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Bidentate Organophosphorus Extractants: Purification, Properties and Applications to Removal of Actinides from Acidic Waste Solutions

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NOTICE

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BIDENTATE ORGANOPHOSPHORUS EXTRACTANTS: PURIFICATION, PROPERTIES AND APPLICATIONS TO REMOVAL OF ACTINIDES FROM ACIDIC WASTE SOLUTIONS

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ABSTRACT

At both Hanford and Idaho, DHDECMP (dihexyl-N,N-diethylcarbamylmethylene phosphonate) continuous countercurrent solvent extraction processes are being developed for removal of americium, plutonium, and, in some cases, other actinides from acidic wastes generated at these locations. Bench and, eventually, pilot and plant-scale testing and application of these processes, has been substantially enhanced by the discovery of suitable chemical and physical methods of removing deleterious impurities from technical-grade DHDECMP. Flowsheet details, as well as various properties of purified DHDECMP extractants, are enumerated.

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INTRODUCTION

Bidentate organophosphorus extractants such as carbamylmethylene phosphonates extract trivalent actinides (Am^{3+}, Cm^{3+}) and lanthanides very well from moderately concentrated (2-5$\underline{M}$) HNO_3 solutions. Common monodentate extractants such as tri-n-butyl phosphate (TBP) and di-n-butylbutyl phosphonate (DBBP) do not.

The favorable extraction properties of certain bidentate organophosphorus compounds, first disclosed by Siddall[1-3], are being exploited at the U. S. Energy and Development Administration Idaho Falls and Hanford sites to develop solvent extraction processes for removal of ^{241}Am and other actinides from acidic wastes generated at these locations. We have made considerable progress in developing and demonstrating suitable extraction processes and also in characterizing and purifying commercially available bidentate reagents. One of us (Lyle D. McIsaac) has also started detailed studies of the use of dihexyl-N, N-diethylcarbamylmethylene phosphonate to extract +4 and +6 as well as +3 actinides from Purex process high-level liquid wastes.

This paper summarizes our latest findings and updates results presented earlier at New Orleans[4] and Baden Baden[5] or published elsewhere.[6]

BIDENTATE EXTRACTANT CHARACTERIZATION AND PURIFICATION

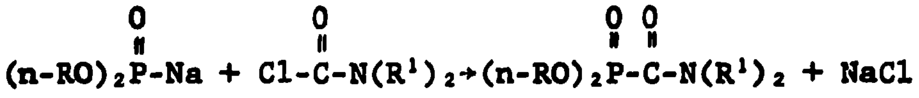
TYPES

There are obviously many organic functional groups which could be possibly combined with a phosphoryl (PO) group to yield a neutral bidentate organophosphorus reagent potentially suitable for use in solvent extraction applications. All the workers in the field have, however, confined their attention to bidentate compounds where the phosphoryl group is combined with a carbonyl (CO) group or another phosphoryl grouping. Thus, Siddall[1,2] and later McIsaac and Schulz[4-6] have studied the extraction properties of various methylene diphosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{P}}(-OR)_2]$, carbamylphosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}-N(-R)_2]$, and carbamylmethylene phosphonates $[(RO-)_2\overset{O}{\overset{\|}{P}}-CH_2-\overset{O}{\overset{\|}{C}}-N(-R)_2]$. O'Laughlin[7] has reviewed the synthesis and extraction properties of various neutral bidentate organophosphorus compounds.

Screening tests at both Idaho Falls and Hanford have shown that carbamylmethylene phosphonates are far superior to either carbamyl phosphonates or methylene diphosphonates for extracting Am(III) from nitric acid solutions of interest. In particular, because of its commercial availability, suitably low aqueous phase solubility, and other favorable properties, the preferred bidentate extraction reagent at both Idaho Falls and Hanford is dihexyl-N, N-diethylcarbamylmethylene phosphonate, DHDECMP. Much work at Idaho Falls has also been done with the dibutyl analogue, DBDECMP.

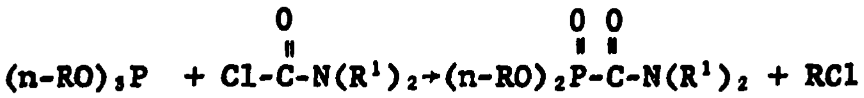
SYNTHESIS

Carbamylmethylene phosphonates as well as methylenediphosphonates and carbamyl phosphonates can be prepared (in 40-60% yield) most conveniently via the Michaelis reaction as illustrated in Equation 1.



$$(n\text{-}RO)_2\overset{O}{\overset{\|}{P}}\text{-}Na + Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}N(R^1)_2 \rightarrow (n\text{-}RO)_2\overset{O}{\overset{\|}{P}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}N(R^1)_2 + NaCl \qquad (1)$$

The Arbuzov rearrangement (Equation 2) can also be used to prepare these classes of bidentate extractants.



$$(n\text{-}RO)_3P + Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}N(R^1)_2 \rightarrow (n\text{-}RO)_2\overset{O}{\overset{\|}{P}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}N(R^1)_2 + RCl \qquad (2)$$

Siddall[2] notes that, especially with larger alkoxy substituents, the Arbuzov rearrangement takes place with dialkylcarbamyl chloride and N, N-dialkylhaloacetamides [$(R)_2N\text{-}CH_2X$] only at temperatures around 200 °C. Visible degradation of product occurs at such temperatures.

REAGENT SOURCE AND COST

Wateree Chemical Company, Lugoff, South Carolina, has been and is currently, as far as we know, the major U.S. supplier of neutral bidentate organophosphorus compounds. On a custom synthesis basis, Wateree Chemical Company has made a wide assortment of diphosphonates, carbamyl phosphonates and carbamylmethylene phosphonates including all the DHDECMP used in the studies reported here. Multiliter amounts of technical-grade DHDECMP are currently (spring 1977) available from Wateree Chemical at a cost of $75-100 per liter.

Very recently, one of us (Lyle D. McIsaac) has been in contact with the Eastman Chemical Company, Rochester, New York, regarding their interest and ability to supply large amounts of technical-grade DHDECMP. Although no commitments have been made, Eastman Chemical Company has indicated their interest in producing and marketing this chemical and, hence, may someday be a second U.S. source of multiliters of DHDECMP.

Gram quantities of purified (99%) dibutyl-N, N-diethylcarbamyl phosphonate (DBDECP) are available as an *off-the-shelf* item from Richmond Organics, Richmond, Virginia. In 1975, this company estimated 1000-kilogram (~1000 liters) amounts of DBDECP would cost about $50-$60 per kilogram.

Experimental quantities of diisopropyl-N, N-diethylcarbamyl phosphonate have also been made by Richmond Organics.

PURITY

Not unexpectedly, technical-grade DHDECMP and other commercially available carbamyl and carbamylmethylene phosphonates made by either the Michaelis reaction or Arbuzov rearrangement contain unreacted starting materials and a whole host of impurities. Research to identify at least some of these impurities has been performed over the last two years by three different groups of scientists in the U.S.: (1) by P. Fagerness and T. Elwood at the University of Utah under the sponsorship of the Allied Chemical Corporation; (2) by E. Martin of Battelle's Pacific Northwest Laboratories in Richland, Washington under the sponsorship of the Atlantic Richfield Hanford Company; and (3) by R. Shoun, W. McDowell, and C. Bahner at the Oak Ridge National Laboratory.* Using modern physicochemical techniques, including coupled gas chromatography and mass spectrometric methods as well as NMR analyses, these scientists successfully identified many of the impurities in as-prepared DHDECMP. Table I lists some of the compounds identified by the Utah group.[9] P. Fagerness and T. Elwood note that many of the impurities

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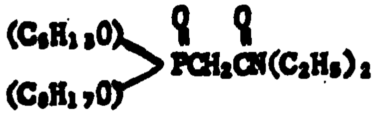
*A detailed account of the researches of Shoun, Bahner, and McDowell was in press[8] when this paper was written.

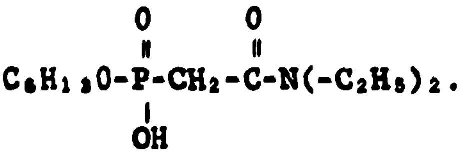
TABLE I

COMPOUNDS IDENTIFIED IN TYPICAL TECHNICAL-GRADE DIHEXYL-N, N-DIETHYLCARBAMYLMETHYLENE PHOSPHONATE

Compound	Wt %	Compound	Wt %
DHDECMP	49	 $C_6H_{13}\overset{\overset{O}{\|}}{P}(C_6H_{13}O)_2$	9.2
 $ClCH_2\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$	0.9	 $(C_6H_{13}O)_3\overset{\overset{O}{\|}}{P}$	10.2
 $Cl_2CH\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$	0.4	 $(C_6H_{13}O)_2\overset{\overset{O}{\|}}{P}CH_2\overset{\overset{O}{\|}}{C}OC_6H_{13}$	12.1
 $(C_2H_5)_2NCH_2\overset{\overset{O}{\|}}{C}(CH_3)_2$	0.7	 $\left.\begin{matrix}(C_6H_{13}O)\\(C_8H_{17}O)\end{matrix}\right>\overset{\overset{O}{\|}}{P}CH_2\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$	3.7
$HOP(OC_6H_{13})_2$	3.4		
 $(C_6H_{13}O)_2\overset{\overset{O}{\|}}{P}CH_3$	4.1		

*Results of P. Fagerness and T. Elwood[9] remain unidentified because of the complexities associated with interpreting mass spectral data; assignments that have been made (Table I) are derived from molecular weights, mass fractionation patterns found in the literature, and experienced intuition. Weight percentages cited in Table I were determined by current integration in the mass spectrometer, assuming equal response functions for all compounds, and must be considered only as estimates.

Unquestionably, the most important and offensive impurity in technical-grade DHDECMP is:



$$C_6H_{13}O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-N(-C_2H_5)_2.$$

The presence and identity of this contaminant has recently been established by Shoun, McDowell, and Bahner[8] at Oak Ridge and also by Martin of the Pacific Northwest Laboratory. This particular acidic impurity has a very high affinity for Am^{3+}, Pu^{4+} (and other actinides) at low HNO_3 concentrations (Figure 1); its removal is essential to permit use of dilute HNO_3 solutions for partitioning of trivalent actinides from coextracted tetravalent and/or hexavalent actinides.

Much effort, described in the succeeding text, at both Hanford and Idaho Falls has been devoted to establishing techniques for obtaining satisfactorily pure DHDECMP solutions

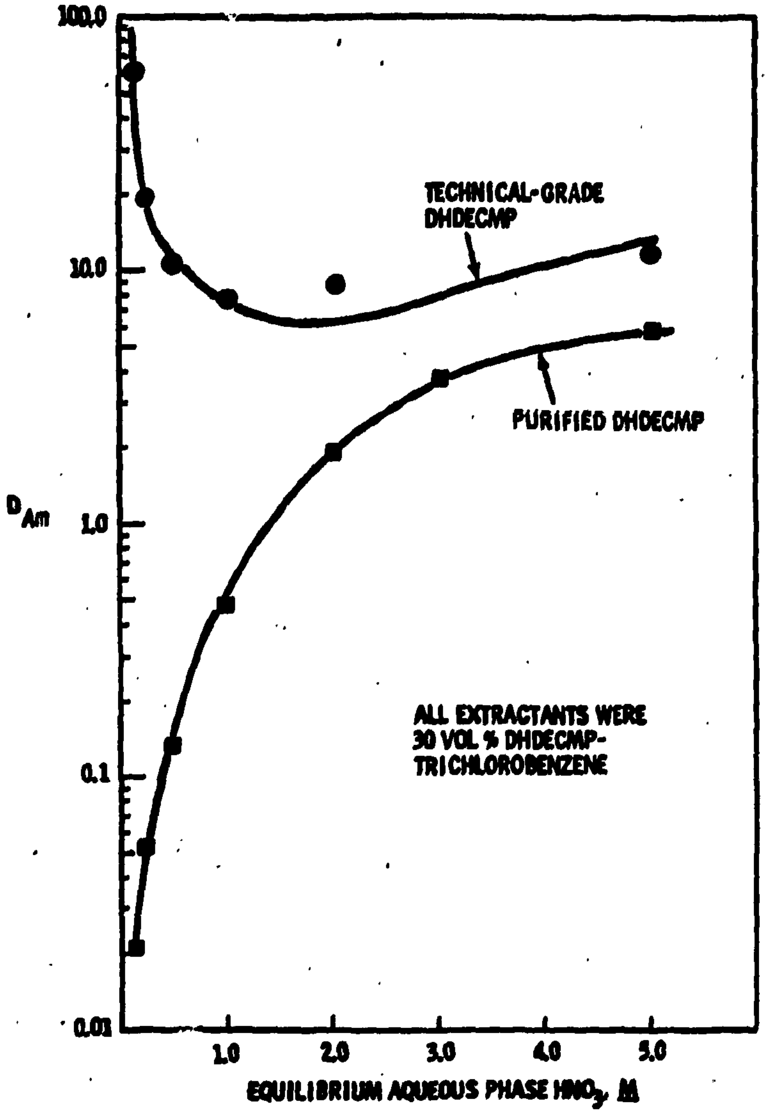


FIGURE 1

EXTRACTION OF AMERICIUM BY PURIFIED AND TECHNICAL-GRADE DHDECMP for use in proposed actinide removal processes. (Most of this work was done before the identity of the deleterious acidic impurity was established.) Solvent purification studies at Idaho Falls have emphasized vacuum distillation and, more recently, liquid chromatography methods to separate DHDECMP from the acidic contaminant and also from most of the neutral impurities. Conversely, special solvent washing and/or ion exchange procedures have been developed at Hanford to remove the acidic impurity from DHDECMP and the other neutral components present in technical-grade material. Simple washing of DHDECMP or its solutions in a carrier solvent with Na_2CO_3 or NaOH solutions does not remove the acidic impurity.

PURIFICATION

Vacuum Distillation

From technical-grade DHDECMP, the DHDECMP fraction distills at 0.001 torr and ∿110 °C. At the Idaho site, an all-glass pot still of a design used by Hickman and Sanford[10] has been used to prepare liter quantities of ∿86% pure DHDECMP. Such vacuum-distilled DHDECMP can be used without further treatment for actinide extraction and stripping studies. Martin, at the Pacific Northwest Laboratories, has prepared less pure, but still equally acceptable pure DHDECMP by distilling at 0.2 torr and 140 °C.

Liquid Chromatography

Very recent research at the Idaho site has demonstrated that >98% pure DHDECMP can be obtained by high pressure liquid chromatography with silica gel as the stationary phase. Preparative liquid chromatography working in tandem with a centrifugal molecular still (e.g., CVC Products, Inc. Lab 5 Still) is being considered for preparing kiloliters of purified DHDECMP for engineering-scale flowsheet tests.

Solvent Wash/Ion Exchange Resin Purification Methods

At Hanford, 30% DHDECMP-trichlorobenzene (and other diluent) solutions have been satisfactorily purified by washing them once with an equal volume of ethylene glycol at 25 °C and then passing the washed solvent through a bed of 25-50 mesh, hydroxide-form Amberlyst A-26 (Rohm and Haas Co.) macroreticular strong base anion exchange resin. Actinide extraction properties (Figure 2) of such solvent are comparable to those of extractant prepared from vacuum-distilled DHDECMP. Before proceeding with a more detailed discussion of the combined wash-ion exchange procedure, it is convenient to summarize purification results achieved by repetitive ethylene glycol washing without subsequent ion exchange treatment.

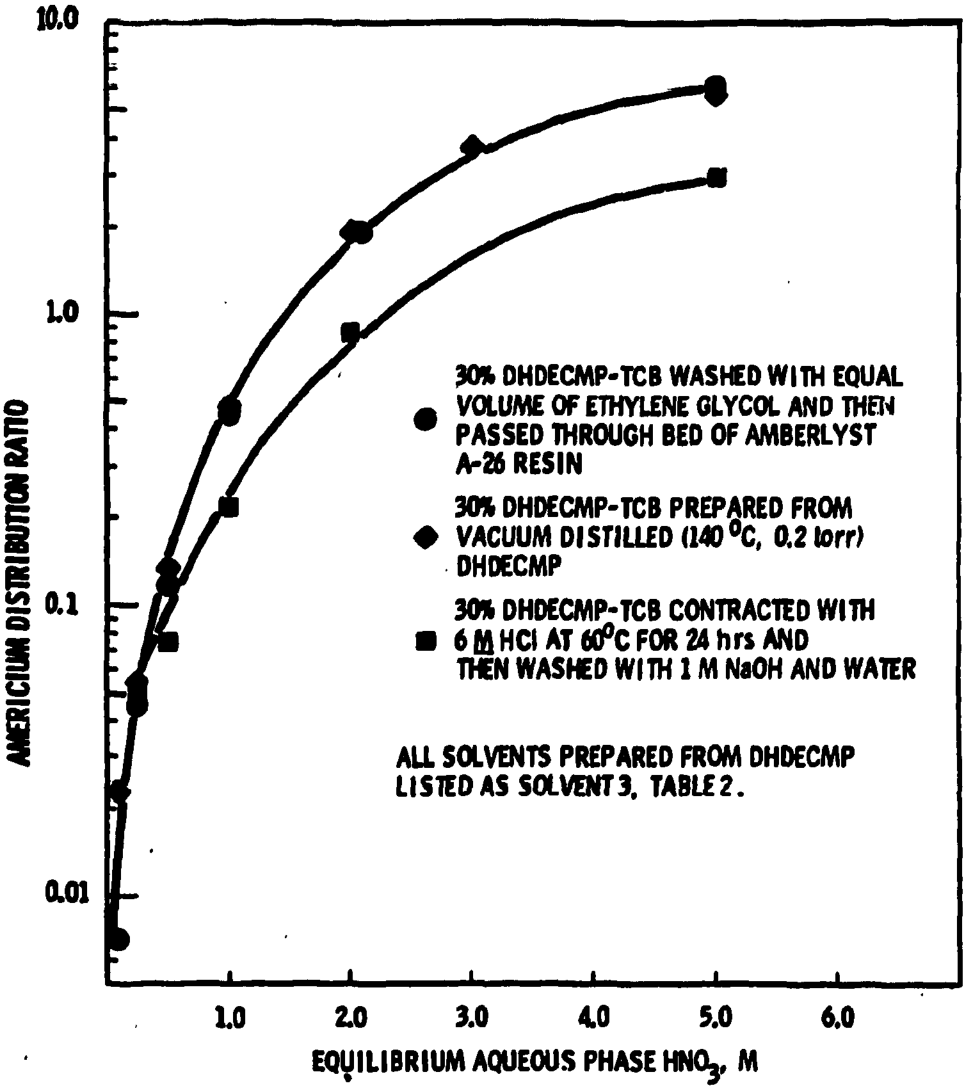


FIGURE 2

AMERICIUM EXTRACTION BEHAVIOR OF VARIOUS PURIFIED DHDECMP SOLVENTS

Ethylene Glycol Washing. Stewart and Crandall[11] developed an ethylene glycol wash procedure for removing mono(2-ethylhexyl) phosphoric acid from bis(2-ethylhexyl) phosphoric acid and its solutions. Ethylene glycol washes also remove most of the acidic impurity from solutions of technical-grade carbamylmethylene phosphonates (Table II). All the washing tests listed in Table II were performed with as-received DHDECMP and DBDECMP (dibutyl-N, N-diethylcarbamylmethylene phosphonate) reagents diluted with trichlorobenzene (TCB); dilution of the bidentate reagent with a water-insoluble solvent such as TCB or perchloroethylene (PCE) is necessary because the undiluted bidentate reagent is completely miscible with ethylene glycol.

Data in Table II clearly show that ethylene glycol washing effectively removes the offensive acidic impurity from solutions of bidentate extractants. Thus, D_{Am} at 0.1$\underline{M}$ HNO_3 for 30 volume percent DHDECMP and DBDECMP solvents washed three times with fresh equal-volume portions of ethylene glycol is 100- to 200-fold lower than for unwashed solvents. The efficiency of ethylene glycol washes in removing the acidic impurity is a function of the number of washes, the volume ratio of ethylene glycol to bidentate extractant, and wash temperature. Washing at 60 °C is definitely more effective than washing at 25 °C. For batch-type washing, three equal volume washes at 60 °C, preferably,

TABLE II

ETHYLENE GLYCOL WASHING OF BIDENTATE ORGANOPHOSPHORUS SOLVENTS

Conditions: 30 volume % DHDECMP (or DBDECMP) - TCB solvents washed as shown with ethylene glycol; americium extraction of washed extractants determined by contacting them at 25 °C three times with equal portions of 0.1M HNO_3 containing ~10^5 μCi/liter ^{241}Am.

Solvent[(b)] Number	Wash Conditions[(a)] Number of Washes	Wash Temperature, °C	Volume Ratio Ethylene Glycol: Solvent	D_{Am} at[(c)] 0.1M HNO_3
1		NOT WASHED		11.4
	1	25	1:1	0.937
	2	25	1:1	0.232
	3	25	1:1	0.109
	3	60	1:1	0.0621
	3	25	1:4	0.596
	3	25	1:10	0.607
	3	25	2:1	0.0657
2		NOT WASHED		4.14
	3	25	1:1	0.0971
3		NOT WASHED		70.8
	3	25	1:1	0.620

(a) All washes were for 10 minutes.

(b) For identification purposes only; Batches 1 and 3 - DHDECMP; Batch 2 - DBDECMP.

(c) D_{Am} = Concentration Am in organic phase/concentration Am in aqueous phase.

or at 25 °C are recommended. (A smaller volume ratio of ethylene glycol to bidentate extractant may be suitable in counter-current extraction equipment.) Other results, not shown in Table II, indicate that transfer of the acidic impurity to the ethylene glycol phase proceeds rapidly--wash times as little as five minutes are suitable.

The ethylene glycol wash procedure meets most of the desiderata for a method for removing the offending acidic contaminant from technical-grade bidentate extractants. It is a simple, inexpensive procedure which can be routinely performed in stainless steel equipment and which yields suitably purified (^{D}Am at 0.1$\underline{M}$ HNO_3 $\leq$ 0.1) extractant in most cases. Unfortunately, the ethylene glycol washing procedure will not completely and satisfactorily purify bidentate reagents containing large amounts of the acidic impurity (e.g., Solvent 3, Table I). In addition to this very serious disadvantage, the second and succeeding ethylene glycol washes disengage only very slowly, even at 60 °C, from the bidentate phase. Centrifuging is required to obtain satisfactory phase separation.

<u>Combined Ethylene Glycol Washing - Resin Purification</u>. Previously, Schulz[12] showed that Amberlyst A-26 resin could be used to remove dibutylphosphoric acid from tri-n-butyl phosphate solutions. Schulz and Honaker[13] have also recently

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	3	25	1:4	0.596
	3	25	1:10	0.607
	3	25	2:1	0.0657
2		NOT WASHED		4.14
	3	25	1:1	0.0971
3		NOT WASHED		70.8
	3	25	1:1	0.620

(a) All washes were for 10 minutes.

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Combined Ethylene Glycol Washing -- Resin Purification. Previously, Schulz[12] showed that Amberlyst A-26 resin could be used to remove dibutylphosphoric acid from tri-n-butyl phosphate solutions. Schulz and Honaker[13] have also recently made use of the Amberlyst A-26 resin in an ion exchange method for preparing highly-purified bis-(2-ethyl-hexyl) phosphoric acid. Work at the Hanford and Idaho sites as well as by Navratil[14] at the U.S. Energy Research and Development Administration Rocky Flats site has shown that the A-26 resin will also remove acid impurities from solutions of DHDECMP.

Because most technical-grade DHDECMP contains such a high concentration of acid impurities, a single pass of a DHDECMP solvent through a bed of A-26 resin will not yield extractant for which ^{D}Am at $0.1\underline{M}$ HNO_3 is the required 0.1 or less (Figure 3). Satisfactorily pure extractant can be prepared, as Navratil[14] has demonstrated, by passing the resin-treated solvent through one or two more beds of fresh or regenerated A-26 resin. Alternatively, the DHDECMP-diluent solution can be washed once with an equal volume of ethylene glycol and the washed solvent then flowed through a bed of A-26 resin. Removal of the bulk of the acid impurities by a preliminary ethylene glycol wash substantially extends the capacity of the A-26 resin to yield acceptably pure extractant (Figure 3).

Very successful pilot-plant scale tests of the combined ethylene glycol wash–A-26 resin system were recently performed at Hanford. In these runs, three separate 40-liter batches of ethylene glycol washed 30% DHDECMP diluted with either TCB,

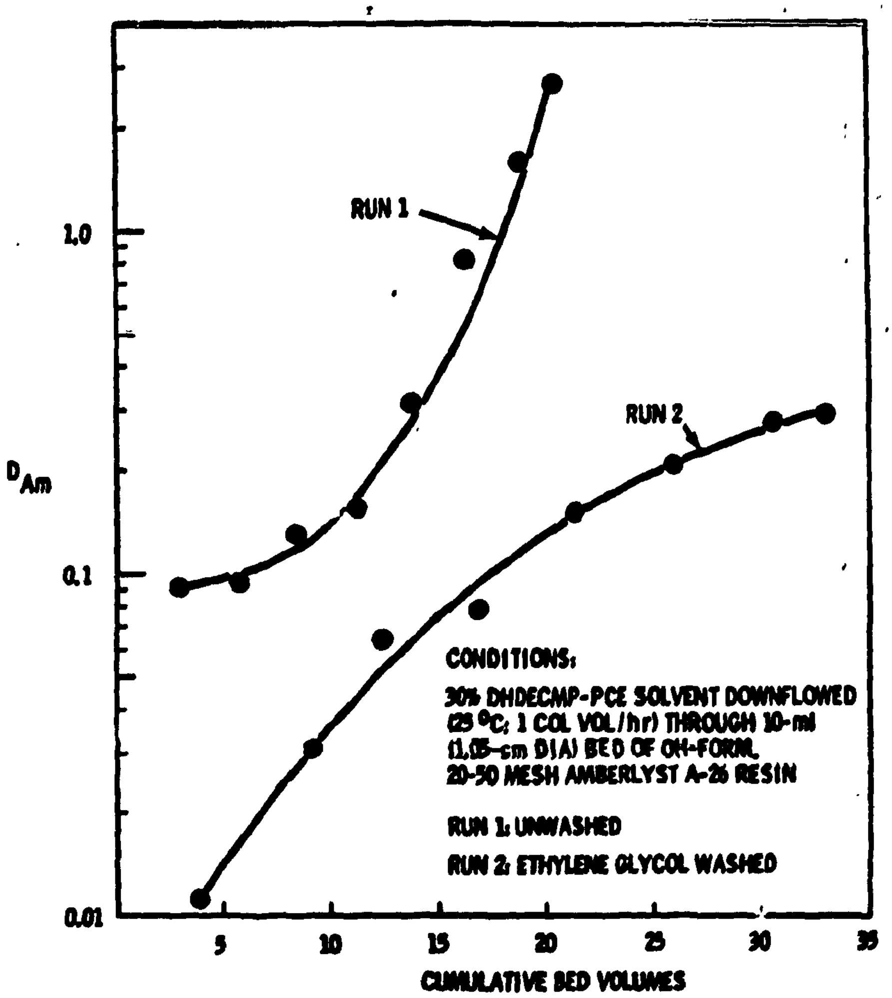


FIGURE 3

AMBERLYST A-26 RESIN PURIFICATION
OF DHDECMP EXTRACTANT

PCE, or a mixture of TCB and PCE were downflowed at ~25 °C through a 25-liter bed of A-26 resin. The resin bed between each load cycle was regenerated by successive water, 3M HNO, and 2M NaOH washes. Americium extraction properties of the DHDECMP solvent batches before and after resin treatment are tabulated in Table III. All the final products easily met the specified $^{D}Am \leq 0.1$.

Hydrochloric Acid Hydrolysis

Siddall[1], in his pioneering researches, observed that the acidic impurity in bidentate organophosphorus reagents could be removed by contacting an 0.5M benzene solution of the bidentate compound with 6M HCl for four hours at 60 °C and then washing the resulting solvent with NaOH and water. Such treatment presumably converts the monobasic impurity to a dibasic entity soluble in NaOH solutions. Subsequently, the acid hydrolysis procedure was studied extensively at Hanford and used to satisfactorily purify several different batches of DHDECMP.[4] The key element, which is difficult to judge, in this purification scheme is how long to contact the bidentate-diluent solution with 6M HCl at 60 °C. Short hydrolysis times (1-4 hours) are adequate to purify technical-grade bidentate solvents containing only small concentrations of the acid impurity. But, long (24 hour - even 48 hour) hydrolysis times are needed with highly-impure bidentate solutions such as Solvent 3, Table I.

TABLE III

PILOT-PLANT SCALE PURIFICATION OF 30% DHDECMP SOLVENTS

Run[b] Number	Diluent	D_{Am} at 0.1M HNO_3[a] After Ethylene Glycol Washing[c]	D_{Am} at 0.1M HNO_3[a] After A-26 Resin Treatment
1	PCE	2.02	0.0347
2	TCB	2.53	0.0604
3	30% PCE - 70% TCB	2.08	0.0470

(a) D_{Am} before ethylene glycol washing was 60.5.

(b) 150 liters of solvent purified in each run.

(c) 22 hours washing at ∿25 °C.

The acid hydrolysis procedure suffers from a number of disadvantages which preclude its being recommended for laboratory-scale, let alone plant-scale, applications. Foremost of these is that the bidentate compound as well as the acidic impurity is attacked by HCl with a concomitant decrease in the power of the purified extractant to extract actinides from moderately concentrated (e.g., 2-5M) HNO_3 solutions. This effect is illustrated in Figure 2 for 30% DHDECMP-TCB solvent contacted 24 hours at 60 °C with 6M HCl. For plant-scale usage specialized, corrosion-resistant equipment would be needed to perform the HCl hydrolysis step.

EXTRACTANT PROPERTIES

SOLUBILITY IN AQUEOUS SOLUTIONS

Data for the solubility of DHDECMP and DBDECMP in various aqueous solutions were reported earlier.[5,6] Dibutyl-N,N-diethylcarbamylmethylene phosphonate is highly soluble (60 g/liter) in 0.1M HNO_3 at 23 °C and still appreciably soluble (9 g/liter) when diluted to 15 volume percent with xylene. The solubility of DHDECMP in 0.1M HNO_3 at 23 °C, however, is low (0.5 g/liter) and comparable to that of tri-n-butyl phosphate (TBP) in water (0.4-0.5 g/liter). The relatively large aqueous phase solubility of DBDECMP is obviously a serious drawback to its plant-scale use.

EXTRACTION MECHANISMS

Logarithmic plots of DHDECMP concentration versus americium distribution ratios from either 1M HNO_3 or synthetic ICPP zirconium-aluminum first-cycle raffinate are straight lines of slope 2.9. Assuming that the slope of such plots indicates the dependency of the extraction reaction on bidentate reagent concentration, extraction of Am(III) by DHDECMP can be represented as:

$$Am^{3+} + 3NO_3^- + 3DHDECMP \rightleftarrows Am(NO_3)_3 \cdot 3DHDECMP \qquad (3)$$

Siddall[2] also observed a third power extractant dependency in extraction of Ce(III) by dihexyl-N, N-dibutylcarbamylmethylene phosphonate (DHDBCMP).

Siddall's studies with DHDBCMP also indicated that at least two molecules of HNO_3 were associated with each Ce-DHDBCMP moiety. Our acid dependency results (Figure 4) with 30% DHDECMP-DIPB (diisopropyl benzene) solvent indicate an acid dependency significantly less than two. The discrepancy between our data and that of Siddall has not yet been resolved. Additional studies of reagent and acid dependencies of DHDECMP and other carbamylmethylene phosphonates have very recently been made by Shoun, McDowell, and Bahner.[8]

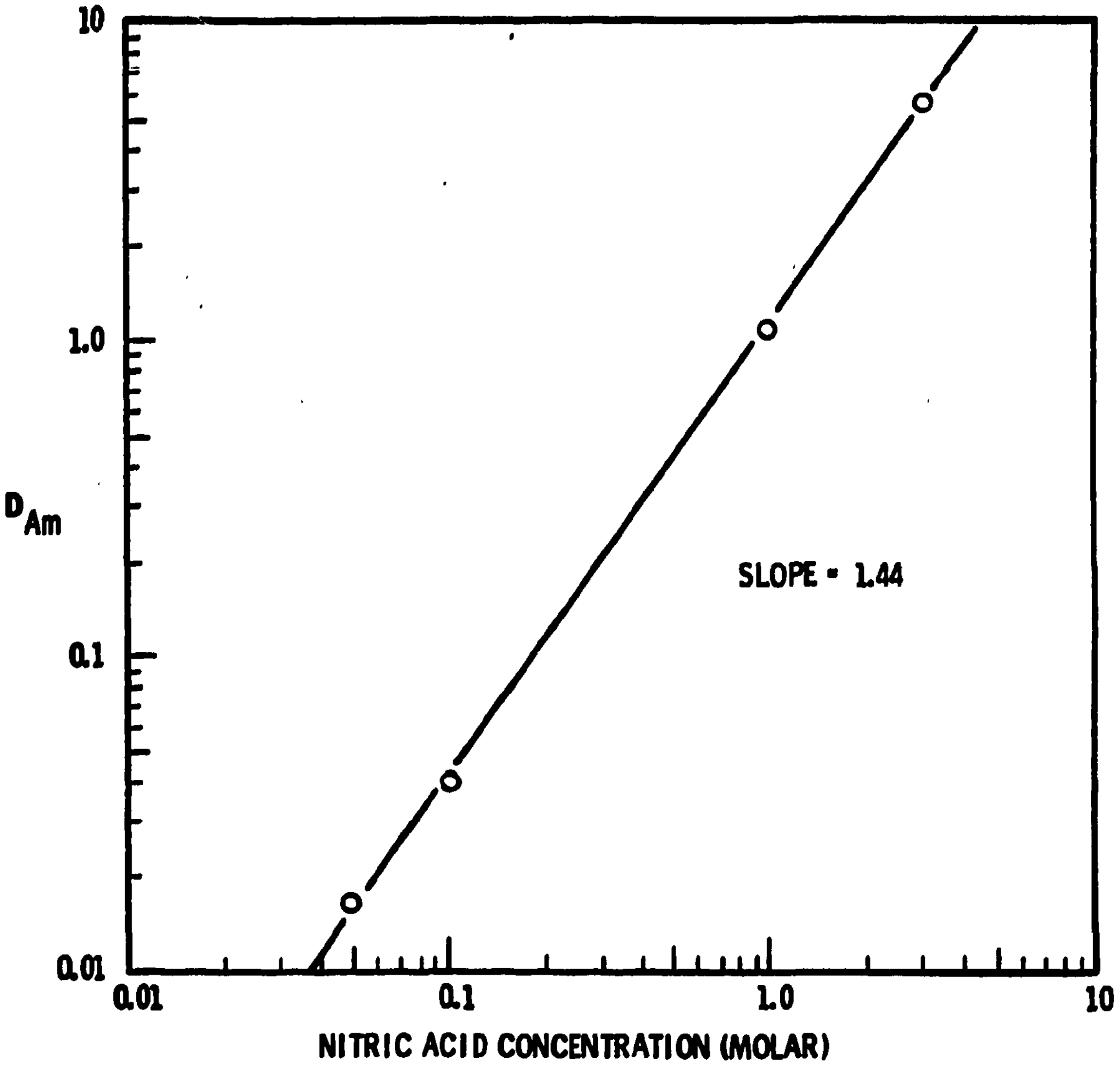


FIGURE 4

ACID DEPENDENCY OF Am(III) EXTRACTION
BY DHDECMP

DILUENT EFFECTS

Just as in many other solvent extraction systems, DHDECMP extraction of Am^{3+}, and other actinides as well, from HNO_3 solutions is strongly dependent upon the particular carrier solvent used to dilute the DHDECMP (Table IV). (Similar data for diluent effects on DBDECMP extraction of Am^{3+} from synthetic ICPP waste solution were presented earlier.[6])

A second organic phase forms when solutions of DHDECMP (or DBDECMP) dissolved in straight chain aliphatic hydrocarbons are contacted with aqueous HNO_3 solutions. Formation of a second phase in such systems can be avoided by diluting the DHDECMP with aromatic or chlorinated (e.g., CCl_4, PCE, TCB, etc.) diluents. Decalin, decahydronaphthalene, is somewhat of an intermediate diluent in that a second organic phase forms only when DHDECMP-decalin extractants are contacted with $\geq 3\underline{M}$ HNO_3 solutions. Addition of a small amount of an aromatic solvent like xylene or toluene to a DHDECMP-decalin extractant prevents formation of a second organic phase even at aqueous acidities as high as $6\underline{M}$ HNO_3.

Because of current existing equipment design limitations, bidentate solvent extraction applications at Hanford are restricted to use of a heavier-than-water diluent such as CCl_4, PCE, or TCB. At Idaho, much of the laboratory work has

TABLE IV

INFLUENCE OF DILUENT ON EXTRACTION OF AMERICIUM(III) BY 33 PERCENT DHDECMP SOLUTIONS

Diluent	D_{Am} (a,b)
Decalin	21.0
3-Heptanone	14.6
Cyclohexane	14.1
Diisopropyl benzene	13.6
2-Ethylhexyl Acetate	10.3
p-Cymene	9.7
Dimethyl benzene	9.4
Mesitylene	7.8
Toluene	7.5
Xylene	7.2
Carbon Tetrachloride	4.0
Heptane	(c)
Trimethylpentane	(c)
Kerosene	(c)

(a) DHDECMP solvent contacted 5 minutes at 23 °C with equal volume of ^{241}Am-spiked synthetic Idaho Chemical Processing Plant (ICPP) zirconium-aluminum first cycle raffinate of composition listed in reference 5.

(b) All values have an estimated uncertainty of ± 10%.

(c) Second organic phase formed.

been done with xylene solutions of DHDECMP; for plant-scale applications, consideration is being given to use of diisopropyl benzene as a diluent.

TYPICAL ACTINIDE DISTRIBUTION DATA

Plotted in Figure 5 are typical data for the equilibrium distribution at 22 °C of selected +3, +4, and +6 actinides between aqueous HNO_3 solutions and 30% DHDECMP in diisopropyl benzene. Some distribution data for other elements in relevant acidic waste solutions at the Idaho site are reported elsewhere in this paper (p. 38); additional distribution data for non-actinide elements are cited in references 4 and 9.

The 30% DHDECMP-DIPB used to obtain the results shown in Figure 5 was prepared from vacuum-distilled (86% purity) DHDECMP and was sequentially washed with 0.5$\underline{M}$ Na_2CO_3 and water prior to use. Equal volume portions of aqueous and organic phases were shaken for five minutes. Adjustments of Pu(IV) and Pu(VI) oxidation states were made with 0.025$\underline{M}$ $NaNO_2$ and 0.025$\underline{M}$ $NaBrO_3$ - 0.001$\underline{M}$ $Ce(NH_4)_2(NO_3)_6$, respectively. Neptunium(IV) and neptunium(VI) states were adjusted with 0.025$\underline{M}$ $Fe(NH_2SO_3)_2$ and 0.025$\underline{M}$ $NaBrO_3$ - 0.001$\underline{M}$ $Ce(NH_4)_2(NO_3)_6$, respectively. Erratic results, not shown here, were obtained for the distribution of Pu(III) between HNO_3-$Fe(NH_2SO_3)_2$ solutions and 30% DHDECMP-DIPB extractant.

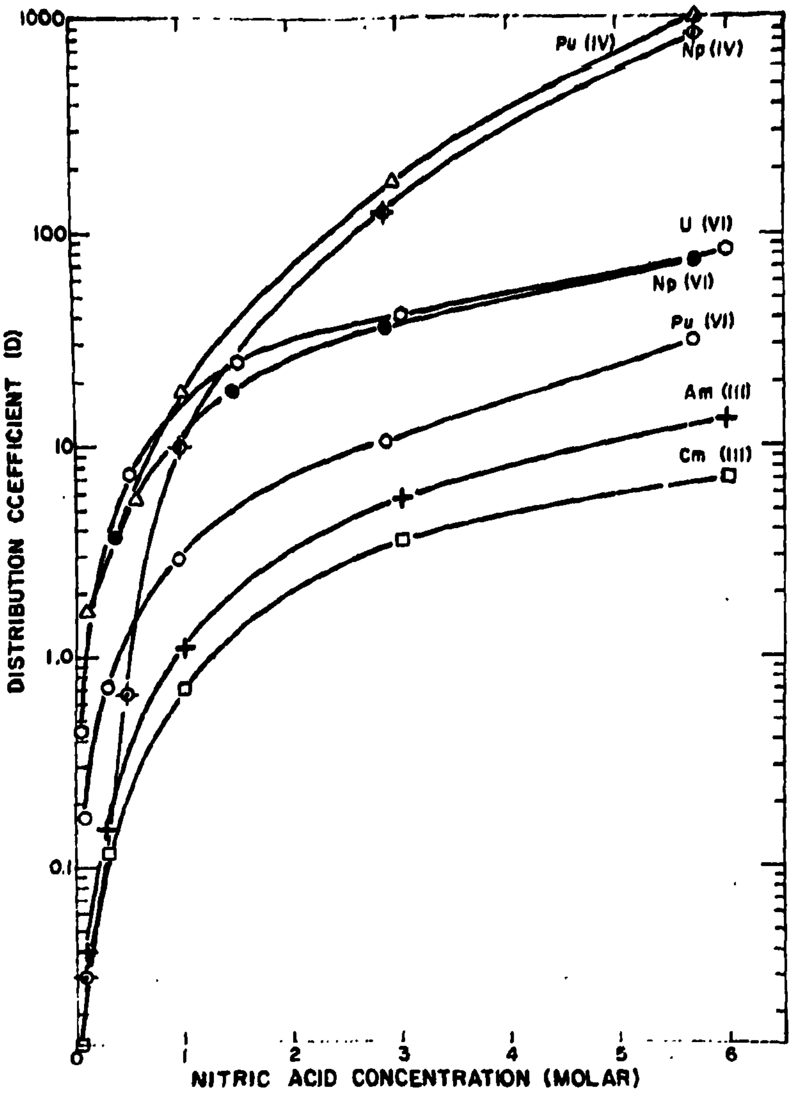


FIGURE 5

EXTRACTION OF +3, +4, AND +6 ACTINIDES
FROM HNO_3 SOLUTIONS BY 30% DHDECMP-DIPB SOLVENT

REACTION KINETICS

Empirical batch contact studies at both Hanford and Idaho show that Am(III) and Pu(IV) both transfer rapidly at 23-25 °C between DHDECMP-diluent solutions and aqueous HNO_3 media. In such tests, the equilibrium distribution ratio in both extraction and stripping modes was attained in approximately 30 seconds of mixing. Such rapid mass transfer rates indicate DHDECMP extraction systems can be operated satisfactorily in short residence time contactors, e.g., centrifugal contactors.

RADIOLYTIC EFFECTS

Alpha radiolysis of DHDECMP-TCB solvents has been investigated at Hanford;[4] while at Idaho, the effects of exposing DBDECMP-xylene solutions to gamma (^{60}Co) radiation have been determined.[15] The principal effect of radiolysis of either DHDECMP or DBDECMP solvents is to increase the amount of americium and plutonium not readily strippable by dilute HNO_3 or HNO_3-HF solutions. Deleterious liquid radiolysis products of DHDECMP and DBDECMP can be effectively removed by washing irradiated solutions with dilute aqueous carbonate solutions. Because of the low dose expected per extraction cycle (0.01 to 0.05 watt-hr/liter) in the proposed Hanford application and considering the expected solvent inventory turnover time,[5] performance of a DHDECMP-diluent extractant is expected to be satisfactory even without intercycle carbonate washing. However, even when performed in centrifugal contactors, anticipated bidentate extractant radiation dose rates in projected Idaho site process applications are such that intercycle carbonate solvent washing will be necessary.

GAS CHROMATOGRAPHY

Gas chromatographic methods have been developed at both Idaho and Hanford to monitor the effectiveness of various methods for purifying crude DHDECMP and to measure the concentration of DHDECMP in various solutions. The Idaho work has been done with a Varian Aerograph (Varian Associates, Palo Alto, California) Model 2740 dual column machine equipped with a flame ionization detector and automatic linear temperature programmer. Stainless steel and glass columns packed with 1.5% OV-101 on Chromosorb G-HP have both been used successfully. A typical gas chromatographic spectrum of technical-grade DHDECMP obtained with the Idaho instrument is shown in Figure 6; the temperature was programmed from 100 to 260 °C at 8 °C per minute. Only the peak corresponding to the DHDECMP component is labeled in Figure 6. Spectra of increasingly pure DHDECMP, up to 98% purity, indicate thermal degradation during gas chromatographic analysis is negligible.

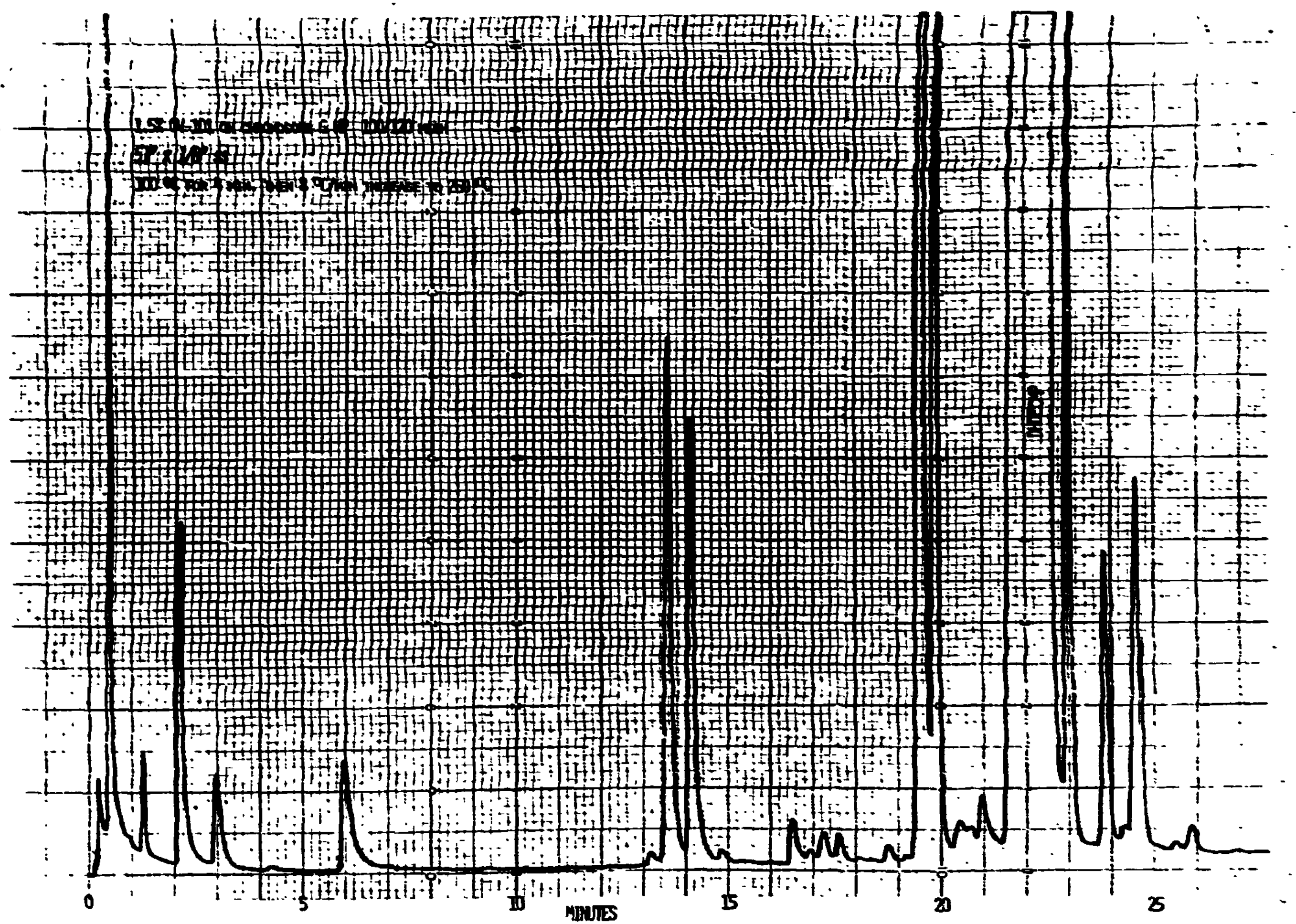


FIGURE 6

TYPICAL GAS CHROMATOGRAPH OF CRUDE DHDECMP

PROCESS APPLICATIONS

AMERICIUM-PLUTONIUM EXTRACTION FROM HANFORD PLUTONIUM RECLAMATION FACILITY WASTE

Research at Hanford on the properties of bidentate organophosphorus compounds relates to the potential use of such reagents to recover Am(III) and Pu(IV) from the acid waste (CAW stream) resulting from operation of Hanford's Plutonium Reclamation Facility. (Typically, the CAW stream contains 0.002 to 0.01 g/liter each of americium and plutonium [Table V]). The Plutonium Reclamation Facility is operated to recover and purify plutonium from a wide variety of metallurgical scrap including metal, oxide, and alloys. Chemical flowsheets for the reflux-type TBP solvent extraction process employed to recover plutonium from HNO_3 and HNO_3-HF solutions of such scrap have been described elsewhere.[16,17]

The latest bidentate extraction flowsheet for direct operation with CAW solution is presented in Figure 7; this flowsheet supersedes and updates earlier[4,5] versions. Americium and plutonium losses cited in Figure 7 are based on laboratory-scale mixer-settler tests in which four mixer-settler stages were used in extraction column runs and three mixer-settler stages in Am-partition and Pu-strip column runs. Principal features of the flowsheet in Figure 7 include:

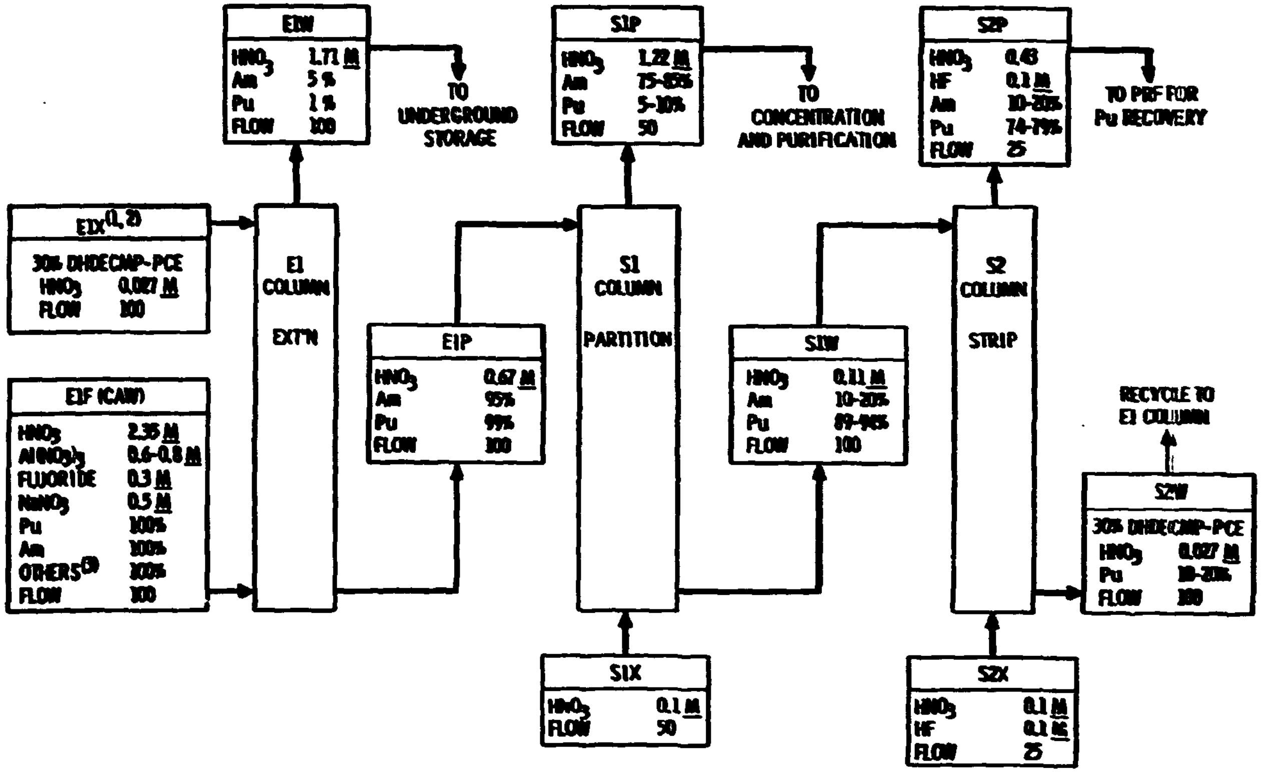
TABLE V

TYPICAL COMPOSITION OF HANFORD AND ICPP ACTINIDE WASTES

Hanford CAW Solution		ICPP First-Cycle Waste[(a,b)]	
Component	Concentration	Component	Concentration
NO_3	5.0M	F	3.12M
H	2.2M	NO_3	2.36M
Al	0.8M	H	1.51M
Na	0.5M	Al	0.68M
F	0.3M	Zr	0.44M
Fe	0.009M	B	0.22M
Si	0.002M	Fe	0.005M
Ca	0.001M	^{239}Pu	1.4×10^{-3} g/liter
Ce	0.007M	^{238}Pu	5.0×10^{-4} g/liter
Mg	0.0006M	^{240}Pu	3.4×10^{-4} g/liter
Ni	0.0003M	^{241}Pu	1.5×10^{-4} g/liter
Pu	0.002-0.01 g/liter	^{242}Pu	4.8×10^{-5} g/liter
^{241}Am	0.002-0.01 g/liter	^{241}Am	4.4×10^{-5} g/liter
		^{237}Np	1.2×10^{-5} g/liter
		^{243}Am	1.2×10^{-6} g/liter
		^{244}Cm	7.3×10^{-7} g/liter

(a) From co-processing of Zr-clad and Al-clad fuels.

(b) Partial analysis of actual waste from tank WM-185; estimates of concentrations of other components of ICPP first-cycle waste given in Reference 6.



NOTES:

(1) TCB MAY BE SUBSTITUTED FOR PCE

(2) DOES NOT INCLUDE RECYCLED Pu

(3) INCLUDES SMALL CONCENTRATIONS OF Ca, Mg, Fe, Cr, Ni, etc.

FIGURE 7

DHDECMP FLOWSHEET FOR Am-Pu RECOVERY FROM HANFORD CAW SOLUTION

- Coextraction of 95 to 98% of the americium and >99% of the soluble plutonium from acidic CAW solution with 30% DHDECMP-PCE (or TCB) solvent; equal flows of CAW and organic solvent are used in the extraction column.

- Use of a small volume of 0.1M HNO_3 to strip 75 to 85% of the extracted americium and 5 to 10% of the plutonium. The recovered americium and plutonium can be concentrated either by simple evaporation or, alternatively, by cation exchange prior to final separation and purification of the ^{241}Am.

- Stripping of residual americium and about 80 to 90% of the plutonium still left in the organic phase into a small volume of dilute HNO_3-HF solution for return to the mainline TBP plutonium recovery process.

The Hanford DHDECMP extraction scheme of Figure 7 is designed and intended to replace the present DBBP process which has been operated since 1970 to recover americium and plutonium from neutralized (0.1 to 0.25M HNO_3) CAW solution. In-line neutralization (with NaOH) of unbuffered CAW solution is a sensitive, difficult-to-control, head-end step. Failure to adjust the acidity of the CAW solution to the proper range for use with a DBBP solvent coupled with marginal extraction equipment and restricted aqueous-to-organic flow ratios is reflected in poor (~60%) plant-scale recovery of ^{241}Am. The DHDECMP process largely overcomes these disadvantages. Mixer-settler data in Table VI evidence the advantages of the DHDECMP process over the DBBP scheme in providing easier and better recovery of americium and plutonium. Even under the presently-used feed: extractant flow ratio of 4.2, the DHDECMP solvent recovers more americium (and plutonium) than does the DBBP extractant from a feed adjusted to near optimum acidity. (The superiority of the DHDECMP process over the DBBP extraction method is even more striking when the latter process operates with a more acidic [pH 0.33] feed.) Finally, at a more favorable feed: extractant ratio of 1, the DHDECMP flowsheet readily recovers over 95% of both the americium and plutonium from acid CAW solution.

The present DBBP Am-Pu recovery process operates with a nominal inventory of about 1000 liters of 30% DBBP-CCl_4 which is replaced about twice a year. Assuming a similar inventory and replacement frequency for a 30% DHDECMP extractant, approximately $30,000 to $45,000 of technical-grade DHDECMP, at present prices, would be required per year. Considering the improved recovery of valuable ^{241}Am which the DHDECMP flowsheet provides, this cost does not appear

TABLE VI

HANFORD BIDENTATE FLOWSHEET: TYPICAL MIXER-SETTLER EXTRACTION COLUMN TESTS

Aqueous feed for all runs was actual PRF CAW solution of composition listed in Table V.

	Stages		Relative Flows			Percent In Raffinate	
Extractant[(a)]	Extraction	Scrub	Feed	Extractant	Scrub	Am	Pu
30% DHDECMP	4	0	1	1	0	4.4	0.55
30% DHDECMP	4	0	2	1	0	15.6	2.9
30% DHDECMP	3	1	4.2	1	0.2[(b)]	22.7	2.6
30% DBBP	3	1	4.2[(c)]	1	0.2[(d)]	33.8	8.0
30% DBBP	3	1	4.2[(e)]	1	0.2[(d)]	51.8	7.7

(a) Diluent in all cases was TCB

(b) Scrub was 0.01$\underline{M}$ HNO_3

(c) Feed was adjusted to 0.26$\underline{M}$ HNO_3, pH = 0.66

(d) Scrub was 0.1$\underline{M}$ HNO_3 - 4$\underline{M}$ $NaNO_3$

(e) Feed was adjusted to 0.51$\underline{M}$ HNO_3, pH = 0.33

prohibitively high and, hopefully, might be reduced by improved solvent inventory management practices.

ACTINIDE EXTRACTION FROM IDAHO HIGH-LEVEL WASTE

The Idaho Chemical Processing Plant, located at the Idaho National Engineering Laboratory near Idaho Falls, is a multipurpose reprocessing facility for irradiated reactor fuels containing highly enriched uranium. Fuels routinely processed at ICPP include stainless-steel-clad fast-reactor fuels, aluminum-clad test-reactor fuels, and zirconium-clad fuels for which the enrichment before burnup varies from 50 to 93%.[18] The stainless-steel-clad fuel is electrolytically dissolved in HNO_3, the aluminum-clad fuels are dissolved in HNO_3-$Hg(NO_3)_2$, and zirconium-clad fuels are dissolved in HF. These multi-head-end dissolver solutions provide the feed for a single-solvent extraction system that is composed of a first cycle of TBP extraction followed by two cycles of methyl-isobutyl ketone extraction. The uranyl nitrate product from the extraction system is denitrated in a fluidized-bed denitrator to UO_3 for shipment.

The aqueous fission product wastes resulting from the ICPP solvent extraction operations contain small amounts of uranium and transuranium elements, primarily neptunium, plutonium, and americium, with traces of curium and transcurium isotopes. The safe and effective management of these nuclear wastes has been a primary goal of the ICPP operation for the past 25 years. The major technique has been to store the liquid waste safely for a period not to exceed five years and then solidify it into a granular oxide for storage in stainless steel bins inside a concrete vault. A program has been under way for the past three years now to assess the feasibility of removing alpha-emitting elements from ICPP liquid wastes prior to calcination. Because the estimated life of the calcine storage vaults is 1000 years, the goal of the program is to develop and demonstrate a process that will reduce the alpha activity in the calcined waste to less than 10 nCi/gram after 1000 years of decay.

The bulk of the waste generated at the ICPP to date has resulted from co-processing of Al- and Zr-clad fuel. A chemical analysis of a typical tank containing first-cycle raffinate from such co-processing is listed in Table V. The only actinides of significance in such raffinate after 1000 years of decay are americium and plutonium. A decontamination factor for these actinides of approximately 200 is needed to reach the 10 nCi/gram criteria 1000 years after calcination.

Early studies indicated DBDECMP was an effective extractant for removing actinides from ICPP first-cycle raffinate. However, as noted earlier, the high aqueous phase solubility of DBDECMP is a major deterrent. For this reason, current bidentate flowsheet development studies at Idaho are concentrated on the use of DHDECMP as the extractant.

Comprehensive data for the distribution of actinide, fission product, and inert constituents of ICPP high-level waste into 30% DHDECMP-xylene solvent are presented in Table VII. Also listed are partial data for the distribution of these elements between the DHDECMP extractant and potential scrub (6M HNO_3) and strip (0.05M HNO_3 - 0.05M oxalic acid) solutions. The extraction data were obtained by contacting synthetic Zr-Al raffinate, containing appropriate radiotracers, for five minutes at 23 °C with 30% DHDECMP-xylene solvent prepared from vacuum-distilled (80% pure) DHDECMP. (Neutron activation techniques were used to obtain data for extraction of aluminum and fluorine.) Distribution data for neptunium cited in Table VII were obtained with synthetic raffinate to which Cr(VI) had been added to oxidize Np(V) to Np(VI). The oxidation state of neptunium in actual ICPP first-cycle raffinate is not known; a mixture of Np(V) and Np(VI) is suspected. These data illustrate the efficiency of the DHDECMP solvent in extracting actinides and lanthanides [and Hg(II)] from ICPP first-cycle waste. Palladium, technetium, and ruthenium also extract fairly well into the DHDECMP solvent but, unlike Hg(II), can be removed by scrubbing the organic extract.

TABLE VII

DISTRIBUTION DATA FOR IDAHO 30% DHDECMP-XYLENE EXTRACTION SYSTEMS

	Distribution Coefficient				
Feed	Extraction(a,b)	Scrub(a,c)	Strip Contacts(a,d)		
Component	Contact	Contact	1	2	3
U(VI)	91.	27.	9.2	0.076	0.014
Np(VI)(e)	44.	29.	4.8	<0.10	
Pu(IV)	7.6	43.	0.04	<0.01	
Am(III)	5.0	3.7	0.34	0.006	
Ce(III)	3.6	3.8	0.52	0.015	
La(III)	3.5	4.2	0.48	0.016	
Nd(III)	3.1	3.4	0.34	<0.1	
Hg(II)	2.6	8.5	$\sim$30.	$\sim$20.	
Eu(III)	2.1	2.7	0.22	0.002	
Pd(II)	1.65	0.23	0.45	$\sim$3.	
Tc(VII)	1.10	0.25	1.8	2.3	
Ru(III,IV)	0.58	0.34	6.7	5.7	5.4
H^+	0.34				
Y(III)	0.30	0.66	0.039	<0.02	
Mo(VI)	0.27	0.14			
Nb(V)	0.13	0.074	0.032		
Rh(III)	0.12	0.056			
F^-	0.043				

TABLE VII (Continued)

Feed Component	Distribution Coefficient				
	Extraction Contact[a,b]	Scrub Contact[a,c]	Strip Contacts[a,d]		
			1	2	3
Ag(I)	0.032				
Zr(IV)	0.015	0.066	0.044		
Sr(II)	0.0094	<0.006			
Cr(III)	0.0087				
Ba(II)	0.0075	0.053			
Al(III)	0.0025				
In(III)	<0.004				
Cu(II)	<0.002	<0.02			
Fe(III)	<0.002	<0.005			
Co(III)	<0.001				
Cs(I)	0.00026	<0.004			
Rb(I)	0.00018				

(a) All values, except where noted, have an estimated uncertainty of ±10%.

(b) Measured with synthetic ICPP first-cycle high-level waste: 1.7M HNO_3 - 3.0M F - 2.11M NO_3 - 0.6M Al - 0.5M Zr containing 2.2 g/liter B, 0.24 g/liter Fe, 0.24 g/liter Na, 0.32 g/liter Sn, and 0.10 g/liter La.

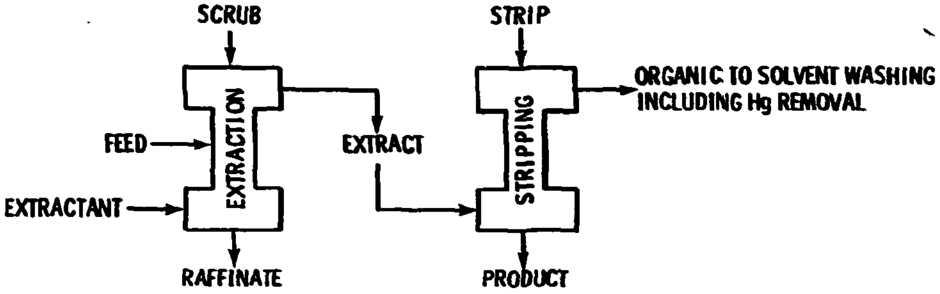
(c) Organic phase from extraction contact contacted with one-fifth volume of 6M HNO_3.

(d) Organic phase from scrub contact stripped three times with fresh equal volume portions of 0.05M HNO_3 - 0.05M $H_2C_2O_4$.

(e) Synthetic extraction feed adjusted to 0.01M Cr(VI).

The data in Table VII were used to draw up a conceptual flowsheet (Figure 8), a slightly modified version of which was subsequently successfully tested in miniature mixer-settler equipment with actual ICPP-produced waste.[19] The aqueous raffinate from the extraction column test (8 stages) contained, without any decay, only 6.6 nCi/gram of total actinides corresponding to decontamination factors from americium and plutonium of 1000 and 2700, respectively. (These decontamination factors are larger than the required 200, thus providing a safety margin to take care of possible variations in feed actinide concentration.) The organic raffinate from the strip column (8 stages) contained no detectable americium or curium, ^{106}Ru as the only gamma emitting fission product radionuclide, and only 0.2% of the plutonium in the extraction column product. Unstripped plutonium in this experiment represents, it is thought, material tightly bound by radiolysis products of DHDECMP generated during the 80 minutes the extractant was in contact with the high-level waste. Such bound plutonium can be effectively removed by contacting the DHDECMP phase with dilute oxalic acid solution. Radioruthenium can be removed from the bidentate solvent by washing with 0.5$\underline{M}$ Na_2CO_3 solution.

A flowsheet step still requiring resolution is how to remove mercury from the DHDECMP extractant before recycle to the extraction column. Electrolytic methods for removal of mercury have been demonstrated but need to be scaled up.



	FEED	EXT'NT	SCRUB	RAFF	EXTRACT	STRIP	PROD	ORG
FLOW RATE ℓ/hr	20	10	2	22	10	10	10	10
DHDECMP		30%			30%			30%
XYLENE		70%			70%			70%
F (M)	3.2			2.91				
NO_3 (M)	2.4		6.0	2.48	0.66	0.05	0.652	0.008
H (M)	1.6		6.0	1.70	0.66	0.05	0.652	0.008
Al (M)	0.6			0.55				
Zr (M)	0.5			0.45				
$H_2C_2O_4$ (M)						0.05	0.05	
Hg (M)	0.002				0.004			0.004
Pu (μg/ℓ)	2200			1.0	4398		4398	
Am (μg/ℓ)	40			0.036	79.92		79.92	
U (μg/ℓ)	1000				2000		2000	

FIGURE 8

CONCEPTUAL FLOWSHEET FOR DHDECMP
EXTRACTION OF ACTINIDES FROM ICPP HIGH-LEVEL WASTE

Efficiency of intercycle Na_2CO_3 washing for adequately removing solvent radiolysis products also remains to be demonstrated in continuous countercurrent tests with actual feed. No decision has been made on final disposition of separated actinides.

REMOVAL OF ACTINIDES FROM PUREX PROCESS HIGH-LEVEL WASTE

A study to determine the technical feasibility of partitioning actinides from Purex process high-level waste solutions is currently under way in the United States under the direction of the Oak Ridge National Laboratory. As part of this program, work is in progress at Idaho to explore possible applications of DHDECMP (and perhaps other bidentate extractants) for removing actinides from Purex process first-extraction cycle aqueous raffinate (HAW solution). The principal thrust of the Idaho investigations so far has centered on extraction-scrub-strip contacts (Table VIII) to measure distribution of various ions between a 30% DHDECMP-DIPB extractant and synthetic HAW solution containing 2.9<u>M</u> HNO_3, and 0.1<u>M</u> $NaNO_2$, and the various other constituents listed in Reference 19. Experimental and analytical techniques used in these distribution ratio measurements were identical to those used with synthetic ICPP waste (*cf.* p. 37).

As expected, 30% DHDECMP-DIPB extractant has a very high affinity for Pu(IV) and U(VI) in Purex process HAW

TABLE VIII

DHDECMP EXTRACTION-SCRUB-STRIP STUDIES WITH SYNTHETIC PUREX PROCESS FIRST-CYCLE WASTE (HAW) SOLUTION

Feed Component	Distribution Coefficients					
	Extraction Contact(a,b)	Scrub Contacts(a,c)		Strip Contacts(a,d)		
		1	2	1	2	3
Pu(IV)	304.	122.	25.	0.70	0.068	0.16
U(VI)	51.	62.	52.	13.9	2.74	2.40
La(III)	6.5	6.1	7.8	1.01	0.16	0.085
Ce(III)	5.8	5.2	7.1	1.02	0.18	<0.1
Pr(III)	5.3					
Nd(III)	4.3					
Am(III)	4.3	4.1	5.7	0.70	0.13	0.18
Pm(III)	4.2					
Sm(III)	3.4					
Eu(III)	2.9	3.2	3.3	0.46	0.086	0.048
Tc(VII)	2.3					
Np(V,VI)	2.2	2.0	3.6			
Gd(III)	2.1	2.4	2.6	0.33	0.061	
Zr(IV)	1.8	0.022	0.0028			
Y(III)	0.60	0.66	0.70	0.076	<0.1	
Pd(II)	0.53	0.47	0.41	1.10	1.20	2.8
Nb(V)	0.51	0.017	0.75			
Mo(VI)	0.39	0.10	0.041			

TABLE VIII (Cont'd)

Feed Component	Distribution Coefficients					
	Extraction Contact[a,b]	Scrub Contacts[a,c]		Strip Contacts[a,d]		
		1	2	1	2	3
Ru(III,IV)	0.27	0.96		15.	15.	
H^+	0.23					
Ag(I)	0.028	0.026				
Rh(III)	0.018					
Sr(II)	0.017	0.019				
Ba(II)	0.013	0.012				
Cd(II)	0.0067					
Cr(III)	0.0033					
Fe(III)	0.0015					
Rb(I)	0.00064					
Cs(I)	0.00050					

(a) All values, except where noted, have an estimated uncertainty of ±10%.

(b) Synthetic HAW solution of composition given in Reference 19 made $0.1\underline{M}$ $NaNO_2$, spiked with appropriate radio-tracers, and contacted five minutes at 23 °C with an equal volume of 30% DHDECMP-DIPB.

(c) Organic extract contacted twice with fresh one-fifth volume portions of $3\underline{M}$ HNO_3 - $0.05\underline{M}$ $H_2C_2O_4$ solution.

(d) Organic phase from final scrub contact stripped three times with fresh equal portions of $0.05\underline{M}$ HNO_3 - $0.05\underline{M}$ $NH_2OH \cdot HNO_3$.

solution. Distribution coefficients for Am^{3+} (and likely for Cm^{3+}) are similar to those for the lanthanides; hence, trivalent actinides and lanthanides will report to the DHDECMP phase along with Pu(IV) and U(VI). Under the conditions used, (0.1$\underline{M}$ $NaNO_2$ in the HAW) neptunium extraction was marginal; presumably, the HAW solution contained both Np(V) and Np(VI). Extraction behavior of Np(IV) from HAW solution containing a reducing agent such as N_2H_4 or $NH_2OH \cdot HNO_3$ has not yet been established. Of the non-actinide and lanthanide constituents of HAW solution, only Tc, Zr, Y, Pd, Nb, Mo, and Ru are extracted to any large extent by the DHDECMP solvent. Zirconium, niobium, and molybdenum are easily scrubbed from the DHDECMP phase by a 3$\underline{M}$ HNO_3 - 0.05$\underline{M}$ oxalic acid solution.

Dilute HNO_3 solutions containing a reducing agent such as $NH_2OH \cdot HNO_3$ readily strip trivalent lanthanides and actinides including Pu(III) from the DHDECMP-DIPB phase. Rare earth oxalate precipitates form when the DHDECMP solution resulting from extraction of synthetic HAW feed are contacted with dilute oxalic acid strip solution. Uranium is tightly held in the DHDECMP phase and is not removed by $HNO_3 \cdot NH_2OH$; it can, however, be stripped with 0.05$\underline{M}$ HNO_3 - 0.05 $\underline{M}$ $H_2C_2O_4$ solution. Uranium is also efficiently removed from DHDECMP solvents by washing them with 0.5$\underline{M}$ Na_2CO_3 solution. Alkaline solvent washes also remove ruthenium from the organic extractant. Behavior of technetium and palladium during scrubbing, stripping, and solvent washing steps has not yet been determined.

The very preliminary work completed thus far certainly indicates a satisfactory DHDECMP flowsheet can be devised for adequate removal of actinides from acidic Purex process waste streams. Much more batch data with both synthetic and actual wastes are required, however, before a conceptual flowsheet suitable for testing in laboratory and pilot plant scale continuous countercurrent extraction equipment can be prepared.

SUMMARY - FUTURE WORK

Research at both Idaho and Hanford has established efficient, practicable physical and chemical methods for preparing satisfactorily pure DHDECMP extractants from commercially-available technical-grade reagent. Mixer-settler tests at both sites have also demonstrated the capability and utility of DHDECMP-based solvent extraction processes for adequate removal of +3, +4, and +6 actinides from acid aqueous waste solutions. These actinide removal processes are now judged ready for engineering-scale tests with both synthetic and actual waste solutions.

Future bench-scale studies, in addition to developing new and/or improved DHDECMP extraction flowsheets, should emphasize determination of the properties of pure DHDECMP including identification of its gaseous and liquid radiolysis products. Studies to elucidate the nature and type of interactions between DHDECMP and carrier solvents and the consequences of such interactions upon actinide and lanthanide extraction are also needed. New, simplified, and hopefully, cheaper methods of synthesizing DHDECMP and other bidentate reagents may prove fruitful.

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