Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Truex Process and the Management of Liquid Tru Uwaste

W. W. Schulz[a]; E. P. Horwitz[b]
[a] Westinghouse Hanford Company, Richland, Washington, USA [b] Chemistry Division, Argonnne National Laboratory, Argonne, Illinois, USA

To cite this Article Schulz, W. W. and Horwitz, E. P.(1988) 'The Truex Process and the Management of Liquid Tru Uwaste', Separation Science and Technology, 23: 12, 1191 — 1210
To link to this Article: DOI: 10.1080/01496398808075625
URL: http://dx.doi.org/10.1080/01496398808075625

SEPARATION SCIENCE AND TECHNOLOGY, 23(12&13), pp. 1191-1210, 1988

THE TRUEX PROCESS AND THE MANAGEMENT OF LIQUID TRU WASTE

W. W. Schulz
Westinghouse Hanford Company
MISN-R2-23, P. O. Box 1970
Richland, Washington, USA

E. P. Horwitz
Chemistry Division
Argonnne National Laboratory
Argonne, Illinois, USA

ABSTRACT

The TRUEX (TRansUranium EXtraction) process is a new generic actinide extraction/recovery process for the removal of all actinides from acidic nitrate and chloride nuclear waste solutions. A brief review of the relevant chemistry of the TRUEX process and a summary of the current status of development and deployment of TRUEX process flowsheets to treat specific acidic waste solutions at several U.S. DOE sites is presented.

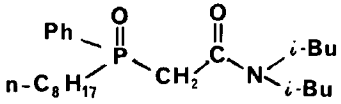
INTRODUCTION

The TRUEX (TRansUranium EXtraction) process is a new generic liquid-liquid extraction process for removal of all actinides from acidic (nitrate or chloride) nuclear waste solutions (1,2). Because of its high efficiency and great flexibility, the TRUEX process appears destined to be widely used in the U.S. and possibly in other countries for cost-effective management and disposal of transuranic (TRU) wastes. In the U.S., TRU wastes are those that contain $>3.7\text{x}10^6$ Bq/kg) of TRU elements with half-lives greater than 20 y.

This paper gives a brief review of the relevant chemistry and summarizes the current status of development and deployment of the TRUEX process flowsheets to treat specific acidic waste solutions at several U.S. Department of Energy (DOE) sites.

TRUEX Process Chemistry

General. The TRUEX process was developed by E. P. Horwitz and co-workers at the Argonne National Laboratory (3-7). The key ingredient in TRUEX is the new actinide-lanthanide selective extractant called octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [abbreviated OϕD(iB)CMPO or simply CMPO]. Its structural formula is:



CMPO is commercially available in solvent extraction (SX) grade purity (>95% pure) from M&T Chemicals, Inc., Rahway, N.J. One of the critical specifications for SX-grade CMPO is that it contain less than ≤0.02 wt% of certain acidic impurities such as octylphenylphosphinic acid, which reduces the stripping efficiency of Am(III) with dilute nitric acid (8a). CMPO has a unique combination of substituent groups which give it very favorable properties as an actinide extractant (8b). Most noteworthy are its ability to extract trivalent actinides from low to high concentrations of nitric acid and from moderate to high concentrations of HCl and its phase compatibility with a wide variety of diluents when mixed with TBP. In the extraction of both the nitrato and chloro complexes of trivalent (as well as tetra- and hexavalent) actinides and tri- and tetravalent lanthanides, CMPO behaves as a neutral extractant. The stoichiometries of the extracted species have been determined by extractant dependency and loading studies (8b,9). The extraction equilibria for Am(III) from nitric and hydrochloric acid may be represented by the following equations:

$$\mathrm{Am}^{3+} + 3\mathrm{NO}_3^- + \overline{3\mathrm{E}\cdot(\mathrm{HNO}_3)_n} \rightleftarrows \overline{\mathrm{Am}(\mathrm{NO}_3)_3\cdot\mathrm{E}_3(\mathrm{HNO}_3)_m} + (3n-m)\mathrm{HNO}_3 \qquad n = 0 \text{ to } 2,\ m = 0 \text{ to } 3 \tag{1}$$

$$\mathrm{Am}^{3+} + 3\ \mathrm{Cl}^- + \overline{3\mathrm{E}\cdot(\mathrm{HCl})_n} \rightleftarrows \overline{\mathrm{AmCl}_3\cdot\mathrm{E}_3\cdot(\mathrm{HCl})_m} + (3n-m)\mathrm{HCl}\ , \qquad n = 0 \text{ to } 1,\ m = 0 \text{ to } 1 \tag{2}$$

where E represents the extractant and the bar denotes a species in the organic phase. In both cases the complexes appear to be anhydrous, i.e., the water of hydration of the Am(III) is removed by the strong ion-dipole bond formed between the tripositive actinide and the electronegative phosphoryl oxygen. As shown in the above equations, the protonated form of the extractant, which is present at high acidities, is able to extract Am(III) despite the competition between hydrogen ions and Am(III) for the basic phosphoryl oxygen donor group. This property is characteristic of extractants containing the carbamoylmethylphosphoryl moiety and may be explained by the protonation of the carbonyl groups while the phosphoryl group bonds to the metal ion. The protonated carbonyl group is probably acting as a shield against incoming acid through electrostatic interactions. We named this property the intramolecular buffering effect (8b). The effect does not exist when a monofunctional phosphine oxide is mixed with an aliphatic amide. This hypothesis is supported by FTIR studies (10) and chemical analysis of solutions containing macroconcentrations of neodymium(III) nitrate and chloride extracted by OϕD(iB)CMPO (9). (Nd is a good stand-in for Am.) Both studies show the presence of HNO_3 and HCl associated with the metal ion-CMPO complex. The infrared studies indicate that the carbonyl group in the Nd complex is protonated when extraction occurs.

The efficiency of CMPO solutions for extracting tri-, tetra-, and hexavalent actinides from a wide range of HNO3 concentrations and from moderate to high hydrochloric acid concentrations is shown in Figures 1, 2, and 3, respectively. The differences in the distribution ratios, D, of actinides in the III, IV, V, and VI oxidation states is typical of their behavior with less complex monofunctional extractants, although the D values are greatly elevated with CMPO.

The data in Figures 1, 2, and 3 show that the Am nitrato-CMPO complex is much more extractable than the Am chloro-CMPO complex at low to moderate acid concentrations. This difference in extractability is due to the soft donor properties and greater hydration energy of the chloride ion relative to the nitrate ion. However, extraction of Am chloro complexes is feasible because the activity coefficient of hydrochloric acid increases very rapidly with concentration. Because D_{Am} is third-power dependent on chloride ion activity (see Eq. 2), one observes very rapid increases in the distribution ratio above 1 M HCl, as shown in Fig. 3. The noteworthy feature of the nitrate system in Fig. 1 is the region between 0.7 M and 6 M HNO3 where D_{Am} is relatively insensitive to acidity. This is the region where the intramolecular buffering effect takes place. A similar region in the chloride system is less evident because HCl concentrations above 8 M HCl cannot be studied due to third phase formation.

TRUEX process solvent. Table 1 summarizes the compositions of the TRUEX process solvents used for various types of waste solutions. When processing nitric acid wastes solution, TRUEX process solvent always contains TBP. The primary function of TBP is to prevent the formation of a second organic phase ("third phase" formation) which occurs when CMPO-paraffinic hydrocarbons mixtures are equilibrated with metal nitrate and/or nitric acid solutions (4,5,11). However, using CMPO in an excess of TBP has a number of other beneficial effects besides improving phase compatibility. TBP reduces the sensitivity of D_{Am} to acidity above 1 M HNO3, enhances D_{Am} above 2 M HNO3, reduces D_{Am} below 1 M HNO3 and reduces the effects of acidic degradation products (1,2,4,5).

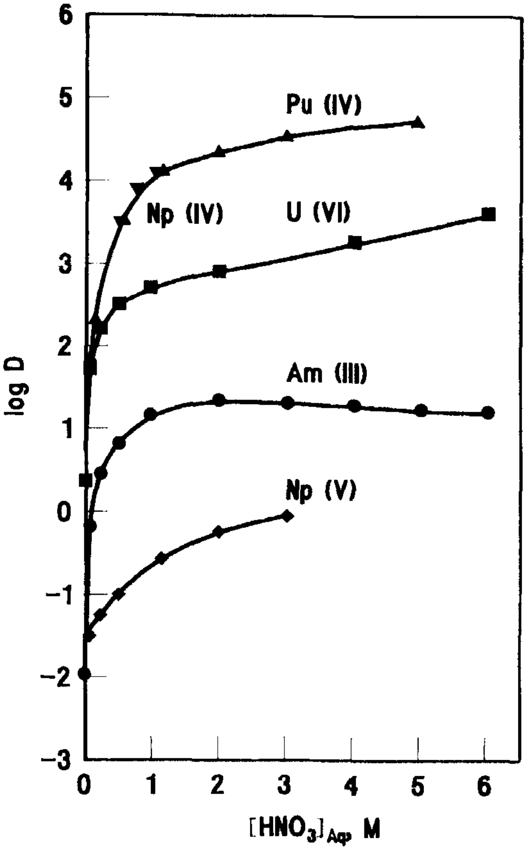


Fig. 1. Distribution ratios of selected actinide ions as a function of the aqueous nitric acid concentration. 0.20 M CMPO - 1.2 M TBP-dodecane. 25°C

Although third phase formation does not readily occur with CCl_4 and TCE diluents, except at high solvent loadings, TBP also improves phase compatibility in both the TCE/HNO_3 and TCE/HCl systems (9,11,12). However, only in the TCE/HNO_3 system does TBP have the beneficial effects on D_{Am}. In the corresponding chloride system TBP has a slight suppressing effect on D_{Am} (9,12).

TRUEX flowsheet features. Table 2 summarizes the flowsheet features of the TRUEX process for different kinds of waste. The

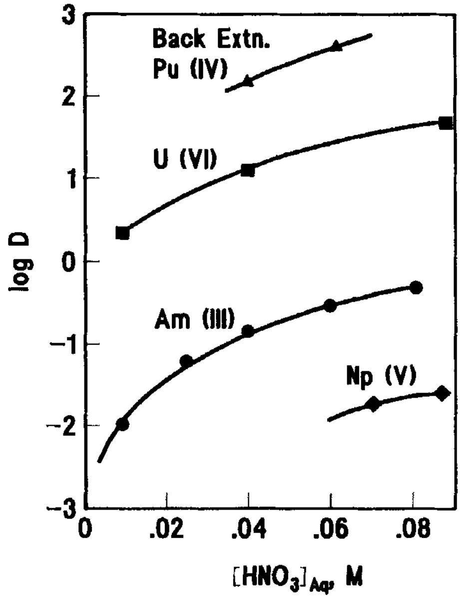


Fig. 2. Distribution ratios of selected actinide ions from low nitric acid concentration. 0.20 M CMPO - 1.2 M TBP-dodecane. 25°C

basic features of all TRUEX flowsheets are essentially the same; extraction of a feed containing high nitrate or chloride concentration, a scrub step to achieve additional decontamination from impurities, and a strip step performed at low nitrate or chloride concentration aided by the presence of a complexing agent such as fluoride or oxalate ion.

Aside from the lanthanides, the TRUEX process provides very good decontamination from most common metallic and nonmetallic impurities when the feed is an aqueous nitrate solution. Differences in flowsheets for treating nitric acid waste streams are dictated primarily by the presence or absence of fission products. Aside from actinides, CMPO extracts trivalent light lanthanides, and to a lesser extent Zr, Tc, Pd, and Fe (1-6). High HNO_3 concentrations enhance the extraction of Zr and Fe, whereas moderate HNO_3 concentrations favor extraction of Tc and Pd (8). Co-extraction of Fe and Zr and to some extent Pd can be largely suppressed by addition of oxalic acid to the feed. A HNO_3-oxalic acid scrub gives additional decontamination of these elements.

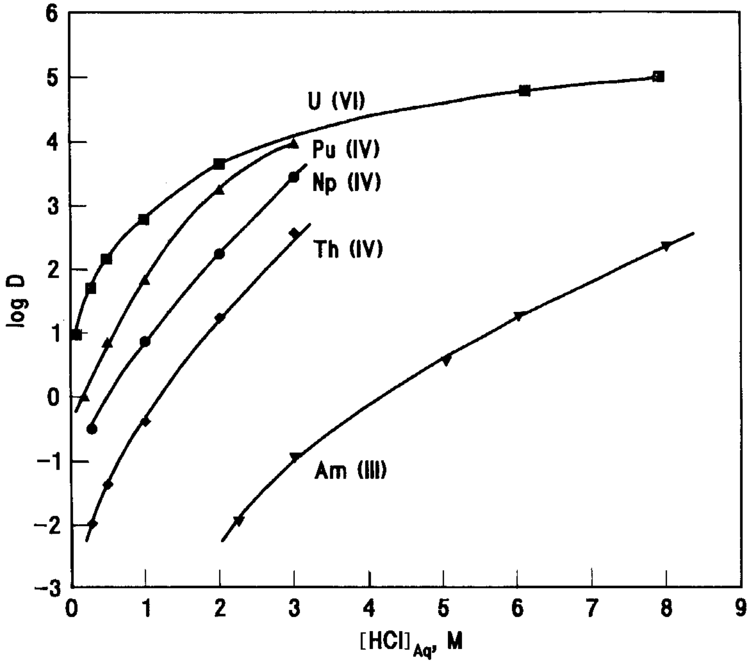


Fig. 3. Distribution ratios of selected actinide ions as a function of the aqueous hydrochloric acid concentration. 0.50 M CMPO in TCE. 25°C

One of the noteworthy features of CMPO is that it is capable of extracting tri-, as well as tetra-, and hexavalent actinides from chloride media. However, unlike extractions in nitrate media, to effectively extract Am(III) one must have a high chloride concentration supplied by either HCl and/or $MgCl_2$ or $CaCl_2$ (8). Furthermore, CMPO does not have the high selectivity for actinides over many metallic impurities when extraction takes place from aqueous chloride solution. For example, Zr, Fe(III), Ga, Sn, Zn, and Cd are all effectively extracted by CMPO from HCl solutions. Nevertheless, CMPO will selectively extract actinides from alkali and alkaline earth chlorides and from aluminum chloride. Alkali and alkaline earth chlorides are the major constituents in chloride salt wastes.

One of the attractive features of the TRUEX process is that selective partitioning of trivalent actinides (and lanthanides) from tetra- and hexavalent actinides can be achieved through pro-

TABLE 1. TRUEX Process Solvents

CMPO, M	TBP, M	Diluent	Use
0.20	1.2 to 1.4	Normal Paraffinic Hydrocarbon C_{12}-C_{13}	HLW
0.25	1.2	Iso-Paraffinic Hydrocarbon C_{12}	HLW
0.25	0.75 to 1.0	CCl_4, TCE*	Pu Scrap Waste
0.50	0 to 1.0	TCE*	Chloride Salt Waste

*TCE = tetrachloroethylene

TABLE 2. TRUEX Flowsheet Features

Application	Scrub	Strip	Concentration Factor*
HLW	Dilute HNO_3 or	Dilute HNO_3 (Am,Cm)	TRU (III) - 3
	HNO_3-oxalic acid	HF or $H_2C_2O_4$ (Pu,Np)	TRU's (III,IV) - 10 to 25
Pu Scrap Waste	Dilute HNO_3	Dilute HNO_3 (Am)	Am (III) - 3
		Dilute HNO_3-HF (Pu)	Pu (IV) - 6
Chloride Salt Waste	6 $\underline{M}$ HCl	1 to 2 $\underline{M}$ HCl (Am,Th)	Am - 5 to 10
		HF or $H_2C_2O_4$ (Pu,Np,U) or Reductant (Pu,Np)	Pu, Np - 5 to 10

*Conc. Factor = [TRU] in Strip/[TRU] in Feed per choice of nitric acid concentrations as shown in Fig. 2 in the expanded D vs. 0.02 M to 0.1 M HNO_3 curve and in Fig. 3. For example, 0.04 M HNO_3 or 2 M HCl selectively strips Am(III) (and trivalent lanthanides if present), while tetra- and hexavalent actinides largely remain in the organic phase. Dilute aqueous HNO_3-HF solution effectively removes tetravalent actinides [e.g., Pu(IV), Np(IV)] and any residual Am(III). Hexavalent actinides are removed during the solvent cleanup with 0.25 M Na_2CO_3 solution. On the other hand, tri-, tetra-, and hexavalent actinides can be stripped together using 0.1 M oxalic acid.

Solvent degradation and cleanup. Hydrolytic and radiolytic degradation of CMPO has been studied extensively over the last two years by the Argonne group (13,14). Hydrolytic and radiolytic degradation of CMPO both lead to the formation of neutral and acidic compounds. The only deleterious degradation product identified is octyl(phenyl)phosphinic acid H[O(ϕ)P]. H[O(ϕ)P] will reduce the efficiency of Am(III) stripping; however, it is readily removed during the solvent cleanup step by 0.25 M Na_2CO_3. The degradation studies performed to date have subjected the TRUEX process solvent to more severe treatment than it will likely see under actual process applications. Even under most of these treatments the process solvent can be largely restored to its original condition. Therefore, it seems unlikely that either hydrolysis or radiolysis will have a significant harmful effect on the performance of the TRUEX process solvent.

TRUEX Process Deployment

Deployment incentive. Engineers and scientists at three U.S. DOE Sites [Hanford, Los Alamos National Laboratory (LANL), Idaho Falls] are actively pursuing application of the TRUEX process to various candidate acidic wastes generated at these sites. Work to deploy the TRUEX process at Hanford and LANL Sites is relatively far along while TRUEX process feasibility studies are just underway at the Idaho Site.

Practical waste management concerns at all three DOE sites provide strong motivation to consider deployment of the TRUEX process. Removal of TRU elements, particularly ^{241}Am, from large volumes of certain acidic wastes generated at each of these sites will convert them from a TRU-type ($>3.7\times10^6$ Bq kg^{-1}) waste requiring expensive deep geologic disposal to a low-level waste which can, in many instances, be disposed of safely and inexpensively in near-surface facilities.

Hanford Site

PFP waste. The principal application of the TRUEX process at the Hanford Site is the removal of ^{241}Am and plutonium from the Plutonium Finishing Plant (PFP) aqueous acidic waste (Table 3). The uranium concentration of PFP waste ranges from zero up to a maximum of about 0.02 M depending on whether or not scrap containing uranium is processed. The PFP waste normally does not contain either inert or radioactive lanthanides, and other species (e.g., Zr, Tc, Pd) which are extracted to some extent by CMPO are also not present. Thus, in many respects, the PFP acidic waste is an "ideal" feed to the TRUEX process.

Process flowsheet. The generic TRUEX process chemical flowsheet for removal of plutonium and americium from acidic nitric acid wastes of the typical composition listed in Table 3 is shown in ref. 9.

Features of the flowsheet used for processing the PFP waste include:

- Countercurrent contact of the aqueous acidic PFP waste with TRUEX process solvent (0.25 M CMPO - 0.75 M TBP-TCE) to extract soluble ^{241}Am and plutonium values. Conditions (5 stages, organic/aqueous flow ratio = 0.333) are chosen to reduce the total concentration of TRU elements in the aqueous raffinate to 3.7×10^5 Bq kg^{-1} (10 nCi/g), a factor of 10 below the limit for TRU waste.

- Any uranium in the PFP waste co-extracts with the plutonium and americium; small amounts of iron also co-extract. The distribution ratio for Fe(III) under countercurrent extraction column conditions is about 0.29. Other components (Table 3) of the PFP waste are not extracted by the TRUEX process solvent.

- Co-extracted iron can be removed from the CMPO extract by contacting it with a small volume of 0.25 M HNO_3. Generally four scrub stages are recommended.

- Essentially all the ^{241}Am, accompanied by less than 1% of the plutonium, can be effectively stripped from the scrubbed CMPO phase by countercurrent contact (5 stages) with an equal volume of 0.05 M HNO_3. Most of the iron not previously scrubbed from the organic phase reports to the ^{241}Am strip solution.

- Following removal of ^{241}Am, the organic phase is contacted (4 stages) with one half its volume of 0.05 M HNO_3 - 0.05 M HF solution to strip the plutonium, along with residual ^{241}Am and iron. The plutonium product solution is suitable for recycle to a TBP extraction circuit in the Plutonium Reclamation Facility (PRF), a part of the PFP.

- Very little uranium, which is co-extracted with the ^{241}Am and plutonium, strips with either TRU element. But, dilute Na_2CO_3 solution, through formation of anionic tris

TABLE 3. Composition of Candidate TRUEX Process Feeds at the U.S. DOE Hanford Site

PFP[a] Waste		CC[b] Liquid Waste	
Constituent[c]	Concentration, M	Constituent[d]	Concentration
NO_3^-	3.0	Na	9.9 M
HNO_3	1.5	NO_3^-	3.6
Al	0.43	NO_2^-	1.1
F^-	0.09	CO_3^{2-}	1.1
U	0 to 0.02	$Al(OH)_4^-$	0.37
Pu	10^{-5} to 10^{-4}	OH^-	0.18
^{241}Am	10^{-6} to 10^{-5}	TOC[e]	0.039 kG L^{-1}
		^{137}Cs	1.4×10^6 Bq mL^{-1}
		$^{89,90}Sr$	6.4×10^5
		^{241}Am	1.9×10^3
		$^{239,240}Pu$	2.1×10^2

[a] Plutonium Finishing Plant.

[b] Complexant Concentrate.

[c] Concentrations of Be, Cr, Ni, Cu, Zn, and Pb all $<6 \times 10^{-4}$ M.

[d] Small ($<10^{-2}$ M) concentrations of Mg, Mo, Cr, Zn, Cd, Ca, Cu, Pb, Zr, Ba, La, Ni, and Nd also present.

[e] TOC = Total Organic Carbon.

> carbonato uranium(VI) species, effectively removes uranium from the CMPO-TBP-diluent phase. Aqueous carbonate solutions, as noted previously, also serve to wash the TRUEX process extractant free of degradation products of both TBP and CMPO. Because the preceding HNO_3-HF step so effectively removes both plutonium and ^{241}Am from the CMPO reagent, spent carbonate solvent washes are low-level wastes.

One product of TRUEX process operation with PFP waste is a dilute HNO_3 aqueous solution containing ^{241}Am and small amounts of plutonium and iron. Currently, it is anticipated that this americium concentrate would be converted to a high density solid form suitable for interim storage at the Hanford Site and eventual shipment and disposal at the Waste Isolation Pilot Plant repository in New Mexico. Of course, if desired for some reason, the ^{241}Am could be purified from plutonium and iron to produce a product, e.g., AmO_2, suitable for beneficial use.

Although not indicated in Table 3, PFP aqueous waste typically contains varying amounts of finely divided (~1 micrometer diameter) TRU-bearing solids. These solids include PuO_2, magnesium silicate (added to improve phase disengaging in the PRF TBP extraction process), and other unidentified miscellaneous solids introduced into the PRF extraction process. Because the particulate matter usually contains high concentrations of TRU elements, it must be removed to assure that the aqueous raffinate from the TRUEX process contains less than 3.7×10^6 Bq kg^{-1} (<100 nCi/g) of TRU elements. Adequate removal of TRU-bearing solids can be accomplished by filtration of the PFP aqueous waste prior to TRUEX process operation and by post-TRUEX process deep-bed (diatomaceous earth) filtration of the aqueous raffinate.

Development/implementation status. Under the direction of Westinghouse Hanford Company, Argonne National Laboratory (ANL) personnel completed at the end of FY1987 development of all required TRUEX process technology including reference flowsheet conditions for routine cleanup of the CMPO-TBP-TCE solvent. A key part of the ANL development effort included a very successful countercurrent demonstration of the TRUEX process in 4-cm dia. centrifugal contactors. The ANL test employed synthetic PFP waste spiked to full feed levels of ^{241}Am, plutonium, and uranium. The aqueous raffinate at steady state contained only about 10^5 Bq kg^{-1} of TRU elements, well below the design basis of 3.7×10^5 Bq kg^{-1} or the required 3.7×10^6 Bq kg^{-1} for low-level waste.

To facilitate transfer of TRUEX process technology, ANL fabricated and shipped to the Hanford Site eight 4-cm centrifugal contactors and also assisted in procurement of kilogram quantities of solvent-extraction grade CMPO. Engineers (Rockwell Hanford and, later Westinghouse Hanford Company) at the Hanford Site assembled and tested, with non-radioactive solutions, a suite of

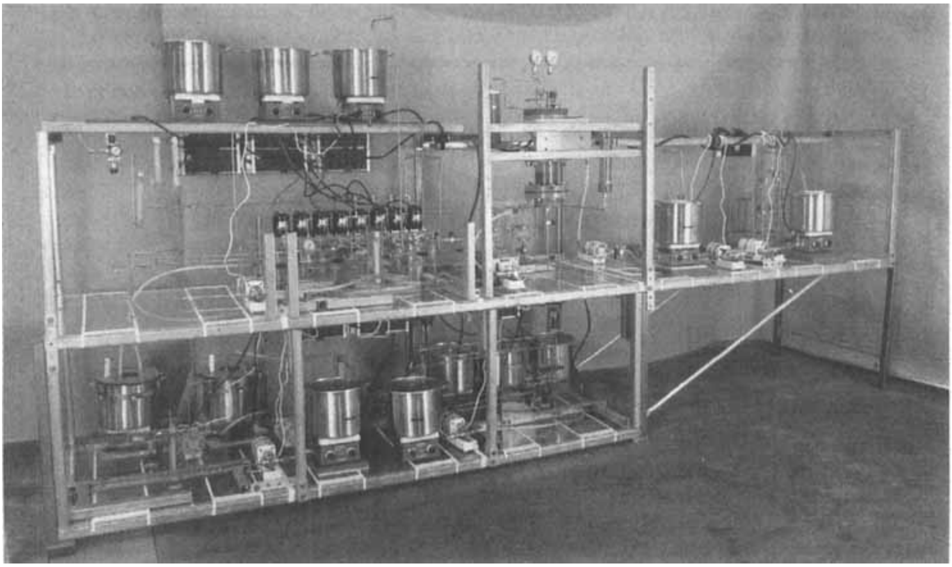


Fig. 4. Laboratory-scale TRUEX process equipment for tests with PFP waste.

TRUEX process solvent extraction and solid-liquid separation equipment and associated tankage and transfer lines (Figure 4). Late in FY1987, this suite of laboratory-scale equipment was installed in a glove box facility in the PFP to conduct a planned sequence of TRUEX process tests with actual PFP aqueous waste.

Table 4 lists conditions and results of the first two very successful countercurrent TRUEX process runs made with actual PFP waste. All units of the laboratory-scale equipment functioned extremely well. The cross-flow microfilter unit efficiently and satisfactorily removed finely-divided solids from the sample of PFP waste. In each of the duplicate runs 10 liters of clarified feed were processed without any difficulty through the centrifugal contactor equipment in about 40 minutes. Most importantly, the TRU element content of the aqueous raffinate in each run was about a factor of 10 to 100 below the 100 nCi/g specification for a TRU-type waste. Additional TRUEX process tests using 16 rather than eight contactors are in progress with PFP waste containing varying concentrations of TRU elements.

TABLE 4. Initial TRUEX Process Tests with Actual PFP Waste

Feed: Clarified PFP Waste Containing 603 uCi/L Pu + ^{241}Am

Solvent: 0.25 M CMPO - 0.75 M TBP-TCE

Scrub: 0.1 M HNO_3

Stages[a]: 5 Extraction, 3 Scrub

Flows: Feed/Scrub/Solvent = 250/50/100

Aqueous Raffinate: TRU uCi/L

Run 1	Run 2
1.1	3.2

Initial plans for deployment of the TRUEX process in the PFP envisioned start-up of prototype-scale (10-cm dia. centrifugal contactors) process operation in FY1991. Because of several presently-unresolved important Hanford Site issues (i.e., restart of N Reactor, future PFP mission, etc.) the actual date for implementation of a production-scale TRUEX process in the PFP is highly uncertain. Present (FY1988) plans call for continued operation of the installed laboratory-scale solvent extraction/solid-liquid separation equipment with actual PFP waste. Results from such tests are expected to enhance the technology base to support a deployment decision and to provide valuable TRUEX process operating experience for operation of a TRUEX process with other candidate Hanford Site wastes.

Other Hanford wastes. In addition to the PFP waste, the TRUEX process is also applicable to removal of TRU elements from several other Hanford Site wastes including Complexant Concentrate (CC), Neutralized Cladding Removal Waste (NCRW), and, if a decision should be made to retrieve them, Single-Shell Tank (SST) wastes. In each case there appears to be a substantial economic incentive to partition these TRU wastes to a large volume of low-level waste suitable for near-surface disposal and a small volume of TRU waste destined for deep geologic disposal.

Complexant Concentrate (Table 3) is an alkaline liquid waste containing high concentrations of various organic complexing agents such as EDTA, HEDTA, and citric acid as well as many radiolytic and chemical degradation products of the primary organic species. CC wastes were generated during previous recovery of ^{90}Sr from neutralized pre-1983 Hanford PUREX process high-level waste. Results (15) of bench-scale scouting tests with simulated waste solutions clearly demonstrate that the TRUEX process provides excellent removal of TRU elements from acidified CC waste. Limited batch extraction tests with actual CC waste confirm the simulated waste data.

There are currently about 2,300 m^3 of Neutralized Cladding Removal Waste (NCRW) stored at the Hanford Site. This waste consists of the solids (principally $ZrO_2 \cdot XH_2O$) which precipitated when the spent NH_4F-NH_4NO_3 waste produced during chemical decladding of Zircaloy-clad N-Reactor fuel was made alkaline. The NCRW contains sufficient TRU elements to be classified a TRU waste. Preliminary tests with the actual NCRW indicate it can be dissolved in HNO_3 or HNO_3-HF solutions to yield a satisfactory TRUEX process feedstock.

The 149 single-shell tanks at the Hanford Site contain 150,000 m^3 of a mixture of solid salt cake (e.g., water-soluble sodium salts), solid sludge [primarily hydrated iron(III) oxide] and a small volume of interstitial liquid. Essentially all the plutonium, ^{241}Am, and ^{90}Sr in the SST waste are contained in the sludge fraction. How and where the SST waste will be finally disposed of has not yet been decided. It is anticipated, however, that any SST waste which might be retrieved would be treated with water to dissolve the salt cake fraction. The resulting aqueous solution, after separation from the undissolved sludge, would presumably be a low-level waste suitable for disposal in near-surface facilities. The dissolved sludge fraction is a suitable feed for the TRUEX process. From extensive experimental evidence with simulated dissolved sludge waste, the TRUEX process has been shown to be applicable to the removal of all TRU elements from an acidic (HNO_3 or HNO_3-oxalic acid) solution of the sludge (6). Processing of the TRU-bearing sludge by the TRUEX process would greatly reduce the amount of waste requiring deep geologic disposal.

Idaho Site.

The Idaho Chemical Processing Plant (ICPP), located at the U.S. DOE Idaho Site, is a multipurpose reprocessing facility for irradiated reactor fuels containing highly-enriched uranium. Materials routinely processed at the ICPP both currently and in the past include Zr-clad fuels for which the uranium enrichment before burnup varies from 50 to 93% as well as stainless-steel-clad fast reactor fuels and Al-clad test-reactor fuels. The Fluorinel Process used to dissolve the various highly-enriched fuels employs as a dissolvent a HNO_3-HF solution containing cadmium and boron as neutron poisons.

At the ICPP, high-level aqueous wastes resulting from solvent extraction of uranium from Fluorinel Process dissolver solution are calcined to a mixture of oxides which is then stored in large stainless-steel bins at the Idaho Site. The unique nature of fuels processed at the ICPP and the process chemicals required to dissolve the fuels results in a large amount of inert material in the waste calcine. For example, calcine obtained from the reference Fluorinel Process contains, typically, (wt%) 56.5 CaF_2, 23.2 ZrO_2, 6.0 CdO, 5.5 Al_2O_3, 4.1 CaO, 0.5-2 total nitrate, and 0.5-1.5 miscellaneous. (Prior to calcination, calcium is added in excess to the waste solution to convert the fluoride to inert CaF_2.) Significantly, actinides and fission products comprise less than 1 wt% of the calcine.

Approximately 3,000 m^3 of calcined high-level waste, produced from about 20,000 m^3 of high-level waste, are currently stored at the U.S. DOE Idaho Site (16). By 2030, as much as 180,000 m^3 of high-level waste will have been generated as the result of anticipated increased fuel reprocessing activity. Intensive laboratory and engineering studies are in progress at the Idaho Site to develop, demonstrate, and select technology for disposal of current and future calcined waste (16). One part of the technology development effort is concentrated on methodology for conversion of the calcine to a glass or ceramic form suitable for disposal in a geologic repository. Driven by economic considerations, other technology studies are focussed on procedures or processes (e.g., TRUEX) which can be used to greatly reduce the amount of calcine which must be converted to a glass or ceramic form.

At the Idaho Site the TRUEX process is being considered for treatment of both retrieved (and acidified) calcine and currently-generated high-level solvent extraction waste. In both applications the goal is to partition the waste into a small volume of highly radioactive (e.g., TRU elements plus fission product lanthanides and ^{99}Tc) waste and a large volume of low-level waste containing nearly all the inert constituents (e.g., Ca, Al, B, etc.) and relatively short-lived fission products. The former material, after conversion to a suitable immobile form, may be disposed of in a deep geologic repository while the large amount of low-level waste may be disposed of in grout form in near-surface facilities.

Current experimental TRUEX process tests at the Idaho Site are closely modeled after the investigation performed a decade earlier by McIsaac and associates using dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) in place of CMPO (17,18). Thus, batch extraction TRUEX process tests with simulated ICPP high-level waste spiked with radioactive tracers and a CMPO-TBP-NPH solvent have been completed; results for TRU and other elements were in good agreement with behavior expected from the data of Horwitz, et al. (5,6). Data from these tests clearly demonstrated, as expected, that the TRUEX process is applicable to selective and efficient removal of TRU elements from Idaho Site high-level waste. Preparations are now in progress to execute TRUEX process batch contact tests with actual high-level waste. Subsequent countercurrent process tests in centrifugal contactors installed in a hot cell are planned; the required contacting equipment is now being procured.

Los Alamos Site.

Various pyrochemical processes, e.g., electrorefining, direct oxide reduction, molten salt extraction, etc., for production and purification of plutonium metal are routinely performed at the U.S. DOE Los Alamos Site (19). These processes, which typically employ molten NaCl, KCl, $MgCl_2$ and/or $CaCl_2$, generate large amounts of waste salts containing mg to g amounts of plutonium and mg amounts of ^{241}Am.

Figure 2 and Tables 1 and 2 illustrate the general conditions for removing TRU elements from any aqueous acidic chloride solution. The TRUEX process, for example, is applicable to extraction of plutonium and ^{241}Am from aqueous solution of the individual spent chloride salts from the ER, DOR, or MSE processes or mixtures of such salts (7). The generic TRUEX process chloride flowsheet derives from and is based upon the process chemistry described earlier. Because CMPO extraction of TRU elements from aqueous chloride media depends so greatly on chloride ion concentration, extraction feed preparation must be carefully controlled to provide sufficient salting strength (7). Also, to further assure satisfactory extraction of TRU elements, the CMPO concentration in the TRUEX-chloride process flowsheet is set at twice what it is in the TRUEX-nitrate process flowsheet (0.5 $\underline{M}$ vs. 0.25 $\underline{M}$). (See Table 1.) Once extracted into the CMPO phase, Am can be stripped with 2 $\underline{M}$ HCl and Pu can be reductively stripped with a dilute HCl-ascorbic acid solution or 0.1 $\underline{M}$ sodium formaldehyde sulfoxylate. Alternatively, both Am and Pu can be stripped with dilute HCl-oxalic acid solutions.

Some of the spent chloride solid wastes which are candidate TRUEX process feedstocks contain relatively large amounts of plutonium. Other types of spent chloride salts contain large amounts of one or more metal impurities which are appreciably extracted by the TRUEX process CMPO solvent. For these reasons, it may be desirable, in some cases, to couple the TRUEX process to a preceding solvent extraction process employing a monofunctional extractant (e.g., TBP, TOPO, quaternary ammonium compound, etc.) intended to remove plutonium or contaminant metals. The purpose of this initial extraction process is to prepare a feed solution more suitable for TRUEX process extraction, decontamination and separation of plutonium and ^{241}Am than that obtained when the spent chloride salt is dissolved in aqueous HCl.

Development/implementation status. A broad-based experimental program is underway at the LANL to investigate and demonstrate application of the TRUEX process to removal of TRU elements from all of the various types of spent chloride salts generated there. The key element in this experimental work is a bank of 16 ANL-type centrifugal contactors (4-cm dia.) constructed of chloride-resistant Hastelloy-F. Presently, this extraction equipment is being used to develop a TRUEX process for treatment of the spent chloride salt produced in various pyrochemical process operations. The objective is to develop a TRUEX process which satisfactorily couples with the TBP extraction scheme used to recover most of the plutonium values in certain pyrochemical process salt; aqueous raffinate from the TBP process is the feed to the TRUEX process. Initial countercurrent TRUEX process tests indicate satisfactory extraction of plutonium and ^{241}Am can be accomplished provided the feed solution contains a sufficiently high chloride ion concentration.

ANL personnel in a cooperative effort with the LANL staff are continuing their studies of the fundamental chemistry of the TRUEX process when applied to chloride media. A major goal of these studies is to improve and optimize the generic TRUEX process for routine recovery and purification of large amounts of plutonium from high concentrations of coextractable impurities.

ACKNOWLEDGMENT

The development of the TRUEX process and associated chemistry was funded by the Division of Chemical Sciences, Office of Basic Energy Sciences, DOE. The testing and implementation of TRUEX for PFP waste and chloride salt waste was funded by Rockwell Hanford Operations and the Los Alamos National Laboratory, respectively.

REFERENCES

1. Horwitz, E. P. and W. W. Schulz, Solvent Extraction and Recovery of the Transuranic Elements from Waste Solutions using the TRUEX Process, in "Solvent Extraction and Ion Exchange in the Nuclear Feed Cycle," Eds. D. H. Logsdail and A. L. Mills, Ellis Horwood Limited, Chichester, England, September 1985, p. 137.

2. Horwitz, E. P. and W. W. Schulz, "Application of the TRUEX Process to the Decontamination of Nuclear Waste Streams," presented at the International Solvent Extraction Conference (ISEC-86), Munich, FRG, September 11-16, 1986.

3. Horwitz, E. P., H. Diamond, D. G. Kalina, L. Kaplan, and G. W. Mason, "Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine Oxide as an Extractant for Actinides from Nitric Acid Waste," presented at the International Solvent Extraction Conference (ISEC'83), Denver, Colorado, August 27-September 2, 1983.

4. Horwitz, E. P. and D. G. Kalina, Solvent Extr. Ion Exch., 2, 179 (1984).

5. Horwitz, E. P., D. G. Kalina, H. Diamond, George Vandegrift, and W. W. Schulz, Solvent Extr. Ion Exch., 3, 75 (1985).

6. Horwitz, E. P., D. G. Kalina, H. Diamond, L. Kaplan, G. F. Vandegrift, R. A. Leonard, M. J. Steindler, and W. W. Schulz, "TRU Decontamination of High-Level PUREX Waste by Solvent Extraction Utilizing a Mixed Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine Oxide/TBP/NPH (TRUEX) Solvent" in Lanthanide/Actinide Separations, Eds., G. R. Choppin, J. D. Navratil, and W. W. Schulz, World Scientific Publications, Singapore, 1985.

7. Horwitz, E. P., H. Diamond, and K. A. Martin, Solvent Extr. Ion Exch., 5, 447 (1987).

8. a. Gatrone, R. C., L. Kaplan, and E. P. Horwitz, Solvent Extr. Ion Exch. 5(6) (1987).; b. Horwitz, E. P., K. A. Martin, H. Diamond, and L. Kaplan, Solvent Extr. Ion Exch., 4, 449 (1986).

9. Horwitz, E. P., H. Diamond, K. A. Martin, and R. Chiarizia, Solvent Extr. Ion Exch., 5, 419 (1987).

10. Martin, K. A., E. P. Horwitz, and J. R. Ferraro, Solvent Extr. Ion Exch., 4 1149 (1986).

11. Kolarik, Z. and E. P. Horwitz, Solvent Extr. Ion Exch., 6, 61 (1988).

12. Kolarik, Z. and E. P. Horwitz, Solvent Extr. Ion Exch., 6, (1988), in press.

13. Chiarizia, R. and E. P. Horwitz, Solvent Extr. Ion Exch., 4, 667 (1986).

14. Nash, K. L., R. C. Gatrone, G. A. Clark, P. G. Rickert, and E. P. Horwitz, "Hydrolytic and Radiolytic Degradation of OϕD(iB)CMPO: Continuing Studies," 5th Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 26-29, 1986.

15. Chiarizia, R. and E. P. Horwitz, Solvent Extr. Ion Exch., 5, 175 (1987).

16. Knecht, D. A., J. R. Berreth, N. A. Chipman, H. S. Cole, B. A. Stables and W. B. Kerr, "Scoping Studies to Reduce ICPP High-Level Radioactive Waste Volumes for Final Disposal," Waste Management, 86, R. G. Post, Editor, Vol. 2, 461, 1986.

17. McIsaac, L. D., J. D. Baker, and J. W. Tachyk, U.S. ERDA Report ICP-1080, Allied Chemical Co., Idaho Falls, ID, 1975.

18. McIsaac, L. D., J. D. Baker, D. H. Meikrantz, and M. C. Schroeder, "Experimental Studies at the Idaho Chemical Processing Plant on Actinide Partitioning from Acid Nuclear Wastes," Proceedings of Intl. Conf. on Nuclear Transmutation, July 22-25, 1980, University of Texas, Austin, TX, 407, 1981.

19. Christensen, D. C., J. D. Williams, J. A. McNeese, and K. W. Fife, "Plutonium Metal Preparation and Purification at Los Alamos - 1984," in Actinide/Lanthanide Separations, G. R. Choppin, J. D. Navratil, W. W. Schulz, Eds., World Scientific Pub. Co., Singapore, 238, 1985.