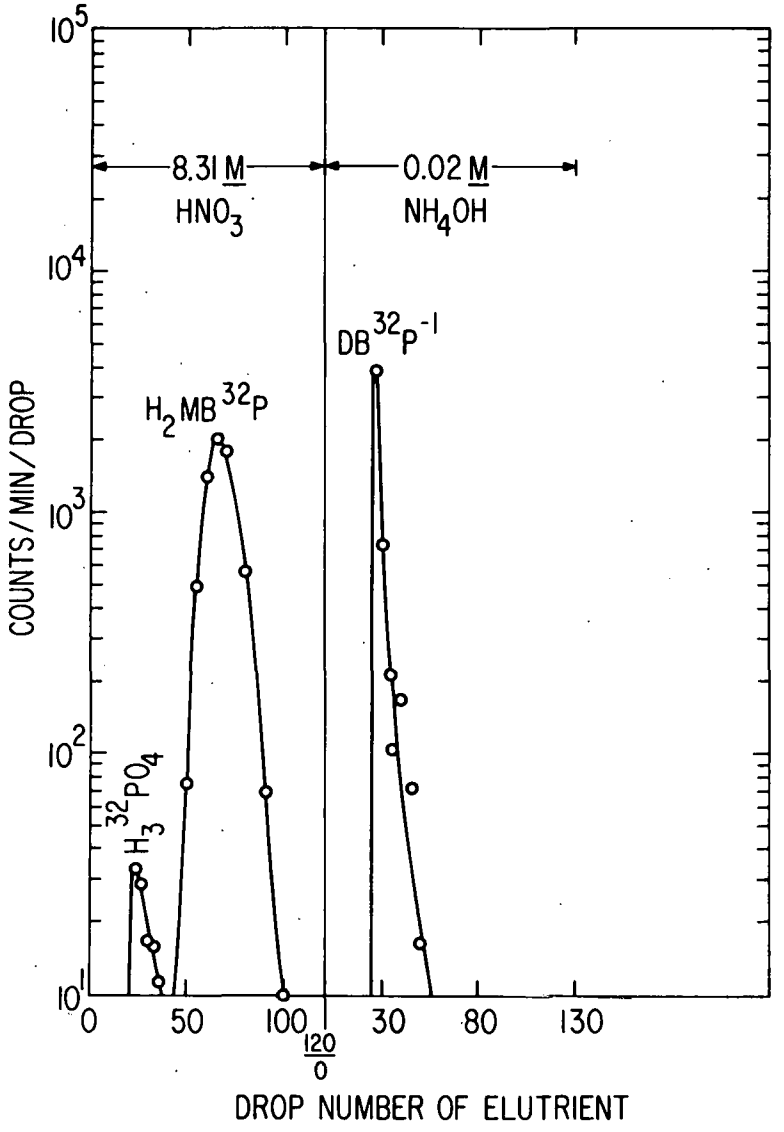

Fig. 14. Elution Curves for the LLC Separation of H_2MBP and HDBP. Column material = 43 wt % 1-decanol on Porasil® B (37–60 μm). Column size = 5.0 cm x 2.6-mm ID. Free-column volume = 13 drops. Mobile-phase velocity = 4.6 cm/min. T = 25°C.

K. Flowsheet Development

The flowsheet for processing Na_2CO_3 scrub solutions is based on the use of 2-EHOH to extract TBP degradation products, primarily DBP and MBP, and to leave the actinides in the aqueous phase raffinate. The raffinate can then be recycled to the HLLW and processed using DHDECMP. Equations describing the basic chemical equilibria, using uranyl-DBP and -MBP complexes as examples, are

$$[UO_2(DBP)_2]_{n(aq)} + 2nH^+_{(aq)} + 2nEHOH_{(org)} \rightleftarrows 2nEHOH{\cdot}HDBP_{(org)} + nUO^{2+}_{2(aq)} \quad (10)$$

and

$$[UO_2(MBP)]_{m(aq)} + 2mH^+_{(aq)} + 2mEHOH_{(org)} \rightleftarrows m(EHOH)_2{\cdot}H_2MBP_{(org)} + mUO^{2+}_{2(aq)}, \quad (11)$$

where n and m equal the state of aggregation of the DBP and MBP complexes, respectively.

The feed solution for the process is the combined TBP- and DHDECMP-Na_2CO_3 scrub solutions. Many process-related variables determine the composition and volume of the Na_2CO_3 scrub solution; for example, the radiation and hydrolytic damage to the TBP and DHDECMP extractant solutions, which, of course, depends on the cooling time of the fuel and residence time of the extractants in the LLE equipment, the actinide and fission-product composition of the organic extractants during stripping operations, and the relative flow rate of extractant and Na_2CO_3 scrub streams.

These processing parameters are not known exactly at this time. Therefore, certain assumptions were made in selecting a reasonable composition and volume of the Na_2CO_3 waste to use in developing a tentative flowsheet. First, the total quantity of actinides contained in the Na_2CO_3 scrub waste is ~6 kg/MTHM. Uranium would total 5.9 kg, 5 kg coming from TBP,[1] and 0.9 kg coming from DHDECMP.[3] The remaining 0.1 kg of actinides would consist of a mixture of neptunium, plutonium, americium and curium. Second, the primary constituent of the Na_2CO_3 scrub waste, $UO_2(DBP)_2$, must stay within solubility limits when the carbonate solution is acidified. Therefore, the uranyl complex concentration should not exceed 0.01 M in the Na_2CO_3 solution (0.02 M in DBP), which requires a carbonate scrub volume of 2500 L/MTHM. Third, the concentration of MBP is in the range of one-third to one-fourth that of DBP, assuming no losses of MBP during HNO_3 scrubbing.[22] This concentration of MBP is probably high since some MBP is lost during scrubbing operations.

In addition to the above constituents, the Na_2CO_3 scrub waste will also contain a certain amount of $NaHCO_3$ and $NaNO_3$ from the neutralization of HNO_3 present in the TBP and DHDECMP. From data in Refs. 1 and 3, 96 moles of $NaHCO_3$ and 96 moles of $NaNO_3$ will be formed in the Na_2CO_3 scrub solution from the neutralization reaction. However, neither the presence of variable amounts of $NaHCO_3$ and $NaNO_3$ nor actinides would alter the flowsheet in any significant detail. Thus, the Na_2CO_3 scrub waste used in the flowsheet development consists of 2500 L/MTHM of 0.21 M Na_2CO_3 containing 6 kg of actinides, 0.02 M DBP, 0.0067 M MBP, 0.038 M $NaHCO_3$, and 0.038 M $NaNO_3$. Approximately 100 g of fission products, primarily zirconium and ruthenium, may also be present.[1] Zirconium was the only fission product that showed any degree of extractability by H_2MBP and HDBP mixtures in 2-EHOH. It was assumed that one-half of the fission product was Zr(IV), and that therefore its concentration in the carbonate feed solution was 2×10^{-4} M. All other fission products were excluded from further consideration in this study.

Preliminary single-stage extraction tests were performed using the above carbonate feed composition and varying the relative amounts of U(VI) and Pu(IV). Sufficient 8 M HNO_3 was added to the carbonate feed to give a final acidity of 3.5 M HNO_3. The phase ratio (R) of 2-EHOH to acidified carbonate feed solution was 0.5, and the temperature was 50°C. Neutralization of carbonate feed by 8 M HNO_3 was carried out simultaneously with the extraction by 2-EHOH by mixing carbonate feed solution with 2-EHOH and then adding dropwise the required amount of HNO_3. This technique avoids the precipitation of U(VI) and Pu(IV)-DBP and -MBP complexes, which will occur when the carbonate feed is neutralized with acid before equilibration with 2-EHOH. The U(VI) and Pu(IV)-DBP and -MBP precipitates will dissolve if they do form when mixed with 2-EHOH, but this process is much slower than the extraction procedure described above.

Single-stage extraction tests were performed first on carbonate feed solutions containing 0.01 M uranyl ions. The tests were performed initially in centrifuge tubes and then in a single-stage centrifugal contactor. A photograph of the single-stage centrifugal contactor is shown in Fig. 15. In order to more easily determine the distribution of HDBP and H_2MBP, individual experiments were performed using ^{32}P-labeled HDBP and H_2MBP. These tests showed that all constituents partitioned between the alcohol and aqueous phases according to predictions based on the data in Figs. 4 and 9 for 3.5 M HNO_3.

L. Eight-stage Continuous Countercurrent Extraction Run

Using the same composition of feed (0.01 M UO_2^{2+}) and phase ratios as in the single-stage tests, an eight-stage countercurrent extraction run using the minicentrifugal contactor was carried out. The flow diagram for this run is shown in Fig. 16. The eight-stage centrifugal contactor is shown in Fig. 17. Uranium analyses showed that steady-state conditions had been achieved after the collection of 450 mL (15 min run time) of raffinate. A total of 3 L of raffinate was collected before terminating the run.

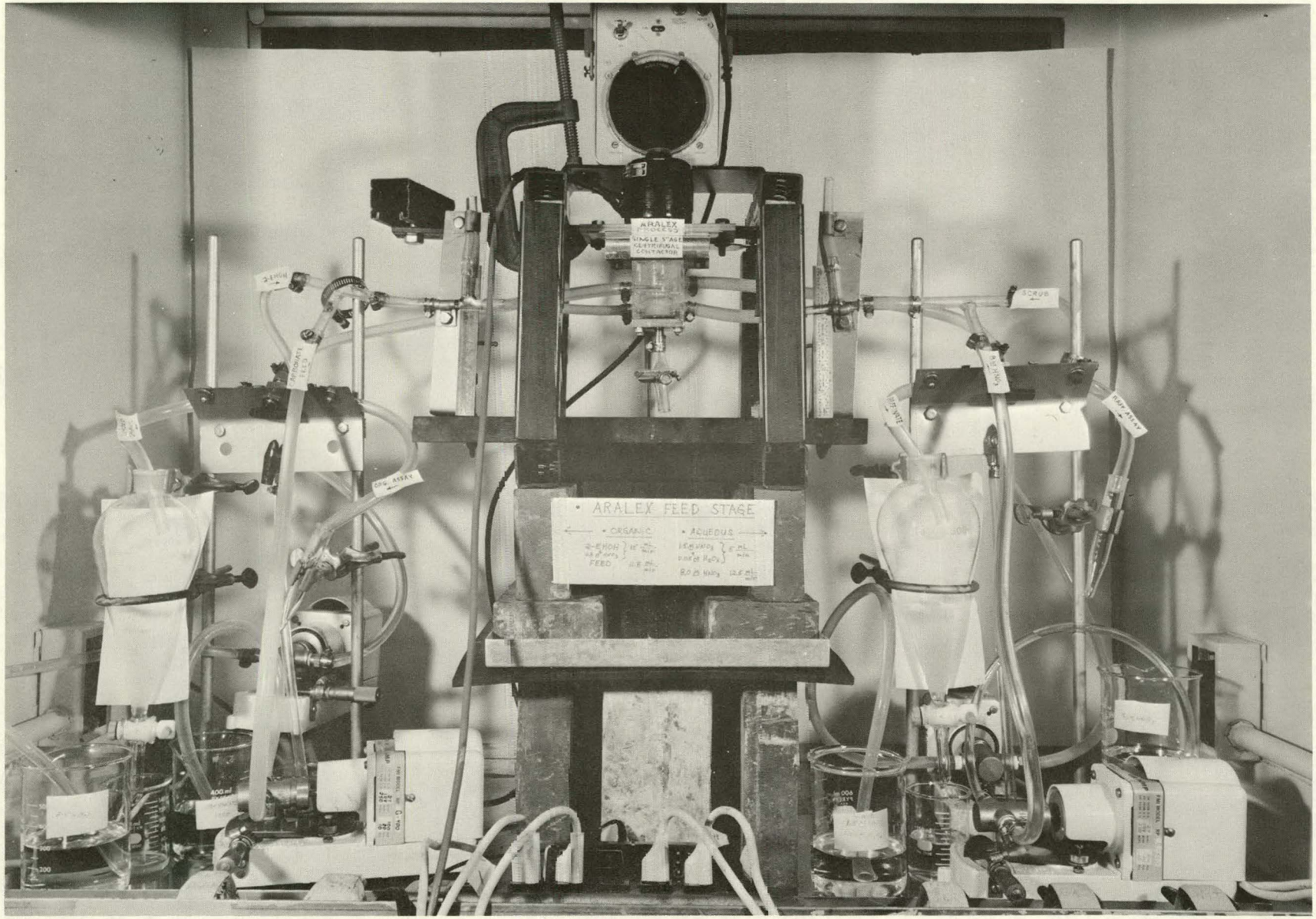

Fig. 15. Single-stage Minicentrifugal Contactor Showing Aqueous and Organic Phase Inlets and Outlets. ANL Neg. No. 122-78-871.

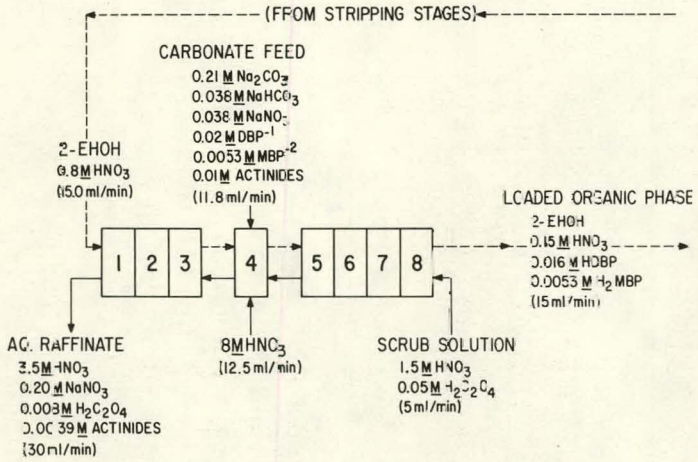

Fig. 16

Eight-stage Countercurrent Liquid-Liquid Extraction Flow Diagram for the Extraction of HDBP and H_2MBP from Na_2CO_3 Scrub Waste Solutions. Actinide = 0.01 M U(VI). T = 23-26°C.

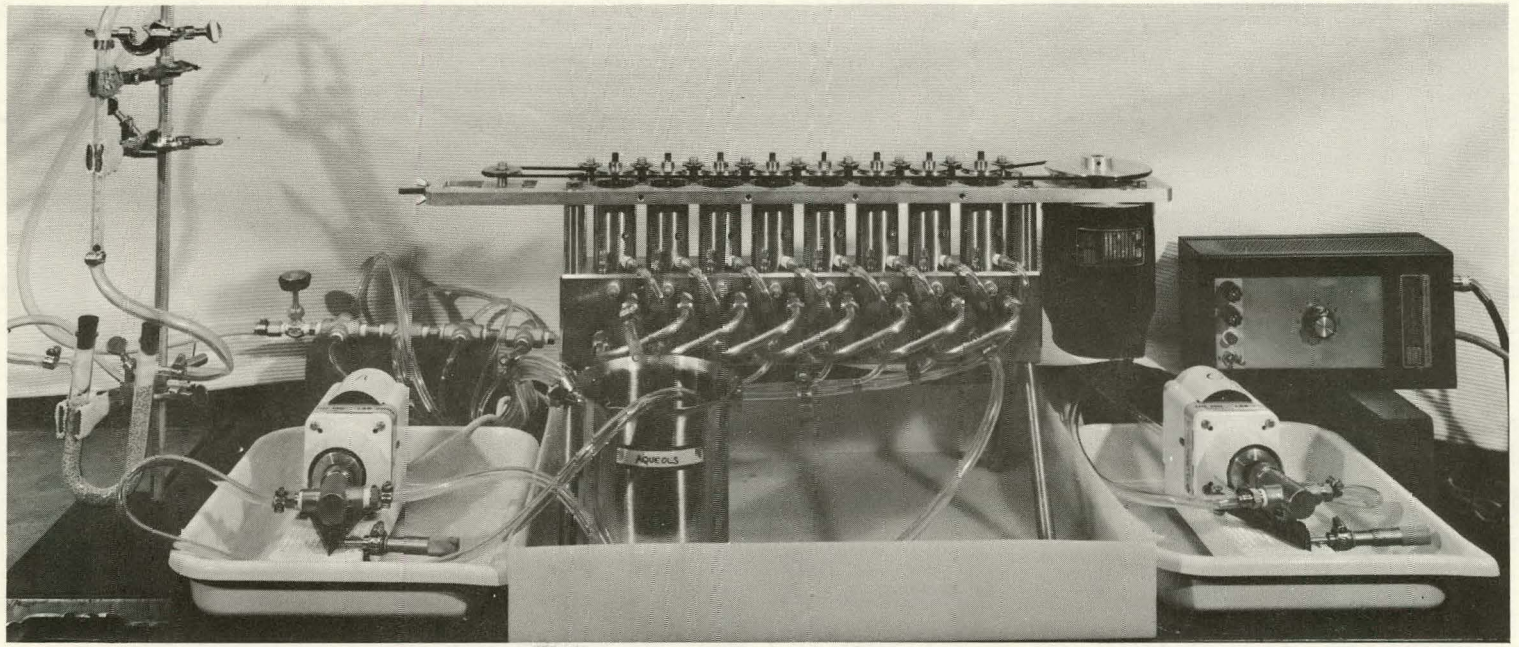

Fig. 17. Eight-stage Minicentrifugal Contactor. ANL Neg. No. 308-77-598.

After the pumps were shut off, the aqueous and organic phases were removed from the rotors, allowed to disengage on standing, and then separated. Uranium analyses were performed on the aqueous and organic phases from all eight stages, whereas H_2MBP and HDBP analyses (by ion chromatography) were performed only on selective phases from stages 1, 4, and 8. The results are shown in Table IV. The data in Table IV show that only one part in 5×10^3 of the total uranium was present in the organic phase leaving stage 8. The decontamination factors (D.F.'s) of HDBP and H_2MBP from the raffinate were >100 and ~10, respectively. Stages 5-8 contained a small quantity of white precipitate in the organic phase, which is believed to be a Zr-MBP compound.

TABLE IV. Eight-stage Continuous Countercurrent Extraction

Flow rates: Feed = 11.8 mL/min Organic Phase = 15 mL/min
8 M HNO_3 = 12.5 mL/min Raffinate = 30 mL/min
Scrub = 5.0 mL/min
Temperature = 24°C Volume of Raffinate Collected = 3L

Stage Number		Molarity of U(VI)		Molarity of H_2MBP		Molarity of HDBP	
		Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
Ext. Stage	1	4.0×10^{-3}	3.0×10^{-4}	2×10^{-4}	--	$<10^{-4}$	--
	2	4.1×10^{-3}	4.0×10^{-4}	--	--	--	--
	3	4.2×10^{-3}	4.4×10^{-4}	--	--	--	--
Feed Stage	4	4.2×10^{-3}	5.5×10^{-5}	1.3×10^{-3}	4.6×10^{-3}	1.5×10^{-4}	1.5×10^{-2}
Scrub Stages	5	1.5×10^{-3}	2.4×10^{-4}	--		--	--
	6	7.1×10^{-4}	6.0×10^{-5}	--	--		--
	7	2.0×10^{-4}	1.1×10^{-5}	--	--	--	--
	8	4.1×10^{-5}	1.5×10^{-6}	--	4.4×10^{-3}	--	1.5×10^{-2}

The D.F.'s achieved for U(VI), H_2MBP, and HDBP agree closely with the calculated values using ~90% stage efficiency and the average D's obtained per stage. In general, effective distribution ratios achieved in the eight-stage run were close to those measured in single-stage experiments, although the D for H_2MBP in the number four extraction stage was somewhat low and the D's for U(VI) in the scrub stages were higher than expected.

M. Seven-stage Batch Countercurrent Extraction Runs

Additional studies on flowsheet testing by countercurrent extraction were performed using macro concentrations of plutonium(IV). Macro quantities of Pu(IV) in Na_2CO_3 solution form Pu(IV) hydroxide. Although the precipitate dissolved during acidification and extraction, mechanical problems could be encountered in pumping the carbonate feed solution with Pu(IV) hydroxide precipitate present. In addition, preliminary experimental studies involving

plutonium concentrations in the 10^{-2} M to 10^{-4} M range showed that polymeric Pu(IV) will extract into H_2MBP-alcohol solutions. Although Pu(IV) polymer did not readily form during the preparation of the carbonate feed solutions, if insoluble U(VI)-DBP and -MBP complexes are formed on neutralization of the carbonate waste solution, some Pu(IV) (usually less than 10%) would be extracted by the 2-EHOH-HDBP-H_2MBP mixtures. This extractable plutonium (presumably Pu polymer) could not be readily removed by scrubbing with HNO_3-$H_2C_2O_4$ mixtures.

To obviate this problem and the problem of Pu(IV) hydroxide formation, diethylenetriaminepentacetic acid (H_5DTPA) was added to the Na_2CO_3 scrub solution (prior to back-extracting the actinide-DBP and -MBP complexes from TBP-nDD) in approximately the stoichiometric amount required to complex the actinides present. The presence of DTPA should prevent the formation of plutonium polymer during the transition from pH = 9 to less than pH = 0.3. Above 1 M in hydrogen ion concentration, H_5DTPA is no longer very effective as a chelating agent and thus does not affect the D's of actinides in the ARALEX process.

Figure 18 shows the flow diagram for a seven-stage countercurrent extraction run using the U(VI)-Pu(IV) carbonate (DTPA) waste solution. Jacketed separatory funnels maintained at 50°C were used for the test run. The carbonate feed solution was introduced into stage 4 while stirring the mixture of oxalic acid scrub, 8 M HNO_3, and 2-EHOH. No precipitation was observed in stage 4, but small quantities of interfacial precipitates were observed in stages 5-7. Phase disengagement (by gravity) was complete in less than 30 s. A total of 484 mL of raffinate (11 fractions) was collected.

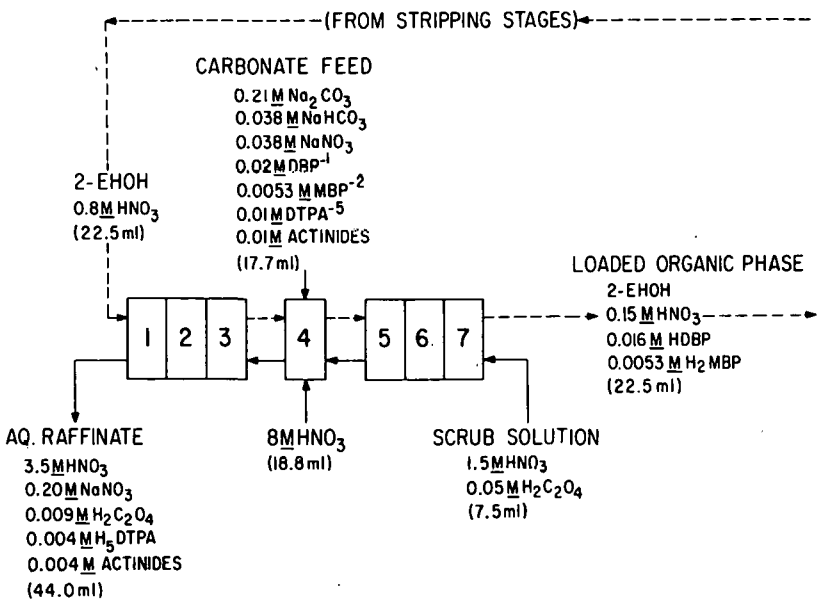

Fig. 18. Seven-stage Countercurrent Liquid-Liquid Extraction Flow Diagram for the Extraction of HDBP and H_2MBP from Na_2CO_3 Scrub Waste Solutions. Actinides = 0.01 M U(VI) and 2.5×10^{-4} M Pu(IV). T = 50°C.

To obtain complete organic and aqueous phase analyses for both H_2MBP and HDBP and U(VI) and Pu(IV), two separate runs were carried out. The first run contained labeled H_2MBP, unlabeled HDBP, and 0.01 M U(VI) in the feed solution. The second run contained unlabeled H_2MBP, HDBP, 0.01 M U(VI), and 2.5×10^{-4} M Pu(IV). Both feed solutions were 0.01 M in DTPA. Uranium was determined by isotopic dilution analyses, plutonium by radiometric analyses, and H_2MBP and HDBP by a combination of radiometric and ion chromatographic analyses. Complete H_2MBP and HDBP analyses were performed only on the run that did not contain Pu(IV). However, H_2MBP, HDBP, and uranium analyses were carried out on the aqueous phase in stage 1, on the organic phase in stage 7, and on both the aqueous and organic phases in stage 4 to ensure that the two separate countercurrent runs were equivalent. The data are tabulated in Table V. The aqueous and organic phase concentrations for each stage were measured after the final pass.

TABLE V. Seven-stage Batch Countercurrent Extraction

Volumes : Feed = 17.7 mL Org. Phase = 22.5 mL Temperature = 50°C
8 M HNO_3 = 18.8 mL Aq. Raff. = 44.0 mL Volume of Raffinate
Scrub = 7.5 mL Collected = 484 mL

Stage Number		Molarity of H_2MBP		Molarity of HDBP		Molarity of U(VI)		Molarity of Pu(IV)	
		Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
Ext. Stages	1	1.0×10^{-4}	3.5×10^{-4}	$<10^{-5}$	$<10^{-5}$	4.0×10^{-3}	4.4×10^{-4}	1.0×10^{-4}	8.8×10^{-6}
	2	3.2×10^{-4}	9.7×10^{-4}	$<10^{-5}$	5×10^{-5}	4.2×10^{-3}	5.2×10^{-4}	1.1×10^{-4}	6.0×10^{-6}
	3	6.2×10^{-4}	2.0×10^{-3}	5×10^{-5}	2.4×10^{-4}	4.4×10^{-3}	5.5×10^{-4}	1.1×10^{-4}	5.4×10^{-6}
Feed Stage	4	1.2×10^{-3}	4.7×10^{-3}	1.5×10^{-4}	1.7×10^{-2}	4.3×10^{-3}	8.0×10^{-4}	1.1×10^{-4}	8.2×10^{-6}
Scrub Stages	5	1.2×10^{-3}	4.6×10^{-3}	1.3×10^{-4}	1.6×10^{-2}	2.1×10^{-3}	4.0×10^{-4}	2.4×10^{-5}	3.4×10^{-6}
	6	1.3×10^{-3}	4.5×10^{-3}	1.2×10^{-4}	1.7×10^{-2}	1.0×10^{-3}	1.0×10^{-4}	8.0×10^{-6}	2.0×10^{-6}
	7	0.6×10^{-3}	4.4×10^{-3}	1.3×10^{-4}	1.7×10^{-2}	4.2×10^{-4}	3.3×10^{-5}	3.8×10^{-6}	4.0×10^{-7}

The D.F.'s of the raffinate from H_2MBP and HDBP were 20 and $>10^3$, respectively. (The aqueous phases from stages 1 and 2 were analyzed, and lower limits for HDBP were set by spiking these phases with labeled HDBP and measuring the corresponding D's.) These D.F.'s are larger than those measured for the eight-stage run. However, the D.F. of the organic phase from uranium was only 358, which is three times lower than the corresponding D.F. achieved in seven stages during the eight-stage run. This difference is the result of the slightly higher average D's for U in the scrub stages of the seven-stage run, which may be due to poor stage efficiency.

The D.F. of the organic phase from plutonium was 500. This was a separate run; however, the data were normalized using the uranium concentrations. The efficiency of the oxalic acid scrub for Pu(IV) can be seen from the data for stages 5, 6, and 7.

Improved decontamination factors for the actinides as well as the HDBP and H_2MBP could be achieved by increasing the number of stages. However, the concentrations of HDBP and H_2MBP in the raffinate would not have to be lowered well below the concentrations of these esters present in the TBP used to extract the actinides from the raffinate. Likewise, the desired level of decontamination of plutonium from the 2-EHOH would be governed by the levels of plutonium present in other waste streams.

N. Five-stage Batch Countercurrent Stripping Runs

Countercurrent stripping of HDBP and H_2MBP from the loaded 2-EHOH was performed using H_2O to remove excess HNO_3 and 0.1 M NaOH to remove the phosphorus esters. The feed solution used for the stripping run was prepared separately. It contained only 0.016 M HDBP (^{32}P-labeled), 0.0053 M H_2MBP, and 0.15 M HNO_3 in 2-EHOH. Using labeled HDBP enables one to check the stripping efficiency of the least extractable constituent in the organic feed. Separatory funnels maintained at 50°C were used for the test. Complete phase disengagement required ~2 min (especially stage 3), but no emulsion or precipitate formation occurred.

A total of 240 mL of stripped 2-EHOH was collected from stage 5. The flow diagram is shown in Fig. 19, and the concentrations of DBP and MBP in each stage (after the final pass) are tabulated in Table VI. Decontamination

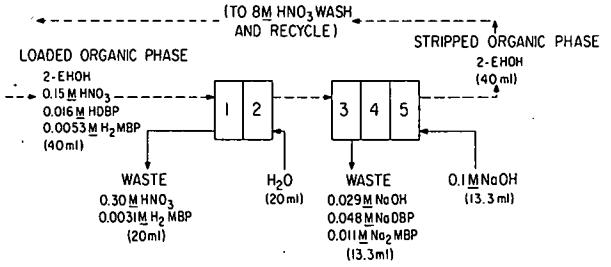

Fig. 19

Five-stage Countercurrent Liquid-Liquid Extraction Flow Diagram for the Stripping of HDBP and H_2MBP from 2-ethyl-1-hexanol (2-EHOH). T = 50°C.

TABLE VI. Five-stage Batch Countercurrent Extraction

Volumes : Organic Phase = 40 mL , 0.1 M NaOH Strip = 13.3 mL
H_2O Strip = 20 mL
Temperature = 50°C
Volume of Stripped Organic Phase Collected = 240 mL

Stage	Molarity of H_2MBP		Molarity of HDBP	
Number	Aqueous	Organic	Aqueous	Organic
1	2.6×10^{-3}	3.9×10^{-3}	1.0×10^{-4}	1.6×10^{-2}
2	4.0×10^{-3}	3.1×10^{-3}	2.0×10^{-4}	1.6×10^{-2}
3	9.4×10^{-3}	$<10^{-4}$	4.5×10^{-2}	3.1×10^{-4}
4	$<10^{-4}$	$<10^{-4}$	1.9×10^{-3}	1.8×10^{-5}
5	$<10^{-4}$	$<10^{-4}$	1.4×10^{-4}	2.6×10^{-6}

of the 2-EHOH from DBP is 10^4. The D.F. for MBP is probably much higher, since it has smaller D's than DBP. Stripping experiments performed on the loaded organic phases from the seven-stage runs were equally effective in stripping not only DBP and MBP, but also any U(VI), Pu(IV), and Zr(IV).

O. Conceptual Flowsheet and Actinide Recovery.

Figure 20 shows a conceptual flowsheet based on one MTHM. Based on the countercurrent extraction experiments, the flowsheet is feasible. The recovery of U(VI) and Pu(IV) from the acidic raffinates obtained from the alcohol extraction process can be readily carried out with TBP or preferably DHDECMP.[3] (The latter extractant will also extract Am(III) and Cm(III).)

The presence of H_5DTPA and dissolved 2-EHOH (the solubility of 2-EHOH in 3.5 M HNO_3 at 50°C is 2.0×10^{-2} M) in the raffinate did not interfere with the extraction, or (in the case of 2-EHOH) with the stripping of actinides with TBP or DHDECMP. However, 2-EHOH does build up in recycled TBP or DHDECMP and, in the range of 5-10 wt % in these solvents, noticeably reduces the D's of the actinides.

The buildup of 2-EHOH in the TBP or DHDECMP extractant solutions can be prevented by prior removal of the soluble 2-EHOH from the ARALEX raffinate. This can be accomplished by either steam-stripping the raffinate or solvent-scrubbing with dodecane or DIPB. The alcohol extraction process was not tested using neptunium, americium, or curium in the carbonate waste solution, since Np(IV) and (VI) are chemically similar to Pu(IV) and U(VI), and Np(V), Am(III), and Cm(III) are considerably less complexed than the tetra- and hexavalent actinides.

P. Other Uses of the ARALEX Process

The ARALEX process can also be used to extract detergents from aqueous solutions containing actinides; for example, contaminated laundry solutions. Detergents from all three classes (anionics such as alkyl sulfates and alkyl benzene sulfonates, cationics such as N-benzyl-N-alkyl dimethyl ammonium chloride, and nonionics such as polyoxyethylenated alkyl phenols) are readily extracted by 2-EHOH from acidic and neutral (and in some cases alkaline) solutions (see Fig. 8). Once the detergent is extracted from the actinides, the acidified raffinate may be evaporated or processed directly for actinide recovery.

However, detergents of the types listed above cannot be back-extracted from the 2-EHOH, and thus one would have to incinerate the loaded organic phase. In addition, the ARALEX process can be used to scrub residual TBP, HDBP, and H_2MBP from various actinide product streams, such as americium and curium nitrate or neptunium (IV, V, VI) nitrate streams. This alcohol scrubbing step prevents eventual precipitation of phosphates or back-extraction problems that might arise on further processing with TBP.

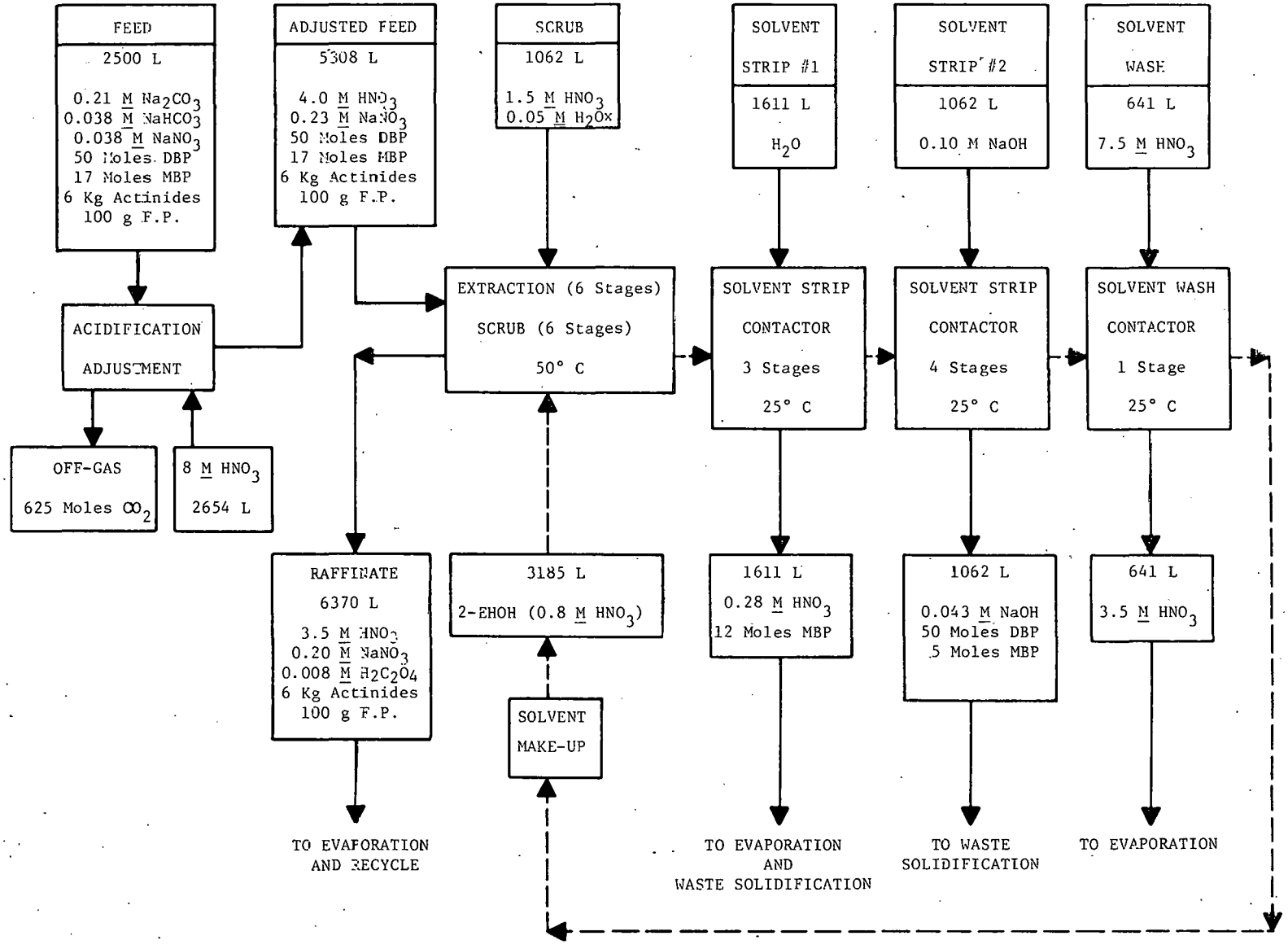

Fig. 20. Conceptual Flowsheet for the Recovery of Actinides from TBP–Na_2CO_3 Scrub Solutions. Basis: One MTHM.

If TBP and HDBP are the only extractants one is concerned with in a product stream, then a scrubbing step using 10-20 vol % 2-EHOH in dodecane or diisopropylbenzene would be sufficient to remove these esters. The use of the more dilute alcohol solution would reduce the concentration of 2-EHOH in the aqueous phase. A 2-EHOH solution used for actinide product stream scrubbing could probably be recycled many times before the phosphorus-based extractants would build up to sufficiently high concentrations to cause problems.

SUMMARY

A flowsheet for the recovery of actinides from TBP Na_2CO_3 scrub-waste solutions has been developed, based on batch extraction data, and tested, using laboratory-scale countercurrent extraction techniques. The process, called the ARALEX process, uses 2-ethyl-1-hexanol (2-EHOH) to extract the TBP degradation products (HDBP and H_2MBP) from acidified Na_2CO_3 scrub waste leaving the actinides in the aqueous phase. Dibutyl and monobutyl phosphoric acids are attached to the 2-EHOH molecules through hydrogen bonds. These hydrogen bonds also diminish the ability of the HDBP and H_2MBP to complex actinides, and thus all actinides remain in the aqueous raffinate. Dilute sodium hydroxide solutions can be used to back-extract the dibutyl and monobutyl phosphoric acid esters as their sodium salts. The 2-EHOH can then be recycled.

After extraction of the acidified carbonate waste with 2-EHOH, the actinides may be readily extracted from the raffinate with DHDECMP or, in the case of tetra- and hexavalent actinides, with TBP.

The ARALEX process is relatively simple and involves inexpensive and readily available chemicals. The ARALEX process can also be applied to other actinide waste streams which contain appreciable concentrations of polar organic compounds that interfere with conventional actinide ion exchange and liquid-liquid extraction procedures. One such application is the removal of detergents from laundry or cleanup solutions contaminated with actinides.

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