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CONF-790415--36

**THE EXTRACTION OF DBP AND MBP FROM ACTINIDES: APPLICATION
TO THE RECOVERY OF ACTINIDES FROM TBP-Na₂CO₃ SCRUB SOLUTIONS**

by

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Prepared for

American Chemical Society Meeting

Honolulu, Hawaii

April 2-5, 1979

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The Extraction of DBP and MBP from Actinides: Application to the Recovery of Actinides from TBP-Na₂CO₃ Scrub Solutions*

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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 Na₂CO₃. As much as 5 kg of actinides may be present in the Na₂CO₃ scrub solutions used to "clean-up" TBP-nDD solutions from the reprocessing of one metric ton of LWR fuel irradiated to 33,000 MWD/MTHM (1). In addition, Na₂CO₃ scrub waste will be generated in the clean-up of the dihexyl-N,N-diethyl carbamoylmethylene phosphonate (DHDECMP) extractant which is to be used to process high-level liquid waste (HLLW) (2).

Na₂CO₃ scrub solutions from TBP-nDD consist essentially

*Work performed under the auspices of the Office of Basic Energy Sciences and the Office of Nuclear Waste Management of the U.S. Department of Energy.

of a NaHCO_3 - NaNO_3 solution containing varying amounts of the sodium salts of dibutylphosphoric and monobutyl phosphoric acids (HDBP and H_2MBP , respectively) and carbonato- and hydroxo-complexes of the tetra- and hexavalent actinides and zirconium. The actual quantities of DBP, MBP, and actinides 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 phosphonic and degradation products of DHDECMP (4).

The efficient removal of actinides from the Na_2CO_3 scrub waste solution presents several problems. Acidification of the carbonate solution with excess HNO_3 followed by extraction with TBP (or, preferably, DHDECMP) results in the rapid build-up of acidic degradation products (HDBP and H_2MBP in the case of TBP) which prevent efficient back extraction. In addition, acidification of Na_2CO_3 scrub waste results in the precipitation of actinide-DBP and -MBP complexes which are difficult to dissolve and make subsequent processing difficult. Cation and anion exchange methods are also not feasible because of precipitate formation and/or poor actinide recoveries. 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.

This paper describes a process for the recovery of actinides from Na_2CO_3 scrub waste solutions which involves the extraction of the HDBP and H_2MBP from acidified solutions using a water-immiscible aliphatic alcohol. All the actinides remain in the aqueous phase, which may then be processed using conventional TBP or DHDECMP procedures. This paper also describes the extraction equilibria measurements performed in the development of the process.

Experimental

Reagents and Labeled Compounds. The sources of all solvents and reagents and the preparation and purification of ^{32}P labeled HDBP and H_2MBP were described by the authors in a previous publication (5). ^{32}P -labeled phosphoric acid (H_3PO_4), ^{32}S -labeled dodecyl sulfuric acid (DSA), ^3H -labeled diethylenetriamine pentacetic acid (H_5DTPA), and ^3H -labeled 2-ethyl-1-hexanol (2-EHOH) were obtained from the Amersham Corporation, Arlington Heights, Illinois.

Measurements of D. Distribution ratios, D, were measured at 25 and 50°C by a procedure described previously (5,6). The D's for HDBP and DSA were measured by reverse or back extraction to minimize the influence of traces of H_2MBP and H_2SO_4 , respectively. D's 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 the case of the actinides, D's were usually measured by forward extraction because of the low values of D. When possible, 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-SolvTM GP scintillation solution.

Counter-Current Liquid-Liquid Extractions. Two experimental arrangements were used to carry out counter-current liquid-liquid extractions. One system consisted of seven jacketed glass separatory vessels equipped with stainless steel centrifugal stirrers. The vessels were maintained at $50^\circ C$ by means of a constant temperature bath. The counter-current transfer of phases was performed manually. The other system consisted of an eight stage counter-current mini-centrifuge contactor (7). The eight stage mini-contactor has a continuous throughput and short phase contact times (~ 10 sec) and thus steady state conditions are attained rapidly. No provision was available for operating the centrifugal contactor at elevated temperatures; therefore, room temperature conditions were used for all experiments.

Flowsheet Testing. Na_2CO_3 scrub waste solutions were prepared by extracting measured amounts of U(VI) and Pu(IV) into dodecane solutions containing 0.02 M - 0.04 M HDBP and 0.0067 M - 0.0134 M H_2MBP . The resultant organic phase plus precipitates were then slurried with the required amount of Na_2CO_3 until all the precipitate dissolved.

All uranium and plutonium analyses were performed by isotopic dilution and radiometric techniques, respectively. HDBP and H_2MBP mixtures were analyzed by first separating the HDBP and H_2MBP from each other using a liquid-liquid chromatographic column containing 2-EHOH as the stationary phase and 8 M HNO_3 and 0.002 M NH_4OH as mobile phases. The separated HDBP and H_2MBP were then decomposed by oxidation and the resultant H_3PO_4 measured colorimetrically. NaDBP and Na_2MBP mixtures were analyzed by ion chromatography (8). Where feasible, HDBP and NaDBP were analyzed radiometrically by spiking known quantities of HDBP with the ^{32}P -labeled ester.

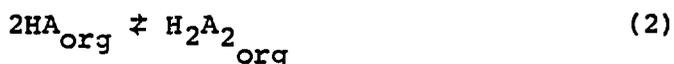
Results and Discussion

Dimerization of HDBP in Various Solvents. Dyrssen, et al. (9,10) has shown that polar solvents are better extractants for HDBP than non-polar solvents because of the formation of a stable hydrogen bonded complex between the polar groups of the solvent and the phosphoryl and

acidic hydrogen groups of the HDBP. In order to ascertain the suitability of different solvents as extractants for HDBP and H₂MBP, measurements were made of the partitioning and dimerization constants of HDBP in a number of polar solvents.

The partitioning and dimerization constants, K_p and K_2 , respectively, are defined by the following equations:

$$K_p = \frac{[HA]_{org}}{[HA]_{aq}} \quad (1)$$



$$K_2 = \frac{[H_2A_2]_{org}}{[HA]_{org}^2} \quad (3)$$

where $[HA]$ and $[H_2A_2]$ are the equilibrium concentrations of the monomeric and dimeric forms of HDBP. K_p and K_2 were calculated from the following equation derived by Dyrssen (9) and Hardy and Scargill (11):

$$D = \frac{K_p}{\phi} + \frac{2K_2K_p^2 C_{aq}}{\phi^2} \quad (4)$$

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 $\mu = 0.1$ (9). Plots of D vs C_{aq} for HDBP using 2-ethyl-1-hexanol (2-EHOH), 2-ethyl-1-hexanoic acid (2-EHA), and p-diisopropylbenzene (p-DIPB) vs. 0.1 M HNO₃ at 25°C are shown in Figure 1. At

low concentrations of C_{aq} , the horizontal asymptote gives

$$\log D = \log K_p \phi^{-1}. \quad (5)$$

The point of intersection of the two asymptotes gives the value for $\log 2K_p K_2 \phi$.

Values for K_p and K_2 for a variety of solvents are shown in Table I. Some data obtained by Dyrssen and Hay (10) and Hardy and Scargill (11) were included for comparison. The data in Table I show clearly that, as the partitioning constant increases, the dimerization constant decreases. Thus, those solvents which have 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 the case of aliphatic alcohols the interaction between the solvent and HDBP is sufficiently strong that the D is independent of C_{aq} (see Figure 1). Thus, K_p divided by two gives D . The high K_p and low K_2 using 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 Figure 2.

It is interesting to note that the data in Figure 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 which are similar in structure to the very stable HDBP dimer. Such structures have resonance stabilization and favorable hydrogen bond angles. 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 dialkylphosphoric acids (9). 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 prior to 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 show 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 have both donor and acceptor properties. For example, in Figure 2, an increase in electron density on the alcohol oxygen would enhance the hydrogen bond strength with the acidic hydrogen of HDBP, but diminish the hydrogen bond strength with the phosphoryl oxygen. 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 and 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, and is less expensive than the straight chain alcohols. In addition, the D for H_2MBP using 2-EHOH is greater than one; all other non-alcoholic solvents have D's for H_2MBP much less than one. The flash point and water solubility of 2-EHOH are 85°C (12) and 0.10 parts per 100 parts of H_2O at 20°C (13), respectively, which are within acceptable limits for fuel reprocessing.

Extraction of HDBP, H_2MBP , and H_3PO_4 . Figure 3 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 Figure 3 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. 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 very difficult to extract into a water-immiscible solvent (11). The probable structure of the H_2MBP -alcohol complex is shown in Figure 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 concentration due to the competition from organic soluble HNO_3 for donor oxygens in the 2-EHOH and phosphorous compounds. Figure 4 shows the extraction of HNO_3 by 2-EHOH and 2-EHA.

The effect of temperature on the D vs. HNO_3 curves is, in general, relatively small and insignificant from a practical standpoint. 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 approximately 5% higher at 50°C than 25°C , which probably accounts for the lower D's at the higher temperature and acidities.

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.

Extraction of DSA and H_5DTPA . Figure 3 also 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) and therefore were included in the study. DSA behaves similar to HDBP, as expected. Hydrogen-bonded complexes analogous to those shown in Figure 2 can be formed between the -OH group of the alcohol and the $-\text{OSO}_3\text{H}$ 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.

Interaction Effects of H_2MBP and HDBP. Hardy and Scargill (11) 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. However, one would not expect interaction between HDBP and H_2MBP in a highly polar solvent, such as 2-EHOH, unless the concentration of one of the esters was above 0.1 M. The extraction of labeled H_2MBP was measured in 2-EHOH 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.

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. The data are shown in Table II below.

Table II. Distribution ratios, D, of NaDBP and Na_2MBP
Aqueous Phase - 0.25 M Na_2CO_3
Temperature 50°C

| | 2-EHOH | |
|-------------------------|----------------------|----------------------|
| | <u>1st. Ext.</u> | <u>2nd. Ext.</u> |
| NaDBP | 1.5×10^{-2} | 1.9×10^{-2} |
| Na_2MBP | 3.5×10^{-4} | 2.2×10^{-4} |

The low D's for the extraction of NaDBP and Na_2MBP from 2-EHOH affords a convenient method for stripping these compounds from the solvent.

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

The second objective in the development of a process for removing TBP degradation products from acidified Na_2CO_3 scrub solution is to effectively retain the actinides in the aqueous phase during the extraction of HDBP and H_2MBP . In order 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 . Dyrssen et al. (14) found that the 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

up to 2 M in concentration. Mason et al. (15,16) reported similar effects on the D's of certain actinides and lanthanides using HDEHP in 1-decanol and 2-ethyl-1-hexanoic acid.

Figure 5 shows the extraction of U(VI), Pu(IV), and Am(III) as a function of the concentration of HDBP and H₂MBP in 2-EHOH, at a constant HNO₃ concentration of 3.5 M. It can be seen that neither HDBP nor H₂MBP is an effective extractant in 2-EHOH for these actinides, although ester concentrations above 0.05 M give D's that are greater than one for Pu(IV). For comparison, the D for Pu(IV) using 0.02 M HDBP in p-diisopropyl benzene 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 H₂MBP decrease, the D's for U(VI) and Pu(IV) gradually approach that of the pure 2-EHOH in equilibrium with 3.5 M HNO₃.

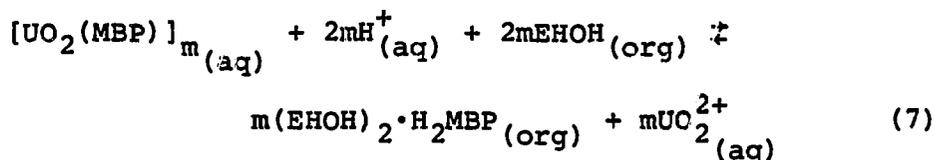
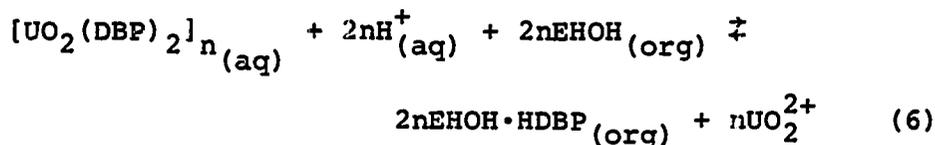
It is important to note that the D's for U(VI), Pu(IV), and Am(III) are higher for H₂MBP than HDBP. However, since the H₂MBP concentration produced by radiolysis and hydrolysis of TBP is always significantly less than HDBP (17), the net effect of the two esters on D's is approximately the same.

Additional studies on the effect of HNO_3 concentration (in the 1 M to 8 M range) on the D's of U(VI) and Pu(IV), using fixed concentrations (0.02 M) of H_2MBP and HDBP in 2-EHOH and using pure 2-EHOH, showed very poor extractions of both metal ions even at the lowest acid concentration. These studies also showed that 2-EHOH makes a significant contribution to the D's at the 0.02 M ester concentration, especially for U(VI) at all acidities and for Pu(IV) at the high (6-8 M) acidities. The highest D's were found for the Pu(IV)- H_2MBP system at 1 M HNO_3 ($D = 1$). However, the addition of 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ to the 1 M HNO_3 reduced the D to less than 0.1 for Pu(IV) and to less than 0.01 for U(VI).

Since the concentrations of HDBP and H_2MBP in Na_2CO_3 scrub waste solution will fluctuate (although in all probability H_2MBP would not exceed 0.01 M (5)), the use of a small quantity of oxalic acid in the HNO_3 scrub solution would ensure an efficient removal of any Pu(IV) and U(VI) that extracts into 2-EHOH along with the HDBP and H_2MBP .

Flowsheet for Processing Na_2CO_3 Scrub Solutions. 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, leaving the actinides in the aqueous phase raffinate. The raffinate can then be recycled to the HLLW and processed using DHDECMP (2). Equations

describing the basic chemical equilibria, using uranyl-DBP and -MBP complexes as examples, are as follows:



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

The feed solution for the process is the TBP- Na_2CO_3 -scrub waste solution. 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 extractant solutions, which, of course, depend 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. Therefore, certain assumptions were made in selecting a reasonable composition and volume of the Na_2CO_3 waste to use in developing a flowsheet. First, the total quantity of actinides contained in the Na_2CO_3 scrub waste is ~ 6 Kg/MTHM (1). Uranium would total 5.9 Kg, and the remaining 0.1 Kg

of actinides would consist of a mixture of Np, Pu, Am, and Cm (1). Second, the primary constituents of the Na_2CO_3 scrub waste (NaDBP, Na_2MBP , and the UO_2^{2+} -carbonato complex) must stay within solubility limits. Therefore, the uranyl complex and NaDBP concentrations should not exceed 0.01 M and 0.02 M , respectively, in the Na_2CO_3 solution, which requires a carbonate scrub volume of 2500 liters/MTHM. Third, the concentration of Na_2MBP is approximately one-third that of NaDBP, assuming no losses of H_2MBP during HNO_3 scrubbing (17). 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. Using data in references 1 and 2, 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 liters/MTHM of 0.21 M Na_2CO_3 containing 6 Kg of actinides, 0.02 M NaDBP and 0.0067 M Na_2MBP (which are present as actinide complexes), 0.038 M NaHCO_3 , and 0.038 M NaNO_3 . Approximately 100 g of fission product, primarily Zr and Ru, is also present (1). Figure 6 shows a conceptual flowsheet based on one MTHM.

Flowsheet testing using counter-current liquid-liquid extraction was performed first using the eight stage mini-centrifugal contactor. The compositions and flow rates of the feed, organic phases, scrub, and raffinate are shown in Figure 7. (The feed solution was also 2×10^{-4} M in Zr(IV).) It can be seen from the flow diagram that the carbonate feed, 8 M HNO_3 , scrub solution from stage 5, and organic solution from stage 3 all meet and are mixed in stage 4. Thus, the neutralization of carbonate feed by HNO_3 and the extraction by 2-EHOH occur simultaneously. This technique avoids the extensive precipitation of actinide (VI and IV)-DBP and -MBP complexes which occurs when the carbonate waste solution is acidified prior to equilibration with 2-EHOH. The actinide (VI and IV)-DBP and -MBP precipitates (when they do form) will eventually dissolve and dissociate when mixed with 2-EHOH and HNO_3 solution, but this process requires several minutes.

Uranium(VI) was the only actinide present in the carbonate waste solution used in the counter-current run shown in Figure 7. Subsequent U(VI), HDBP, and H_2MBP analyses showed that steady state conditions had been already achieved after the collection of 450 ml (15 min run time) of raffinate. A total of over 3 liters of raffinate was collected before terminating the run. Only one part in 5×10^3 of the total uranium was present

in the organic phase leaving stage 8. The decontamination factor for HDBP and H_2MBP from the raffinate was >100 and ≈ 20 , respectively. Distribution ratios of HDBP and H_2MBP in stage 4 were 29 and 2, respectively. These values are somewhat lower than the D's shown in Figure 3, which may be due to the interaction between $UO_2(VI)$ and HDBP and H_2MBP in the aqueous phases. After completion of the run, the aqueous and organic phases were removed from the rotors and examined for insoluble material and interfacial precipitates. Stages 5 through 8 contained a small quantity of white precipitate in the organic phase, which is believed to be a Zr-MBP compound.

Additional studies on flowsheet testing were performed on carbonate feed solutions containing $0.01 \text{ M } U(VI)$, $2.5 \times 10^{-4} \text{ M } Pu(IV)$, and $2 \times 10^{-4} \text{ M } Zr(IV)$. Preliminary experimental studies involving macro plutonium concentrations (10^{-4} M to 10^{-2} M) showed that polymeric $Pu(IV)$ will extract into H_2MBP -alcohol mixtures. 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 could not be readily removed by scrubbing with HNO_3 - $H_2C_2O_4$ mixtures. In order to obviate

this problem, diethylenetriamine pentacetic acid (H_5DTPA) was added to the Na_2CO_3 scrub solution (prior to back extracting the actinide-DBP and -MBP complexes from nDD) in approximately the stoichiometric amount required to complex the actinides present.

Figure 8 shows the flow diagram for a seven stage counter-current extraction run using the U(VI)-Pu(IV) carbonate (DTPA) waste solution. Jacketed separatory funnels maintained at $50^\circ C$ 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 and no interfacial precipitates were observed in stages 5-7. Phase disengagement (by gravity) was complete in less than 30 seconds. A total of 484 ml of raffinate (11 fractions) were collected. Only an average of one part of Pu (and U) from a total of 2×10^4 of each actinide was detected in the organic phases from stage 7. The HDBP and H_2MBP decontamination factors from the raffinate were >100 and ~ 40 , respectively. Thus, the concentration of both HDBP and H_2MBP is $<10^{-4}$ M in the raffinate.

The improvement in D.F for uranium over that obtained using the 8 stage mini-centrifugal contactor was largely due to improved stage efficiency using the separatory funnels

and higher temperature. However, the presence of DTPA chelating agent in the Na_2CO_3 scrub does ensure a good decontamination of plutonium from the organic phase and prevents the formation of interfacial precipitates, which probably improves the behavior of H_2MBP . Improved decontamination factors for the actinides as well as the HDBP and H_2MBP could be achieved by increasing the number of stages. However, it would not be necessary to lower the concentrations of HDBP and H_2MBP in the raffinate 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.

Counter-current stripping of the 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 flow diagram is shown in Figure 9. Separatory funnels at a temperature 50°C were used for the stripping run. 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. Decontamination of the 2-EHOH from the NaDBP and Na_2MBP was 350 and $\gg 100$, respectively. After stripping, the 2-EHOH is recycled.

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 (2). (The latter extractant will also extract Am(III) and Cm(III).) The presence of H₅DTPA and dissolved 2-EHOH (solubility of 2-EHOH in 3.5 M HNO₃ at 50°C is 2.0 x 10⁻⁴ M) in the raffinate do not interfere with the extraction, or (in the case of 2-EHOH) with the stripping of actinides with TBP or DHDECMP. The alcohol extraction process was not tested using neptunium, americium, or curium in the carbonate waste solution since Np(IV) and (VI) are 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.

The alcohol extraction 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 alkylphenols) are readily extracted by 2-EHOH from acidic and neutral (and in some cases alkaline) solutions. Once the detergent is extracted from the actinides, the acidified raffinate may be evaporated or processed directly with DHDECMP.

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.

Summary and Conclusions

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 counter-current extraction techniques. The process utilizes 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 alcohol extraction (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} clean-up solutions contaminated with actinides.

Acknowledgments

The authors wish to acknowledge the assistance of Walter H. Delphin, now with DuPont de Nemours, Inc., for help in the preparation of the ^{32}P -labeled HDBP and H_2MBP , and the assistance of Anton Ziegler and Herbert Diamond for their help with the counter-current liquid-liquid extraction experiments involving the mini-centrifugal contactor, and jacketed separatory funnels, respectively. The authors also wish to thank Florence Williams for performing the ion chromatographic analyses of the HDBP and H_2MBP . We especially thank Dr. D. William Tedder of ORNL for many helpful discussions throughout the course of this project, as well as Dr. J. O. Blomeke (ORNL) and Dr. Martin J. Steindler (ANL) for securing the funding which made portions of this project possible.

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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 <u>M</u> HNO ₃ | 2.25 ± 0.03 | <-0.2 | This work |
| 4-methyl-2-pentanol/0.1 <u>M</u> HNO ₃ | 2.21 ± 0.05 | <1 | 10 |
| 1-octanol/0.1 <u>M</u> HNO ₃ | 2.16 ± 0.02 | <1 | This work |
| 1-decanol/0.1 <u>M</u> HNO ₃ | 2.15 ± 0.02 | <1 | This work |
| 1-octanoic acid/0.1 <u>M</u> HNO ₃ | 1.80 ± 0.02 | N.D. ^a | This work |
| 2-ethyl-1-hexanoic acid/0.1 <u>M</u> HNO ₃ | 1.76 ± 0.02 | 0.54 | This work |
| methyl isobutylketone/0.1 <u>M</u> HNO ₃ | 1.36 | 1.19 | 10 |
| isopropyl ether/0.1 <u>M</u> HNO ₃ | 0.52 | 2.29 | 10 |
| benzene/1 <u>M</u> HNO ₃ | -0.42 | 4.88 | 11 |
| p-diisopropylbenzene/0.1 <u>M</u> HNO ₃ | -1.36 | 5.38 | This work |
| kerosene/1 <u>M</u> HNO ₃ | -1.96 | 5.78 | 11 |
| carbon tetrachloride/0.1 <u>M</u> HNO ₃ | -1.44 | 6.49 | 10 |

^aN.D. - Not Determined.

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Figure Captions

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 . $T = 25^\circ\text{C}$.
2. Structure of hydrogen-bonded complexes between an aliphatic alcohol and HDBP and H_2MBP .
3. Distribution ratios of dibutyl phosphoric acid (HDBP), monobutyl phosphoric acid (H_2MBP), phosphoric acid (H_3PO_4), dodecyl sulfuric acid (DSA), and diethylenetriamine tetraacetic acid (H_5DTPA) vs. aqueous HNO_3 concentration. Organic phase - 2-ethyl-1-hexanol. $T = 25$ and 50°C .
4. Equilibrium curve for the extraction of nitric acid using 2-ethyl-1-hexanol (2-EHOH) and 2-ethyl-1-hexanoic acid (2-EHA). $T = 25^\circ\text{C}$.
5. 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 . $T = 50^\circ\text{C}$.
6. Conceptual flowsheet for the recovery of actinides from $\text{TBP-Na}_2\text{CO}_3$ scrub solutions. Basis: One MTHM.
7. Eight stage counter-current liquid-liquid extraction flow diagram for the extraction of HDBP and H_2MBP from Na_2CO_3 scrub waste solution. Actinide - 0.01 M U(VI). $T = 23-26^\circ\text{C}$.

8. Seven stage counter-current liquid-liquid extraction flow diagram for the extraction of HDBP and H₂MBP from Na₂CO₃ scrub waste solution. Actinides - 0.01 M U(VI) and 2.5×10^{-4} M Pu(IV). T = 50°C.
9. Five stage counter-current liquid-liquid extraction flow diagram for the stripping of HDBP and H₂MBP from 2-ethyl-1-hexanol (2-EHOH). T = 50°C.

Figure Captions

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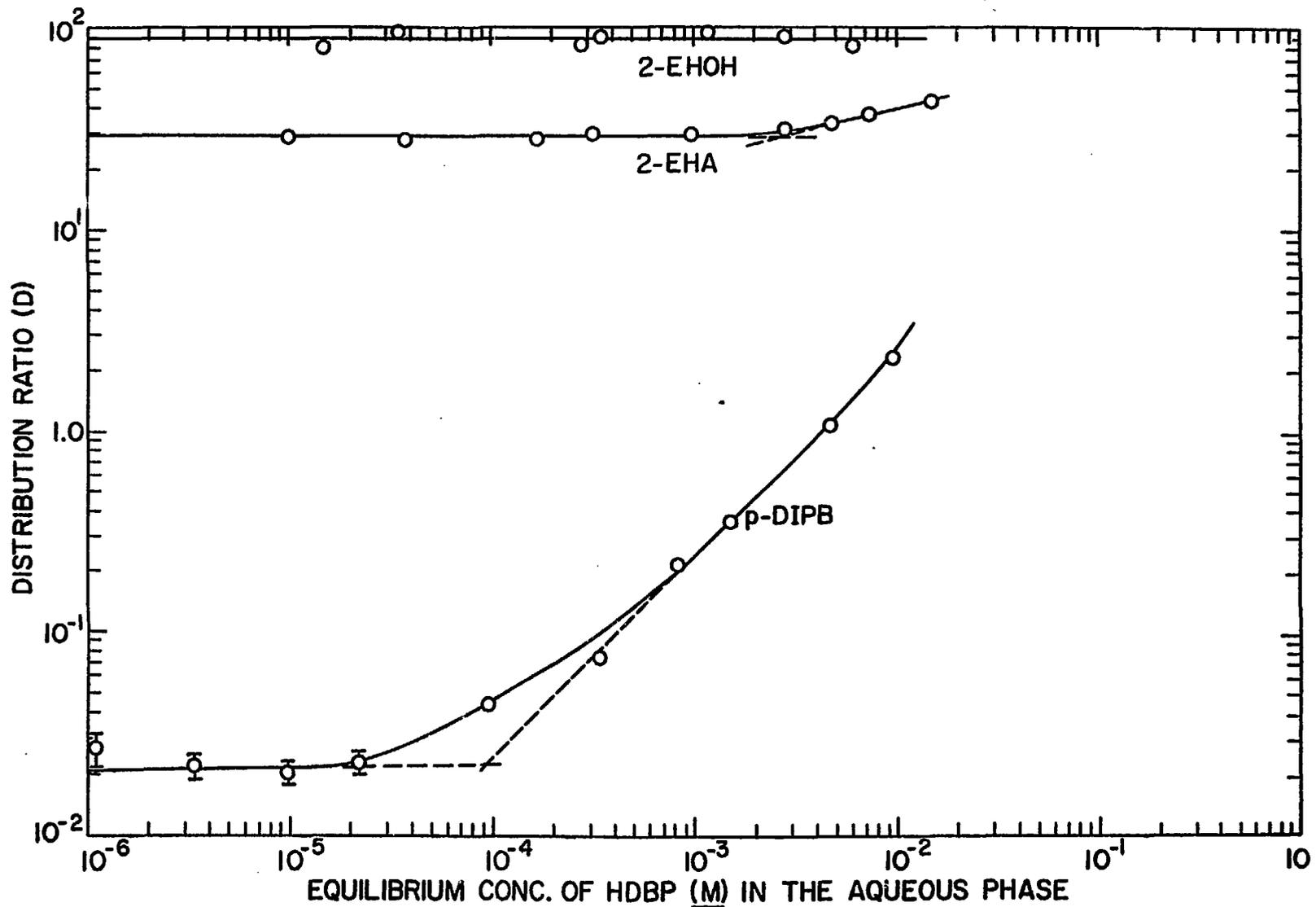
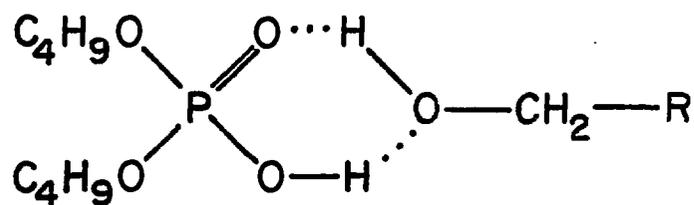


Fig 1

HDBP-ALCOHOL



H₂MBP-ALCOHOL

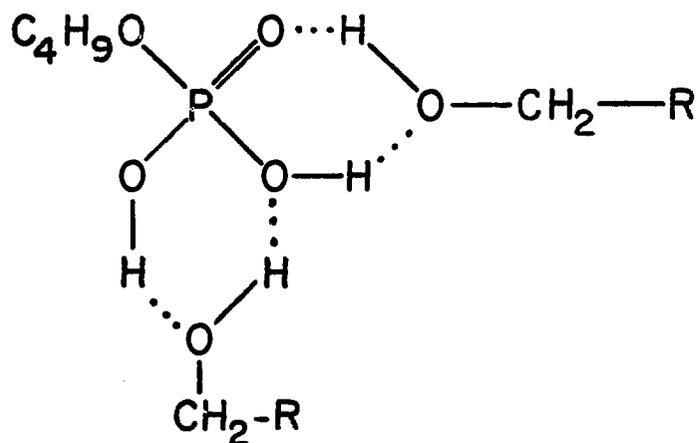


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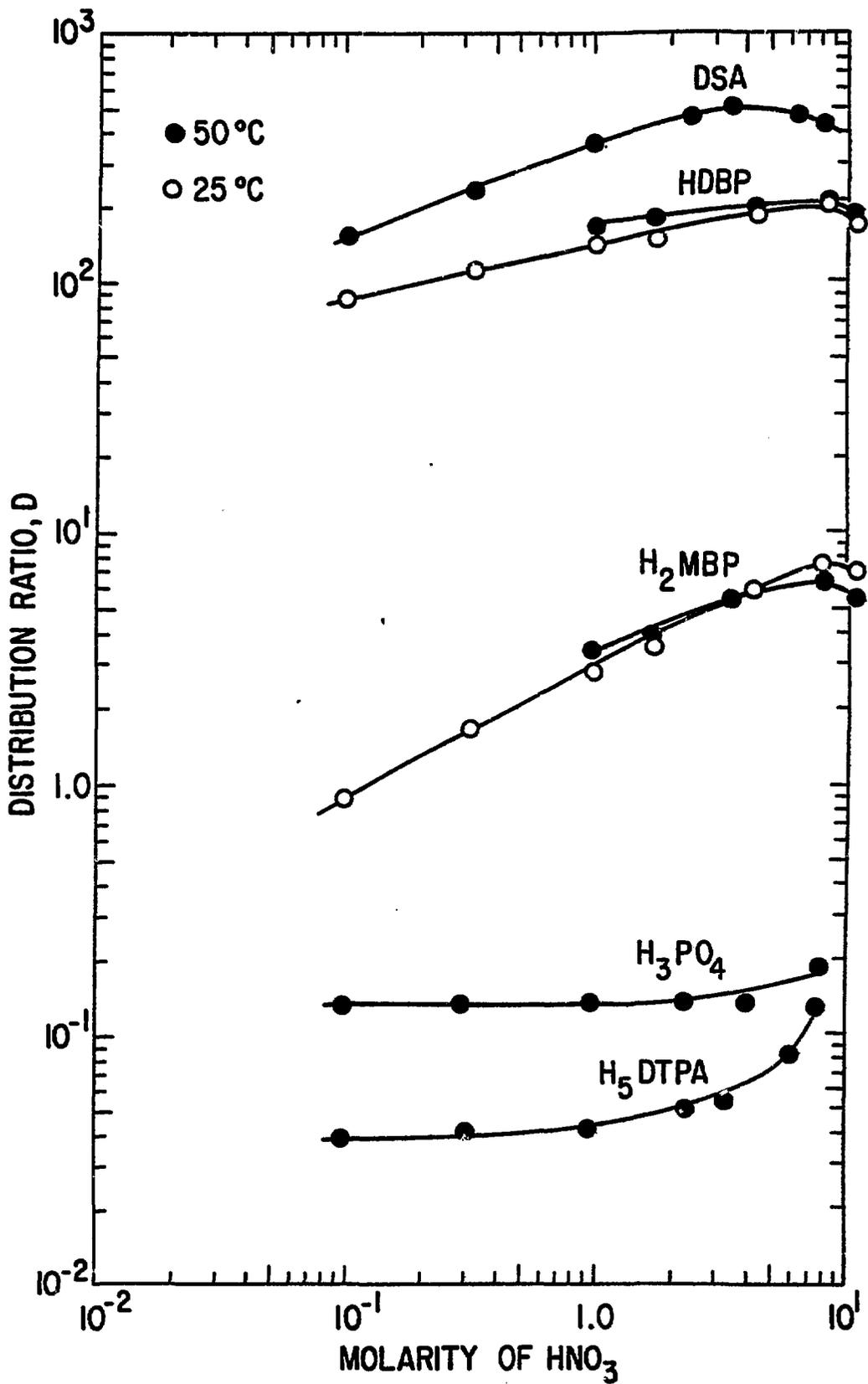


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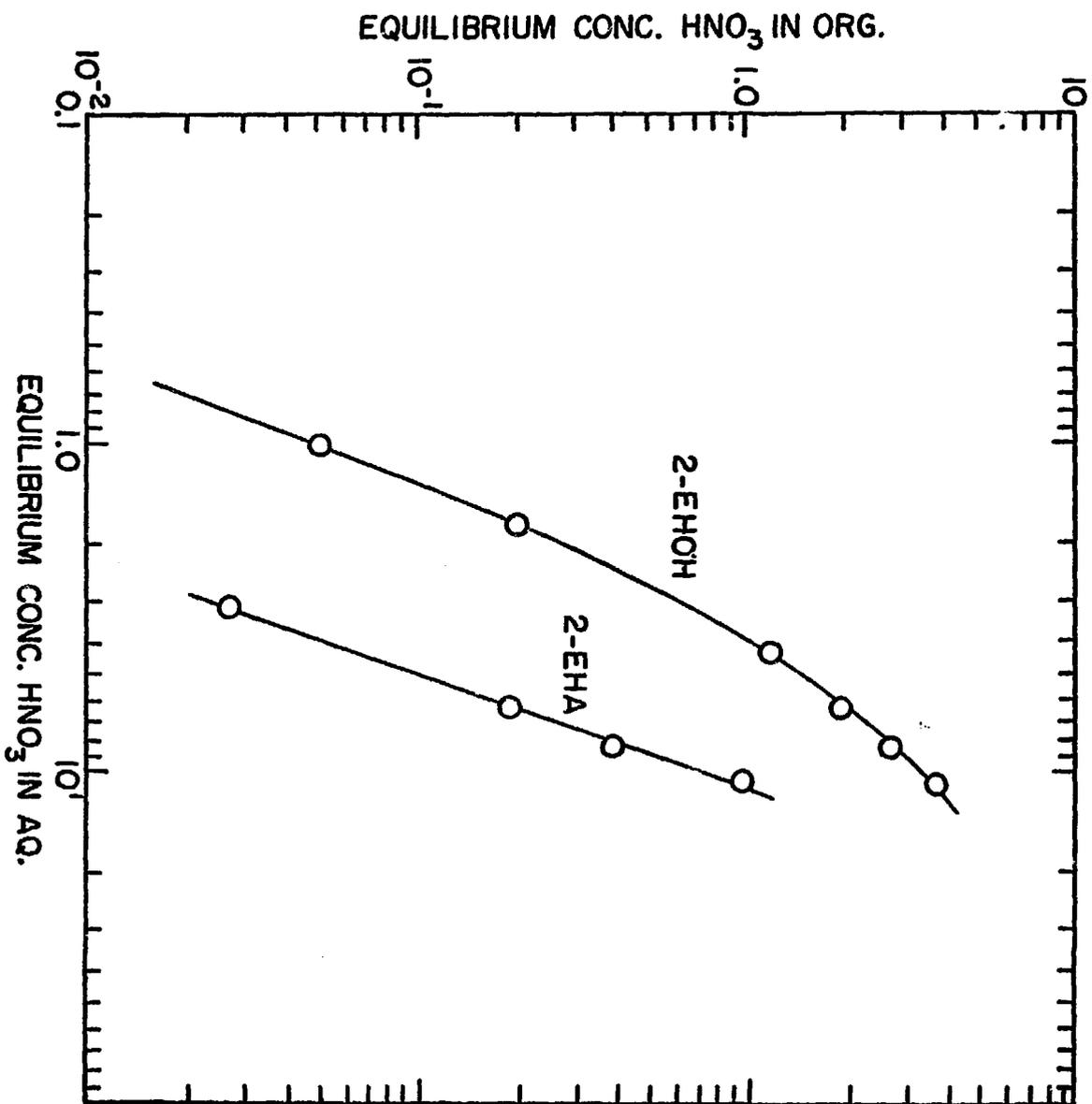


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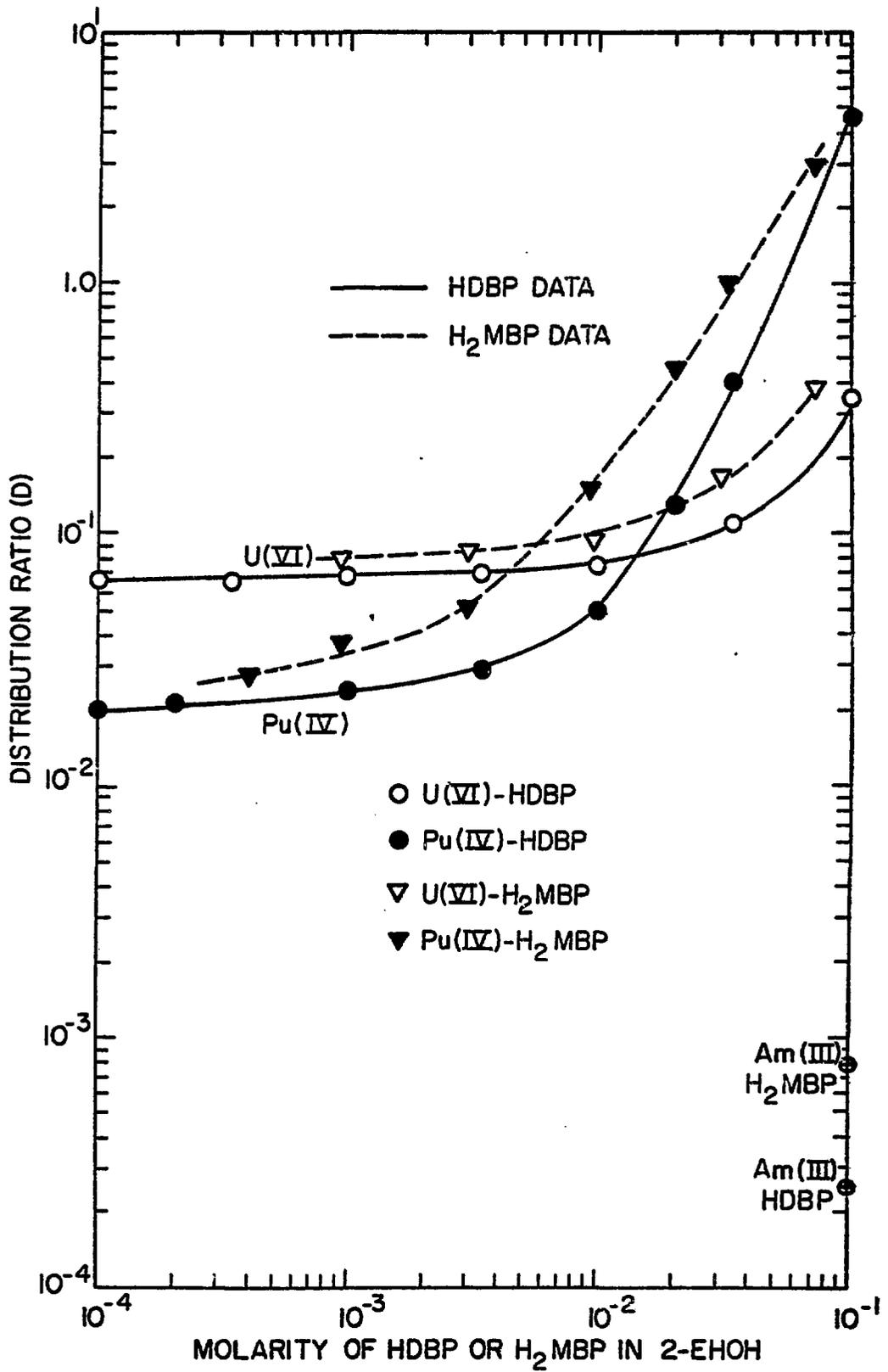


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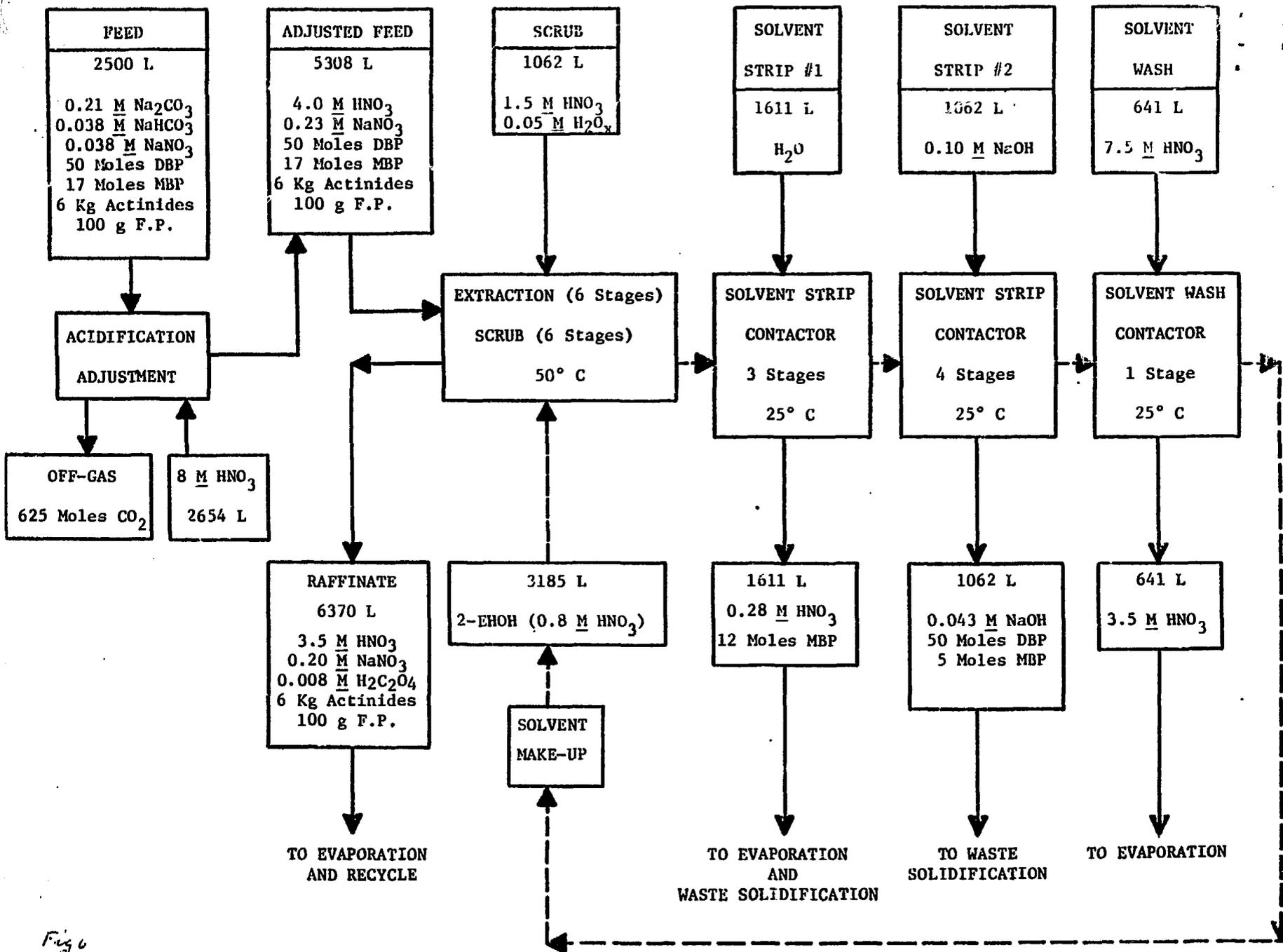


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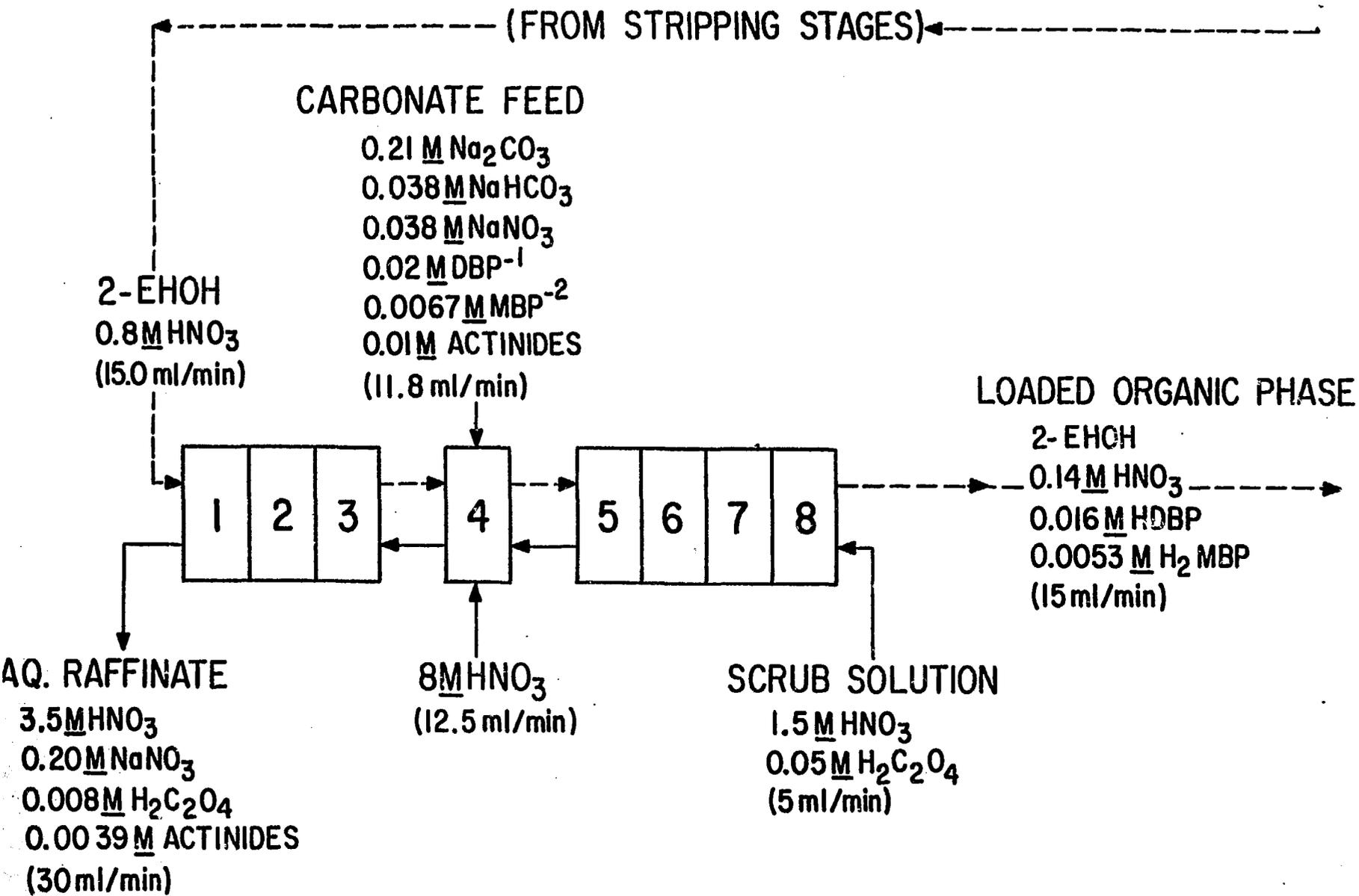


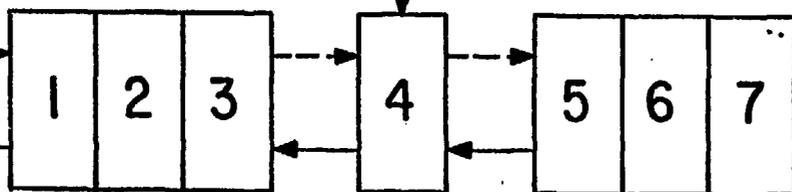
Fig 7

(FROM STRIPPING STAGES) ←

CARBONATE FEED

0.21 M Na_2CO_3
0.038 M NaHCO_3
0.038 M NaNO_3
0.02 M DBP^{-1}
0.0067 M MBP^{-2}
0.01 M DTPA^{-3}
0.01 M ACTINIDES
(17.7 ml)

2-EHOH
0.8 M HNO_3
(22.5 ml)



LOADED ORGANIC PHASE

2-EHOH
0.14 M HNO_3
0.016 M HDBP
0.0053 M H_2MBP
(22.5 ml)

AQ. RAFFINATE

3.5 M HNO_3
0.20 M NaNO_3
0.009 M $\text{H}_2\text{C}_2\text{O}_4$
0.004 M H_5DTPA
0.004 M ACTINIDES
(44.0 ml)

8 M HNO_3
(18.8 ml)

SCRUB SOLUTION

1.5 M HNO_3
0.05 M $\text{H}_2\text{C}_2\text{O}_4$
(7.5 ml)

Fig 8

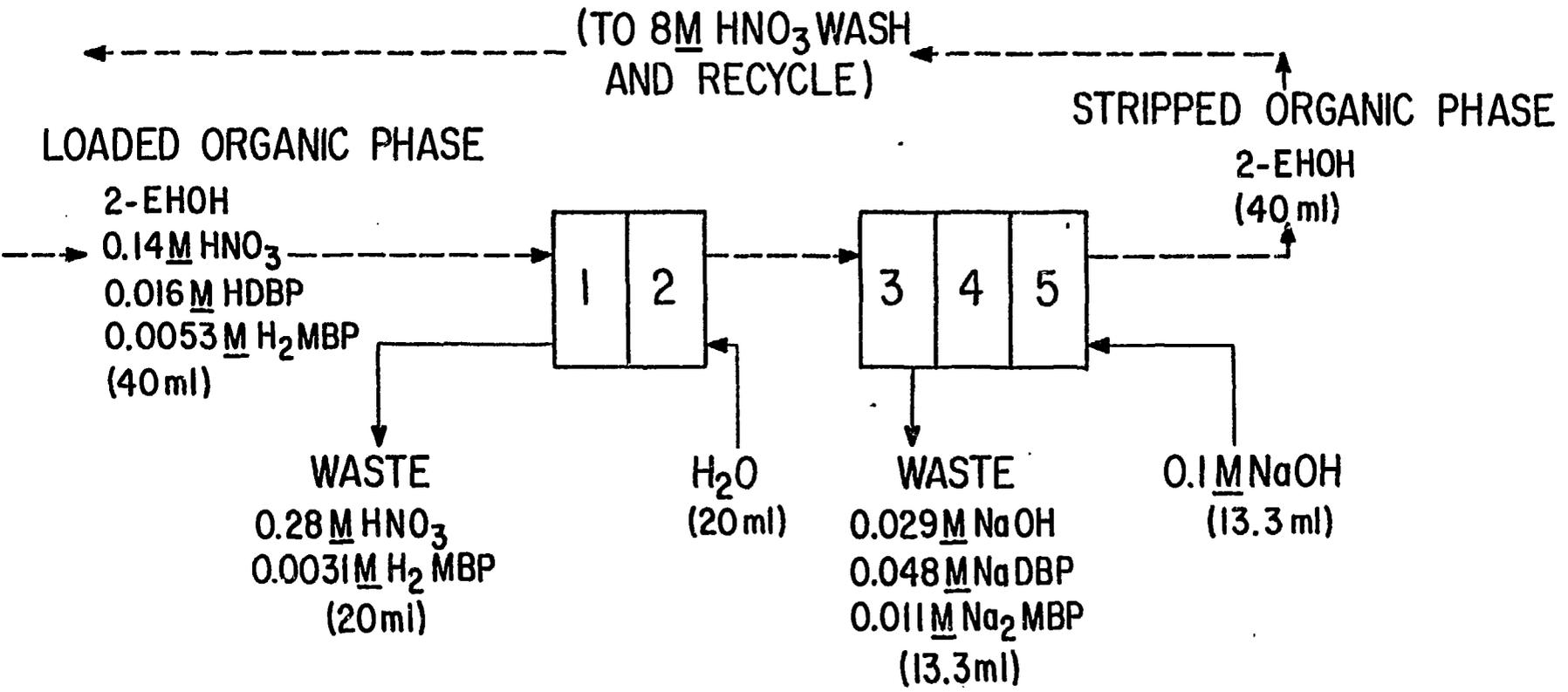


Fig 9