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## ORNL Review of TRUOX Flowsheet Proposed for Deployment at the Rockwell Hanford Plutonium Finishing Plant

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Chemical Technology Division

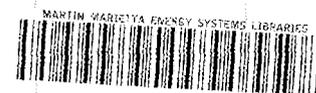
ORNL REVIEW OF TRUEX FLOWSHEET PROPOSED FOR DEPLOYMENT  
AT THE ROCKWELL HANFORD PLUTONIUM FINISHING PLANT\*

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ABSTRACT

The Transuranium Extraction (TRUEX) process will be installed at the Rockwell Hanford Operations (RHO) Plutonium Finishing Plant (PFP). The purposes are to process the PFP waste to recover the plutonium, to isolate the americium, and to have the remaining waste converted to a non-TRU waste. Rockwell requested that ORNL provide an outside review of the process and its implementation. This review addresses the generation of the TRUEX feed, the chemical flowsheet, and the products and raffinates. It suggests that present PFP operations be modified to reduce the amount of transuranium elements that will be in the TRUEX process feed. This review also includes an assessment of the TRUEX solvent extraction flowsheet on the bases of material balance, adequate extraction and stripping stages, and solvent cleanup. The final part of the review includes results of three-party discussions [RHO, ORNL, and Argonne National Laboratory (ANL)] of some major issues.

1. INTRODUCTION

The TRansUranic EXtraction (TRUEX) process<sup>1</sup> was developed at Argonne National Laboratory (ANL) for removal and recovery of transuranium (TRU) elements from certain nuclear waste solutions. The process is a multi-stage solvent extraction system that uses two mixed extractants, octyl-(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and tributyl phosphate (TBP), in a diluent that is best selected based on the particular application. The selected diluent is tetrachloroethylene (TCE) for use at the U.S. DOE Hanford Site Plutonium Finishing Plant (PFP).

Rockwell Hanford Operations (RHO) decided to implement the TRUEX process at the PFP (1) to recover plutonium from the PFP waste, (2) to remove americium for storage, and (3) to remove all actinides to a level well below the 100 nCi/g limit for transuranium (TRU) waste. Rockwell plans to begin TRUEX processing of PFP wastes by midyear 1991, and they

requested that ORNL provide an outside review of the process and its deployment at the PFP.

The PFP recovers plutonium in the Plutonium Reclamation Facility (PRF) from scrap materials which also contain some  $^{241}\text{Am}$  from  $^{241}\text{Pu}$  decay. The plutonium is worth recovering while the americium has little value and is best isolated for future shipment to the Waste Isolation Pilot Plant (WIPP). The PRF separation scheme is a pulsed column solvent extraction facility using TBP in  $\text{CCl}_4$ , and the aqueous raffinate from the first extraction column is the primary waste to be treated by the TRUEX process. This aqueous raffinate will periodically include the interfacial crud that accumulates in the extraction column. Five other process streams that may be added to the TRUEX process feed are: (1) the carbonate scrub of the solvent cleanup, (2 and 3) the distillates from two evaporators, (4) laboratory wastes, and (5) the HF scrubber waste.

This review will include (1) the PRF processing, (2) the PFP wastes or the TRUEX feed, (3) the TRUEX flowsheet and chemistry, and (4) the products and raffinates.

## 2. PRF PROCESSING

Management and operation of PRF can affect the amount of transuranium actinides in the PFP waste. Since the success of the TRUEX process will be determined by an assured long term production of only low-level waste from the PFP waste, it was prudent to examine the PRF operations. Several points are stressed that, if implemented, could improve the nature of the PFP waste and hence promote a successful use of the TRUEX process.

In PRF operation, the TBP- $\text{CCl}_4$  phase is scrubbed with sodium carbonate and then washed and reacidified with 3 M  $\text{HNO}_3$ . The regenerated solvent generally is stored until it is needed and the storage period can be several weeks. Storage after high acid treatment promotes chemical degradation of TBP to form HDBP (dibutyl phosphoric acid) and HMBP (monobutyl phosphoric acid) which are primary contaminants that form complexes with actinides that are not stripped from the organic phase

during the stripping cycle. The complexed actinides are stripped from the organic with the next sodium carbonate scrub and become part of the PFP waste. The PRF solvent cleanup operation could be changed to minimize the TBP degradation by washing the organic phase after the carbonate scrub with dilute nitric acid (not greater than 0.1 M). It should not be necessary to further acidify the organic phase before it is contacted with the high-acid PRF feed.

Another operation of PRF that contributes actinides to the aqueous waste is the transfer of interfacial crud from the extraction column to the aqueous waste. Separation of this crud from the aqueous waste and special management of this relatively small volume of crud could greatly relieve stress on the TRUEX process. The amount of interfacial crud is a function of solvent degradation and should be reduced if the preceding suggestion on solvent acidification is adopted.

The PRF feed generally is not a clean solution. It has been centrifuged but not with high technology centrifugation, and therefore the feed solution contains very fine suspended solids. These solids, which probably have high actinide content, also contribute to the interfacial crud in the extraction column. A further cleanup of the PRF feed (use a better centrifuge and return the solids to the dissolver) can improve the PRF extraction-stripping with fewer solids and actinides in the PFP wastes. However, this improved clarification of the PRF feed does not eliminate the clarification steps in the TRUEX process.

A general cleanup of the PFP and a commitment for cleaner operation would help reduce the actinide level in the PFP waste. This latter suggestion and those above may appear to permit the TRUEX implementation to control the PFP. However, the main objective is to assure a low-level waste after PFP operation; and the overall attitude concerning both the PFP and TRUEX processes must be directed to that goal.

### 3. THE PFP WASTES - THE TRUEX FEED

Six streams from the PFP have been identified as the feed for the TRUEX process (Fig. 1). Two of these are clearly TRU wastes, the aqueous

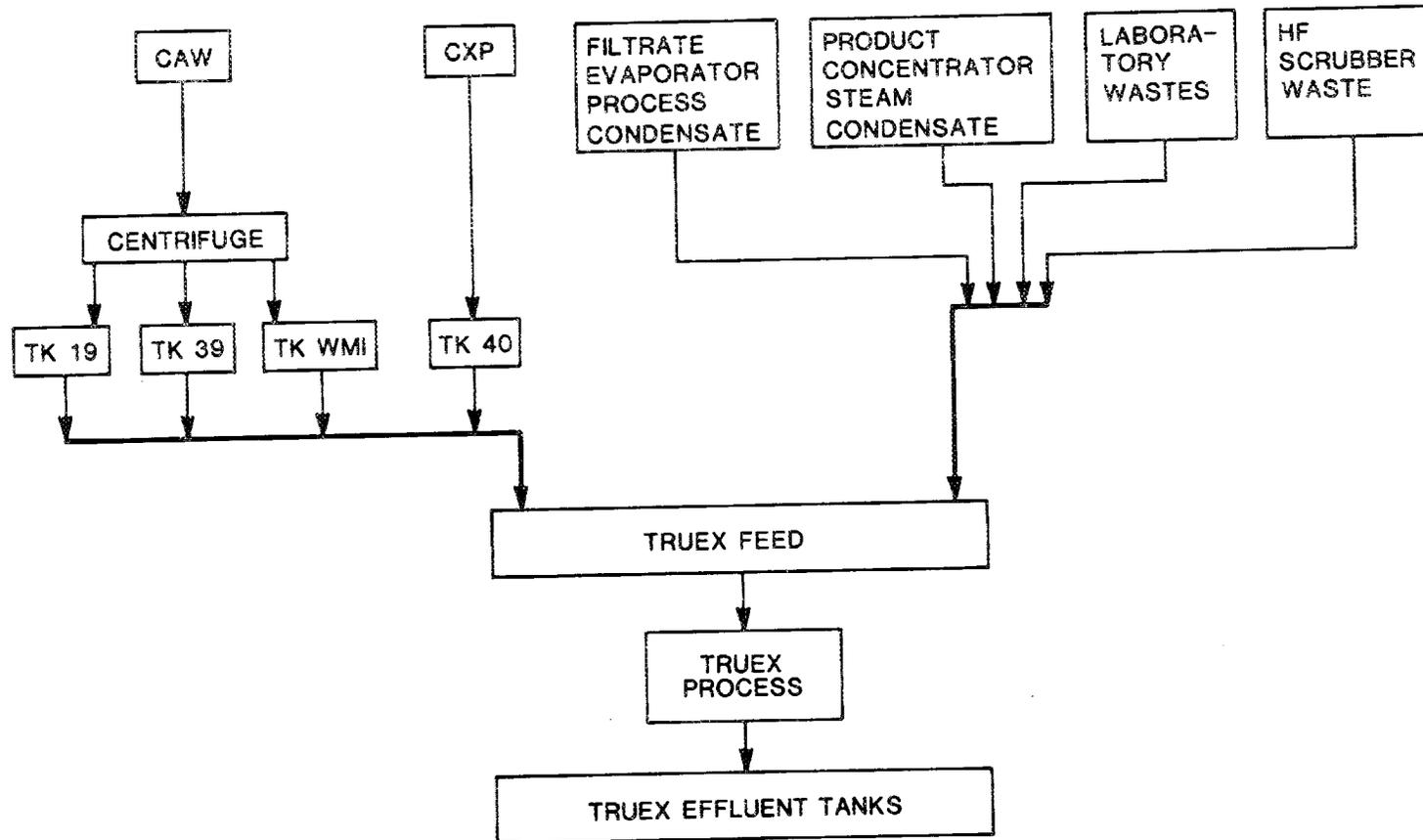


Fig. 1. Diagram of PFP wastes that make up the PFP TRUEX feed. The CAW is the aqueous raffinate from the RRF main extraction column. The CXP is the solvent cleanup waste.

raffinate from the RRF main extraction column (CAW) and solvent cleanup waste (CXP) from the PRF process. These are also the streams expected to present particular problems because of the presence of insoluble and refractory material which contains alpha activity. It might be preferable to consider treating them for clarification before they are mixed with the other streams.

The other four streams can be substantially reduced in volume by judicious operation. Two streams are condensates which should not normally be TRU wastes; it might be worthwhile to take additional measures to improve evaporator performance and assure that the two condensates are not TRU wastes. The HF scrubber waste contains aluminum and fluoride and should not normally contain refractory plutonium or alpha materials; thus, any alpha-activity may be soluble and not present as solids. The laboratory waste consists partly of a condensate (which again should not be a TRU waste) and partly from other sources such as hot drains. The amount of this material that is a TRU waste might be significantly reduced.

Thus, a combination of hardware improvements and appropriate administrative procedures might substantially reduce the total volume of TRU wastes. Such actions have been effective at other locations. As a somewhat extreme example, in a program to reduce the waste management problems at the Prototype Fast Reactor (PFR) reprocessing plant at Dounreay, United Kingdom, all analytical procedures were revised to eliminate chlorides and certain complexing agents and other chemicals commonly used in analyses. Furthermore, the use of hot drains was limited so that analytical labs had to process their own waste to a solid or very small liquid volume. In spite of initial objections, once this procedure was done it apparently worked out reasonably well. It is not clear to what extent such an approach has been considered at the PFP.

For the reference case, the six PFP waste streams are combined as shown in Fig. 1. Leonard, et al.<sup>2</sup>, have estimated the composition of the resulting TRUEX feed. The molar concentrations of uranium, plutonium, and americium should usually be about 3, 30, and 6  $\mu\text{M}$ , respectively. The aluminum concentration is very high, 0.43  $\text{M}$ , and the iron concentration is 0.03  $\text{M}$ . The feed is adjusted to 1.5  $\text{M}$   $\text{HNO}_3$  and the total nitrate concentration is then 3.06  $\text{M}$ .

Solids suspended in the TRUEX feed, which depend largely on the PRF operation, may contain both TRU and non-TRU components; and plutonium should be the only TRU component in the solids that remain after a digestion period in 1.5 M acid. Characterization of the solids in terms of physical properties and chemical composition will enable better decisions on the management of the solids. For now, it is proper to plan for the best practical removal of the solids from the TRUEX feed before the extraction step. If the volume and the plutonium content of the solids are acceptably low, the solids may be directly prepared for transfer to WIPP or added to the americium waste resulting from the TRUEX process operation. Otherwise, the solids can be recycled through the PRF dissolvers.

Solids that are not separated from the TRUEX process feed before extraction and solids that form because of excursions in the TRUEX process operation, generally will follow the aqueous stream. Hence, the aqueous raffinate and any other aqueous process discharge could contain solids which include TRU material and the efficiency of TRUEX processing would be diminished. Therefore, the overall TRUEX process deployment should include a polishing filtration of the aqueous process discharge streams, probably by deep bed filtration.

#### 4. TRUEX SOLVENT EXTRACTION FLOWSHEET ASSESSMENT

An assessment of the TRUEX solvent extraction flowsheet for processing PFP waste at Hanford was made to determine: (1) that the process is based on feasible chemistry, (2) that no appreciable quantities (or volumes) of secondary TRU wastes are created in removing plutonium and americium from the PFP waste, and (3) that modest variations in process variables such as acidity of the PFP waste will not cause less than required removal of transuranium elements. The assessment consisted first of a careful review of the chemistry and equilibrium distribution data which forms the basis of the TRUEX process and the results from "tracer level" flowsheet tests of the process at ANL. This review consisted of discussions with ANL staff and an examination of their published information. Subsequently, a detailed analysis was carried out on

the ANL reference flowsheet for the TRUEX process. The detailed analysis was conducted without involving ANL personnel and included preparation of a material balance flowsheet which identified all waste and product streams. Then, the effects of modest changes in the nitric acid concentration in the process feed on the americium and plutonium concentrations of process output streams were determined from calculations of equilibrium conditions. This assessment presumed (1) that the aqueous feed had been sufficiently clarified and (2) the solvent extraction process generated no TRU-bearing solids.

#### 4.1 PROCESS CHEMISTRY AND EQUILIBRIUM DATA

The TRUEX process developed by ANL is based on solvent extraction chemistry that has been thoroughly studied and is well understood. The ANL staff are to be commended for the quality and thoroughness of their work. A broad base of data has been obtained by ANL which includes (1) the equilibrium distribution coefficients of both TRU and non-TRU elements and their dependency on aqueous solution acidity, (2) the stability of the solvent (0.25 M CMPO - 0.75 M TBP in TCE diluent) to the radiation and chemicals present during the processing, and (3) the important physical properties (phase separations times, density, etc.). This broad base of data permits reliable estimates for compositions of product and waste streams and reliable judgment of solvent performance.

Process chemistry data show that the required degree of removal of plutonium and americium can be achieved using very modest additions of process reagents for scrubbing and stripping operations. Because of the low radiation dosages [ $\sim 2.9$  kJ/L ( $\sim 0.8$  Wh/L) each year] to the solvent and its excellent chemical stability, solvent degradation is not an anticipated major problem. The only deleterious degradation product identified is dibutyl phosphoric acid (HDBP) formed from TBP which can be easily removed by scrubbing with an alkaline solution. The HDBP generation rate is quite low and even after one year of routine operation with no removal, its concentration would build up only to about 1 mM, which is a concentration that should not be a problem in TRUEX process operation. For routine operation it may eventually prove unnecessary to clean

the solvent for each flowsheet pass; initially, however, it is recommended that the HDBP be removed by alkaline scrubbing after each extraction-scrub-strip cycle. This conservative approach will not increase total salt waste volumes significantly (see Sect. 4.2).

Numerous preliminary tests will be needed to establish the operability of a TRUEX plant with regard to equipment, safety, and adequacy of process control systems. These tests will involve numerous startup and shut-down (planned and unplanned) operations. Such operations can often lead to much longer solvent contact times (or solvent aging with dissolved chemicals) than in routine operations at reference process conditions. After the plant becomes fully operational and has operated for a significant duration, better information from actual plant data will enable a decision on the frequency of solvent cleanup. In fact, this frequency may eventually depend on the proven ability to adequately scrub or strip species such as iron, which forms highly insoluble compounds with HDBP, from the solvent.

#### 4.2 MATERIAL BALANCE FLOWSHEET FOR THE REFERENCE TRUEX PROCESS AND THE COMPOSITION OF PROCESS STREAMS

A material balance (Table 1) was carried out on the reference flowsheet (Fig. 2) for the nominal daily processing rate of PFP waste at Hanford. Results are summarized in Table 2 on an annual throughput basis for product and waste streams. Output process stream compositions and their TRU content were estimated by calculations from equilibrium data<sup>2</sup> and are in good agreement with ANL's predictions. In our calculations, we assumed that the extraction coefficients of TRU and non-TRU elements remained constant at values given in Table III-1 of ref. 1 throughout the multiple contacts in the extraction scrubbing and in the stripping operations. The methods similar to those described by Alders<sup>3</sup> were used to calculate end-stream compositions.

It was assumed that the americium product stream could be converted to a solid waste form without generating a significant volume of secondary TRU waste<sup>4</sup>. Then the only secondary TRU waste generated by TRUEX processing is the solvent scrubber waste (SSW). The SSW is estimated to

Table 1. Complete material balance for reference TRUEX flowsheet (shown in Fig. 2)

Process Stream	2EF Feed	2EW Waste	4XP Americium	5XP Plutonium	5ES	SSW Waste	3SF	4XP	5XP
<b>Volumetric flow</b>									
Absolute (L/d)	9.60×10 <sup>3</sup>	1.08×10 <sup>4</sup>	3.60×10 <sup>3</sup>	1.80×10 <sup>3</sup>	3.60×10 <sup>3</sup>	1.80×10 <sup>2</sup>	1.20×10 <sup>3</sup>	3.6×10 <sup>3</sup>	1.80×10 <sup>3</sup>
Relative to feed	1.000	1.125	0.3750	0.1875	0.3750	1.875×10 <sup>-2</sup>	0.1250	0.3750	0.1875
<b>Concentrations</b>									
HNO <sub>3</sub> , M	1.5	1.3	1.1×10 <sup>-1</sup>	5.0×10 <sup>-2</sup>	1.0×10 <sup>-2</sup>		0.25	5.0×10 <sup>-2</sup>	5.0×10 <sup>-2</sup>
HF, M				5.0×10 <sup>-2</sup>					5.0×10 <sup>-2</sup>
Am, mg/L	1.45	1.90×10 <sup>-4</sup>	3.87	1.0×10 <sup>-3</sup>	3.23×10 <sup>-6</sup>	6.46×10 <sup>-6</sup>			
Pu, mg/L	7.17	nil	1.2×10 <sup>-2</sup>	3.8×10 <sup>1</sup>	3.9×10 <sup>-3</sup>	7.80×10 <sup>-2</sup>			
U, mg/L	7.1×10 <sup>-1</sup>	nil	5.7×10 <sup>-2</sup>	4.4×10 <sup>-1</sup>	1.62	3.24×10 <sup>1</sup>			
Non-TRU metals, g/L	1.85×10 <sup>1</sup>	1.64×10 <sup>1</sup>				9.2			
Non-TRU salts, g/L	1.18×10 <sup>2</sup>	1.05×10 <sup>2</sup>				3.4×10 <sup>1</sup>			
<b>Mass flow</b>									
Am, g/d	1.39×10 <sup>1</sup>	2.04×10 <sup>-3</sup>	1.39×10 <sup>1</sup>	1.80×10 <sup>-3</sup>	1.16×10 <sup>-5</sup>	1.16×10 <sup>-5</sup>			
Pu, g/d	6.88×10 <sup>1</sup>	nil	4.3×10 <sup>-1</sup>	6.84×10 <sup>1</sup>	1.39×10 <sup>-2</sup>	1.39×10 <sup>-2</sup>			
U, g/d	6.80	nil	2.0×10 <sup>-1</sup>	7.8×10 <sup>-1</sup>	5.83	5.83			
Non-TRU metals, Mg/d	1.80×10 <sup>-1</sup>	1.8×10 <sup>-1</sup>				1.65×10 <sup>-3</sup>			
Non-TRU salts, Mg/d	1.11	1.11				6.12×10 <sup>-3</sup>			
HNO <sub>3</sub> , mol/d	1.44×10 <sup>4</sup>	1.45×10 <sup>4</sup>	3.96×10 <sup>2</sup>	9.0×10 <sup>1</sup>	3.6×10 <sup>1</sup>		3.00×10 <sup>2</sup>	1.80×10 <sup>2</sup>	9.0×10 <sup>1</sup>
HF, mol/d				9.0×10 <sup>1</sup>					9.0×10 <sup>1</sup>
<b>TRU activity<sup>a</sup></b>									
Am, nCi/L	4.96×10 <sup>6</sup>	6.50×10 <sup>2b</sup>	1.32×10 <sup>7</sup>	3.42×10 <sup>3</sup>	1.11×10 <sup>1</sup>	2.21×10 <sup>2c</sup>			
Pu, nCi/L	6.56×10 <sup>5</sup>	nil	1.10×10 <sup>4</sup>	3.47×10 <sup>6</sup>	3.57×10 <sup>2</sup>	7.13×10 <sup>3d</sup>			
Am, Ci/d	4.76×10 <sup>1</sup>	7.0×10 <sup>-3</sup>	4.76×10 <sup>1</sup>	6.16×10 <sup>-3</sup>	3.97×10 <sup>-5</sup>	3.97×10 <sup>-5</sup>			
Pu, Ci/d	6.30	nil	3.93×10 <sup>-2</sup>	6.25	1.27×10 <sup>-3</sup>	1.27×10 <sup>-3</sup>			

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<sup>a</sup>Calculated using Am = 3.4230 Ci/g and Pu = 9.1441×10<sup>-2</sup> Ci/g.

<sup>b</sup>After neutralization the waste would be 2.6 nCi/g on basis of the 250 g/L of non-TRU salts.

<sup>c</sup>6.1 nCi/g on basis of 34 g salt/L.

<sup>d</sup>210 nCi/g on basis of 34 g salt/L.

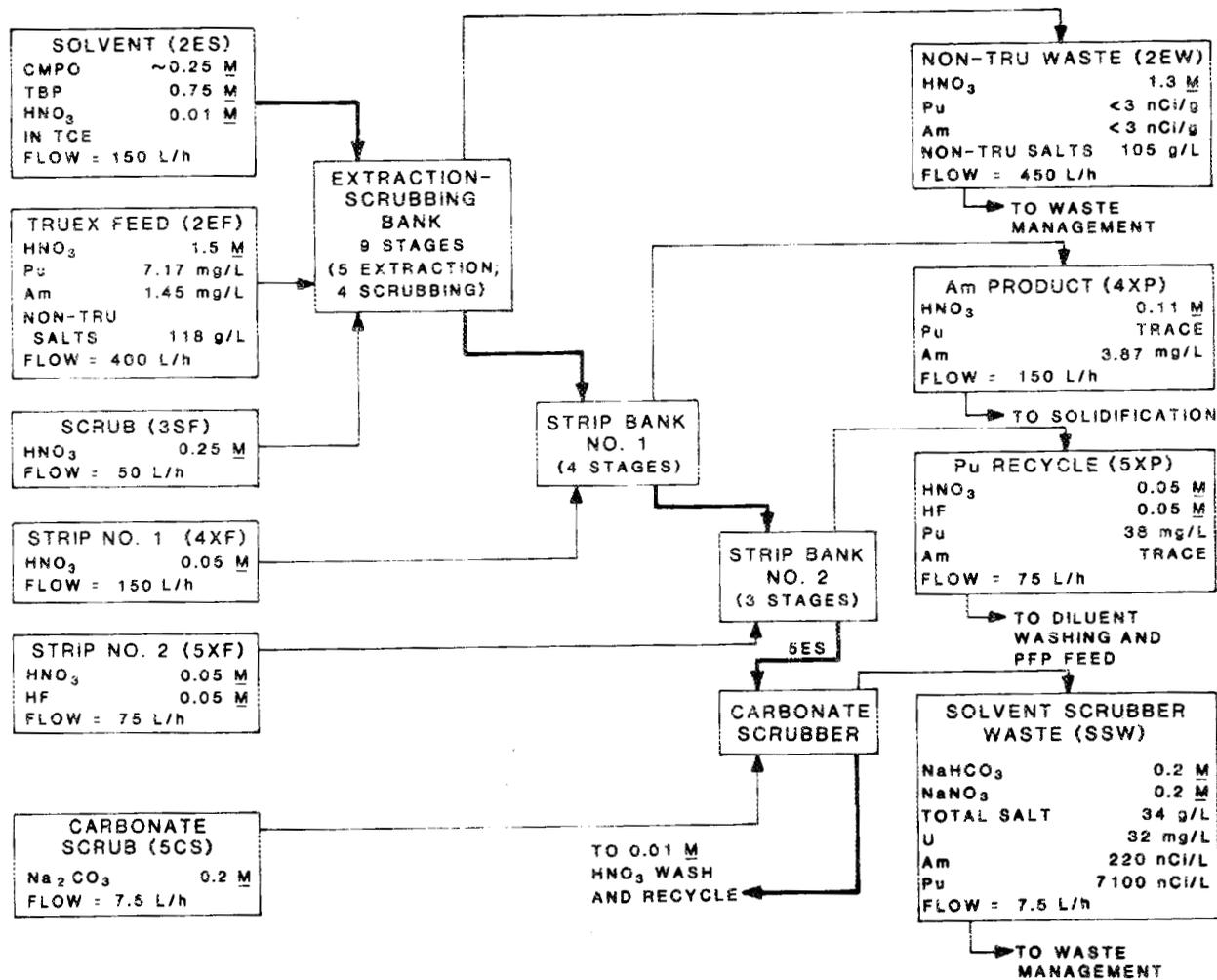


Fig. 2. Reference TRUEX flowsheet for removing americium and plutonium from PFP wastes.

Table 2. Annual throughputs for TRUEX processing of PFP waste  
(250 days operation)

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Americium Product (4XP)

kg of americium	3.5
$^{241}\text{Am}$ curies	$1.2 \times 10^4$

Plutonium Product (5XP)

kg of plutonium	17
Plutonium, curies	$1.6 \times 10^3$

Non-TRU Waste (2EW)

Acid waste:

Non-TRU salts, kg	$2.8 \times 10^5$
$\text{HNO}_3$ , kg	$2.2 \times 10^5$

Neutralized waste:

Volume, L	$2.7 \times 10^6$
Non-TRU salts, kg	$5.8 \times 10^5$
Americium, curies	<1.7
Spec. act. of salt, nCi/g	<3
Total nitrate, kg	$4.5 \times 10^5$

Spent Solvent Scrubber Waste (SSW)

Sodium salts, kg	$1.5 \times 10^3$
Americium, curies	$9.95 \times 10^{-3}$
Plutonium, curies	$3.17 \times 10^{-1}$
Uranium, kg	1.5

---

contain  $\sim 200$  nCi Pu/g (sodium salt content basis). However, only 180 L/d of SSW (6.1 kg Na salts) is generated, and it could be converted to a non-TRU waste by (1) blending this SSW with the 10,800 L of 2EW waste or (2) adding one additional stage in plutonium stripping to reduce the SSW to  $\sim 12$  nCi/g. The first option to blend together the wastes may not be prudent because of the uranium content in the SSW; thus, the second option is preferred.

The ANL reference flowsheet utilizes the basic separation chemistry of CMPO to optimum advantage. Americium is removed from the waste while achieving a concentration factor of  $\sim 2.7$  and the plutonium product is recycled to PRF for recovery. Process chemical addition is quite low; and even with no reagent recycle, it only increases the salt waste mass by  $\sim 5\%$ . The total aqueous volume generated in TRUEX processing is  $\sim 170\%$  of the initial feed volume and is typical of a good solvent extraction process. Most of this excess volume is water, and it can be recycled to the processing. Some small fraction of the water may require decontamination for discharge to the environment. The highest degree of decontamination for water (for recycle or discharge) is needed in the conversion of the americium product (4XP) to a solid waste form.<sup>4</sup>

Although the reference TRUEX process flowsheet can be modified to permit the production of a more concentrated americium product, it is not obvious that the potential benefits will outweigh the increased complexity of process operations. To accomplish high product concentrations of americium, either back cycle of americium to the PRF feed or internal reflux of the americium is required. Detailed process and equipment flowsheet analyses, plus additional experimental work, are required to establish if any flowsheet has potential merit for increasing the americium concentration. Also, major changes in the TRUEX process flowsheet at this point could significantly delay the processing of PFP waste.

#### 4.3 EFFECT OF VARIATIONS IN THE NITRIC ACID CONCENTRATION IN TRUEX PROCESS FEED ON AMERICIUM STRIPPING

Since the stripping of americium is third power dependent on nitric acid concentration, the amount of nitric acid extracted in the extraction-

scrubbing bank (Fig. 2) will influence the subsequent stripping of americium in Strip Bank No. 1. The extraction of actinides in the extraction-scrub bank is essentially independent of nitric acid concentration in the 1 to 3 M range. Since the distribution coefficient of  $\text{HNO}_3$  is only 0.2, most of the acid will be stripped from the organic phase in Strip Bank No. 1, and there is essentially no effect on plutonium stripping in Strip Bank No. 2. In an operating plant, modest variations ( $\pm 10\%$ ) in feed acid concentrations are to be expected, and an occasional error in feed adjustment may cause much wider variations.

Calculated profiles for nitric acid in the americium strip bank (No. 1) are given in Table 3 for TRUEX process feeds ranging from 1.0 to 4.0 M  $\text{HNO}_3$ . The effect of increasing  $\text{HNO}_3$  concentrations in the feed to the strip bank will significantly increase  $\text{HNO}_3$  concentrations in Stage 1, which will result in poorer stripping of americium in that stage. Nitric acid concentrations in Stages 2 and 3 are not greatly increased by increasing the  $\text{HNO}_3$  concentration of the TRUEX feed reference flowsheet conditions from 1.5 M to 4.0 M  $\text{HNO}_3$ . Stage 4 concentrations are virtually the same for all feed concentrations. Thus, there can be no problem caused by acid changes in the subsequent stripping of plutonium in Strip Bank No. 2. Thus, small variations of  $\pm 10\%$  in TRUEX process feed acidity would have essentially no effect on americium stripping. The use of four scrub stages in the extraction step (Fig. 2) is beneficial in reducing the effect of feed acidity on subsequent stripping.

The only severe problem that will occur if americium is not sufficiently stripped will be the production of a TRU-contaminated solvent wash waste. However, our calculations show that even if feed acidities of up to 4 M were employed, the americium activity of solvent wash waste would only increase from 6.5 to 20 nCi/g of dissolved salts. Americium contamination of the plutonium product would be increased about three-fold (up to 0.3% of the americium in the feed); but since the plutonium product is recycled to PRF, this is of little concern. Also, the increase in the SSW activity could be eliminated by adding an extra strip stage in americium stripping or, if preferred, to plutonium stripping.

Table 3. Effect of the nitric acid concentration of TRUEX process feed on the HNO<sub>3</sub> stage profiles for americium stripping

TRUEX process feed	HNO <sub>3</sub> concentration, M				
	1.0	1.5	2.0	3.0	4.0
Americium stripping					
Organic feed	5.975×10 <sup>-2</sup>	6.594×10 <sup>-2</sup>	7.213×10 <sup>-2</sup>	8.452×10 <sup>-2</sup>	9.691×10 <sup>-2</sup>
Stage concentrations <sup>a</sup>					
Aqueous phase:					
Stage 1	9.968×10 <sup>-2</sup>	1.059×10 <sup>-1</sup>	1.121×10 <sup>-1</sup>	1.244×10 <sup>-1</sup>	1.368×10 <sup>-1</sup>
Stage 2	5.987×10 <sup>-2</sup>	6.110×10 <sup>-2</sup>	6.233×10 <sup>-2</sup>	6.479×10 <sup>-2</sup>	6.725×10 <sup>-2</sup>
Stage 3	5.191×10 <sup>-2</sup>	5.215×10 <sup>-2</sup>	5.239×10 <sup>-2</sup>	5.286×10 <sup>-2</sup>	5.334×10 <sup>-2</sup>
Stage 4	5.032×10 <sup>-2</sup>	5.036×10 <sup>-2</sup>	5.040×10 <sup>-2</sup>	5.048×10 <sup>-2</sup>	5.056×10 <sup>-2</sup>
Organic phase:					
Stage 1	1.994×10 <sup>-2</sup>	2.117×10 <sup>-2</sup>	2.241×10 <sup>-2</sup>	2.489×10 <sup>-2</sup>	2.736×10 <sup>-2</sup>
Stage 2	1.197×10 <sup>-2</sup>	1.222×10 <sup>-2</sup>	1.247×10 <sup>-2</sup>	1.296×10 <sup>-2</sup>	1.345×10 <sup>-2</sup>
Stage 3	1.038×10 <sup>-2</sup>	1.043×10 <sup>-2</sup>	1.048×10 <sup>-2</sup>	1.057×10 <sup>-2</sup>	1.067×10 <sup>-2</sup>
Stage 4	1.006×10 <sup>-2</sup>	1.007×10 <sup>-2</sup>	1.008×10 <sup>-2</sup>	1.010×10 <sup>-2</sup>	1.011×10 <sup>-2</sup>

<sup>a</sup>Organic feed enters at Stage 1 and stripped organic exits Stage 4. An aqueous strip solution of 0.05 M HNO<sub>3</sub> enters Stage 4 and the aqueous product exits from Stage 1.

## 5. MAJOR ISSUES DISCUSSED BY THREE PARTIES (RHO, ANL, AND ORNL)

Several questions on the TRUEX process flowsheet and its related chemistry have been discussed by members of the RHO, ANL, and ORNL staff. These questions and the ORNL answers based on those discussions are given here for reference purposes. Only the questions related to the flowsheet are given here.

### 5.1 WHAT IS THE MOST VULNERABLE PART OF THE TRUEX PROCESS FLOWSHEET FOR PFP WASTE?

The PFP waste contains solids that likely will not dissolve completely in 1.5 M  $\text{HNO}_3$ . Those residues will contain TRU elements and must be separated from the TRUEX process feed. A good High-Gradient Magnetic Fractionation (HGMF) or centrifugation technique will separate the major particulates, but a complete separation of the particulates will be difficult. The very small particulates will likely proceed into the solvent extraction system and will probably remain with the aqueous stream. It is not clear where particulates will reside in centrifugal contactors, but at least some particles will trace the aqueous stream to the raffinate waste. There, the effect of the particles will be determined by their TRU element content. To minimize the TRU element content of the TRUEX process raffinate, the flowsheet should include a polishing filter, such as a deep bed filter, for the raffinate. Solid particles containing TRU elements passing through the system and contaminating the raffinate could be a major problem but proper filtration can eliminate or minimize this problem.

### 5.2 WHAT IS THE EXPECTED OPERATING LIFETIME OF THE CENTRIFUGAL CONTACTORS?

There are no long-term "hot" operations from which an accurate expected lifetime can be determined. The ANL staff believes that the contactor lifetime should be at least five years, and even then the commercially available motor is the most likely component to fail.

Since the motor can be replaced easily, quickly, and inexpensively, ANL believes that the expected operating lifetime is acceptable. The ORNL has some reservations on the lifetimes and suggests that a careful quality assurance program be established for production of the contactors and that a careful testing procedure be required before accepting the contactors.

### 5.3 WHAT IS THE EFFECT OF PLUTONIUM POLYMER IN THE PFP WASTE OR IN THE TRUEX PROCESS?

The PFP waste may contain some plutonium polymer that formed during the PFP processing, even though processing conditions should not support polymer formation. Depending on the PRF extraction and scrubbing performance, the PRF solvent wash could produce some polymer in the carbonate wash. The general operation of PFP leads to the conservative conclusion that there will be small amounts of polymer in the PFP wastes. Any polymer in the PFP waste probably will be "aged" polymer and will proceed into the TRUEX process. There, some of the polymer may appear as interfacial crud, and the remainder should stay in the aqueous phase. There is no present information to predict the quantity of polymer that might reach the aqueous raffinate from the TRUEX process.

The most likely places for polymer formation in the TRUEX process are in the stages where the solution for americium stripping is introduced and where the plutonium stripping is done. The low acid americium strip solution, 0.05 M  $\text{HNO}_3$ , may strip some plutonium from which some polymer may form before the aqueous phase strips enough acid from the organic to prevent polymer formation. Any such plutonium polymer formed in the americium stripping cycle probably will follow the americium and be a problem unless the polymer is removed with the americium. The plan for americium recovery is to load it onto a cation exchange resin, and the resin is not likely to also remove the plutonium polymer. Some R&D work is needed to answer these questions concerning plutonium polymer.

The formation of plutonium polymer in the plutonium stripping stages should be less likely because of the presence of 0.05 M fluoride. However, the low acid concentration, 0.05 M, suggests that some plutonium

polymer may form; but it should remain with the aqueous portion and proceed into the plutonium product. Therefore, polymer formation in the plutonium stripping stages should not be a problem, providing that the plutonium product is recycled to a high acid PRF dissolver rather than to the extraction feed. The depolymerization of aged polymer will require digestion with high,  $>3 \text{ M}$  acid and high temperature,  $>80^\circ\text{C}$ .

#### 5.4 WHAT IS THE BEST SOLVENT TREATMENT PROCEDURE CURRENTLY AVAILABLE FOR TRUEX?

Sodium carbonate scrubbing is the best demonstrated technology. At a processing rate of 400 L/h (9600 L/d) of PFP waste, the solvent wash waste will be generated at a rate of about 1500 kg/year. If it becomes necessary to reduce the amount of this waste, an alternate method of scrubbing with hydroxylamine or the hydrazine salts (carbonates or oxalates) could be used. The hydrazine or hydroxylamine salts probably can be decomposed into the component gases by electrolysis or with  $\text{NO}_x$  sparging, but some development efforts would be required before instituting an alternate method.

### 6. SUMMARY

Rockwell Hanford Operations (RHO) plans to install the TRUEX process in their PFP facility to minimize TRU wastes from the PFP and to recover plutonium. The ORNL staff reviewed and assessed the TRUEX process flow-sheet for PFP waste treatment.

This ORNL effort included consideration of the PRF process, the PFP wastes, and the TRUEX process flowsheet and chemistry. The results include suggestions that (1) minor changes in the PRF operation could reduce the amounts of PFP TRU wastes, (2) the PFP wastes may be better managed if the six waste streams are not combined, and (3) the TRUEX process flow-sheet and its related chemistry represent sound technology.

## 7. REFERENCES

1. E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrift, and W. W. Schulz, The TRUEX Process - A Process for the Extraction of Transuranium Elements from Nitric Acid Wastes Utilizing Modified Purex Solvent, Solvent Extr. Ion Exch. 3, 175 (1985).
2. R. A. Leonard, G. F. Vandegrift, D. G. Kalina, D. F. Fisher, R. W. Bane, L. Burris, E. P. Horwitz, R. Chiarizia, and H. Diamond, The Extraction and Recovery of Plutonium and Americium from Nitric Acid Waste Solutions by the TRUEX Process-Continuing Development Studies, ANL-85-45 (September 1985).
3. L. Alders, "Liquid-Liquid Extraction," Elsevier Publishing Co., New York, pp. 84-155 (1959).
4. J. C. Mailen, D. O. Campbell, J. T. Bell, and E. D. Collins, Americium Solidification and Disposal, ORNL/TM-10226 (1987).

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