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THE TRUEX PROCESS: A VITAL TOOL FOR DISPOSAL OF U. S. DEFENSE NUCLEAR WASTE*

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Summary

The TRUEX (TRansUranium EXtraction) process is a generic actinide extraction/recovery process for the removal of all actinides from acidic nitrate and chloride nuclear waste solutions. Because of its high efficiency and flexibility and its compatibility with existing process facilities, TRUEX has now become a vital tool for the disposal of certain U. S. defense nuclear waste.

The development of TRUEX is closely coupled to the development of bifunctional extractants belonging to the carbamoylphosphoryl class and CMPO in particular. A brief review of the development of CMPO and its relationship to other bifunctional and monofunctional extractants is presented. The effect of TBP on CMPO, the selectivity of CMPO for actinides extracted from acidic nitrate media, the influence of diluents on CMPO behavior and 3rd phase formation, and the radiolysis/hydrolysis of CMPO and subsequent solvent cleanup will be highlighted.

Application of TRUEX in the chemical pretreatment of specific nuclear waste streams and a summary of the current status of development and deployment of TRUEX is presented.

I. INTRODUCTION

The synthesis and chemical properties of multifunctional organophosphorus extractants have been intensively investigated over the last two decades at the Argonne National Laboratory in the U. S. and in the USSR. A major achievement of the Argonne studies was the successful synthesis of the bifunctional extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (1). CMPO is the key reagent in the TRUEX (TRansUranium EXtraction) solvent extraction process, a generic process for the removal and recovery of all actinides from acidic nitrate and chloride nuclear waste solutions (2). Because of its high efficiency and flexibility and its compatibility with existing process facilities, the TRUEX process has now become a vital tool for the disposal of certain U. S. defense wastes.

Development of CMPO and its relationship to other bifunctional and monofunctional organophosphorus extractants is reviewed in this paper. Important parameters including selectivity of CMPO for actinide elements from acidic solutions, the effects of tributyl phosphate (TBP) concentration and type of hydrocarbon diluents on CMPO extraction behavior, third phase formation, and radiolytic effects are highlighted.

The paper concludes with a brief summary of the current status of engineering-scale development and deployment of the TRUEX process at the U. S. Department of Energy Hanford site.

II. CMPO

The key ingredient in the TRUEX process is the extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (abbreviated OøD[iB]CMPO or simply CMPO). CMPO was the result of several years of basic studies on the extraction of Am (III) and Eu (III) from nitrate media by extractants belonging to the carbamoylphosphoryl (CP) class.

The early recognition that the ability to extract Am (III) from high nitric acid concentrations by carbamoylmethylphosphonates was not due to chelation but rather to an

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intramolecular buffering effect was an important discovery (3). This discovery revealed that to design more efficient extractants in the CP class, emphasis should be placed on the basicity of the phosphoryl oxygen, not on the carbamoyl portion of the molecule. The carbamoylmethylphosphine oxides are the end products of attempts to increase D_{Am}. However, much effort had to be devoted to the determination of the role of substituents in modifying the properties of the extractant (4).

CMPO has a unique combination of substituents groups which give it very favorable properties as an actinide extractant. Most noteworthy is its ability to extract trivalent actinides from low to high concentrations of HNO_3 and from moderate to high concentrations of HCl and its phase compatibility with normal paraffinic hydrocarbons when mixed with TBP. (See section III.) Figure 1 shows a comparison of the distribution ratio of Am (III), D_{Am}, as a function of HNO_3 for CMPO and a series of monofunctional extractants of increasing basicity. The presence of intramolecular buffering effect is quite evident in the CMPO as well as the reduced basicity of CMPO relative to TOPO due to the inductive effect of the phenyl group. The latter property improves backextraction. Figure 2 shows the possible solution structure of the Am-CMPO-nitrato complex at high HNO_3 concentration. Structures of this type are supported by infrared and loading studies (5).

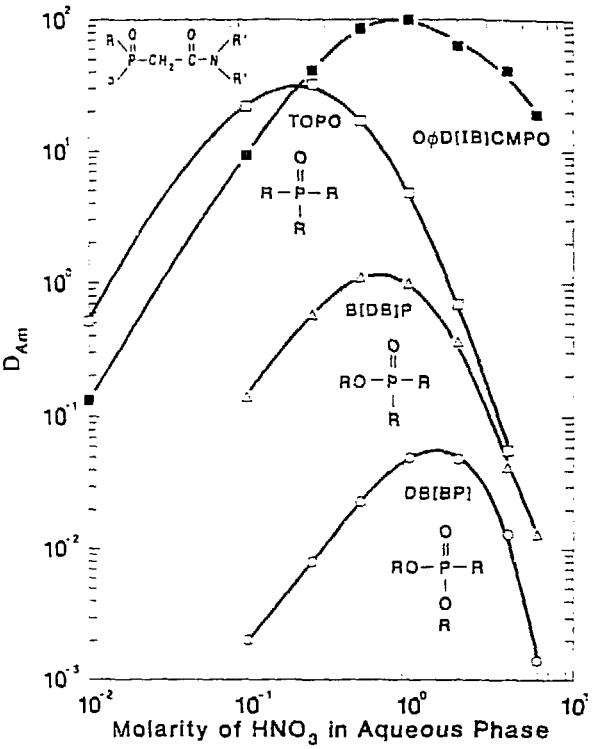

Fig. 1. 0.5 M Extractant in DIPB (di-isoprophylbenzene), 25°C B-butyl, O-octyl

III. TBP MODIFICATION AND THE INFLUENCE OF DILUENT

Although CMPO represented an improvement over other extractants belonging to the CP class, its propensity for third-phase formation when used with paraffinic hydrocarbons diluents was a major disadvantage and made the extractant impractical for use in nuclear fuel reprocessing facilities in the USA. However, it was discovered that a small concentration of CMPO in Purex process solvent (1.2 M TBP in dodecane) largely eliminated third-phase formation (6). In addition, D_{Am} increased at high HNO_3 concentrations, became very insensitive to HNO_3 concentration above 1 M HNO_3, and decreased at low HNO_3 concentrations used for backextraction. Figure 3 illustrates the effect of TBP on D_{Am} using tetrachloro-

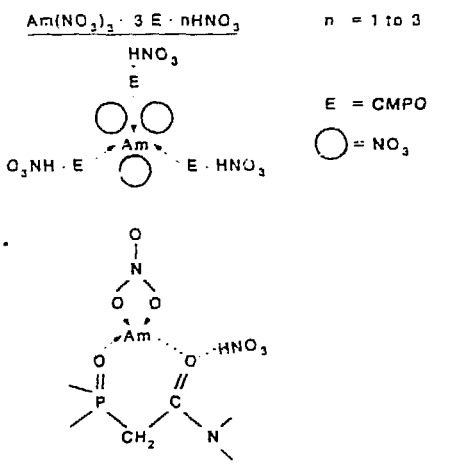

Fig. 2. Possible solution structure of the Americium nitrato-CMPO complex at high HNO_3 concentration

ethylene (TCE) as the diluent. (TCE was selected as the diluent to show the influence of TBP because D_{Am} can be measured with little or no TBP without third-phase formation. This is not possible when using dodecane.) The dramatic improvement in the properties of CMPO when used with an excess of TBP led to the development of the TRUEX process.

Figure 4 shows the effect that hydrocarbon chain length and branching has on the solubility of Nd (III) in 0.2 M CMPO -1.2 M TBP - hydrocarbon mixtures (7). The ordinate shows the maximum concentration of Nd (III) that can be extracted without third-phase formation as a function of the aqueous nitric acid concentration. Short chain length and branching reduce third-phase formation. Process solvent formulations consisting of 0.2 M CMPO -1.2 M TBP-Isoparaffinic C_{12} hydrocarbon (e.g., Isopar®-L) do not form third-phases on loading with Nd(III) at any HNO_3 concentration (7).

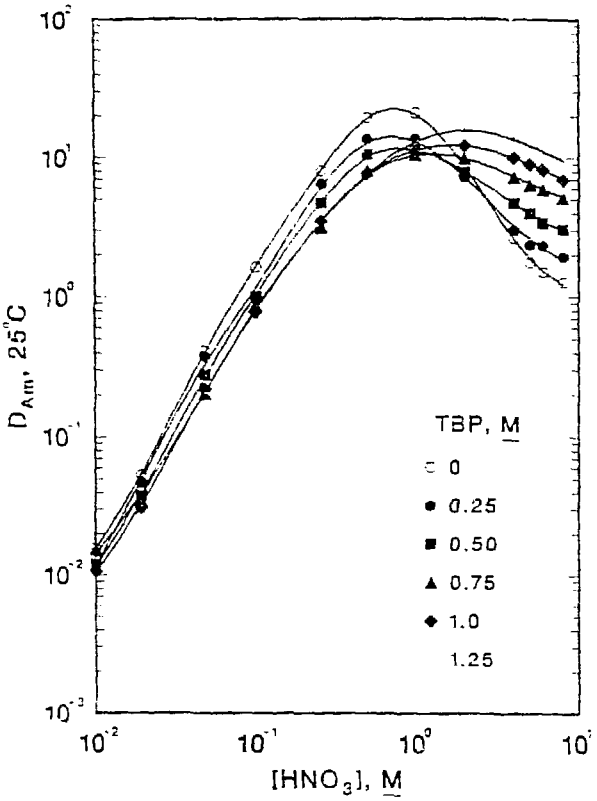

Fig. 3. Acid dependency of D_{Am} with 0.25 M CMPO in TCE for various TBP concentrations

Figure 5 shows the influence of diluent on the distribution ratio of the CMPO, D_{CMPO}. Carbon-14 labeled CMPO was used to make the measurements (8). The data were plotted using regular solution parameters. As expected, the fit is only approximate, but considering the high polarity of CMPO and the wide range of diluents studied, the correlation is very good. Of more practical interest is the correlation between D_{CMPO} and D_{Am}. Diluents that interact strongly with the extractant (through dipole-dipole or dipole-induced-dipole interactions) raise D_{CMPO} but lower D_{Am} (8). Figure 6 shows an approximate inverse first power relationship between log D_{Am} and log D_{CMPO} with CMPO for selected diluents. The large positive deviation for tris-2-ethylhexylphosphine oxide (TEHPO) may be explained by the creation of holes in the diluent structure for the $Am(NO_3)_3 \cdot 3CMPO$ complex as well as for the much smaller CMPO to occupy. Conversely, dodecane shows a negative deviation relative to octane which may be explained by dodecane's significantly larger molar volume and greater cohesiveness, making accommodation of the larger $Am(NO_3)_3 \cdot 3CMPO$ relatively more difficult than accommodation of the

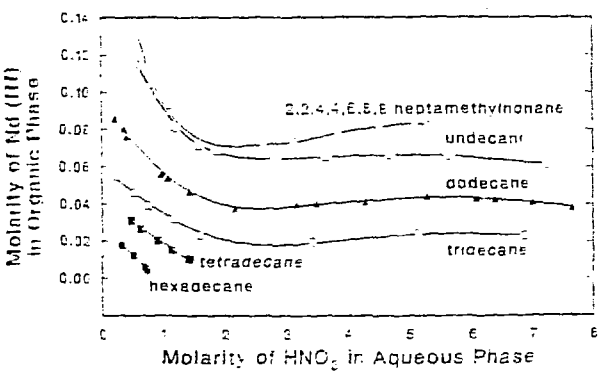

Fig. 4. Maximum loading of Nd(III) in 0.2 M CMPO-1.2 M TBP-NPH as a function of carbon chain length and branching

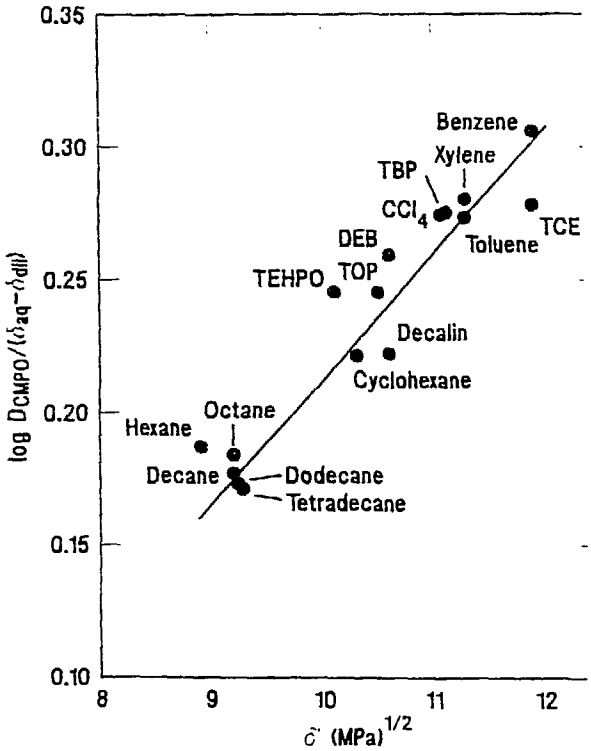

Fig.5. Distribution ratio of CMPO as a function of the solubility parameter of the diluent. (Ref. 8) 0.20-0.25 M CMPO-Diluent/0.25 M HNO_3

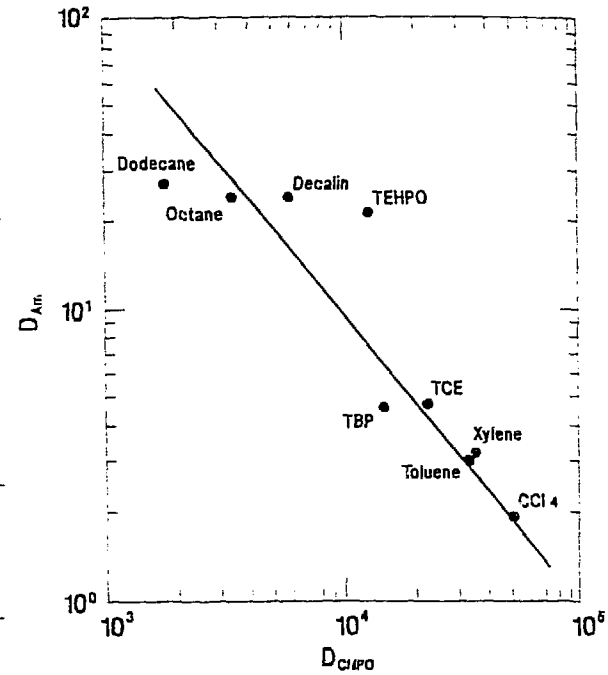

Fig. 6. Distribution ratio of Am(III) as a function of the distribution ratio of CMPO. (Ref 8) 0.20 M CMPO in diluent/0.25 M HNO_3

smaller uncomplexed CMPO. The data in Figs. 3-6 show the significant variations in extraction properties of CMPO that may be achieved by relatively small changes in diluent type and structure. These variations give one considerable flexibility in adapting CMPO to practical solvent extraction processes.

IV. TRUEX PROCESS: NITRATE MEDIA

The generic TRUEX process separation scheme is shown in Figure 7. The TRUEX process as practiced in the USA utilizes three different process solvent formulations: 0.20 M CMPO-1.2 M TBP-dodecane, 0.20 M CMPO-1.4 M TBP-Conoco® C_{12}-C_{14}, and 0.50 M CMPO in TCE. (Conoco® C_{12}-C_{14} is a normal paraffinic hydrocarbon with an average chain length of C_{13}. TCE is tetrachlorolethylene.) The first two process solvents are used for processing nitric acid waste solutions and the latter for processing chloride salt waste solutions. CMPO is commercially available in solvent

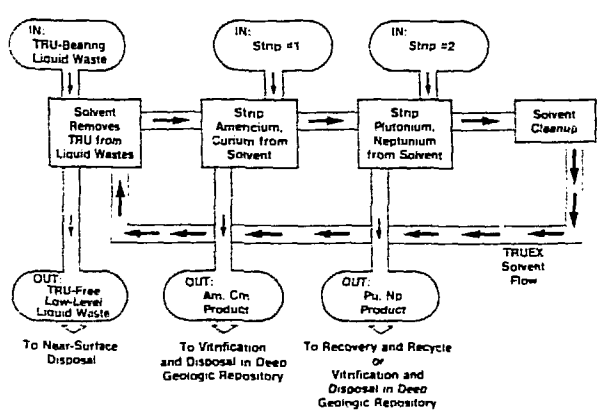

Fig. 7. Basic TRUEX process separation scheme

extraction (SX) grade purity (>95% pure) from Atochem North America, Inc. Philadelphia, PA 19102 (formerly M & T Chemicals, Inc., Rahway, NJ).

The distribution ratios of selected actinide as a function of the aqueous HNO_3 concentration are shown in Figure 8. Two features of these data are noteworthy: first, between 1 and 3 M HNO_3, the D's of actinides in the four different oxidation states differ from one another by an approximately constant factor; second, D_{Am} is insensitive to HNO_3 concentration between 1 and 6 M HNO_3. This latter feature is important from an engineering perspective because ^{241}Am is the major source of alpha activity in defense nuclear waste. Defense waste can vary widely in acidity, even within the same class of waste. Therefore, flowsheet design is substantially simplified having a system in which Am(III) does not vary widely over a wide range of possible feed acidities.

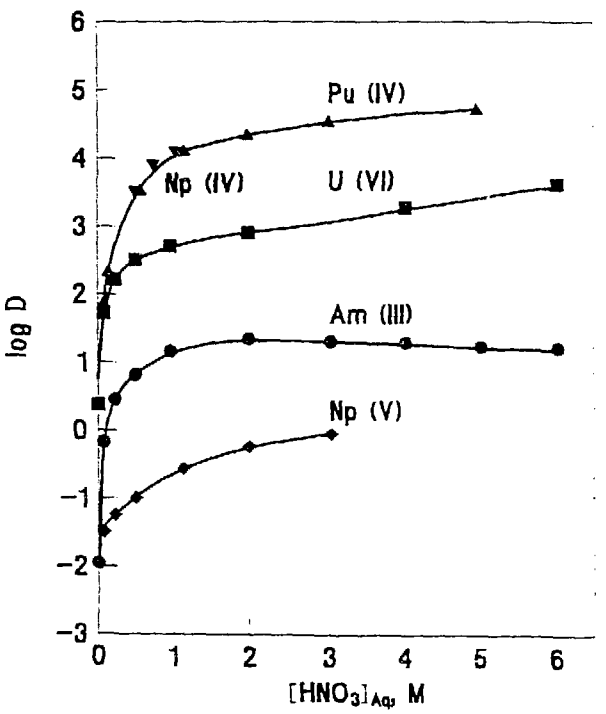

Fig. 8. Distribution ratios of selected actinide ions as a function of the aqueous nitric acid concentration. 0.2 M CMPO-1.2 M TBP-dodecane. 25°C (Ref 9)

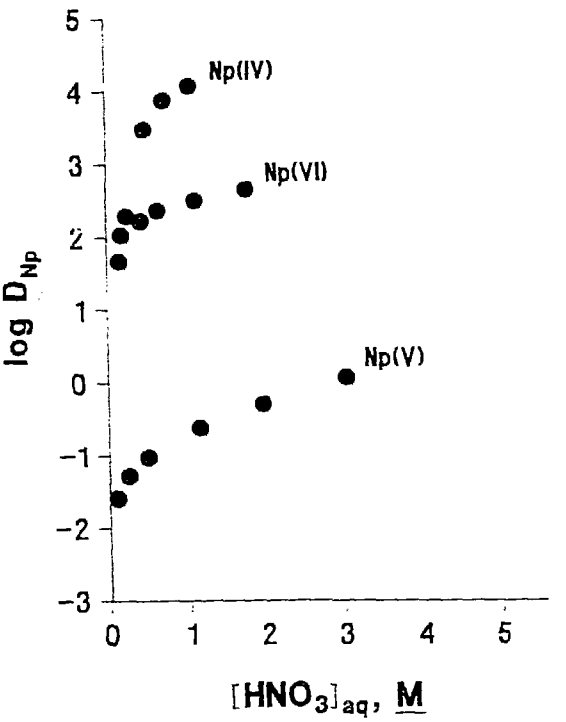

Fig. 9. Distribution ratio of neptunium as a function of the aqueous nitric acid concentration. 0.20 M CMPO -1.2 M TBP-dodecane. 25°C

Since Np(V) is not efficiently extracted by CMPO (Figure 8), the conversion of Np to either the (IV) or (VI) oxidation states is important. Figure 9 compares D_{Np} for the three oxidation states of neptunium commonly confronted in aqueous SX processes. The most effective way to remove Np in TRUEX processing is to reduce Np(VI) and (V) to Np(IV) with ferrous sulfamate. At the same time some Pu(IV) will be reduced to Pu(III). However, Pu(III) is readily oxidized to Pu(IV) in TRUEX process solvent by extracted nitrous acid (7). Thus, Np and Pu will both be in their (IV) oxidation states and remain together during stripping operations.

Table 1 shows the extractabilities of a number of inert constituents, fission products, and actinides from 1 to 3 M HNO_3 waste solutions using either of the TRUEX-NPH (normal paraffinic hydrocarbon) process solvent formulations. In addition to the extraction of U and the TRU's, the lanthanides and Tc are also removed. The extraction of Tc (as $HTcO_4$) (2) is a bonus since this element tends to migrate and its presence in low-level waste is not

acceptable in the USA. Oxalic acid is frequently used with HLW to improve the decontamination factor from Zr and Mo.

Table 1. Extractabilities of Elements from Nitric Acid (1 to 3 M) Waste using TRUEX Process Solvent

Distribution Ratio Range				
<0.05		0.01 to 1	1 to 20	>20
Be	Rb	*Zr	Y	Th
Na	Sr	*Mo(VI)	Tc	U(VI)
Mg	Rh	Ru	La	Np(IV)
Al	Ag	*Pd	Ce	Pu(IV)
K	Cd		Pr	
Ca	In		Nd	
Cr(III)	Sb		Pm	
Mn(II)	Te		Sm	
Fe(III)	Cs		Eu	
Co(II)	Ba			
Ni			Am	
Cu			Cm	
Zn				

* D's lowered by oxalate ion

Backextraction or stripping of loaded TRUEX solvent is usually performed in two steps. The first step involves the selective partitioning of trivalent actinides (e.g., Am) from tetravalent actinides (e.g., Pu) using 0.04 M HNO_3 (see Figure 7). The second stripping step involves the backextraction of tetravalent actinides using a dilute HNO_3-HF mixture or oxalic acid if trace amounts of actinides(IV) are present. Uranyl ion and pertechnetate are stripped with Na_2CO_3 during the solvent washing step. The selective partitioning of Am from Pu on backextraction is an important feature of the flowsheet developed for processing plutonium scrap waste (see Fig. 7). Four separate contercurrent tests runs on PFP waste produced Am product which contained only 7% of the Pu and a Pu product which contained only 1% of the Am. The behavior of Am in the strip stages is closely linked to the purity of the CMPO (10). Therefore, Am stripping has been used to define the specifications for SX-grade CMPO.

All the actinides can be very effectively stripped together using a solution of either vinylidene-1,1-diphosphonic acid or 1-hydroxyethane-1,1-diphosphonic acid (11). The diphosphonic acids are particularly useful stripping agents if the TRU's are to be vitrified rather than recovered for useful purposes.

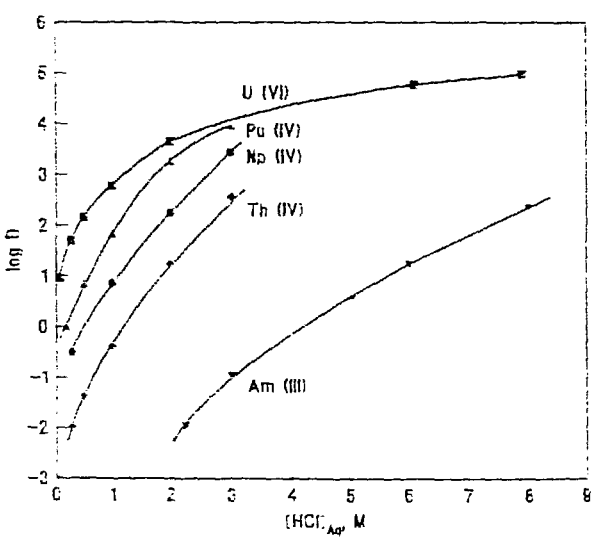

Fig. 10. Distribution ratios of selected actinide as a function of the aqueous hydrochloridic concentration 0.5 M CMPO in TCE. 25°C (Ref 12)

V. TRUEX PROCESS: CHLORIDE MEDIA

The generic TRUEX separation scheme shown in Figure 7 applies also to processing TRU chloride salt waste. However, the extraction of actinide-chloro is considerable ions weaker and less selective than the extraction of the corresponding

nitrate complexes. Figure 10 shows the distribution ratios of selected actinides as a function of the HCl concentrations using 0.5 M CMPO in TCE (11). The data show that at least 6 M HCl is required for efficient extraction of Am(III). However, magnesium and calcium chlorides are effective salting-out agents, and their presence reduces substantially the amount of HCl required for efficient extraction of Am(III).

Table 2 shows the extractabilities of a number of elements from 6 M HCl using 0.5 M CMPO in TCE. Unlike the nitrate system, a number of nonactinide and nonlanthanide elements show significant extraction. Generally, a TRUEX-chloride process would be preceded by a preliminary extraction with a monofunctional extractant, e.g., TBP or TOPO to remove transition and post-transition elements (12). The primary use of the TRUEX-chloride process is to remove ^{241}Am and traces of Pu from chloride salt waste.

Table 2. Extractabilities of Elements from Hydrochloric Acid (6 M) using TRUEX Process Solvent

Distribution Range			
$<10^{-2}$	10^{-2} to 10^{0}	10^{0} to 10^{2}	$>10^{2}$
Be	Mn(II)	V	Fe
Na	Co(II)	Zn	Ga
Mg	Ni	Cd	Zr
Al	Pb(II)	Sn	Mo
K			
Ca		Am	Th
Cr(III)		Cm	U(VI)
			Np(IV)
			Pu(IV)

Selective partitioning of Am from Pu is readily achieved in TRUEX-chloride using 1 to 2 M HCl. Plutonium is then backextracted with dilute HCl and a reducing agent or oxalic acid (12).

VI. RADIOLYSIS AND SOLVENT CLEANUP

The radiolysis, hydrolysis and solvent cleanup of TRUEX process solvent have been studied extensively by the Argonne Separations Group (13-15). G values for the disappearance of CMPO in CMPO-TBP formulations have been calculated for three different media (13). The G (-CMPO) values are: dodecane (1.2± 0.3), TCE (4.5 ± 0.3), and CCl_4 (16.4 ± 1.7). These data show that CMPO is more stable in NPH than it is in chlorinated diluents. Both neutral and acidic degradation products are formed on radiolysis of TRUEX process solvent. Neutral compounds and their concentrations that are formed after 60 watt-hours per liter absorbed dose from ^{60}Co gamma radiation followed by water scrubbing to neutrality (15): methyloctylphenylphosphine oxide (1.7×10^{-3} M), and octyl(phenyl)-N-monoisobutylcarbamoylmethylphosphine oxide (8.6×10^{-3} M). Acidic compounds present under the same conditions are (15): dibutyl phosphoric (3.3×10^{-3} M), octyl(phenyl)phosphinic acid (3.3×10^{-3} M), octyl(phenyl)phosphinylacetic acid (4.2×10^{-3} M). On hydrolysis, only the acidic compounds are observed. The presence of the acidic compounds elevates D_{Am} under stripping conditions and therefore is regarded as deleterious (11).

Sodium carbonate scrubbing will remove a large fraction of the acidic hydrolytic and radiolytic degradation products from the process solvent (15). In the case of hydrolytic degradation, a Na_2CO_3 wash will restore the TRUEX process solvent to pristine condition except for the small loss of TBP and CMPO by hydrolysis (3 to 4% of the CMPO was lost after 8 weeks of continuous mixing with 5 M HNO_3 at 50°C). In the case of radiolysis (up to 100 watt-hours/liter absorbed dose), carbonate washing will not restore the process

solvent to pristine condition, although the quality of the solvent, as measured by D_{Am} at 0.04 M HNO_3, is sufficient for continuous countercurrent stripping, especially if macroquantities of iron or lanthanides are present (10,15). However, a secondary solvent cleanup using a new batch treatment with macroporous anion exchange resin will restore irradiated TRUEX process solvent to pristine condition, even after receiving an absorbed dose of 100 watt-hours/liter (15). (10% of the CMPO was lost after irradiation to 100 watt-hours/liter).

An additional solvent cleanup step using the 1,1-diphosphonic complexants described earlier has been recently developed (11). The diphosphonic acid complexants are used to completely remove the last traces of actinides from spent solvent prior to carbonate washing. This procedure avoids generating a TRU contaminated alkaline wash stream and resin (if secondary cleanup is used). Since the new complexants are designed to be readily destroyed by catalytic oxidation, the strip solution can be recycled into an appropriate feed solution.

VII. TRUEX TEST-RUNS

Table 3 summarizes the test-runs that have been performed at Hanford. The plutonium finishing plant (PFP) waste stream was processed in a continuous countercurrent mode using centrifugal contactors. The test runs performed on the other waste streams involved batch shake-out experiments. In no case was any difficulty encountered in reducing the TRU concentration well below the 100 nCi/g level required for non TRU waste.

Table 3. Summary of Demonstration of TRUEX Process with Representative Nuclear Waste Solutions

Waste Type	Type of Demonstration		System Performance	
	Bench	Pilot	TRU D.F.	Effluent TRU Concentration (nCi/g)
PFP Waste[a]	x	x	10^4	1 - 2
Complexant[b] Concentrate	x		10^2	1
Neutralized Cladding Removal Waste[c]	x		10^3	<1
Fuel Reprocessing HLW[d]	x		5×10^5	2

[a] Hanford Plutonium Finishing Plant acidic waste

[b] Alkaline aqueous waste solution containing large concentrations of organic complexants such as EDTA.

[c] Alkaline Slurry (solution and solids) resulting from addition of NaOH to NH_4F-NH_4NO_3-Zr cladding waste.

[d] Acidic high-level waste from Purex processing of commercial LWR fuel.

VIII. CONCLUSIONS

Although some aspects of CMPO chemistry remain to be studied, e.g., structure of organic phase complexes and the exact role of TBP as a modifier, our knowledge of the synthesis, purification and properties of this extractant is sufficient to predict confidently its performance in engineering-scale TRUEX process applications. Batch and countercurrent tests of the TRUEX process with various actual waste solutions have been uniformly very successful. Pilot plant-scale countercurrent tests of the TRUEX process with an actual Hanford site waste solution will begin in 1992 or 1993; full plant-scale TRUEX process operation at Hanford is scheduled to begin in the 1996-99 time frame.

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