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September 1985

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ABSTRACT

This report summarizes the work done to date at Argonne National Laboratory on the application of the TRUEX solvent extraction process for removing and separately recovering plutonium and americium from a nitric acid waste solution containing these elements, uranium, and a complement of inert metal ions. This simulated waste stream is typical of a raffinate from a tributyl phosphate (TBP)-based solvent extraction process for removing uranium and plutonium from dissolved plutonium-containing metallurgical scrap. The TRUEX process solvent in these experiments was a solution of TBP and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (OΦD[iB]CMPO, or simply CMPO) dissolved in carbon tetrachloride (CCl_4); the composition of the TRUEX-CCl_4 solvent was 0.25M CMPO-0.75M TBP. A flowsheet was designed on the basis of measured batch distribution ratios to reduce the TRU content of the solidified raffinate to $\leq$10 nCi/g and was tested in a countercurrent experiment performed in a 14-stage Argonne-model centrifugal contactor. The process solvent was recycled without cleanup. An unexpectedly high evaporative loss of CCl_4 resulted in concentration of the active extractant, CMPO, to nearly 0.30M in the solvent. Results are consistent with this higher CMPO concentration. The raffinate contained only 2 nCi/g of TRU, but the higher CMPO concentration resulted in reduced effectiveness in the stripping of americium from the solvent. Conditions can be easily adjusted to give high yields and good separation of americium and plutonium. Experimental studies of the hydrolytic and gamma-radiolytic degradation of the TRUEX-CCl_4 showed that solvent degradation would be (1) minimal for a year of processing this typical feed, which contained no fission products, and (2) could be explained almost entirely by hydrolytic and radiolytic damage to TBP. Even for gross amounts of solvent damage (typical of 100 years of processing this waste stream), scrubbing with aqueous sodium carbonate solution restored the original americium extraction and stripping capability of the solvent.

I. INTRODUCTION

The ability of the TRUEX (TRansUranic EXtraction) solvent extraction process to extract, separate, and recover transuranic (TRU) elements from nitrate media containing a wide range of acid, fission-product, and salt concentrations makes this process an important tool for processing a large variety of TRU-containing waste streams. The application of TRUEX processing of nuclear waste streams in the United States would have two important results:

(1) a greatly lessened bulk of waste that must be buried in deep geologic repositories at the Waste Isolation Pilot Plant (WIPP) or as glass in a high-level nuclear waste repository and

(2) the recovery of substantial amounts of TRU elements (e.g., plutonium) that are in these streams and that otherwise would be lost.

The TRUEX solvent extraction process was invented by members of the Chemical Separations Group, Chemistry Division, Argonne National Laboratory through basic studies of a number of neutral, phosphorus-based, bifunctional extractants [HORWITZ-1981A,B, -1982, -1983A,B, -1984, -1985D; KALINA-1981, -1984, -1985A,B; MUSCATELLO]. Process application, flowsheet development, and testing has since become a cooperative effort between this group and the Separations Science and Technology Group, Chemical Technology Division, Argonne National Laboratory [HORWITZ-1985A,B; VANDEGRIFT-1984A, -1985]. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated OΦD[iB]CMPO, or simply CMPO [HORWITZ-1983B, -1984, -1985A; VANDEGRIFT-1984A, -1985]. Its chemical structure is shown in Fig. I-1. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon or a nonflammable chlorocarbon such as carbon tetrachloride or tetrachloroethylene.

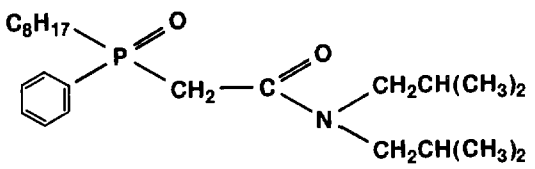

Fig. I-1.

The Chemical Structure of OΦD[iB]CMPO

Described in this report is the application of the TRUEX solvent extraction process to remove plutonium and americium from an aqueous nitric acid waste stream. The stream is a typical raffinate of a TBP-based solvent extraction process used to remove uranium and plutonium from dissolved plutonium scrap. We have designated this waste stream as PFP waste, because it is typical of the waste stream exiting the Hanford Plutonium Finishing Plant

(PFP).* The TRUEX process solvent chosen for this waste stream is 0.25M CMPO-0.75M TBP diluted by carbon tetrachloride, and is designated as TRUEX-CCl_4. Our primary objective has been to demonstrate this process on a simulated PFP waste stream by (1) reducing the alpha activity in the solidified raffinate to <10 nCi/g, (2) providing a purified plutonium product stream, (3) providing a purified americium product stream, and (4) demonstrating the effectiveness of centrifugal contactors for this operation. A second objective was to measure the gamma-radiolytic and hydrolytic degradation of the TRUEX-CCl_4 process solvent under conditions relevant to the processing of PFP waste.

*The specific composition of the synthetic PFP waste solution used in this study was provided by W. W. Schulz, Rockwell Hanford Operations.

II. SUMMARY AND CONCLUSIONS

A flowsheet has been developed and tested for the removal of americium and plutonium from typical PFP waste solutions using the TRUEX process. Americium and plutonium are selectively stripped from the solvent in this process. The flowsheet was demonstrated in a countercurrent experiment with extraction, scrub, and two strip sections, and with solvent recycle using a 14-stage centrifugal contactor unit (five extraction, two scrub, four americium-strip, and three plutonium-strip stages). The conclusions of the demonstration are as follows:

- A raffinate vhat is <10 nCi/g solid is easily attainable with five extraction stages.
- An americium product stream containing >99.9% americium and very little plutonium contamination is attainable under properly selected conditions of solvent composition, phase ratio, aqueous nitric acid concentration, and number of stages in the first strip.
- A plutonium product stream with >99.9% plutonium and very little americium contamination is attainable under properly selected conditions of solvent composition, phase ratio, aqueous nitric acid/hydrofluoric acid concentrations, and number of stages in the second strip.
- Batch distribution ratios measured for tracer concentrations of radionuclides can be used to predict the extraction behavior of Pu(IV) and Am(III) in this process.
- Loss of diluent (CCl_4) with subsequent increases in extractant concentration is an area of concern. The use of a less volatile diluent, tetrachloroethylene, is recommended. However, if CCl_4 is to be the diluent, reduced evaporation must be achieved by, for example, cooling of selected stages or sealing of rotor shafts. We also recommend, particularly if CCl_4 is the diluent, monitoring of the solvent density and/or periodic measurements of americium distribution ratio to check the solvent composition and degradation.
- The major constituent by weight of the americium product stream is iron. If a purer americium product is sought, the flowsheet can be altered by adding additional scrub stages.

The stability of the TRUEX-CCl_4 solvent to hydrolytic and gamma-radiolytic degradation was also studied. The conclusions of this study are as follows:

- Hydrolytic and radiolytic damage to the solvent will be of no consequence for periods equivalent to several years of processing of typical PFP wastes.
- Observed effects on extraction behavior of the solvent can be largely explained by degradation of tributyl phosphate to dibutyl phosphoric acid.

- Scrubbing the degraded solvent with aqueous sodium carbonate solution restored, and in most cases increased, its original capability in regard to extraction behavior of americium and in ease of phase disengagement.

- When fresh, or only slightly degraded, solvent was contacted with aqueous sodium carbonate solutions, phase disengagement was very slow. However, treatment of the solvent before use with macroporous ion-exchange resin in the hydroxide form greatly alleviated the slow disengagement problem and should allow the use of a sodium carbonate cleanup step in Argonne-model centrifugal contactors.

The overall conclusion of this effort is that there are no foreseeable problems in implementing a TRUEX solvent extraction process on solutions having the general composition of a typical PFP waste. The countercurrent demonstration of the flowsheet met its objectives and has led to modifications in the flowsheet to improve its performance.

III. REFERENCE FLOWSHEET FOR PFP WASTE PROCESSING

A reference flowsheet was prepared to describe the removal of americium and plutonium from PFP waste using the TRUEX process. The TRU concentration in the solidified raffinate from the treated PFP waste should be less than 10 nCi/g, i.e., a nonTRU waste. The recovered americium and plutonium are separated from the loaded TRUEX-CCl_4 solvent, and from each other, in successive stripping sections.

In this section, the reference flowsheet is presented, the results of a flowsheet demonstration in a 14-stage centrifugal contactor are given, and the demonstration results are discussed. Based on the flowsheet analysis and a review of the demonstration run results, an outline for a revised flowsheet was worked out and is included in Section III.C.7, in which solvent cleanup and recycle are addressed.

A. Flowsheet Development

A reference flowsheet was designed for the PFP waste from which americium and plutonium are recovered and, subsequently, separated from each other. For the demonstration of this flowsheet, the solvent was recycled without any cleanup. However, the flowsheet modifications outlined in Section III.C.7 include two solvent cleanup steps. The extraction/scrub section recovers most of the TRU elements from the PFP waste, so that the raffinate will be a nonTRU waste. In addition, successive strips are chosen for stripping the organic phase so that the two TRU elements, americium and plutonium, are separated from each other.

1. Calculations

To make the calculations on the flowsheet, shown in Fig. III-1, that are required to meet process constraints, batch distribution coefficients were measured for key components in the PFP waste. These distribution coefficients for the PFP waste are summarized in Table III-1 for each section of the flowsheet. Using the distribution coefficient and the concentration of each component in each input stream (DF, DS, EF, and FF) to the flowsheet, the composition of each output stream (DW, EW, and FW) was calculated using an electronic worksheet. The use of electronic worksheets for such calculations is described by Leonard [LEONARD-1985]. The input concentrations and the calculated output concentrations are listed in Table III-2. Additional results are listed in Appendix A, Section 6. Because the organic phase is recycled from the second strip back to the extraction/scrub section, it is both an input (DX) and output (FP) stream. Thus, the organic phase starts out with only CMPO and TBP in CCl_4. As the process time in the calculation increases, small amounts of HNO_3, Pu, Am, and U build up in the organic phase. The concentrations of these components listed in Table III-2 are for steady-state conditions. Highlights of the worksheet calculations are shown on the flowsheet in Fig. III-1, with each americium and plutonium value in the effluent streams given as a percent of the amount in the aqueous feed (DF).

As shown in Fig. III-1 and detailed in Table III-2, the PFP flowsheet meets all process objectives. The aqueous raffinate (DW) from the extraction/scrub section contains only 3 nCi/g of solid when neutralized

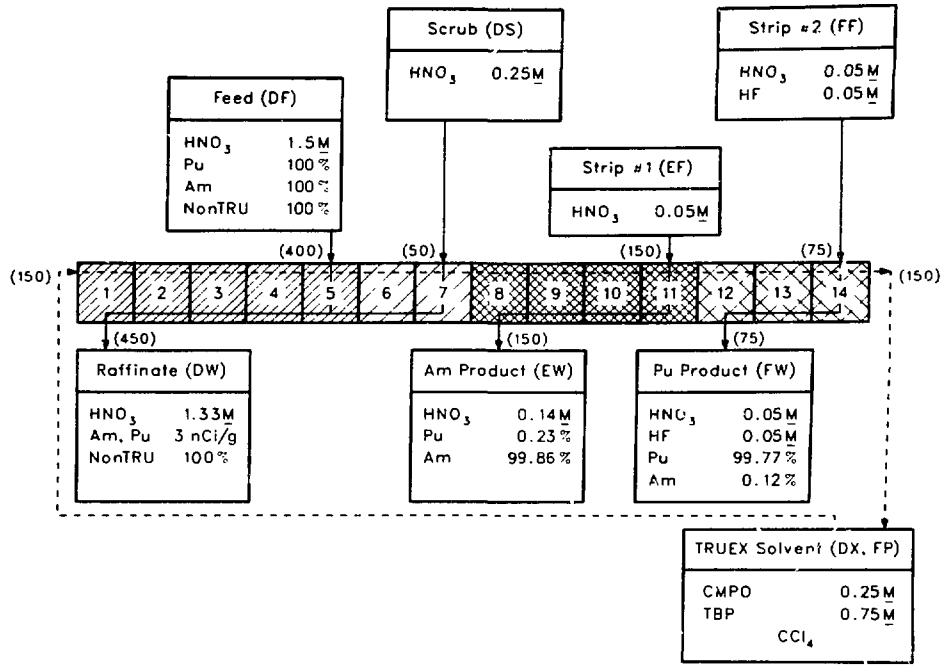

Fig. III-1. Flowsheet for Tests with Synthetic PFP Waste. (Parenthetical entries indicate stream flow rates in mL/min.)

and solidified as a mixture of nitrate salts. The americium product (EW) in the aqueous phase from the first strip contains only 0.2% of the plutonium. The plutonium product (FW) in the aqueous phase from the second strip contains only 0.1% of the americium.

2. Potential Problems

Two potential problems were observed based on the flowsheet calculations. First, because the americium concentration is low relative to that of iron, and because the distribution coefficients for iron are relatively high when compared with other nonTRU components in the PFP waste, significant amounts of iron could be present with the americium in the EW effluent. If this presents a problem, additional stages could be added to the scrub section. With each additional scrub stage, the iron concentration would drop by a factor of two, based on the iron distribution coefficients measured from the demonstration run. This is a smaller factor than would be predicted from the expected value shown in Table III-1. Second, because the extraction factor, the distribution ratio times the organic/aqueous (O/A) flow ratio, is greater than one for uranium in all sections of the flowsheet, the concentration of uranium in the organic phase (DX, FP) will build up until it is 17 times that in the aqueous feed (DF). However, because the concentration of

Table III-1. Distribution Coefficients for Various Constituents of PFP Waste Using TRUEX-CCl_4 Solvent at 30°C

Component	Distribution Coefficients			
	Extraction	Scrub	First Strip	Second Strip
HNO_3	0.23	0.2	0.2	0.2
Be	<0.0	<0.04	a	a
Na	<0.02	<0.02	a	a
Mg	<0.001	<0.001	a	a
Al	<0.0001	<0.0001	a	a
K	<0.03	<0.03	a	a
Fe	0.061	0.061[b]	a	a
Ca, Cr, Mn, Ni, Cu, Zr, Pb	<0.01	<0.01	a	a
U	400	400	33[c]	4.2
Pu	2000	2000	160[d]	0.03
Am	17[e]	3.0[f]	0.11[g]	0.1
F^-	h	h	h	h
SO_4^{2-}	h	h	h	h

[a]Not available. Expect these coefficients to be even less than those for the extraction/scrub section.

[b]This expected value for the Fe coefficient was found to be higher, about 0.25, in the demonstration run.

[c]Coefficient is 110 for the first contact of the organic phase with the aqueous phase and 36 for the second; all others are as shown.

[d]Coefficient is 440 for the first contact of the organic phase with the aqueous phase and 170 for the second; all others are as shown.

[e]Coefficient is 16 for the first two contacts of the organic phase with the aqueous phase; all others are as shown.

[f]Coefficient is 8.8 for the first contact of the organic phase with the aqueous scrub and 6.5 for the second; all others are lower and approach the value shown in the table, which is for the 0.25M HNO_3 aqueous scrub feed.

[g]Coefficient is 0.87 for the first contact of the organic phase with the aqueous phase and 0.13 for the second; all others are as shown.

[h]Very low distribution coefficient; therefore, assumed to be zero.

Table III-2. Concentrations in the Process Flowsheet for Recovery of Americium and Plutonium from PFP Waste

Component	Process Stream Concentrations,[a] M							
	Organic Solvent,[b] DX,FP (150)	Aqueous Feed,[c] DF (400)	Aqueous Scrub,DS (50)	Aqueous Raffinate, DW (450)	Aqueous Am Strip, EF (150)	Aqueous Am Product, EW (150)	Aqueous Pu Strip, FF (75)	Aqueous Pu Product, FW (75)
HNO_3	0.01	1.5	0.25	1.331	0.05	0.141	0.05	0.05
HF	0	0	0	0	0	0	0.05	0.05
Be	0	7E-5	0	6.2E-5	0	<5E-8	0	0
Na	0	0.04	0	0.036	0	2.4E-6	0	0
Mg	0	0.06	0	0.053	0	<1E-10	0	0
Al	0	0.43	0	0.382	0	3.4E-12	0	0
K	0	0.003	0	0.0027	0	<5E-7	0	0
Ca	0	0.06	0	0.053	0	4.7E-7	0	0
Cr	0	4E-4	0	3.6E-4	0	<3E-9	0	0
Mn	0	0.003	0	0.0027	0	<3E-8	0	0
Fe	0	0.03	0	0.027	0	4.6E-5	0	1.19E-9
Ni	0	4E-4	0	3.6E-4	0	<3E-9	0	0
Cu	0	3E-4	0	2.7E-4	0	<3E-9	0	0
Zn	0	6E-4	0	5.3E-4	0	<5E-9	0	0
Pb	0	5E-4	0	4.4E-4	0	<4E-9	0	0
U	5.18E-5	3E-6	0	1.29E-7	0	5.7E-7	0	1.408E-5
Pu	1.62E-8	3E-5	0	8.1E-12	0	1.83E-7	0	1.596E-4
Am	1.25E-10	6E-6	0	8.3E-10	0	1.598E-5	0	3.9E-8
NO_3^-[d]	0.01	3.06	0.25	2.72	0.05	0.141	0.05	0.05
F^-	0	0.09	0	0.08	0	0	0.05	0.05
SO_4^{2-}	0	0.01	0	0.009	0	0	0	0

[a]Parenthetical entries in the heading indicate stream flow rates in mL/min.

[b]Without solvent wash or cleanup steps, solvent is recycled directly from the second strip section to the extraction section as the organic feed.

[c]The PFP waste reference composition is as specified by Rockwell Hanford.

[d]Calculated values. Includes nitrate from nitric acid as well as nitrate salts.

uranium in the aqueous feed (DF) is low, it is not a problem. A complete process flowsheet could include a solvent wash to remove any uranium from the solvent, thereby eliminating the potential problem (see Section III.C.7).

3. Dependence of Flowsheet Performance on Component Concentration

a. Aqueous Feed

The performance of the flowsheet focuses on the removal of americium from the aqueous raffinate (DW) and on how that removal depends on the concentration of the various components in the aqueous feed. Because it is the least extractable of the three actinides present in the PFP waste, Am(III) is the key component in TRU removal from PFP waste and, hence, the most likely to be affected by variations in acidity, nitrate salt concentration, and temperature. [The distribution ratios of Pu(IV) and U(VI) from the PFP feed in the extraction section are $>10^2$; therefore, the influence of small fluctuations in the process conditions on uranium and plutonium decontamination factors would be negligible.] Fortunately, the distribution coefficient, or ratio, of americium (D_{Am}) is insensitive to HNO_3 concentration above 0.6M. In the limiting case, with only nitrate ion from HNO_3 present, an increase from 0.8 to 3.0M HNO_3 would decrease D_{Am} only 10%. With five stages in the extraction section, the resulting decontamination factor for americium would be smaller; and the TRU concentration in the solidified aqueous raffinate (DF) would increase from 3 to 5 nCi/g.

Scrub and stripping sections are more sensitive to HNO_3 concentration because, at low HNO_3 levels (<0.8M), D_{Am} varies approximately as the second power of the HNO_3 concentration. Thus, HNO_3 concentrations in the scrub and strip feeds must be controlled carefully to get the desired stripping of americium from the solvent. Variations of HNO_3 concentrations in the scrub and strip feeds will have almost no effect on the decontamination factor for americium in the extraction section.

A decrease in salt concentration would also result in a small decrease in D_{Am}. If the concentration of nitrate salts in the feed were essentially zero, D_{Am} would decrease 38%. In this limiting case, the reduced decontamination factor for americium would allow the TRU concentration in the solidified aqueous raffinate (DW) to increase from 3 to 33 nCi/g. On the other hand, an increase in nitrate salt concentrations would produce an increase in D_{Am}, particularly if the salt were aluminum nitrate.

The value of D_{Am} increases with a decrease in temperature. Distribution ratios for flowsheet development studies were measured at 30°C, which is probably higher than the actual processing temperature for PFP waste. Therefore, processing performed at 25°C would result in somewhat more efficient removal of TRU elements from the aqueous feed and somewhat less efficient stripping of the organic solvent.

b. Organic Feed

As with the aqueous feed, flowsheet performance focuses on the removal of americium from the aqueous raffinate (DW) and on how that removal depends on the concentration of various components in the organic feed. The

distribution coefficient for americium varies as the third power of the concentration of CMPO in the solvent.* Thus, it is important to hold the CMPO concentration in the solvent to fairly close tolerances to realize the calculated flowsheet performance. To this end, CCl_4 was added to the recycled organic solvent during the countercurrent demonstration of the flowsheet to replace expected CCl_4 losses.

Another factor that could affect flowsheet performance is an inadequate solvent strip or solvent cleanup. If americium concentration builds up in the recycled organic phase, the extent to which americium can be removed in the aqueous raffinate (DW) will be limited, no matter how many extraction stages are used.

B. Flowsheet Demonstration Results

The flowsheet described in Section III.A was demonstrated in a 14-stage centrifugal contactor; the experimental procedure for this experiment is described in Appendix A, Section 1. Before the requisite amounts of uranium, plutonium, and americium were added to the feed, the process was run to obtain samples of outlet streams for measuring concentrations of inert elements. Following this run, referred to as the cold run, actinide elements and $NaNO_2$ (0.01M) were mixed into the feed and left to stand for 18 hours before the hot run was begun.

The americium and plutonium concentrations in the aqueous raffinate waste stream (DW), americium product stream (EW), plutonium product stream (FW), and spent process solvent (FP) are shown in Tables III-3 to III-6, respectively. Table III-7 shows the decontamination factors achieved for americium and plutonium from the aqueous feed (DF) and the level of alpha activity in the neutralized and solidified raffinate (solidification by evaporation to a nitrate salt mixture). The compositions of the americium and plutonium product streams (EW and FW) with respect to inert constituents in solution are shown in Table III-8. Total composition of both streams on a weight basis is shown in Table III-9. Table III-10 shows the distribution ratios of americium, D_{Am}, that were obtained by equilibrating the aqueous and organic phases collected from each contactor stage after the termination of the hot test run. Because distribution ratio and density measurements of FP fractions indicated that the final CMPO concentration was about 0.30M, Table III-10 also gives calculated D_{Am} values obtained when the CMPO concentration was corrected from 0.30 to 0.25M.

1. Decontamination of Feed Stream (DF)

The data in Tables III-3 and III-7 show that the TRUEX process, when operated as described in the flowsheet in Fig. III-1, reduces the TRU concentration in the feed to well below the goal of 10 nCi/g of disposed waste form. The decontamination factors and activities were calculated using the average ^{241}Am activity in samples DW-4, -5, and -6 and the plutonium activity in

*The plutonium and uranium distribution coefficients vary as the second power of the CMPO concentration, and that for HNO_3 is assumed to vary as the first power.

Table III-3. Plutonium and Americium Concentrations in the DW Stream Samples

Sample Number[a]	Concentration in Aqueous Raffinate Stream (DW)			
	Americium[b]		Plutonium[c,d]	
	10^5 dpm/L	10^{-10}M	10^5 dpm/L	10^{-8}M
DW-1	2.1	1.1	-	-
DW-2	1.5	0.81	-	-
DW-3	1.5	0.81	3.0	0.62
DW-4	2.4	1.3	-	-
DW-5	3.2	1.7	-	-
DW-6	2.7	1.5	5.4	1.1

[a]Taken at three-minute intervals during run; see Section 1 of Appendix A for details.

[b]Specific activity = 7.6×10^{12} dpm/g.

[c]Specific activity = 2.03×10^{11} dpm/g.

[d]Measured by isotopic dilution and mass spectrometric analysis. Mass spectrometric analysis was performed by E. L. Callis, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

Table III-4. Plutonium and Americium Concentrations in the EW Stream Samples

Sample Number[a]	Concentration in Americium Product Stream (EW)			
	Americium[b]		Plutonium[c,d]	
	10^{10} dpm/L	10^{-5}M	10^6 dpm/L	10^{-8}M
EW-1	0.80	0.43	-	-
EW-2	1.8	0.97	-	-
EW-3	1.9	1.0	3.7	7.6
EW-4	2.2	1.2	-	-
EW-5	2.5	1.4	-	-
EW-6	2.6	1.4	3.4	7.0

[a]Taken at three-minute intervals during run; see Section 1 of Appendix A for details.

[b]Specific activity = 7.6×10^{12} dpm/g.

[c]Specific activity = 2.03×10^{11} dpm/g.

[d]Measured by isotopic dilution and mass spectrometric analysis. Mass spectrometric analysis was performed by E. L. Callis, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

Table III-5. Plutonium and Americium Concentrations in the FW Stream Samples

Sample Number[a]	Concentration in Plutonium Product Stream (FW)			
	Americium[b]		Plutonium[c]	
	10^9 dpm/L	10^{-6}M	10^9 dpm/L	10^{-5}M
FW-1	0.10	0.054	0.79	0.16
FW-2	0.82	0.45	7.0	1.4
FW-3	2.2	1.2	7.9	1.6
FW-4	3.7	2.0	8.1	1.7
FW-5	4.1	2.2	8.0	1.6
FW-6	4.4	2.4	8.3	1.7

[a]Taken at three-minute intervals during run; see Section 1 of Appendix A for details.

[b]Specific activity = 7.6×10^{12} dpm/g.

[c]Specific activity = 2.03×10^{11} dpm/g.

Table III-6. Plutonium, Americium, and CMPO Concentrations in the FP Stream Samples

Sample Number[a]	Concentration in Recycled Solvent Stream (FP)				
	Americium[b]		Plutonium[c]		CMPO,[d] M
	10^7 dpm/L	10^{-8}M	10^6 dpm/L	10^{-7}M	
FP-1'					0.26
FP-2'					0.26
FP-3'					0.27
FP-1	0.15	0.081	-	-	0.27
FP-2	0.69	0.37	-	-	0.27
FP-3	1.9	1.0	-	-	0.27
FP-4	3.3	1.8	-	-	0.28
FP-5	5.0	2.7[e]	-	-	0.28
FP-6	4.7	2.5[e]	5.8	1.2[f]	0.28

[a]Taken at three-minute intervals during the cold (1', 2', 3') and hot demonstrations; see Appendix A for details.

[b]Specific activity = 7.6×10^{12} dpm/g.

[c]Specific activity = 2.03×10^{11} dpm/g.

[d]Based on the measurements of D_{Am} between 2.0M HNO_3 and the FP samples and the known D_{Am} value (12) between 2.0M HNO_3 and 0.25M CMPO-0.75M TBP in CCl_4.

[e]Average of americium in samples 5 and 6 represents 0.17% of the total americium.

[f]Represents 0.14% of the total plutonium.

Table III-7. Decontamination Factors for Plutonium and Americium Extracted from Simulated PFP Waste

Radionuclide	Activity in Feed, nCi/L	Activity in Raffinate,[a] nCi/L	Decontamination Factor[b]	Activity in Solid Raffinate,[c] nCi/g
$^{238,239,240}Pu$	6.58×10^5[d]	2.4×10^2	2.4×10^3	1.2 (0.80)[e]
^{241}Am	5.00×10^6[f]	1.2×10^2	3.7×10^4	0.58
Total		3.6×10^2		1.8 (1.38)[e]

[a]Based on the plutonium concentration in sample DW-6 and the average ^{241}Am concentrations in samples DW-4, -5, and -6.

[b]Corrected for dilution of feed by scrub.

[c]Assuming that the weight of a liter of neutralized raffinate after evaporation is 206 g.

[d]Based on 7.2×10^{-3} g(Pu)/L and a specific activity of the plutonium mixture (0.05% ^{238}Pu, 86.46% ^{239}Pu, and 11.84% ^{240}Pu) of 2.03×10^{11} dpm/g.

[e]Parenthetical entry is based on the plutonium all being ^{239}Pu (specific activity of 1.36×10^{11} dpm/g).

[f]Based on 1.4×10^{-3} g(^{241}Am)/L and a specific activity of 7.6×10^{12} dpm/g.

Table III-8. Concentrations of Inert Constituents in EW and FW Product Streams during the Cold Run[a]

Element[c]	Concentration in Stream Samples,[b] 10^{-6}M					
	EW-1'	EW-2'	EW-3'	FW-1'	FW-2'	FW-3'
Cr	3.0	<2.4	<2.4	4.2	3.6	<2.4
Mn	2.2	<0.56	<0.56	3.0	5.1	1.6
Fe	570	700	720	200	570	570
Ni	2.4	2.2	<2.1	3.9	14	3.5
Cu	39	13	9.0	33	16	8.4
Zn	1.2	0.09	0.09	4.1	0.95	2.0

[a]Data were obtained by E. A. Huff, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory, using inductively coupled plasma/atomic emission spectroscopy.

[b]These sample numbers bear prime symbols because they were generated during the operation using feed containing no U, Pu, or Am; see Appendix A.

[c]The concentrations of Be, Al, Mg, Ca, and Pb were all below the detectability limits of 3.9×10^{-6}M, 23×10^{-6}M, 1.3×10^{-6}M, 7.8×10^{-6}M, and 1.5×10^{-6}M, respectively.

Table III-9. Composition of the Americium (EW) and Plutonium (FW) Product Streams

	Composition in Product Stream			
	Americium (EW)		Plutonium (FW)	
Element	mg/L	wt %	mg/L	wt %
Mn	-	-	0.009	0.013
Fe	40	91	31	45
Ni	-	-	0.020	0.028
Cu	0.06	1.4	0.053	0.075
Zn	0.006	0.014	0.013	0.018
Pu	0.017	0.038	38	54
Am	3.5	7.9	0.39	0.55

Table III-10. Distribution Ratios of Americium by Stage after Termination of the Demonstration Run

Stage No.	Stage Type	Distribution Ratio of Americium	
		Measured[a]	Calculated[b]
1	Extraction	31	18
2	Extraction	29	17
3	Extraction	27	16
4	Extraction	35	20
5	Extraction/Feed	32	19
6	Scrub	17	9.8
7	Scrub	15	8.7
8	Strip 1	4.0	2.3
9	Strip 1	0.69	0.40
10	Strip 1	0.30	0.17
11	Strip 1	0.30	0.17
12	Strip 2	0.31	0.18
13	Strip 2	0.25	0.14
14	Strip 2	0.20	0.12

[a]Based on the measured D_{Am} values in the extraction section, the CMPO concentration was assumed to be 0.30M.

[b]Distribution ratio that should have occurred had there been no evaporative losses of CCl_4; i.e., for a 0.25M CMPO concentration.

sample DW-6. However, the americium and plutonium contents of the DW samples are not constant and generally increase in magnitude with the time of sampling. If sample DW-3 had been used to calculate the alpha activity in the raffinate, the level would have been only 1 nCi/g.

Worksheet calculations of the alpha activity in the raffinate predicted 3 nCi/g of solid neutralized raffinate, based on a D_{Am} of 17 to 18 and a plutonium distribution ratio (D_{Pu}) > 10^2 in the extraction stages. Thus, the americium decontamination factor was greater than expected. The plutonium decontamination factor, on the other hand, was much lower than anticipated and much lower than achieved during an earlier test of TRUEX using a dissolved sludge waste feed [VANDEGRIFT-1984A].

2. Americium Product Stream (EW)

The data in Table III-4 show that a steady buildup of [Am]* occurred in the americium product stream (EW). The total americium recovered in the EW stream was 88%, based on an average concentration in samples EW-5 and -6. Worksheet calculations predicted that 99.86% of the americium would be stripped into the EW stream.

Table III-4 also shows the [Pu] lost to the EW stream. Worksheet calculations predicted 0.23% of the plutonium would report to the EW stream, whereas the stream contained only ∿0.09% plutonium.

3. Plutonium Product Stream (FW)

The data in Table III-5 show that, after an initial buildup to steady-state conditions, essentially all the plutonium was stripped into the FW stream. However, the ineffective stripping of americium in stages 8 through 11 resulted in ∿12% of the americium reporting to the FW stream, instead of <0.1%, as predicted.

4. Spent Process Solvent Stream (FP)

Table III-6 shows the [Am] and [Pu] remaining in the stripped TRUEX process solvent. The average [Am] in FP-5 and -6 and the [Pu] in FP-6 represent 0.17% and 0.14% of the total americium and plutonium, respectively. Calculations predicted 0.001% of the americium and 0.02% of the plutonium would be in the FP stream.

Table III-6 also shows the calculated [CMPO] in FP fractions based on D_{Am} measurements. The FP fractions collected during the cold run are also included. Both sets of samples show a gradual increase in [CMPO]. Gas chromatographic analysis of sample FP-6 confirmed that [CMPO] was in the range of 0.28-0.30M.†

*Brackets around a chemical symbol indicate concentration.

†Analysis performed by A. S. Boparai, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

5. NonTRU Constituents in EW and FW Product Streams

Table III-8 shows the concentrations of nonTRU constituents in the americium (EW) and plutonium (FW) product streams collected during the cold run (their concentrations in the feed are presented in Table III-2). The concentrations of all nonTRU feed constituents except iron are reduced to undetectable or insignificant levels in the EW and FW product streams. Table III-9 gives the compositions of the americium and plutonium product streams on a weight basis. Iron is a major constituent in both products.

C. Discussion

Overall, the flowsheet demonstration run went well. Based on the results, modifications to the reference flowsheet in the extraction, scrub, and both strip sections can be recommended with a high degree of confidence. The solvent cleanup operations, discussed in Section III.C.7, are given a conditional recommendation pending further laboratory and flowsheet tests, because they were determined from laboratory tests discussed in Section V and have not yet been subjected to a full countercurrent flowsheet demonstration.

In this section, the solvent loss rate is discussed first, because it impacted on all other results. This is followed by a discussion of four key components (HNO_3, Fe, Pu, and Am), which did not behave quite as expected, either because of unexpected values of their distribution coefficients or because of higher-than-expected evaporative losses of the diluent. Then, other constituents are discussed. Finally, flowsheet modifications that address the problems reviewed are outlined.

1. Evaporative Loss Rate of CCl_4

Based on the evaporative loss tests discussed in Section IV.B, we expected that an overall evaporative loss rate of the CCl_4 diluent in the solvent would be 3 mL/min during the demonstration run. Carbon tetrachloride was added at this rate during the run to make up for its expected loss. After the run, the evaluation of the data by four different methods (density measurements of the solvent, gas chromatographic analysis of the solvent, determination of D_{Am} of the various solvent samples, and an overall material balance of all solvent fractions accumulated during the demonstration run) indicated that the CCl_4 loss rate had actually been substantially higher, about 11 mL/min, on the assumption that the loss occurred only while the contactor was operating.

Precautions had been taken to ensure that the evaporative loss rate for CCl_4 would be the same for the demonstration run as it had been earlier for the evaporative loss tests. To keep the solvent in a closed container and minimize evaporative losses, a 4-L glass reaction kettle was used as the solvent feed tank. The ground-glass joints in the cover of the reaction kettle allowed connection of the solvent feed (DX) and return (FP) lines without exposing the kettle contents to the outside air. The room temperature was kept low, close to or below that for the earlier evaporative loss tests. The lines going to and from the contactor and the interstage lines were free of leaks, and the same solvent pumps were used. When this experimental setup was used for the evaporative loss tests, the rate of CCl_4 evaporation was

found to be higher than, but close to (within 50%), the rate predicted from the energy input into the system by the contactor rotors. The higher evaporative loss rate observed during the demonstration run suggests that an additional source of heat existed while carrying out the flowsheet demonstration. This heat could have come from the heat of solution released as the aqueous feed containing 1.5M HNO_3 was equilibrated with the organic phase containing almost no HNO_3. Further tests are needed to verify that the energy released by this heat of solution actually caused the additional 8 mL/min of CCl_4 loss. Because of the high loss rate, several techniques to reduce evaporative loss are discussed in Section IV.B. We expect that, by incorporating one or more of these techniques, significantly lower loss rates, i.e., 1% or less of the total solvent flow rate, could be realized.

The high evaporative losses of CCl_4 might have occurred by another means, by evaporation from the contactor stages as the unit sat overnight in the glove box. These losses were expected to be minimal because of the water layer over the solvent. However, the effectiveness of this water layer has never been tested. As detailed in Appendix A, Section 1, the two liquid phases remained overnight in the contactor stages both between the cold and hot (demonstration) runs and between the hot run and the collection (draining) of the stage liquids after the hot run. This possible mechanism for the extra loss is suggested by Table III-6, which shows that the [CMPO] in the solvent during the hot run rose from 0.27 to 0.28M, and by Table III-10, which projects the [CMPO] in the solvent from the stage samples to be 0.30M, as measured the day after the run. Thus, about two-thirds of the unexpected CCl_4 loss may have occurred while the solvent was sitting overnight in the contactor stages or during further handling and aliquoting of the samples.

The [Am] in the aqueous raffinate (DW) was fairly constant, suggesting that only a small fraction of americium leaving in the organic effluent (FP) was getting back to the organic feed port. A look at the overall 20-minute test shows that the [Am] in the organic feed would have been higher with a higher degree of mixing in the solvent feed tank. With 60 to 75 mL of solvent per stage, the americium introduced into the feed stage at time zero takes four or five minutes to flow through the ten stages between the feed stage and the solvent effluent. Thus, the initial [Am] in the effluent is much less than its later steady-state value. The solvent feed and return lines contained about 100 mL of solvent, and the solvent feed tank contained 1550 mL of solvent at the outset. The solvent feed (DX) is taken from the very bottom of the solvent feed tank, whereas the returning organic phase (FP), with a volume loss of up to 7% as a result of the CCl_4 loss, is less dense and floats to the surface of the solvent feed tank, which contains no mixer. Thus, all the solvent free of americium was used before the first solvent containing any traces of americium was used. Eleven minutes is required before the americium-free solvent is gone. Thus, it would be 15 to 16 minutes into the run before the first solvent containing trace amounts of americium was fed to Stage 1 where the aqueous raffinate (DW) was exiting. The six DW effluent samples were taken at 2, 5, 8, 11, 14, and 17 minutes. Sampling time was about 45 seconds. Thus, only the last DW sample might have been affected by americium in the solvent, but the [Am] would still have been very low and, thus, have had little effect. The experimental values for the DW samples show that this was the case.

A second explanation of why the [Am] in the DW stream was fairly constant is that a small but rising fraction of the americium getting back to the DX feed from the organic effluent (FP) was offset by the higher D_{Am} caused by the higher [CMPO]. Thus, the [Am] in the aqueous raffinate (DW) stays about constant. The actual situation of a fairly constant [Am] in the DW stream was probably a result of a combination of these two explanations.

2. Nitric Acid

Because of the evaporative losses of CCl_4, the [CMPO] in CCl_4 rose from its initial value of 0.25 to about 0.30M by the end of the experiment. The distribution coefficient of HNO_3 in the process would also increase, because it is assumed to be proportional to the [CMPO] in the solvent. Thus, the two-stage scrub section, which, among other things, scrubs much of the HNO_3 from solvent, would be somewhat less effective than planned. In addition, with only two stages in the scrub section, the acid concentration in the solvent leaving the scrub section is about twice as high as it would be if more scrub stages were present. The result is a higher acid concentration in the first stages (8 and 9) of the first strip, and a reduced ability of the first aqueous strip to recover the americium from the solvent.

To verify the higher acid concentrations in stages 8 and 9, the aqueous phases collected from these two stages after the hot run were measured and found to have HNO_3 concentrations of 0.26 and 0.10M, respectively. Preliminary batch extraction tests of the flowsheet indicated that these values should have been 0.14 and 0.06M, respectively. On the assumption that the [CMPO] was constant at 0.25M, the difference in acidity in stage 8 (where the EW stream exits) would produce a D_{Am} of 2.6, instead of 1.0.

3. Iron

The distribution coefficient of iron (D_{Fe}) is higher (0.25) than expected (0.061) [HORWITZ-1982, -1985D] in the scrub section, resulting in more iron in the EW effluent. This unexpected behavior of iron may be due to the slow kinetics of Fe(III) extraction into the solvent [KALINA-1981]. The net result is that the D_{Fe} for back extraction is one to two orders of magnitude greater than that determined by forward extraction with a short (1- to 2-minute) period in the mixing zone. The addition of a third scrub stage would reduce the iron concentration in the EW stream by about half. Additional scrub stages would result in similar additional reductions of iron in the americium product until the iron from some other source, for example, from the aqueous feed to the first strip, becomes the controlling factor.

Like the scrub section, the americium stripping section does not effectively remove all the iron from the organic phase. Therefore, iron is also found in the plutonium product stream (FW). This second stripping section does effectively remove iron from the TRUEX process solvent. Thus, as shown in Table III-9, iron is a major constituent in both the americium and plutonium products. This probably will not present any problems if the plutonium is recycled into the feed of a PUREX-type extraction process and the americium product is converted to glass.

4. Plutonium

With the higher than expected nitric acid and CMPO concentrations in the first strip section, less plutonium than expected came out in the americium product effluent. Almost all the plutonium came out in the second strip where the concentration of 0.05M HF in the aqueous phase proved to be effective in stripping the plutonium from the solvent. After the second strip, only 0.15% of the plutonium remained in the organic effluent (FP). This shows the effectiveness of the dilute mixture of nitric and hydrofluoric acids for stripping plutonium from the TRUEX-CCl_4 solvent. Tests made after the demonstration run showed that plutonium remaining in the solvent from the second strip could be washed out using a sodium carbonate solution. Thus, a sodium carbonate wash for the solvent, recommended in Section III.C.7 as part of the flowsheet modifications, would effectively remove any plutonium not recovered by the second strip.

A small amount of the plutonium (0.04%), which may be an inextractable plutonium polymer inasmuch as the distribution coefficient for Pu(IV) in the extraction section is so high and that of Pu(III) is about equal to D_{Am}, came out in the aqueous raffinate (DW). The polymer could have come from the plutonium sample used to make up the feed. Plutonium polymer is believed to have a distribution ratio less than 1.0 for TRUEX process solvent [HORWITZ-1985C].

5. Americium

With the 16 to 20% higher [CMPO] in the solvent, the D_{Am} values given in Table III-1 are increased sharply due to the third-power dependence of D_{Am} on [CMPO]. Thus, a 16 to 20% increase in [CMPO] produces a 56 to 73% increase in D_{Am}, giving better than expected performance in recovery of americium from the aqueous raffinate (DW) and a poorer than expected performance in the stripping of americium from the solvent in the strip sections. Thus, 88% of the americium was recovered in the first strip, whereas 99.9% recovery was expected. Then, 98% of the remaining americium was recovered in the second strip, where the higher O/A flow ratio in this section cuts down on the effectiveness of americium recovery. The remaining 0.2% of the americium ends up in the organic effluent (FP). Tests on the FP samples from the demonstration run show that the americium would have been stripped from the solvent as expected had the [CMPO] in the solvent not increased.

The actual values of D_{Am} for each stage were measured from the demonstration run. These actual values (Table III-10) vary from the expected values (Table III-1) in the way that the observed changes in the HNO_3 and CMPO concentrations, mainly the latter, would predict. The [Am] in each effluent, calculated using an electronic worksheet [LEONARD-1985] (see Appendix A, Section 6), is shown in Table III-11 for these two sets of distribution coefficients, along with the measured effluent [Am].

Also shown in Table III-11 is a third set of americium concentrations calculated for the effluent streams using corrected values of D_{Am}. The corrected coefficients were determined, as discussed in Section 6 of

Table III-11. Measured and Calculated Americium Concentrations in the Effluents near the End of the Demonstration Run

Effluent Stream	Time into Run, min	Measured [Am], 10^{-6}M	Calculated [Am],[a] 10^{-6}M		
			Case 1[b]	Case 2[c]	Case 3[d]
Aqueous Raffinate (DW)	17	1.45E-4	8.8E-4 (8.8E-4)	4.2E-5 (4.2E-5)	1.44E-4 (1.44E-4)
Americium Product (EW)	18	13.6	16.0 (16.0)	12.2 (13.2)	14.1 (14.7)
Plutonium Product (FW)	18	2.3	0.039 (0.039)	3.6 (4.2)	1.47 (1.59)
Organic Effluent (FP)	18	0.026	1.2E-4 (1.2E-4)	0.155 (0.163)	0.025 (0.028)

[a]Shown for the appropriate time into the run. The calculated [Am] at steady-state conditions is given in parentheses.

[b]Uses the expected distribution coefficients given in Table III-1, and assumes immediate recycle of the organic effluent. This is Case A in Table A-5 of Appendix A.

[c]Uses the measured distribution coefficients given in Table III-10, and assumes no recycle of the organic effluent. This is Case C in Table A-5 of Appendix A.

[d]Uses corrected distribution coefficients, as discussed in Appendix A, Section 6, and assumes no recycle of the organic effluent. This is case E in Table A-5 of Appendix A.

Appendix A, by considering the effects of temperature, stage efficiency,* and [CMPO]. The stage efficiency was essentially 100%. The temperature effect appeared to be small. The corrected values of D_{Am}, which correspond to a [CMPO] between 0.27 and 0.28M, as shown in Table III-6, permit prediction of the [Am] in both the aqueous raffinate (DW) and the organic effluent (FP). The approach of the organic effluent (FP) to a steady-state [Am], as calculated by the electronic worksheet using the corrected D_{Am} values and as shown in Table A-9 of Appendix A, matches closely the measured concentrations shown in Table III-6.

As discussed in Appendix A, Section 6, the stripping sections of the contactor were expected to reach steady state well within three residence times (the residence time for the organic phase is six to seven minutes, and those of the aqueous phases are even less). However, because of the high HNO_3 and CMPO concentrations, the two strip stages nearest the EW exit, stages 8 and 9, had americium extraction factors† close to or greater than 1.0. This caused an americium buildup in the solvent in the first stripping section. The buildup occurred slowly, being limited by the rate at which americium was entering the contactor. This slow buildup of americium in the strip sections, while the extraction and scrub sections are at steady state, can be seen in the worksheet results for Case E in Appendix A, Section 6. Thus, the gradual increases of americium in three output streams, EW, FW, and FP, although not seen in worksheet calculations based on the expected coefficients for americium, are in agreement with calculated results using the actual D_{Am} values in the contactor stages.

The [Am] in the aqueous phase, calculated from the corrected values of D_{Am}, is plotted as a function of stage number in Fig. III-2. The measured effluent concentrations are also plotted on the figure, and agree quite well with the calculated values. The aqueous concentrations of americium in the stages, determined after the demonstration run, generally agree with, but are somewhat scattered about, the calculated values. This data scatter results from the way that the run was terminated. The pumps were turned off about five seconds before the rotors were, and continued pumping for only a few seconds. When the rotor motors were turned off, the rotors continued spinning for 10 or 15 seconds. Thus, the spinning rotors continued to pump liquid from stage to stage for a short time while no liquid was coming in from the pumps. The deviations, from the calculated [Am], of the [Am] measured in each stage can be explained qualitatively by the shutdown procedure.

Overall, the americium separation from the nonTRU elements went well. With a reduction of [CMPO] from about 0.275 to 0.25M, more americium would be removed from the solvent in the first strip, and the americium contamination in the plutonium product (FW) would be reduced to the expected values shown in Fig. III-1.

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*Stage efficiency is the ratio of the amount of a component extracted from one phase into the other phase to the amount that would be extracted if the two phases were at equilibrium. Thus, if the exiting effluents from a stage are completely equilibrated, the stage efficiency is 100%.

†The extraction factor for a component is the distribution coefficient for that component times the O/A flow ratio in the stage.

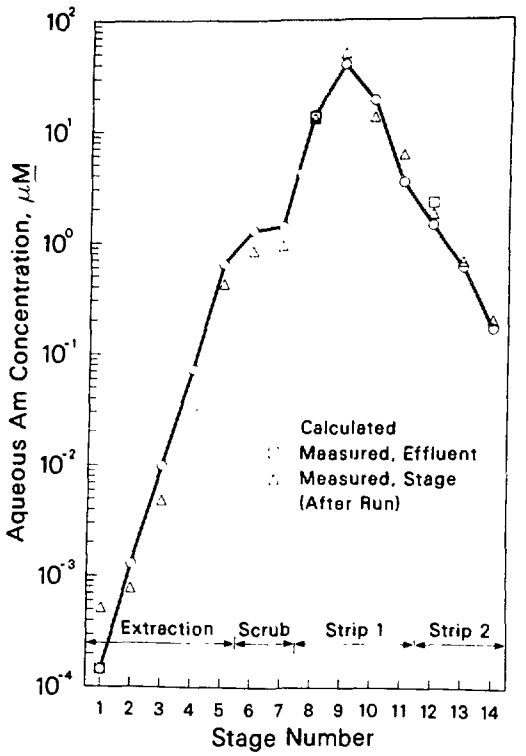

Fig. III-2.

Americium Concentration as a Function of Stage Number at the End of the Demonstration Run

6. Other Constituents

Besides the iron discussed in Section III.C.3, the only detectable nonTRU metals in the americium (EW) and plutonium (FW) product streams are Cr, Mn, Ni, Zn, and Cu, as shown in Table III-8. The presence of Cr, Mn, and Ni in these effluents is likely a result of corrosion of the stainless steel. The source of the Cu is probably from a previous demonstration run of the 14-stage contactor bank. The source of the Zn is not known.

7. Flowsheet Modifications

Based on the above discussion, the flowsheet depicted in Fig. III-1 is being revised. An outline of possible revisions is given here. These include the use of tetrachloroethylene (TCE) instead of CCl_4 as the diluent for the solvent, a lower HNO_3 concentration in the feed to the scrub section and the first strip section, improved control of the diluent concentration in the solvent, and use of solvent cleanup stages.

a. Tetrachloroethylene as Diluent

Because CCl_4 is more volatile than TCE, the latter must be given serious consideration as the diluent in TRUEX process solvent. The lower volatility of TCE is reflected in its higher boiling point (121°C vs. 77°C for CCl_4) and its lower vapor pressure (about 17% of that of CCl_4).

In other respects, the two diluents have very similar properties, including density, viscosity, latent heat of vaporization, and the distribution ratios of Am(III) and Pu(IV) [HORWITZ-1985C]. Thus, if TCE were used as the diluent in place of CCl_4, it would not be necessary to change the CMPO and TBP concentrations in the TRUEX process solvent, the number of stages, or the relative flows. In addition, the plutonium retention number and the amount of Cl^- produced per watthour of irradiation are lower for TCE than for CCl_4 [BARNEY].

b. Scrub

The HNO_3 concentration in the scrub solution should be lowered from 0.25 to 0.20M, and one or two additional scrub stages should be added. These changes would reduce the concentration of HNO_3 in the organic phase entering the first strip stage, which would, in turn, lower D_{Am} in the strip section and improve the stripping factor for the back extraction of americium. The addition of two scrub stages would reduce the iron content of the americium and plutonium products to about 65 and 14 wt % of the product, respectively. The diminution in D_{Am} that will occur in the scrub stages when the HNO_3 concentration is reduced will increase the quantity of americium returned to the feed stage. Although this will result in a somewhat larger buildup of americium in the organic phase feeding into the scrub stages, it will not reduce the decontamination factor for americium between the aqueous feed (DF) and the aqueous raffinate (DW).

c. First Strip

The HNO_3 concentration in the aqueous feed to the first strip should be reduced from 0.05 to 0.04M. This reduction in acidity would reduce D_{Am} by 50%, thereby improving the stripping factor. An additional stage in the first strip is also worthy of consideration. The additional stage would ensure at least 99.9% removal of americium from the organic phase before it enters the plutonium stripping section, even if the acidity in the earlier strip stages is higher than expected.

d. Control of Diluent Concentration

As seen from the demonstration run, the diluent concentration in the solvent must be controlled fairly closely if the flowsheet is to operate as designed. As the diluent (CCl_4 or TCE) evaporates, TRUEX process solvent becomes less dense as a result of the increase in concentration of the less dense components, TBP and CMPO. To monitor this, a continuous-reading densitometer in the solvent feed line (DX) is recommended. The densitometer would control diluent addition using a diluent feed pump. A second option is to install such a densitometer and diluent feed pump in the solvent return line (FP). For this case, continuous stirring of the solvent reservoir is recommended to ensure a uniform diluent concentration in the solvent.

Another method of monitoring the solvent (although not applicable to continous monitoring) is to measure the D_{Am} in the solvent with 2.0 and 0.01M HNO_3. Because D_{Am} is directly third-power dependent on [CMPO], excessive evaporative loss of the diluent will cause significant increases in D_{Am}, as was experienced in the demonstration run. The 2M HNO_3 measurement

enables one to calculate the [CMPO] to within ±2%, whereas the 0.01M HNO_3 measurement indicates the presence of acidic extractants that can reduce stripping efficiency. Both measurements are necessary to assess the quality of the solvent. A standard procedure for these measurements could be devised and easily implemented. The distribution ratio measurements give a more accurate measure of [CMPO] (when performed in triplicate), require less time, and are less costly than a gas chromatographic analysis.

e. Solvent Cleanup

One or two solvent wash stages using Na_2CO_3 are envisioned to remove any uranium and dibutyl phosphoric acid (HDBP) that may be in the organic solvent. In addition, the Na_2CO_3 neutralizes HNO_3 and HDBP in the solvent and strips their sodium salts as $NaNO_3$ and sodium dibutyl phosphate (NaDBP), respectively. The dibutyl phosphate (DBP) ion forms a gel with iron if the DBP is not removed. The solvent wash removes uranium as a carbonate complex. The uranium would otherwise build up in the solvent, because its distribution coefficient in the solvent is greater than 1.0 throughout the rest of the flowsheet. The spent wash solution would be recycled, with the required addition of Na_2CO_3 to maintain its concentration at a constant level, until sufficient buildup of nitrate ion or the trace components required the solution to be discarded. The distribution coefficients of the trace components removed in the solvent wash will vary as the solvent and the wash solutions are recycled. Even if a small amount of Na_2CO_3 solution is entrained in the solvent, it should have no effect on the operation of the rest of the flowsheet.

A second solvent cleanup step, an acid rinse stage, is attractive if minimal aqueous entrainment in the recycled solvent is required. The acid could be either 0.1M oxalic acid or 0.1M HNO_3. Oxalic acid is preferred, as it would provide a further uranium removal step. In either case, the solvent treated by the acid rinse produces a much clearer solvent with less aqueous phase entrainment in the solvent being recycled.

f. Effects of the Revised Flowsheet on Species Concentrations

The revised flowsheet outlined here will have only a minimal effect on the concentrations given in Table III-2. The concentration of HNO_3 will be zero in the recycled organic solvent (DX), unless an acid rinse is used. The iron concentration in the EW effluent will be lower by a factor of about two for each additional scrub stage. The concentrations of Am, Pu, and U in the DX feed will remain low. The uranium concentration in the other effluents will be lowered by about a factor of 20. The plutonium concentration in the EW effluent will be slightly higher, but still under 1% of the total plutonium in the feed. The americium concentration in the plutonium product stream (FW) will be even less than the 0.1% shown in Table III-2.

IV. EVALUATION OF CENTRIFUGAL CONTACTORS

The hydraulic performance of annular centrifugal contactors used with an acidic aqueous phase and an organic solvent such as tributyl phosphate (TBP) in a diluent of n-dodecane (nDD) or other normal paraffinic hydrocarbon (NPH) is well established [BERNSTEIN-1973A,B; LEONARD-1980, -1983; WEBSTER]. The contactors were also expected to work well with chlorinated hydrocarbon diluents such as tetrachloroethylene (TCE) and CCl_4; however, this had never been demonstrated and, therefore, needed to be evaluated. When a chlorinated hydrocarbon is the diluent, the solvent is more dense than the aqueous phase. In this section, we report the operation of centrifugal contactors when the more dense phase is the solvent (organic phase) and verify that the contactors do work as expected. Also discussed are the evaporative losses associated with chlorinated hydrocarbons, which are much more volatile than nDD or NPH.

A. Hydraulic Performance

To test the flowsheet described in Section III, a 12-stage 4-cm contactor, shown in Fig. IV-1, was built and tested for hydraulic performance with PUREX process solutions (aqueous phase, 0.01M HNO_3; organic phase, 30% TBP in NPH). Every stage was checked for rotor leaks, and none were found. Process throughputs of 0.8 L/min were obtained as predicted by the contactor design theory developed at Argonne National Laboratory. The maximum throughput* that was measured was 0.9 ± 0.1 L/min.

After the 12-stage contactor was checked out and fully operational,† it was operated at 300 mL/min of 0.2M HNO_3 for the aqueous phase flow and 300 mL/min of TRUEX-CCl_4 solvent for the organic phase flow. The aqueous- and organic-phase reservoirs held about 1.0 and 2.0 L of each phase, respectively. Contactor operation, with total recycle of both phases, was continued for 90 minutes. No accumulation of organic phase was seen in the aqueous-phase reservoir, and vice versa, which represents excellent hydraulic performance at 75% of the maximum throughput for the PUREX solvent. When operating at this level, one of the contactor effluents typically contains ~0.5 vol % of the other phase. Over the 90-minute period of the test, this would be expected to result in a significant accumulation (~140 mL) of the organic phase in the aqueous reservoir, or vice versa. However, no such accumulation was seen, which indicates that the maximum throughput for the TRUEX-CCl_4 solvent was markedly higher than that for the PUREX solvent.

As a further guide to hydraulic performance of the TRUEX-CCl_4 solvent, dimensionless dispersion numbers (N_{Di})‡ were measured for two acid concentrations (0.001 and 0.2M HNO_3) and for three organic/aqueous (O/A) volume

*Throughput so high that at least one phase effluent contains 1% of the other phase.

†An additional four stages, which had been built and tested earlier, were also used in the flowsheet test. However, they were not used in the hydraulic performance and evaporative loss tests described in this section.

‡The dispersion number is a measure of how easily a dispersion breaks. It is useful because, for a given rotor design and rotor speed, total throughput is proportional to the dispersion number.

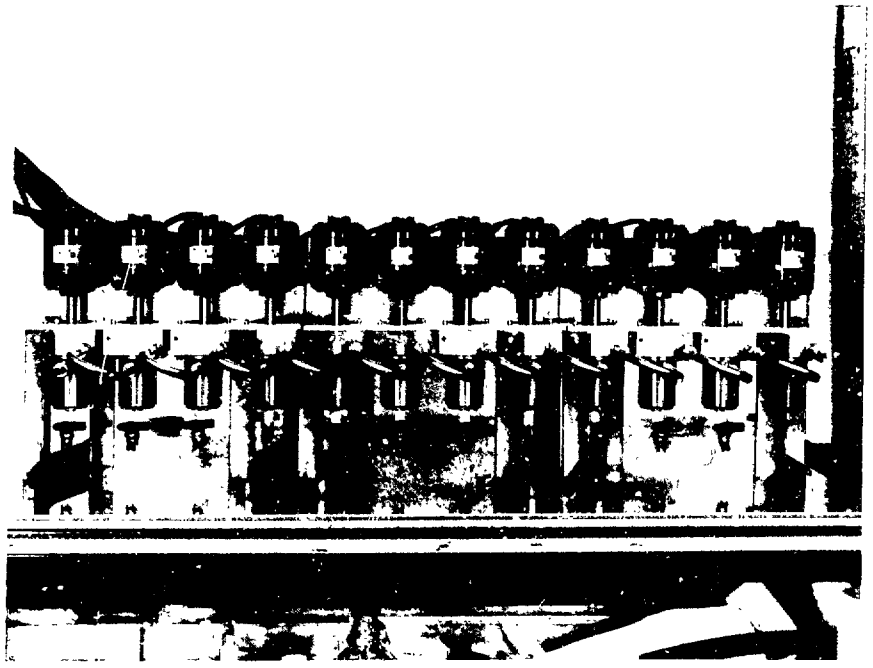

Fig. IV-1. Twelve-Stage 4-cm Annular Centrifugal Contactor

ratios (0.33, 1.0, and 3.0), using a procedure outlined earlier [LEONARD-1981]. The results, given in Table IV-1, show that the dispersion number is variable when the O/A ratio and the acid concentration are both low. This erratic behavior at low O/A ratios disappears at the higher acid concentrations. For the conditions used in the TRUEX flowsheet with CCl_4 as a diluent, the dispersion number is 1.6×10^{-3} or higher. The contactor was designed based on experience with PUREX solvent and nitric acid, a combination that, typically, has a dispersion number of 9×10^{-4}. Thus, based on the higher dispersion numbers for the TRUEX-CCl_4 solvent and nitric acid, contactor throughputs up to 1.5 L/min could, in theory, be realized. In practice, the liquid level in the annular mixing zone of each stage would limit contactor throughput to 1.2 L/min. If the gap in the annular mixing zone of the contactor were enlarged by 60%, with an attendant small loss in extraction efficiency, contactor throughputs up to 1.5 L/min, the limit set by the dispersion number, could be obtained in the 4-cm unit. However, near maximum throughput, one or both effluents would then have an increased carryover of the other phase from some low value, much less than 0.1%, to a value close to 1%.

To conclude the hydraulic performance tests on the 4-cm contactor, the TRUEX flowsheet was evaluated using a synthetic PFP feed without Am, Pu, and U. The flowsheet shown in Fig. III-1 was used with two minor changes: two, rather than three, stages were used for the second strip section and four, rather than five, stages were used for the extraction section. Translucent sections of fluorocarbon tubing permitted observation of liquid flow

Table IV-1. Effect of Acid Concentration on the Dispersion Number for Liquid Systems with CCl_4 as Diluent[a,b]

$[HNO_3]$ in Aqueous Phase (A), M	O/A Volume Ratio	Continuous Phase	Dispersion Number x 10^4
0.001	0.33	A	2.1 to 11.7[c]
	1	O	16 ± 1
	3	O	23.5 ± 1.5
0.2	0.33	A	34 ± 4
	1	O	16 ± 1
	3	O	25 ± 1

[a]Organic phase (O): 1.0M TBP in CCl_4.

[b]Based on batch tests made as described by Leonard, using 100-mL graduated cylinders [LEONARD-1983].

[c]Highest dispersion numbers occur when two phases are initially mixed. Dispersion number decreases as successive tests are made.

in the interstage lines. All effluents were examined for possible other-phase contamination. When the liquid was drained from the stages after testing this flowsheet, a very small amount of loose particles or crud was observed at the interface between the two phases. Loose solids of this type do not impair contactor operation. They will either pass from stage to stage and exit with one of the contactor effluents or be collected in the stage liquid during a run and removed later when the stages are drained. Based on these observations, all stages worked well.

B. Evaporative Losses

To measure the evaporative loss of CCl_4 in the 12-stage contactor, completely closed feed systems were constructed, in which the only route for evaporative losses was the annular gap formed between the rotor shaft as it entered the contactor stage and the splash plate.

The evaporative loss rate was measured for three liquids: water, TCE, and CCl_4. Selected physical properties of these liquids are listed in Table IV-2. For purposes of comparison, the properties of n-dodecane are also listed. Water and TCE have almost the same vapor pressures, whereas that for CCl_4 is greater by a factor of five. Also, TCE and CCl_4 have almost the same latent heats of vaporization, whereas that for water is greater by a factor of 12. Thus, if vapor pressure controls the rate of evaporative loss, the loss rates for TCE and water should be similar. If the latent heat of vaporization controls loss, the loss rates for TCE and CCl_4 should be similar.

Table IV-2. Physical Properties of Various Solvents

Solvent	Vapor Pressure at 20°C, kPa	Latent Heat of Vaporization at 20°C, J/g	Heat Capacity at 20°C, J/(g·K)
nDD[a]	0.01	358	2.09
Water	2.3	2450	4.18
TCE	2.0	210	0.883
CCl_4[b]	11.9	218	0.841

[a]Included for comparison purposes.

[b]For purge gas saturated with CCl_4 at 20°C, the contactor will lose 0.5 mL of CCl_4 (liquid phase) for every liter of purge gas that flows through the system.

Test results, listed in Table IV-3, show that the evaporative loss rates of TCE and CCl_4 are about 12 times that for water, indicating that the latent heat of vaporization is the major factor controlling evaporative loss rates. The TCE loss rates are two to three times lower than those of CCl_4, indicating that vapor pressure is an important secondary factor. As shown in the table, introducing one mole of extractant (TBP) per liter of diluent produces a small reduction in the evaporative loss rate of the diluent.

As a further test of the results, an evaporative loss rate was calculated by assuming that all the energy input to the liquid due to mixing, centrifugation, and pumping was used to evaporate the most volatile liquid component. The results of the calculations, listed in the last column of Table IV-3, show rough agreement of this model with the experimental results. Finally, this model predicts that, when two phases are present so that throughput is doubled, the evaporative loss rate should also be doubled. This effect can be seen by comparing the data in the last two rows of the table.

Based on the evaporative loss data given in the last row of Table IV-3, which show that the solvent loss per stage will be 5.2×10^{-4} mL/min for each mL/min of total liquid throughput in the stage, we have calculated that the evaporative loss rate for the 14-stage flowsheet demonstration would be 3 mL/min. This loss rate is equivalent to 2% of the solvent flow rate through the contactor. As larger units with higher throughputs are built and used, this loss rate will remain at about the same percentage, because the heat input is roughly proportional to contactor throughput. Discussions with Rockwell Hanford personnel indicate that this rate of loss of CCl_4 is about the same as that experienced now in solvent extraction processes using CCl_4 as the diluent in pulsed columns.

Table IV-3. Results of Evaporative Loss Tests in the 12-Stage 4-cm Contactor

Liquid System			Total Liquid Flow Rate, mL/min	Evaporative Loss Rate,[a] mL/h (mL/min)	
More Dense Phase		Less Dense Phase			
Solvent	TBP Concn, M			Measured	Calculated[b]
Water	0.0	None	300	5.5 ± 1.0 (0.092)	5.3 (0.088)
TCE	1.0	None	300	39 ± 5 (0.65)	74 (1.23)
TCE	0.0	None	300	51 ± 5 (0.85)	74 (1.23)
CCl_4	1.0	None	300	90 ± 10 (1.50)	79 (1.32)
CCl_4	0.0	None	300	146 ± 10 (2.4)	79 (1.32)
CCl_4	1.0	0.2M HNO_3	600[c]	225 ± 35 (3.8)	140 (2.3)

[a]For all 12 stages of the 4-cm contactor.

[b]Assuming isothermal operation, with all heat generated due to mixing, centrifugation, and pumping in the contactor serving to evaporate the most volatile component of the liquid.

[c]The O/A flow ratio is 1.0.

As reported Section III.C.1, the apparent loss rate of CCl_4 from the solvent was 11 mL/min, rather than the 3 mL/min expected. The additional loss is about 5% of the total solvent flow rate. One explanation for the additional solvent loss is that it is caused by the heat of solution released as the 1.5M HNO_3 aqueous solution was equilibrated with the organic phase containing about 0.01M HNO_3. If this possibility is correct, the additional diluent loss rate observed will be unchanged, on a percentage basis, as the process is scaled up. A second possibility, also reported in Section III.C.1, is that the apparent high CCl_4 loss rate during the flowsheet demonstration was actually due to evaporative losses of the CCl_4 while the solutions were sitting overnight in the contactor stages. In either case, the total apparent solvent loss rate of 7% is unacceptably high, and future work is needed to control solvent losses.

Three methods for reducing the loss of diluent are envisioned; these methods could be used individually or in combination. First, the opening between the shaft and the splash plate could be indirectly sealed by a redesign of the motor/rotor system of the contactor. A low-flow air-purge stream is required for such a system, which results in some diluent loss that could be controlled by the air-purge flow rate. If desired, diluent in the air purge can be recovered and recycled to the solvent. Second, one or more feeds or one or more stages could be cooled to offset the heat added by the heat of solution, as well as that added by mixing the liquids. Third, CCl_4 could be replaced by TCE, which, with its lower vapor pressure, would reduce the solvent loss rate by a factor of two to five.

V. GAMMA-RADIOLYTIC AND HYDROLYTIC DEGRADATION OF TRUEX-CCl_4 SOLVENT AND SOLVENT CLEANUP PROCEDURES

A. Hydrolytic and Gamma-Radiolytic Degradation Studies

1. Introduction

The stability of the TRUEX-CCl_4 solvent (0.25M CMPO-0.75M TBP diluted by CCl_4) in regard to hydrolytic and gamma-radiolytic degradation has been studied. The experimental procedure is discussed in Appendix A, Section 3. Reported here are the results of experiments run at 50 and 70°C to measure the nitric-acid-catalyzed degradation of the TRUEX-CCl_4 solvent and the results of gamma-radiolytic degradation experiments run at 50°C. Discussions on the predicted effects of temperature on the rate of hydrolytic solvent degradation and absorbed dose on radiolytic degradation are also presented.

2. Measurement of Solvent Degradation

The means chosen to measure the degree of solvent degradation was the one most important to the TRUEX process--the ability to strip americium from the TRUEX solvent by dilute nitric acid solution. Americium is extracted into the TRUEX solvent as a nitrate salt:

$$Am^{3+}_{Aq} + 3NO_3^-{}_{Aq} + 3CMPO_{ORG} \rightleftharpoons Am(NO_3)_3 \cdot 3CMPO_{ORG}$$

Therefore, americium is more extractable by the TRUEX solvent at high aqueous phase nitrate concentrations and less extractable at low ones ($D_{Am} \propto [NO_3^-]^3$). The formation of acidic degradation products is the major concern in the hydrolytic and radiolytic degradation of neutral extractants (e.g., TBP). These acidic degradation products (HA) inhibit the stripping of americium from the TRUEX solvent by low nitric acid solutions through the following mechanism:

$$Am^{3+}_{Aq} + 3(HA)_{2\,ORG} \rightleftharpoons Am(A)_3 \cdot 3HA_{ORG} + 3H^+_{Aq}$$

Americium is far more extractable by acidic extractants at low acidities than at high acidities ($D_{Am} \propto [H^+]^{-3}$).

The D_{Am} was measured between the treated TRUEX-CCl_4 solvents and three aqueous nitric acid solutions with concentrations of 2.0, 0.05, and 0.01M. At 2M HNO_3, D_{Am} is at its maximum, ~11, for this composition of CMPO-TBP-CCl_4 [KALINA-1985B]; this measurement is useful to see if the concentration of the extractant has increased as a result of volatilization of CCl_4 during treatment or decreased because of extensive degradation. The 0.05M HNO_3 contact was the one chosen in the PFP flowsheet to preferentially strip americium while leaving plutonium in the TRUEX solvent. The value of D_{Am} at this acid concentration was monitored for the treated solvents as a

means of evaluating the effects of solvent degradation on stripping. Contact with 0.01M HNO_3 was chosen as a more sensitive measure of acidic impurities. A summary of D_{Am} values at these acidities for fresh, H_2O-washed, and Na_2CO_3-scrubbed TRUEX-CCl_4 solvent is shown in Table V-1.

Table V-1. Replicate Distribution Ratios of Americium Measured at Three Nitric Acid Concentrations vs. Washing of Freshly Prepared TRUEX-CCl_4 Solvent

Treatment	Distribution Ratio of Americium at [HNO_3], 25°C		
	2M	0.05M	0.01M
None	10.6	0.180	0.021
	12.5	0.233	0.034
	12.0	0.200	0.035
	9.96	0.203	0.0315
	10.2	0.196	--
	9.76	0.208	--
Average	10.8	0.203	0.0304
Water Washed	10.9	0.222	0.0238
	11.7	0.214	--
	11.6	0.237	--
Average	11.4	0.224	0.0238
Carbonate Washed	13.2	--	0.0212
	13.0	0.208	0.0285
	12.0	0.238	0.0197
	13.2	0.228	--
	11.9	0.235	--
Average	12.7	0.227	0.0231

3. Hydrolytic Degradation

a. Experimental Results

Presented in Tables V-2 and V-3 are the results of the experiments performed to measure the effects of aqueous phase composition and time of contact on hydrolytic decomposition of the TRUEX-CCl_4 solvent. The effects of washing the degraded solvents with 0.25M Na_2CO_3 are also presented in these tables. (Sodium carbonate washing has been found to wash the hydrolysis products of TBP, dibutyl and monobutyl phosphoric acids, from PUREX solvents [HEALY; VANDEGRIFT-1984B and references cited therein].) The carbonate wash is discussed is more detail in Section V.B.

Table V-2. Hydrolytic Decomposition of TRUEX-CCl_4 Solvent[a] vs. Time and Contact with Various Aqueous Phases at 50 ± 0.2°C[b]

Aqueous Phase Composition	Treatment Time, h	Distribution Ratio of Am at [HNO_3], 25 ± 0.1°C					
		After Treatment			After Carbonate Wash		
		2M	0.05M	0.01M	2M	0.05M	0.01M
0.05M HNO_3	713	14.5	0.205	0.0173	12.0	0.206	0.0199
0.25M HNO_3	23	10.6	0.190	0.0364	11.8	0.206	0.0191
	192	12.1	0.175	0.0128	12.5	0.214	0.0147
		10.7	0.170	0.0098			
	667	12.8	0.213	0.0242	12.3	0.216	0.0160
2.5M HNO_3	22	11.0	0.190	0.0159	11.8	0.192	0.0173
	192	14.0	0.252	0.0264	14.1	0.218	0.0183
		12.3	0.180	0.0290			
		13.0	0.178	0.0249			
	332	16.8	0.264	0.0288	12.4	0.208	0.0171
		13.7	0.203	0.0279			
	714	13.5	0.266	0.0906	13.7	0.212	0.0118
		12.3	0.254	0.0868			
5.0M HNO_3	48	14.4	0.207	0.0252	12.1	0.192	0.0194
	169	14.2	0.191	0.0349	11.7	0.178	0.0171
1/9 0.25M HNO_3, 8/9 Simulated PFP Waste Solution	168	11.7	0.160	0.0083	11.8	0.165	0.0042
	331	12.3	0.182	0.0126	10.2	0.192	0.0062

[a]As measured by distribution ratios of americium at three nitric acid concentrations.

[b]The organic phase was preequilibrated with three contacts of fresh aqueous phase, then mixed vigorously with a fresh aqueous phase during treatment. A 125-mL volume of TRUEX-CCl_4 solvent was contacted with 50 mL of aqueous phase.

Table V-3. Hydrolytic Decomposition of TRUEX-CCl_4 Solvent[a] vs. Time and Contact with Various Aqueous Phases at 69.4 ± 0.3°C[b]

Aqueous Phase Composition	Treatment Time, h	Distribution Ratio of Am at [HNO_3], 25 ± 0.1°C					
		After Treatment			After Carbonate Wash		
		2M	0.05M	0.01M	2M	0.05M	0.01M
0.05M HNO_3	690	12.8	0.206	0.0223	13.2	0.196	0.00784
0.25M HNO_3	380	12.3	0.200	0.0396	11.9	0.220	0.00725
	690	12.1	0.223	0.0321	13.6	0.203	0.00543
2.5M HNO_3	380	8.64	0.723	2.06	10.9	0.163	0.00786
	690	7.15	2.02	11.3	9.00	0.162	0.0125
1/9 0.25M HNO_3, 8/9 Simulated PFP Waste Solution	310	10.9	0.246	0.0951	11.8	0.181	0.00423
	310	11.2	0.241	0.0648	12.4	0.186	0.00391

[a]As measured by distribution ratios of americium at three nitric acid concentrations.

[b]The organic phase was preequilibrated with three contacts of fresh aqueous phase, then mixed vigorously with a fresh aqueous phase during treatment. A 125-mL volume of TRUEX-CCl_4 solvent was contacted with 50 mL of aqueous phase.

For the hydrolysis experiments performed at 50°C (Table V-2), it is important to note that the only meaningful signs of solvent degradation were measured by an increase in D_{Am} for the aqueous phase nitric acid concentration of 0.01M HNO_3. Under the most severe conditions tested (contact with 2.5M HNO_3 for 714 hours), D_{Am} increased by a factor of about five. However, at 0.05M HNO_3 (the conditions chosen for stripping americium from the TRUEX-CCl_4 solvent), the increase in D_{Am} was only ∿35%.

Of special interest in Table V-2 are the results of experiments employing the aqueous phase encountered by the TRUEX-CCl_4 solvent in the feed and extraction stages (8/9 PFP waste solution-1/9 0.25M HNO_3). After the treatment with this aqueous feed, the D_{Am} at 0.01M HNO_3 was less than half its value for the original solvent. This reduction is probably due to the formation of stable metal complexes of acidic compounds that are removed in the water-wash steps. The presence of macro constituents such as iron in the PFP solution appears to actually improve the solvent under these conditions.

Experiments were also performed at 69.4°C. These data are presented in Table V-3. As expected, the rate of degradation appears to be higher at 69.4°C than at 50°C. Under these conditions, substantial degradation is observed for samples treated with 2.5M HNO_3 and the 0.25M HNO_3-simulated PFP waste solution mixture. Especially important is the observation that prolonged treatment with higher acid concentrations at this elevated temperature results in significant increases in D_{Am} at 0.01 and 0.05M HNO_3 and a detectable decrease in D_{Am} at 2M HNO_3. For TRUEX-CCl_4 process solvent treated for 690 h with 2.5M HNO_3 at 69.4°C, the increases in D_{Am} values at low acid concentrations are very obvious. The increase in D_{Am} at 0.01M HNO_3 is on the order of a factor of 400, whereas the value at 0.05M increases by about ten. This very high value would make stripping of americium impossible, under the conditions of the proposed flowsheet design, without cleanup of the solvent. Under these same conditions, a slight decrease in D_{Am} was observed at 2.0M HNO_3. This small but measurable decrease, observed under no other hydrolysis conditions, may be due to (1) degradation of CMPO or (2) binding of the extractant by other degradation products, thus lowering its ability to extract americium.

b. Calculations of Hydrolytic Damage

Studies of nitric acid-catalyzed decomposition of TBP are reviewed by Shoun and Thompson [SHOUN], and recently measured data are presented by Stieglitz and Becker [STIEGLITZ]. The rate data of Stieglitz and Becker for the formation of dibutyl phosphoric acid (HDBP) from hydrolysis of TBP in normal paraffinic hydrocarbon solutions contacted by aqueous nitric acid solutions were used to give an indication of the magnitude of the hydrolytic decomposition expected for TBP alone in the TRUEX-CCl_4 process solvent.

The activation energy for TBP hydrolysis in this system was calculated by plotting ln k vs. 1/T, where k is the rate constant in units of inverse hours for HDBP formation from TBP, and T is the temperature in kelvin. This plot is based on the Arrhenius equation [GORDON]:

$$k = e^{-E_a/RT}$$

where E_a is the activation energy of the reaction, and R is the gas constant. The activation energy calculated from the slopes of these plots (slopes for both 0.5 and 3.0M HNO_3 were the same) was 22.5 kcal/mol. This equates to increasing the rate of TBP hydrolysis at 30°C by a factor of 10 at 50°C and by a factor of 80 at 69.4°C. Table V-4 shows the calculated rates of HDBP formation based on the data of Stieglitz and Becker [STIEGLITZ]. Because the diluent is different and because of the presence of CMPO in the organic phase, this calculation can be considered only as an estimate, possibly useful for showing trends.

c. Evaluation of Hydrolysis Products

For all the degraded solvent samples, it was found that washing with dilute sodium carbonate solution resulted in a reduction of D_{Am} values for 0.01M HNO_3, indicating that the acidic degradation products are readily scrubbed from the TRUEX solvent. This fact, combined with the knowledge that,

Table V-4. Estimated Rate Constant for the Hydrolysis of TBP vs. HNO_3 Concentration and Temperature[a]

$[HNO_3]$, M	Rate Constant, h^{-1}, at Temperature		
	30°C	50°C	69.4°C
0.05	1.3×10^{-8}	1.3×10^{-7}	1.1×10^{-6}
0.25	7.4×10^{-8}	7.4×10^{-7}	5.6×10^{-6}
2.5	8.6×10^{-7}	8.6×10^{-6}	6.6×10^{-5}
5.0	1.8×10^{-6}	1.8×10^{-5}	1.4×10^{-4}

[a]Calculated from data of Stieglitz and Becker [STIEGLITZ].

under most conditions, there was no significant degradation of the CMPO, is consistent with TBP hydrolysis being the major degradation reaction in this system. The primary hydrolysis product of TBP, HDBP, can be successfully removed from PUREX solvent systems by sodium carbonate scrubbing.

To evaluate the importance of TBP hydrolysis, the distribution-ratio data for 0.01M HNO_3 were examined and compared with previous literature results. The most relevant data in the literature concerning the partitioning and extraction behavior of HDBP [DYRSSEN-1960A,B; HARDY] are the bases for the following discussion.

(1) Partitioning of HDBP

Following hydrolysis of the TRUEX-CCl_4 solvent, the organic phase was washed three times with H_2O (O/A = 1:2) to reduce its acidity and preconditioned twice with the appropriate acid prior to measurement of D_{Am}. The partitioning of HDBP between organic and aqueous phases has been found to be strongly dependent on the aqueous phase acid concentration, as well as on the composition of the organic phase.

Hardy and Scargill reported that the distribution ratio of HDBP (D_{HDBP}) between 20% TBP in kerosene and HNO_3 of 0.001 to 10M varies from about 0.14 at 0.001M HNO_3 to a maximum of about 17 at 6M HNO_3 [HARDY]. Because the values of D_{HDBP} are quite small at low acidity, appreciable quantities of HDBP may be washed out during the water washes and preconditioning steps. It was, therefore, important to calculate the extent of HDBP scrubbing in these steps.

It had been shown that D_{HDBP} is quite sensitive to the composition of the organic phase, varying from 0.17 to 47 for 0.01145M TBP in CCl_4 and undiluted TBP, respectively (0.1M HNO_3 aqueous phase) [DYRSSEN -1960A]. The TRUEX-CCl_4 solvent should resemble a solution of 1.0 to 1.25M TBP in CCl_4, in terms of the partitioning of HDBP, as a result of the presence of 0.25M of the more basic CMPO. The value of D_{HDBP} obtained by Dyrssen and Hay for 1.145M TBP in CCl_4/0.10M HNO_3 was 13.8 [DYRSSEN-1960B]. Comparison

of this value with that obtained with 20% TBP in kerosene of 5.18 [HARDY] indicates that the behavior in TRUEX-CCl_4 may be approximated by multiplying the D_{HDBP} value with 20% TBP in kerosene by 2.5 to 3 to determine the partitioning of HDBP between TRUEX-CCl_4 and aqueous phases of varying nitric acid concentrations. Using a value for the distribution ratio of HNO_3 (D_{HNO_3}) of 0.2 for HNO_3 partitioning between TRUEX-CCl_4 and the aqueous phase [HORWITZ -1985C], the aqueous HNO_3 concentration during the H_2O washes and, hence, the partitioning of HDBP may be calculated. The calculated values of D_{HDBP} for the water wash and preconditioning stages for the TRUEX-CCl_4 process solvent treated under different conditions are shown in Table V-5. Based on the approximations above, water washes can be seen to reduce the [HDBP] only slightly for samples that were treated with relatively high [HNO_3]. Preconditioning of the organic phases with 0.01M HNO_3 reduces the [HDBP] by an additional 33%. Preconditioning with the higher concentrations of [HNO_3] would result in smaller reductions.

Table V-5. Calculated Losses of HDBP from TRUEX-CCl_4 Solvent Samples during Experimental Procedures

$[HNO_3]_{Aq}$ in TRUEX Exposure, M	D_{HDBP} for Each Stage of H_2O Washes[a]			% HDBP Retained after H_2O Washes[a]	% HDBP Retained in Organic Phase[b]
	#1	#2	#3		
0.05	4.5	1.8	0.54	37	25
0.25	14	6.0	2.5	74	50
2.5	33	23	15	93	62
5	40	30	18	95	63
1.36c	28	16	9.0	90	60

[a]Values based on D_{HDBP}(TRUEX) = 3 x D_{HDBP} (20% TBP/kerosene) [HARDY], assuming water washes (O:A = 2:1) with D_{HNO_3} = 0.2.

[b]After three water washes and two preconditioning stages (O:A = 1:1) with 0.01M HNO_3 (D_{HDBP} = 4.5).

[c]Composition of 1/9 0.25M HNO_3, 8/9 simulated PFP waste solution (1.5M HNO_3).

(2) Americium Extraction by HDBP

The effect of HDBP on the extraction of americium at 0.01M HNO_3 is quite profound for highly degraded TRUEX-CCl_4 solvent. Values of D_{Am} up to 11 were observed for highly degraded TRUEX-CCl_4 solvent, compared with about 0.02 for untreated solvent. Rate constants for TBP hydrolysis under the conditions of the hydrolytic degradation experiments have been estimated and are presented in Table V-4. Using these values and data for americium extraction by HDBP [DYRSSEN-1960B], an attempt was made to correlate the predicted concentration of HDBP with the observed change in D_{Am} at 0.01M HNO_3 with degraded TRUEX-CCl_4 solvent.

Dyrssen and Hay have studied the extraction of americium by HDBP in a number of diluents, including CCl_4 and undiluted TBP [DYRSSEN -1960B]. Americium extraction by HDBP in degraded TRUEX-CCl_4 solvent should

fall somewhere in between its behavior when diluted by CCl_4 and when diluted by TBP. The D_{Am} at 0.10M HNO_3 with HDBP in CCl_4 was found to follow an approximate third-order extractant dependence, as follows:*

$$\ln D_{Am}^{0.10} = 2.79 \ln [HDBP] + 7.15 \quad (1)$$

Assuming an inverse third-power dependence on $[H^+]$, this equation becomes, at 0.01M HNO_3:

$$\ln D_{Am}^{0.01} = 2.79 \ln [HDBP] + 14.06 \quad (2)$$

For HDBP in TBP, the extractant dependence at 0.10M HNO_3 is nonlinear due to the extraction of americium by the TBP. Assuming that the limiting value of D_{Am} in this system (about 3×10^{-3}) is due to extraction by TBP, a fairly good straight-line dependence of D_{Am} vs. [HDBP] can be obtained by subtracting 3×10^{-3}, the distribution ratio of TBP (D_{TBP}), from all D_{Am} values to yield the values due to HDBP extraction. The resulting line may be described by the equation:

$$\ln D_{Am}^{0.10} = 1.96 \ln [HDBP] + 0.44 \quad (3)$$

At 0.01M HNO_3, Eq. 3 becomes:

$$\ln D_{Am}^{0.01} = 1.96 \ln [HDBP] + 7.35 \quad (4)$$

Equations 2 and 4, in conjunction with the calculated [HDBP] based on time, temperature, and acidity during degradation, can be used to correlate changes in $D_{Am}^{0.01}$ with [HDBP].

For the various hydrolytic degradation conditions employed, the calculated [HDBP] values range from 7.0×10^{-5} to 3.4×10^{-2}M. This range of concentrations would correspond to increases in $D_{Am}^{0.01}$ of 3.3×10^{-6} (undetectable) to 103 using Eq. 2 and to increases of 1.12×10^{-5} (undetectable) to 2.06 using Eq. 4. The actual range of values for $D_{Am}^{0.01}$ is about 0.02 for untreated TRUEX-CCl_4 to 11.3 for the most highly hydrolyzed solution. For solutions with intermediate [HDBP], the observed changes in $D_{Am}^{0.01}$ generally fall within the range of values predicted by Eqs. 2 and 4. Considering experimental errors and the assumptions involved in these calculations, the agreement is quite good. The observed values of $D_{Am}^{0.01}$ and the theoretical values predicted by Eqs. 2 and 4 are plotted in Fig. V-1.

No calculations based on extraction due to the acidic degradation products of CMPO were performed. Because of the predicted higher hydrolytic stability of the CMPO and the poorer expected extraction of americium by its degradation products, HDBP should be the predominant species responsible for elevated D_{Am} values at low acid concentrations.

The data in Fig. V-1 are not corrected for the loss of HDBP due to partitioning of the acidic compound during water washes and preconditioning. Taking the data of Table V-5 into account, the calculated

*In the designation D_{Am}^{x}, x refers to $[HNO_3]$ of xM.

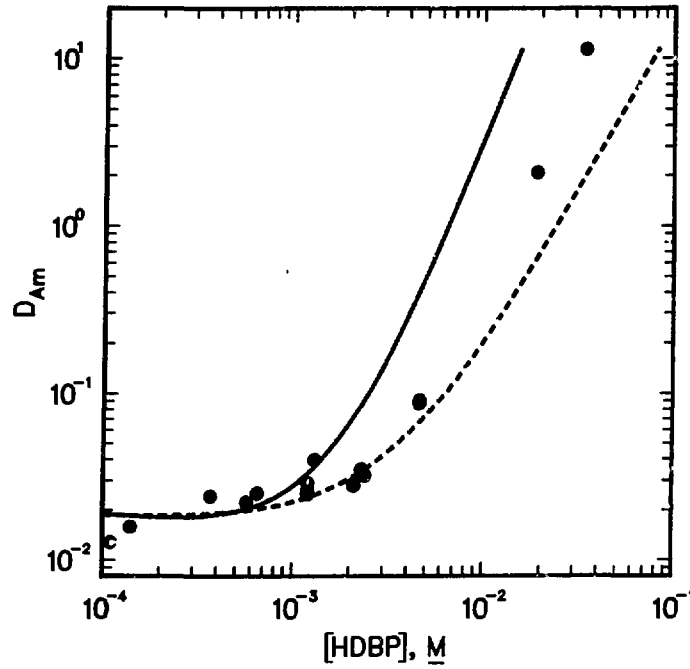

Fig. V-1. The Distribution Ratio of Americium vs. the Concentration of HDBP, Aqueous Phase = 0.01M HNO_3, T = 25°C. The dashed line represents data for HDBP dissolved in TBP; the continuous line represents data for HDBP dissolved in CCl_4. The data points represent our measured D_{Am} values vs. the [HDBP] calculated from TBP degradation rates from the literature under the conditions of time and temperature in our experiments.

increases in $D_{Am}^{0.01}$ would be reduced to about 0.24-0.40 of those tabulated for solutions treated with $[HNO_3] \geq 1.36M$ (based on Eqs. 2 and 4). For 0.05 and 0.25M HNO_3, the calculated changes would be reduced by factors of 15-48 and 4-7, respectively.

d. Effect of Hydrolysis on the PFP Process

Based on a PFP process (1) having five extraction, two scrub, four americium-strip, and three plutonium-strip stages; (2) operating for 250 days per year; and (3) employing a 2.5M HNO_3 solution to simulate the PFP waste extraction/feed aqueous phase, the amount of HDBP formed per year can be estimated using the following equation:

$$[HDBP]_{formed} = [TBP]\ \Sigma\ (k \cdot \Delta t)$$

where k values for each section are taken from Table V-4, and Δt is 2050 h for the extraction/feed, 820 h for the scrub, and 2870 h for the two strips. The calculation indicates that a concentration of 1.4×10^{-3}M HDBP would be formed in one year of processing. This inconsequential amount of degradation would have little effect on solvent quality, even with no solvent cleanup in the process.

4. Radiolytic Degradation

a. Experimental Results

The calculated yearly dose (primarily due to alpha radiation) that the TRUEX-CCl_4 solvent would experience during processing of PFP waste is 0.82 Wh/L. The gamma doses that the solvents received in the experiments reported in this study were substantially higher than this. The conditions for these experiments, which were run in a ^{60}Co radiation field, are presented in Table V-6.

The D_{Am} data at 2M HNO_3 for irradiation doses up to ∿10 Wh/L show only slight differences when compared with the original solvent (D_{Am} = 10.8). Even at the extremely high dose of 102 Wh/L, the reduction in the value of D_{Am} at 2M HNO_3 is slight. This drop may indicate that CMPO is being destroyed by irradiation; it may also be a sign that some of the degradation products are binding up the extractant, thereby impairing its ability to extract americium.

The effect of gamma irradiation on D_{Am} at 0.05M HNO_3 is also small and could be interpreted as a mix of two parameters: (1) the decrease in the concentration of CMPO as a result of its destruction and (2) the formation of acidic degradation products. In any case, this variation would not have a significant effect on the TRUEX processing of PFP waste.

The effect of gamma-radiolytic degradation is more evident in the D_{Am} values at 0.01M HNO_3. However, here too, the effect at reasonable doses (up to about 10 Wh/L) is nil.

A much more dramatic effect than the changes in D_{Am} values for the degraded solvents was the direct correlation of the yellowing of the TRUEX-CCl_4 solvent with (1) accumulated gamma dose and (2) the concentration of nitric acid in the aqueous phase with which it was contacted during irradiation. The yellow color varied from almost imperceptible at 6.5 Wh/L with 0.05M HNO_3 to brilliant at 102 Wh/L with the PFP aqueous feed solution. Both the aqueous and organic phases were colored. No solid formation was noted for any of the irradiations, but the volume of the organic phase was noticeably lessened; after long irradiations it dropped from 125 to ∿110 mL.

Much as had been observed in the hydrolytic degradation studies of TRUEX-CCl_4, we found that low doses of gamma irradiation in the presence of the PFP waste solution were actually beneficial in reducing D_{Am} at 0.01M HNO_3. A similar effect was observed in the cases where, due to cracking of

Table V-6 Decomposition of TRUEX-CCl_4 Solvent[a] vs. Gamma Radiation Dose and Contact with Various Aqueous Phases at 49 ± 2°C[b]

Aqueous Phase Composition	Dose,[c] Wh/L	Distribution Ratio of Am at [HNO_3], 25 ± 0.1°C					
		After Exposure			After Carbonate Wash		
		2.0M	0.05M	0.01M	2.0M	0.05M	0.01M
0.05M HNO_3	0.37	12.6	0.218	0.0145	12.5	0.203	0.00766
	1.1	12.0	0.196	0.00611[d]	12.6	0.206	0.00494
	6.5	9.93	0.176	0.0229	12.3	0.203	0.0107
	9.4	9.80	0.182	0.0345	12.5	0.189	0.0122
	70	7.97	0.144	0.287	10.4	0.108	0.0105
	102	8.64	0.165	0.425	11.5	0.122	0.0144
0.25M HNO_3	0.37	14.2	0.227	0.00711[d]	13.8	0.247	0.00627
	1.1	11.9	0.155	0.00555[d]	12.1	0.173	0.00548
	5.9	9.80	0.175	0.0252	11.4	0.205	0.0110
	8.5	10.3	0.174	0.0283	11.9	0.227	0.0115
	70	8.46	0.203	0.279			
		7.83	0.203	0.352	9.17	0.105	0.0152
	102	9.55	0.196	0.492			
		9.18	0.204	0.467	10.8	0.132	0.0190
1/9 0.25M HNO_3, 8/9 Simulated PFP Waste Solution	0.50	12.4	0.168	0.00548	11.8	0.172	0.00451
	1.5	11.8	0.176	0.0125	12.0	0.175	0.00715
	5.9	11.7	0.168	0.00739	13.6	0.201	0.00552
	8.5	11.2	0.167	0.00765	12.0	0.157	0.00505
	70	8.33	0.191	0.256	11.2	0.118	0.00467
	102	7.15	0.302	1.31	10.9	0.116	0.00508
					10.2	0.0947	0.00392

[a]As measured by distribution ratios of americium at three nitric acid concentrations.

[b]The organic phase was preequilibrated with three contacts of fresh aqueous phase, then mixed vigorously with a fresh aqueous phase during exposure. A 125-mL volume of TRUEX-CCl_4 solvent was contacted with 50 mL of aqueous phase.

[c]Total dose to the solvent. This value is based on a calculated electron density of the solvent of [e^-] = 700M (compared with 555M for water). Thus, water absorbs 100 erg/(g·rad), and the TRUEX-CCl_4 solvent absorbs 126 erg/(g·rad). Because TBP and CMPO make up 20 vol % and 10 vol %, respectively, their fractional doses are 0.2 and 0.1 of the total dose, respectively.

[d]This lower-than-expected value is likely due to the presence of dissolved iron in the aqueous and organic phases. The Teflon cover of the magnetic stirring bar cracked due to radiation damage during this run.

the Teflon stir bar cover as a result of radiolytic damage, the aqueous phase contained high iron concentrations. This reduction in D_{Am} at 0.01M HNO_3 is probably due to complexation of acidic degradation products by the iron.

b. Calculations of Radiolytic Damage

Based on a reasonable range of G values* for TBP degradation to HDBP of 0.3-3 [DAVIS], the expected amounts of HDBP formed at each dose given to the TRUEX-CCl_4 can be calculated. Concentrations of HDBP would be expected to range from 4.14×10^{-5}M (0.37 Wh/L) to 1.140×10^{-2}M (102 Wh/L) for a G value of 0.3. For G = 3.0, the HDBP concentrations would be expected to be a factor of ten higher.

Alternatively, the G values for TBP degradation can be calculated for these solutions based on the increase in D_{Am} at 0.01M HNO_3 and Eqs. 2 and 4. The results of these calculations for all samples that showed an increase in extraction of americium at low acid concentration are shown in Table V-7.

These calculations, which are based on a calculated [HDBP] and are, therefore, subject to the same errors as discussed in Section V.A.3.b, yield a range of G values for the samples. These values range from an average of 0.24 for the lower limit of the extraction power of HDBP in the TRUEX-CCl_4 process solvent to 0.55 for the upper limit. These values are in reasonable agreement with the G values that have been determined previously for two-phase (TBP in diluent and aqueous HNO_3) degradation studies of TBP [DAVIS].

c. Evaluation of Radiolysis Products

As in the hydrolytic degradation experiments, it appears that the gamma-radiolysis of TRUEX-CCl_4 process solvent is dominated by TBP decomposition. Only after very high radiation doses to the solvent (>10 Wh/L) is there any significant change in the extraction behavior. Radiolytic degradation manifests itself primarily by increased D_{Am} at 0.01M HNO_3, indicative of the formation of relatively small concentrations of acidic materials.

Evidence for CMPO degradation is found only at the very high absorbed doses. The reduction of D_{Am} at 2M HNO_3 after doses of 70 or 102 Wh/L may be indicative of loss of CMPO. However, because the degradation products of TBP are expected to be more powerful acidic extractants than the CMPO decomposition products, it is the HDBP formed by TBP radiolysis that should be of major concern in solvent cleanup.

d. Effect of Radiolysis on the PFP Process

The data in Table V-6 show that, even after doses of ~10 Wh/L, the TRUEX-CCl_4 solvent performs almost identically to freshly prepared material. From this information, it appears that radiolytic damage to the

*The number of molecules destroyed or produced for each 100 eV of energy absorbed.

Table V-7. Calculated G Values for TBP Radiolysis in TRUEX-CCl_4 Solvent

Aqueous Phase Composition	Dose,[a] Wh/L	$\Delta D_{Am}^{0.01}$ [b]	Calculated Value [HDBP], M[c]	Calculated Value G
0.05M HNO_3	6.5	2.9×10^{-3}	8.0×10^{-4}–1.2×10^{-3}	0.33–0.49
	9.4	1.45×10^{-2}	1.4×10^{-3}–2.7×10^{-3}	0.40–0.77
	70	2.67×10^{-1}	4.0×10^{-3}–1.2×10^{-2}	0.15–0.46
	102	4.05×10^{-1}	4.7×10^{-3}–1.5×10^{-2}	0.12–0.39
0.25M HNO_3	5.9	5.2×10^{-3}	9.8×10^{-4}–1.6×10^{-3}	0.45–0.73
	8.5	8.3×10^{-3}	1.2×10^{-3}–2.0×10^{-3}	0.37–0.64
	70	2.96×10^{-1}	4.2×10^{-3}–1.3×10^{-2}	0.16–0.50
	102	4.60×10^{-1}	4.9×10^{-3}–1.6×10^{-2}	0.13–0.42
1/9 0.25M HNO_3, 8/9 Simulated PFP Waste Solution	70	2.36×10^{-1}	3.9×10^{-3}–1.1×10^{-2}	0.15–0.43
	102	1.29×10^{0}	7.1×10^{-3}–2.7×10^{-2}	0.19–0.70
Average				0.24–0.55

[a]Total dose to the solvent. See footnote c of Table V-6.

[b]Determined by subtracting 0.020 from each measured $D_{Am}^{0.01}$ value.

[c]Range of concentrations calculated on the basis of Eqs. 2 and 4.

solvent, even after extended use, should be inconsequential, because the expected yearly dose is only 0.82 Wh/L. It seems that the hydrolytic degradation of the solvent (discussed in Sec. V.A.3) will be more of a problem in the operation of the TRUEX process with PFP waste.

B. Sodium Carbonate Scrub Solvent Cleanup

1. Solvent Behavior

Contact with aqueous sodium carbonate solution has been the chief means of cleaning up degraded PUREX solvent from TBP degradation products [HEALY; VANDEGRIFT-1984B and references cited therein]. All the treated TRUEX-CCl_4 process solvent samples in this study were contacted with 0.25M Na_2CO_3 to see if this treatment would bring the solvent back to its extraction performance before treatment. The effect of a carbonate wash on the untreated solvent was also measured. Following are some general comments on the results of this procedure:

- The harsher the treatment of the TRUEX-CCl_4 process solvent, the more easily the phases separated after mixing.
- After the first contact with a carbonate solution, only the most severely treated samples had complete phase separation in less than three minutes; the original TRUEX-CCl_4 process solvent (as prepared, with no treatment to degrade it) showed no signs of disengagement after 30 minutes.

- After the second contact, some less severely treated samples showed phase disengagement within three minutes.

- Progressive carbonate washes continued to improve phase separation times; even the mildest treatment seemed to improve the phase separation characteristics of the slow-disengaging original TRUEX-CCl_4 process solvent.

- Samples of TRUEX-CCl_4 process solvent that were contacted with 8/9 simulated PFP waste solution-1/9 0.25M HNO_3 broke very well on the first and subsequent contacts with the carbonate wash solution, but did form an interfacial solid with each contact--likely, Fe(III) complexes with acidic degradation products.

- Washing the solvents with water after carbonate washing formed an emulsion with all but the most severely treated samples.

- For carbonate solution washing, centrifuging at about 5000 g for three minutes was adequate for complete phase separation. For water washing, the times had to be increased to an hour or more for the original TRUEX-CCl_4 process solvent and the mildly treated samples.

- In general, the ease of phase separation increased with each water contact.

Also noted was the fact that, when the solvents that were radiolytically degraded in contact with PFP waste solutions were washed with sodium carbonate solution, some of the yellow color in the organic phase reported to the aqueous phase on the first contact, and the TRUEX-CCl_4 process solvent changed from bright yellow to orange-brown. No more color was removed in subsequent contacts; but, a yellow interfacial crud continued to precipitate with each washing.

No yellow color in the aqueous phase developed for sodium carbonate washing of TRUEX-CCl_4 process solvents contacted with other aqueous phases during gamma irradiation; nor was any dramatic color change with Na_2CO_3 solution contact observed. The D_{Am} data collected show that the colors of the degraded and the Na_2CO_3-washed solvents cannot be correlated with their abilities to extract or to be stripped of americium.

2. Efficiency of Sodium Carbonate Scrub

For all TRUEX-CCl_4 solutions subjected to hydrolytic and radiolytic degradation, the values obtained for $D_{Am}^{0.01}$ following sodium carbonate treatment were lower than those measured for untreated solvent. This is especially true for samples hydrolyzed at 69.4°C, where $D_{Am}^{0.01}$ was found to be in the range of 0.0039 to 0.0125 after treatment, and for samples irradiated in the presence of the PFP solution, where $D_{Am}^{0.01}$ for the treated solution was found to be less than 0.0072. For untreated solvent, $D_{Am}^{0.01}$ was found to be $\sim$0.02. We found that sodium carbonate treatment has a much smaller effect on the values of $D_{Am}^{0.01}$ that were obtained for TRUEX-CCl_4 process solvent that has not been contacted

with HNO_3 (Table V-1). Because sodium carbonate has been shown to be very effective at removing HDBP generated during hydrolysis, the inability to reduce $D_{Am}^{0.01}$ in untreated TRUEX-CCl_4 process solvent with sodium carbonate indicates that the TRUEX-CCl_4 process solvent contains some acidic impurity that must be degraded before the carbonate scrub is effective. This fact is made especially apparent in light of the very poor phase separation and emulsion formation observed in the carbonate treatment of fresh TRUEX-CCl_4 process solvent. The apparently high surface activity and low aqueous solubility of the sodium salt of the acidic impurity (or impurities) found in the solvent mixture would indicate that the impurity is associated with the CMPO or CCl_4, rather than the TBP. Reaction of this impurity during the hydrolysis or radiolysis experiments appears to break it down, facilitating scrubbing with carbonate and improving (i.e., reducing) the values of $D_{Am}^{0.01}$.

The effect of sodium carbonate scrubbing on D_{Am} at 2.0M HNO_3 also warrants notice. For highly degraded solutions, the values of D_{Am} decreased to as low as 7.15. Following treatment, the values were found to be nearly as high as for fresh extraction (10.8), indicating that most of the decrease in D_{Am} was probably due to complexation of the CMPO by acidic degradation products, rather than degradation of the CMPO itself.

It should be noted that, in the treatment of degraded TRUEX-CCl_4 solutions, interfacial material was routinely removed with the aqueous scrub phases. This may contribute to the improved performance of the solvent resulting from removal of aqueous-insoluble degradation products of CMPO. This area needs further examination in regard to solvent cleanup and performance of the TRUEX-CCl_4 process.

C. Solvent Cleanup by Strong-Base Macroporous Ion Exchange Resin

The use of a strong-base macroporous anion exchange resin appears to be an ideal method for the secondary cleanup of TRUEX process solvent. It should be possible to quantitatively sorb high molecular weight acidic compounds, whether phosphoric acids generated from TBP or phosphinic acids generated from CMPO, on a macroporous resin in the hydroxyl ion cycle. Hydrolytically and radiolytically degraded process solvent, as well as used, but essentially undegraded, process solvent, have been column treated with BioRad AG™ MP-1. In both cases, the phase disengagement time of the solvent after equilibration with 0.25M Na_2CO_3 improved significantly after resin treatment, as shown in Table V-8. Resin-treated process solvent was also less colored than it was before treatment.

The use of macroporous resin for the treatment of PUREX process solvent has been studied by Schulz [SCHULZ]. The technique was found to improve significantly the plutonium retention number of carbonate-scrubbed PUREX process solvent. (The plutonium retention number is an indirect measure of the presence of acidic extractants.) However, a great deal more work is needed to assess the applicability of the macroporous resin treatment for the cleanup of TRUEX process solvent, particularly in regard to column capacity and flow rate.

Table V-8. Phase Disengagement Times for TRUEX Process Solvent

Solution[a]	Disengagement Time,[b] s	
	Before Resin Treatment	After Resin Treatment
Carbonate-Scrubbed, Degraded TRUEX-CCl_4 Solvent	120	40
TRUEX-CCl_4 Solvent from Cold Run	>>600	40

[a]Defined in Appendix A, Section 5.

[b]After 15 seconds of vortex mixing using 1 mL each of organic and aqueous phase contained in a 13- x 100-mm culture tube.

D. Physical Properties of TRUEX-CCl_4 Solvent

1. Introduction

Samples of TRUEX-CCl_4 process solvent that had been subjected to radiolytic degradation and acid hydrolysis were compared with fresh solvent in regard to density, viscosity, and interfacial tension. The samples that were examined are shown in Table V-9. Samples 3β and D8 should approximate the hydrolytic and radiolytic degradation, respectively, that would result from two years of operation of the TRUEX process in the PFP facility. Sample D5 was examined to determine the effects of radiolysis well in excess of any reasonably expected exposure of the solvent.

Table V-9. Samples of TRUEX-CCl_4 Studied in Physical Measurements

Sample	Treatment
Fresh Solvent	None.
D8	Irradiated to 1.5 Wh/L in ^{60}Co cell at 50°C in contact with 8/9 simulated PFP waste-1/9 0.25M HNO_3.
D5	Same as D8, only 102 Wh/L irradiation.
3β	Hydrolyzed for 310 h at 69.4°C in contact with 8/9 simulated PFP waste-1/9 0.25M HNO_3.

2. Density

Only very slight differences in the densities were observed for the treated and untreated TRUEX-CCl_4 process solvent (Table V-10). Some of the differences may be accounted for by the extraction of water into the organic phase upon water washing (densities of 1.393 and 1.395 g/mL for wet and dry TRUEX-CCl_4 solvent, respectively). Additional differences may be due to the

Table V-10. Densities of TRUEX-CCl_4 Solutions

Sample	Density at 22.5°C, g/mL[a]
Fresh Solvent	1.395 ± 0.001
Water-Washed Solvent[b]	1.393 ± 0.003
D8	1.386 ± 0.003
3β	1.377 ± 0.003
D5	1.387 ± 0.002

[a]Equivalent to kg/dm^3.

[b]Prepared by three contacts with water (O/A phase ratio = 2).

loss of small amounts of the CCl_4 diluent, which has a density of 1.594 g/mL at 20°C [WEAST]. Inasmuch as no significant changes in the extractant concentration in these solutions were detected as measured by the extraction of americium, it appears that selective loss of CCl_4, either by evaporation, decomposition, or aqueous phase solubility, was of minor importance in these degradation experiments.

These small changes in the density of the TRUEX solvent are insignificant compared with the differences in density between the solvent and the various aqueous phases in the process: the feed plus scrub solution (density of 1.117 0.002 g/mL) and the scrub, strip, and Na_2CO_3 wash solutions (density of 1.00 to 1.02 g/mL [WEAST]). Thus, changes in density due to degradation should have no detectable effect on performance of the TRUEX process.

For comparison, 30% TBP in CCl_4 equilibrated with 3M HNO_3 was found to have a density of 1.339 g/cm^3 [ZIELINSKI], whereas the density of 24.8% TBP in CCl_4 is 1.324 g/mL [JOHNSON]. Water-saturated solutions of TBP in CCl_4 have densities of 1.436 (25.5% TBP) and 1.375 g/mL (34.8% TBP) [VAN ARTSEN].

3. Viscosity

The viscosities of the fresh and slightly degraded TRUEX solvents are quite similar (Table V-11). One possible explanation for the slight increase in viscosity after treatment (like the slight decrease in density) is the loss of a small amount of the diluent. Sodium carbonate treatment of the fresh and hydrolyzed samples has only a slight effect on the measured viscosities. From these results it seems clear that mild degradation of the TRUEX-CCl_4 solvent will have little effect on the performance of the TRUEX process due to changes in viscosity.

Only the very highly degraded sample, D5, shows a significant change in viscosity. This is especially true for the value obtained after Na_2CO_3 treatment. Clearly, only after a high dose of gamma irradiation, such as that received by sample D5, would the flow properties of the TRUEX-CCl_4 solvent be altered.

Table V-11. Viscosities of TRUEX Solvents at 22.7 ± 0.3°C

Sample	Viscosity,[a] cp[b]	
	Before Scrub	After Na_2CO_3 Scrub[c]
Fresh Solvent	1.28 ± 0.07	1.26 ± 0.01
D8	1.39 ± 0.05	-
3B	1.36 ± 0.01	1.32 ± 0.02
D5	1.93 ± 0.10	2.71 ± 0.07

[a]Standard deviation based on variation in descent time only.

[b]Equivalent to mPa·s.

[c]Samples treated by three contacts with 0.25M Na_2CO_3 followed by five contacts with water (O/A phase ratio = 2).

For comparison, the literature value for the viscosity of CCl_4 is 0.969 cp at 20°C, dropping to 0.843 cp at 30°C [WEAST]. Water-saturated solutions of TBP in CCl_4 were found to have viscosities of 1.19 cp for 25.2% TBP and 1.48 cp for 40.5% TBP at 25°C [BURGER]. Solutions of TBP in normal paraffinic hydrocarbons are more viscous due to the higher viscosity of the diluents (e.g., viscosity of 1.35 cp for dodecane at 25°C [WEAST]). A solution of 24.6% TBP in dodecane has been found to have a viscosity of 1.577 cp (dry) or 1.604 cp (water saturated) at 25°C [JOHNSON]. A typical PUREX solvent (30% TBP in kerosene) has a viscosity of 2.78 cp [COLVEN].

4. Interfacial Tension

The values obtained for the absolute interfacial tensions between the samples of TRUEX-CCl_4 process solvent and various aqueous phases are summarized in Table V-12. Interfacial tensions were in the range of 8 to 13 mN/m when the TRUEX-CCl_4 solutions were in contact with the PFP waste/HNO_3 solution. Higher values (10-15 mN/m) were observed when the aqueous phase was 0.05M HNO_3. In addition to the differences caused by variation due to acid concentration of the aqueous solutions, these differences may be in part attributable to surface active metal-extractant complexes (as proposed by Cox and Flett [COX]) lowering the interfacial tension when the TRUEX-CCl_4 solvent is in contact with the PFP waste solution. The higher values of interfacial tension for the degraded solvents in contact with acidic solutions may be due to the prior decomposition of surface active materials during hydrolytic and gamma-radiolytic treatment or to aqueous phase solubilization of surfactants during treatment and work-up.

The low values of interfacial tension when the extractant solutions are in contact with sodium carbonate are not surprising considering the poor phase-separation behavior observed during Na_2CO_3 scrubbing. The interfacial tension between the solvent and Na_2CO_3 is considerably higher following the treatment, indicating that a significant amount of surface active material is removed thereby.

Table V-12. Values of Absolute Interfacial Tension between Solvent and Aqueous Phases

Sample	Interfacial Tension for Aqueous Phase,[a] mN/m[b]		
	8/9 Simulated PFP Waste-1/9 0.25M HNO_3	0.05M HNO_3	0.25M Na_2CO_3
Fresh Solvent	8.5 ± 0.1 (6.7 ± 0.7)	10.6 ± 0.3 (9.9 ± 0.7)	2.2 ± 0.1 (0.8 ± 0.1)[c]
D8	13.2 ± 0.1 (13.8 ± 0.3)	14.7 ± 0.2 (12.3 ± 0.2)	1.0 ± 0.1 (0.6 ± 0.1)
3B	11.2 ± 0.2 (5.5 ± 1.2)	13.1 ± 0.2 (11.2 ± 0.3)	-
D5	12.6 ± 0.3 (10.0 ± 0.6)	12.8 ± 0.2 (10.7 ± 0.7)	-

[a]Measured from aqueous to organic phase. Values in parentheses are organic to aqueous measurements. Standard deviations based on ranges of apparent interfacial tensions.

[b]Equivalent to dyne/cm.

[c]After Na_2CO_3 scrub of the solvent, the interfacial tension increased to 6.3 ± 0.2 (1.7 ± 0.1) mN/m.

Little relevant literature data are available for comparison with these data. Mailen and Tallent have reported an interfacial tension of 10 to 11 mN/m for freshly prepared 30% TBP in NPH and 6.2-7.0 mN/m for used Savannah River Plant PUREX solvent vs. 0.25M Na_2CO_3-0.02M sodium tartrate [MAILEN].

5. Conclusion

The physical properties measured for TRUEX solvent degraded to the equivalent of about two years of use in the PFP process show no significant changes compared with freshly prepared solvent. Viscosity, density, and interfacial-tension measurements, combined with solvent-extraction and phase-disengagement data, indicate that very little effect of degradation can be detected. Following cleanup of the solvent by Na_2CO_3 treatment, it appears that the used TRUEX solvent should be as good as, if not better than, freshly prepared material.

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REFERENCES

BARNEY

G. S. Barney and D. G. Bouse, Alpha Radiolysis of TBP - Effect of Diluents, U.S. Energy Research and Development Administration, ARH-ST-153, Atlantic Richfield Hanford Co., Richland, WA (1977).

BERNSTEIN-1973A

G. J. Bernstein, D. E. Grosvenor, J. F. Lenc, and N. M. Levitz, A High-Capacity Annular Centrifugal Contactor, Nucl. Technol. 20, 200-202 (1973).

BERNSTEIN-1973B

G. J. Bernstein, D. E. Grosvenor, J. F. Lenc, and N. M. Levitz, Development and Performance of a High-Speed Annular Centrifugal Contactor, Argonne National Laboratory, ANL-7969 (1973).

BURGER

L. L. Burger, Comparison of Diluents for Tributyl-Phosphate, General Electric Company, HW-19065 (1950).

COLVEN

T. J. Colven, Jr., Mixer-Settler Development, Savannah River Plant, DP-140 (1956).

COX

M. Cox and D. S. Flett, The Significance of Surface Activity in Solvent Extraction Reagents, Proc. Int. Solvent Extr. Conf., Vol. 1, p. 63 (1977).

DAVIS

W. Davis, Jr., Radiolytic Behavior, in Science and Technology of Tributyl Phosphate, W. W. Schulz and J. D. Navratil, (eds.), Vol. 1, Chap. 7, CRC Press, Inc., Boca Raton, FL (1984).

DYRSSEN-1960A

D. Dyrssen and L. D. Hay, The Distribution and Dimerization of Di-n-Butyl Phosphate (DBP) in Different Solvents, Acta Chem. Scand. 14, 1091 (1960).

DYRSSEN-1960B

D. Dyrssen and L. D. Hay, Solvent Extraction of $^{152,154}Eu$ and ^{241}Am by Di-n-Butyl Phosphate in Different Organic Solvents, Acta Chem. Scand. 14, 1100 (1960).

GORDON

A. J. Gordon and R. A. Ford, The Chemist's Companion, John Wiley and Sons, New York (1972).

HARDY

C. J. Hardy and D. Scargill, Studies on Mono- and Di-n-Butylphosphoric Acids - II. The Solubility and Distribution of Mono- and Di-n-Butylphosphoric Acids in Aqueous-Organic Solvent Systems, J. Inorg. Nucl. Chem. 11, 128 (1959).

HEALY
T. V. Healy, Fuel Reprocessing Solvent Tributyl Phosphate, in Proc. IAEA and NEA (OCD) Symp. on Management of Radioactive Wastes from the Nuclear Fuel Cycle, p. 201, International Atomic Energy Agency, Vienna (1976).

HORWITZ-1981A
E. P. Horwitz, D. G. Kalina, and A. C. Muscatello, The Extraction of Th(IV) and U(VI) by Dihexyl-N,N-Diethylcarbamoylmethylphosphonate from Aqueous Nitrate Media, Sep. Sci. Technol. 16, 403 (1981).

HORWITZ-1981B
E. P. Horwitz, A. C. Muscatello, D. G. Kalina, and L. Kaplan, The Extraction of Selected Transplutonium (III) and Lanthanide (III) Ions by Dihexyl-N,N-Diethylcarbamoylmethylphosphonate from Aqueous Nitrate Media, Sep. Sci. Technol. 16, 417 (1981).

HORWITZ-1982
E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, and H. Diamond, Selected Alkyl(Phenyl)-N,N-Dialkylcarbamoylmethylphosphine Oxides as Extractants for Am(III) from Nitric Acid Media, Sep. Sci. Technol. 17, 1261 (1982).

HORWITZ-1983A
E. P. Horwitz, H. Diamond, and D. G. Kalina, Carbamoylmethylphosphoryl Derivatives as Actinide Extractants, Plutonium Chemistry, Chap. 27, ACS Symposium Series 216, W. T. Carnall and G. R. Choppin, (eds.), American Chemical Society (1983).

HORWITZ-1983B
E. P. Horwitz, 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, Denver, CO, August 21 - September 2, 1983.

HORWITZ-1984
E. P. Horwitz and D. G. Kalina, The Extraction of Am(III) from Nitric Acid by Octyl(Phenyl)-N,N-Diisobutylcarbamoylmethylphosphine Oxide-Tri-n-Butyl Phosphate Mixtures, Solvent Extr. Ion Exch. 2, 179 (1984).

HORWITZ-1985A
E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrift, and W. W. Schulz, The TRUEX Process - A Process for the Extraction of the Transuranium Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent, Solvent Extr. Ion Exch. 3, 175 (1985).

HORWITZ-1985B
E. P. Horwitz, 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, Proceedings of the Symposium on Actinide-Lanthanide Separations, 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, HI (1985).

HORWITZ-1985C
E. P. Horwitz, K. A. Martin, H. Diamond, and R. Chiarizia, unpublished data, Chemistry Division, Argonne National Laboratory (1985).

HORWITZ-1985D
E. P. Horwitz and W. W. Schulz, Solvent Extraction and Recovery of the Transuranic Elements from Waste Solutions Using the TRUEX Process, Proceedings of the International Meeting on Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle, AERE Harwell, United Kingdom, September 3-6, 1985, Ellis Harwood Limited, Market Cross House, West Sussex, England (1985).

JOHNSON
W. F. Johnson and R. L. Dillon, Physical Properties of Tributyl-Phosphate Diluent Solutions, General Electric Company, HW-29086 (1953).

KALINA-1981
D. G. Kalina, E. P. Horwitz, L. Kaplan, and A. C. Muscatello, The Extraction of Am(III) and Fe(III) by Selected Dihexyl-N,N-Dialkyl-carbamoylmethylphosphonates, -phosphinates, and -phosphine Oxides from Nitrate Media, Sep. Sci. Technol. 16, 1127 (1981).

KALINA-1984
D. G. Kalina, Application of Lanthanide Induced Shifts for the Determination of Solution Structures of Metal Ion-Extractant Complexes, Solvent Extr. Ion Exch. 2, 381 (1984).

KALINA-1985A
D. G. Kalina and B. Tansey, A Precautionary Note on the Use of Dibutyl-N, N-Diethylcarbamoylphosphonate in Solvent Extraction, Solvent Extr. Ion Exch. 3, 173 (1985).

KALINA-1985B
D. G. Kalina and E. P. Horwitz, Variations in the Solvent Extraction Behavior of Bifunctional Phosphorus-Based Compounds Modified with TBP, Solvent Extr. Ion Exch. 3, 235 (1985).

LEONARD-1980
R. A. Leonard, G. J. Bernstein, A. A. Ziegler, and R. H. Pelto, Annular Centrifugal Contactors for Solvent Extraction, Sep. Sci. Technol. 15, 925-943 (1980).

LEONARD-1981
R. A. Leonard, G. J. Bernstein, R. H. Pelto, and A. A. Ziegler, Liquid-Liquid Dispersion in Turbulent Couette Flow, AIChE J. 27, 495-503 (1981).

LEONARD-1983
R. A. Leonard, A. A. Ziegler, R. A. Wigeland, R. W. Bane, and M. J. Steindler, Operation with Three Liquid Phases in a Staged Liquid-Liquid Contactor, Sep. Sci. Technol. 18, 1563-1579 (1983).

LEONARD-1985
R. A. Leonard, Use of Electronic Worksheets for Calculation of Stagewise Solvent Extraction Processes, accepted for presentation at the Fourth Symposium on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1985.

MAILEN
J. C. Mailen and O. K. Tallent, Cleanup of Savannah River Plant Solvent Using Solid Sorbents, Oak Ridge National Laboratory, ORNL/TM-9256, (1985).

MUSCATELLO
A. C. Muscatello, E. P. Horwitz, D. G. Kalina, and L. Kaplan, The Extraction of Am(III) and Eu(III) from Aqueous Ammonium Thiocyanate by Dihexyl-N,N-Diethylcarbamoylmethylphosphonate and Related Compounds, Sep. Sci. Technol. 17, 859 (1982).

SCHULZ
W. W. Schulz, Macroreticular Ion-Exchange Resin Cleanup of PUREX Process TBP Solvent, Proc. Int. Solvent Extr. Conf., Vol. I, p. 174, Society of Chemical Industry, London (1971).

SHOUN
R. R. Shoun and M. C. Thompson, Chemical Properties and Reactions, in Science and Technology of Tributyl Phosphate, W. W. Schulz and J. D. Navratil (eds.), Vol. 1, Chap. 5, CRC Press, Inc., Boca Raton, FL (1984).

STIEGLITZ
L. Stieglitz and R. Becker, Chemical and Radiolytic Degradation in the PUREX Process, Proceedings of the American Nuclear Society International Topical Meeting, Fuel Reprocessing and Waste Management, Vol. 1, Jackson, WY, August 26-29, 1984.

VAN ARTSEN
J. J. Van Artsen and A. E. Korvezee, The Ternary System: Carbon Tetrachloride-Water-Tributyl Phosphate (TBP), Recueil 83, 752 (1964).

VANDEGRIFT-1984A
G. F. Vandegrift, R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. J. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, Transuranic Decontamination of Nitric Acid Solutions by the TRUEX Solvent Extraction Process - Preliminary Development Studies, Argonne National Laboratory, ANL-84-45 (1984).

VANDEGRIFT-1984B
G. F. Vandegrift, Diluents for TBP Extraction Systems, in Science and Technology of Tributyl Phosphate, W. W. Schulz and J. D. Navratil (eds.), Vol. 1, CRC Press, Inc., Boca Raton, FL (1984).

VANDEGRIFT-1985

G. F. Vandegrift, R. A. Leonard, E. P. Horwitz, and M. J. Steindler, TRU Removal from Complexant Concentrate Waste by the TRUEX Process, accepted for presentation at the Fourth Symposium on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1985.

WEAST

R. C. Weast (ed.), CRC Handbook of Chemistry and Physics, 65th ed., CRC Press, Inc., Boca Raton, FL (1984).

WEBSTER

D. S. Webster, A. S. Jennings, A. A. Kishbaugh, and H. K. Bethmann, Performance of Centrifugal Mixer-Settler in the Reprocessing of Nuclear Fuel, AIChE Symp. Ser., Nuclear Engineering--Part XX, No. 94, Vol. 65, pp. 70-77 (1969).

ZIELINSKI

A. Zielinski and J. Kulawik, Investigation of Foam Properties in Some Extraction Systems with TBP in Kerosene and in Carbon Tetrachloride, J. Radioanal. Chem. 58, 143 (1980).

APPENDIX A.

EXPERIMENTAL PROCEDURES

1. Flowsheet Demonstration

The TRUEX process was tested using simulated PFP waste containing uranium, plutonium, and americium, as well as the TRUEX-CCl_4 process solvent. Fourteen of 16 stages available in the 4-cm centrifugal contactor were used. Five participants were directly involved in sampling and controlling the experiment during the cold and hot runs. Both runs went smoothly. The flowsheet tested is shown in Fig. III-1, in which the numbers in parentheses indicate the volumetric flow rates that were used in the demonstration run. The concentrations of the feed streams are basically those given in Table III-2. The process solutions in the glove box at the start of the run are listed in Table A-1. Additional solutions in the glove box after the run are given in Table A-2. During the actual 20-minute hot run, six samples were taken from each of four sampling ports. On the day after the run, one sample was taken from the aqueous PFP feed (DF) and the total liquid (organic plus aqueous) in each of the 14 stages was drained for samples. Thus, 39 samples were taken and bagged out for chemical analysis. During the cold run that was accomplished the previous day, three samples were taken from each of the four sampling ports. Samples were collected in the same way and with the same frequency as during the hot test.

Before the hot run, all feed solutions were put in place, and the americium, plutonium, uranium, and $NaNO_2$ stock solutions were introduced to the DF container, mixed, and allowed to equilibrate overnight.* To begin the run,

Table A-1. Initial Solutions in the Glove Box

Code	Name	Concentration, M			Volume, L		Container Type
		HNO_3	HF	Other	Solution	Container	
DF	PFP Waste	1.5	0.0	a	9.0	10.0	HDPE[b]
DS	Scrub	0.25	0.0	-	2.0	2.0	HDPE
EF	First Strip	0.05	0.0	-	4.0	4.0	HDPE
FF	Second Strip	0.05	0.05	-	2.5	4.0	HDPE
DX	Solvent	0.01	0.0	c	2.4	4.0	Glass
C	CCl_4	-	-	CCl_4	0.10	0.118	Glass

[a]Americium, 6×10^{-6}M; plutonium, 3×10^{-5}M.
[b]High-density polyethylene.
[c]0.25M CMPO-0.75M TBP in CCl_4.

*Americium and plutonium stock solutions were prepared and quantitated by D. L. Bowers, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

Table A-2. Additional Solutions in the Glove Box after the Run

Code (Origin)	Name	Concentration, M			Volume, L				Sample Containers	
		HNO_3	HF	Other	Waste[a]	Sample	Sample Container	Total Sample	Quan.	Type[b]
DW (DF+DS)[c]	Raffinate	1.4	0.0	nonTRU	8.4 (15)	0.1	0.25	0.6	6	HDPE[d]
EW (EF)[c]	Am Strip	0.05	0.0	1.6×10^{-5} Am	2.7 (4)	0.05	0.25	0.3	6	HDPE
FW (FF)[c]	Pu Strip	0.05	0.05	1.6×10^{-4} Pu	1.35 (2)	0.025	0.25	0.15	6	HDPE
DF	Feed	1.5	0.0	e	-	0.05[f]	0.25	0.05	1	HDPE
FP (DX)	Solvent	0.01	0.0	g	-	0.05	0.118	0.3	6	Glass[h]
S	Stage Samples	0.05-1.4	0.0-0.05	i	-	∿0.1	0.118	∿1.4	14	Glass[h]

[a]A high-density polyethylene or polypropylene bottle of the size shown in parenthesis was used.

[b]All containers of narrow-mouth type with screw-on caps.

[c]Volume from 20-min run.

[d]High-density polyethylene.

[e]Americium, 6×10^{-6}M; plutonium, 3×10^{-5}M.

[f]This sample is taken from the residual volume left in the DF container.

[g]C.25M CMPO, 0.75M TBP, rest CCl_4.

[h]Containers have Teflon TFE caps.

[i]Varying amounts of americium and plutonium, depending on the stage number.

the DX and FP pumps were started after the contactor rotors were spinning. When organic solvent flow was established through the unit, the aqueous feed pumps for DS, DW, FF, and EF were turned on. When aqueous flow was established in all effluent lines, the DF feed pump was started, at which time the test was considered to be at time zero. Samples of the DW effluent were taken starting two minutes after time zero and every three minutes thereafter. Samples of the EW, FW, and FP effluents were taken starting three minutes after time zero and every three minutes thereafter. Carbon tetrachloride was added to the solvent reservoir (DX) at the rate of 3 mL/min to compensate for expected evaporative losses.

Four of the five participants were positioned at the 2-1/2 module glove box, one at each of its four windows. The fifth participant acted as foreman and timekeeper. The duties of these participants were as follows:

Participant 1 was in charge of the raffinate (DW) pump switch and was the sample taker of the raffinate (DW) and the americium product (EW) lines.

Participant 2 was the sample taker of the plutonium product (FW) line.

Participant 3 was in charge of the switches for five of the rotor motors and the TRUEX solvent (FP) pump to the DX reservoir, and was sample taker of the TRUEX solvent (FP) line.

Participant 4 was in charge of the switches for nine of the rotor motors and for the pumps for the TRUEX solvent (DX) reservoir and the feed (DF), scrub (DS), strip #1 (EF), and strip #2 (FF) lines, and was responsible for adding CCl_4 from a burette into the DX reservoir at 3 mL/min.

Participant 5 was the timer, data taker, and checklist keeper. Table A-3 is the checklist used for the demonstration run. For the cold run, the test was stopped at 11 minutes after time zero (after three samples had been taken at each effluent port). The liquids were not drained from the contactor stages after the cold run; thus, the startup time for the hot run on the following day was decreased. In the first minute of startup for the hot run, the rotors were turned on, the DX and FP pumps were started, and solvent flow was established. In the next five minutes, the DS, DW, FF, and EF pumps were started in sequence and effluent flow was established so that, at the end of this time, the DF pump could be started (time zero). After this point, the checklist given in Table A-3 was followed exactly.

2. Sample Analyses

All DF, DW, EW, FW, FP, and individual-stage samples were gamma-counted to measure ^{241}Am activity. Aliquots of each sample were placed directly in Biogamma™ counting vials. The size of aliquot was determined by the expected activity level of the sample. The vials were counted in a Beckman Biogamma™ automatic gamma counter with a NaI(Tl) well detector. The energy window of the counter was set for measuring the 59.6-keV photopeak of ^{241}Am. Corrections were made for the differences in the counting geometries obtained with different size aliquots. Conversions from counts per minute to disintegrations per minute were accomplished by multiplying the former by factors ranging from 5.02 to 3.74, depending on the sample size.

Table A-3. Checklist for PFP Waste Demonstration Run

Time after Start of Run, min	Participant	Action
-23 (approx.)	3,4	Turn rotors on
-22 (approx.)	4	DX pump on
-12.5 (approx.)	3	Turn on FP pump when solvent appears at exit port
-11 (approx.)	4	Start CCl_4 addition at 3 mL/min when FP effluent starts flowing into DX reservoir
-10.5 (approx.)	4	Mark liquid level in DX reservoir
-10	4	DS pump on
- 6 (approx.)	1	Turn on DW pump when flow appears at the DW port
- 5	4	FF pump on
- 3	4	EF pump on
- 1.5 (approx.)	1	Indicate time that DW and EW start flowing
- 1.5 (approx.)	2	Indicate time that FW starts flowing
- 1.5 (approx.)	3	Check that FP flow is continuing
0	4	DF pump on
2	1	Sample DW
3	1,2,3	Sample EW, FW, FP
5	1	Sample DW
6	1,2,3	Sample EW, FW, FP
8	1	Sample DW
9	1,2,3	Sample EW, FW, FP
11	1	Sample DW
12	1,2,3	Sample EW, FW, FP
14	1	Sample DW
15	1,2,3	Sample EW, FW, FP
17	1	Sample DW
18	1,2,3	Sample EW, FW, FP
20	3,4	Kill all pumps and rotors except DW and FP pumps
20.5	1,3	Kill DW and FP pumps

Selected samples of FW and FP were counted by alpha pulse-height analysis to measure both ^{241}Am and $^{239,240}Pu$. Samples for counting were prepared by heating to dryness small aliquots of FW and FP on a tantalum disk; the FP samples were prepared by heating in an evacuated chamber. A gold-plated surface barrier silicon detector and a Davidson 4096 Multi-Channel Pulse Height Analyzer were used to count the samples.

The plutonium concentration in selected DW and EW fractions was measured by mass spectrometric isotopic dilution analysis.* Aliquots of 4.0 and 40 mL of EW and DW, respectively, were diluted with concentrated HNO_3 to 4-5M HNO_3. Each solution was adjusted to 0.05M in $NaNO_2$ and spiked with an aliquot from a standard ^{244}Pu-4M HNO_3 stock solution. The EW samples were spiked with 9.7×10^{-2} μg of ^{244}Pu; the DW samples were spiked with 9.7×10^{-4} μg of ^{244}Pu. The spiked samples were allowed to stand for 48 hours to attain isotopic equilibrium.

Plutonium was separated from all other constituents by extracting it with 15 vol % Aliquot-336™ nitrate in xylene using an O/A phase ratio of 1:2. The organic phase was scrubbed three times with an equal volume of 5M HNO_3 and stripped three times with an equal volume of 1M formic acid-0.1M HNO_3. The combined strip solution for each sample was evaporated to 2-4 mL, washed with three 2-mL portions of 2-ethylhexanol to remove traces of organic extractant, and then submitted for mass spectrometric analysis.

Samples of EW and FW obtained from the cold test run were analyzed for inert constituents using inductively coupled plasma/atomic emission spectroscopy (ICP/AES).† A 4.0-mL volume of each sample was placed in a 25-mL volumetric flask and diluted to volume with ultrapure water from a Barnstead Nanopure water purification system. Blanks were run on the 0.05M HNO_3 and 0.05M HNO_3-0.05M HF solutions used for the EF and FF streams, respectively.

With the exception of zinc, the blanks showed no detectable quantities of the constituents reported in Table III-8. In the case of zinc, the correction in the EW and FW fractions was about 20%.

3. Hydrolytic and Gamma-Radiolytic Degradation Studies

Five thermostated vessels were set up to measure the hydrolytic degradation of the TRUEX-CCl_4 solvent (0.25M CMPO-0.75M TBP diluted by CCl_4) in contact with several aqueous phases at 50 and 70°C. Two additional vessels, thermostated to 50°C, were placed in the Argonne ^{60}Co Irradiation Facility to measure the gamma-radiolytic degradation of the TRUEX-CCl_4 solvent.

a. Hydrolytic Degradation

Each of several samples of the organic solvent (125 mL) was pre-equilibrated with three contacts of the aqueous phase with which it was to be

*Mass spectrometric analysis was performed by E. L. Callis, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

†ICP/AES analysis was performed by E. A. Huff, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

in contact during treatment. After the preequilibration, the 125-mL samples of the TRUEX solvent and 50 mL of the aqueous phase were stirred vigorously for periods of time between one day and one month in one of two thermostated vessels (at either 50 ± 0.2°C or 69.4 ± 0.3°C), each fitted with a water-cooled condenser. When the treatment period was completed, both phases were poured into a separatory funnel and, after phase separation was completed, the aqueous phase was removed. The organic phase was washed with water to remove nitric acid and, in the case of contacts with the PFP feed solution, ferric ion from the organic phase. Based on a nitric acid distribution ratio of 0.2, three to five water washes of the organic phases (1.2 O/A volume ratio) were sufficient to reduce the nitric acid concentration below 1×10^{-4}M. After washing, the organic phases were stored in glass-stoppered bottles.

b. Radiolytic Degradation

Experiments were run in the ^{60}Co cell in pairs. The two vessels were identical to those used in the hydrolytic degradation studies. Because the samples were located at different distances from the source, their measured dose rates were different (1.9×10^5 and 2.8×10^5 R/h). Experiments were run for irradiation times of 30 to 4500 minutes. Reaction vessels were maintained at 49 ± 2°C. The organic phase (125 mL) was preequilibrated with three 50-mL portions of the appropriate aqueous phase before its final contact in the irradiation cell. The phases were stirred vigorously during exposure. After irradiation, the degraded TRUEX solvents were washed three times with water to remove dissolved nitric acid (2.0 O/A phase ratio).

c. Sodium Carbonate Scrubs

A 6-mL quantity of each organic phase was separated and contacted with three consecutive 3-mL aliquots of 0.25M Na_2CO_3 solution. This operation was followed by three to six water washings in the same phase ratio. The number of water washings was set by the time the water/organic emulsion took to break; as water washing continued, the time for the emulsion to break decreased. In the final water wash, the phases broke within one minute with no centrifugation. Also, in all washes, a white froth was evident at the interface. With continued washing and separating of the white froth from the aqueous phase, both solutions were clear at completion of the washing operation.

d. Distribution Ratio Measurements

Aliquots of 1 mL of TRUEX-CCl_4 were preequilibrated with two consecutive 1-mL aliquots of the appropriate aqueous phase. A spike of ^{241}Am was added to a third 1-mL contact, and the solutions were thermostated at 25°C with intermittent vortex mixing. The samples were then centrifuged, and the phases were separated. Duplicate 50-μL aliquots of both phases were then taken for liquid scintillation counting.

4. Physical Properties of TRUEX-CCl_4 Process Solvent

Samples of TRUEX-CCl_4 subjected to gamma-radiolysis and hydrolysis were compared with fresh material with respect to density, viscosity, and interfacial tension.

a. Density

The densities of the various TRUEX-CCl_4 solutions were determined by weighing samples contained in 10-mL volumetric flasks. The densities were calculated from the average of three separate measurements at 22.5 ± 0.2°C.

b. Viscosity

The viscosities of the TRUEX solvent solutions were measured at ambient temperature (22.7 ± 0.3°C) using a Gilmont falling ball viscometer with a stainless steel ball. The viscometer constant, K, was calculated based on the behavior of water, using values for the density (ρ_{std} = 0.9975 g/mL) and viscosity (μ_{std} = 0.9325 cp) of water at 23°C [WEAST] and the density of the stainless steel ball (ρ_{ball} = 8.02 g/mL) provided by the manufacturer. The average time of descent of the ball in water, t_{std}, was found to be 43.10 ± 1.36 s. The value of K was then calculated using the following equation.

$$K = \frac{\mu_{std}}{(\rho_{ball}-\rho_{std})\ (t_{std})} = 3.08 \times 10^{-3}\ cp\cdot mL/(g\cdot s)$$

This value of K was then used to calculate viscosities of the other solutions using the following equation.

$$\mu = K(\rho_{ball} - \rho)\ t$$

where μ, ρ, and t are the viscosity (cp), density (g/mL), and descent time (s), respectively, for each sample. The viscosity of each sample was calculated from the average of at least five measurements.

c. Interfacial Tension

The interfacial tension measurements were performed at ambient temperature (22.7 ± 0.6°C) using a Fisher Model 21 tensiometer equipped with a platinum/iridium ring 6.065 cm in circumference. Both organic-to-aqueous and aqueous-to-organic interfacial tensions were measured. The aqueous-to-organic measurements were found to be generally higher and more reproducible than the organic-to-aqueous measurements, probably due to better wetting in the aqueous phase, as explained by Goankar and Neuman [GOANKAR]. Measurements were performed using about 15 mL of each phase. Samples were allowed to equilibrate for a minimum of 15 minutes before the measurements were made. At least five measurements for each sample were averaged to obtain the interfacial tension, using the correction factor of Zuidema and Waters [ZUIDEMA], with the ratio of the radius of the ring to that of the wire forming the ring (R/r) equal to 54.3318.

5. Secondary Solvent Cleanup Using Macroporous Anion Exchange Resin

About 2 L of hydrolytically and radiolytically degraded TRUEX process solvent and 1 L of TRUEX process solvent that was not degraded were purified using macroporous anion exchange resin in the hydroxide form. The TRUEX-CCl_4 process solvent fraction that was a mixture of all the solutions tested for hydrolytic and radiolytic degradation was subjected to the carbonate scrub

cleanup before treatment with macroporous resin; the undegraded solvent was not. A 2.5-cm-ID, 25-cm-long Bio-Rad™ column was slurry packed with AG MP-1 (50-100 mesh) resin under 35 to 70 kPa (5 to 10 psi) of N_2 pressure. The 100-cm^3 resin bed was converted to the hydroxide ion cycle by eluting it with 14 bed volumes of 4M NaOH, followed by a water wash to neutral pH. After rinsing, the resin bed was washed with five bed volumes of anhydrous methanol to remove water, followed by five bed volumes of CCl_4 to remove the methanol. During the crossover from methanol to CCl_4, a great deal of heat was produced, which caused the resin bed to separate slightly. After one to two bed volumes of CCl_4 had passed through the column, the heating subsided and voids in the resin bed disappeared. No explanation for this behavior can be given at this time. Flow rates of 1 to 2 mL/(cm^2·min) (5-10 mL/min) were used during the preconditioning steps.

Prior to being passed through the resin bed, both batches of solvent were equilibrated with 0.01M HNO_3 (O/A = 2), followed by one water wash (O/A = 2), to ensure that all sodium salts of acidic extractants that may have been present were converted to the acidic form. The pH levels of the acid washes were checked to ensure that the solvents contained no residual basicity. The 2-L batch of degraded TRUEX process solvent was passed through the column first. The solvent was yellow and cloudy before passing through the resin bed. After passing through the bed, the solvent was much lighter colored and clear. A flow rate of 5 to 10 mL/min was used throughout the cleanup procedure. The 1-L batch of TRUEX-CCl_4 process solvent initially appeared clear before and after column treatment; however, near the end of the procedure the eluate became slightly cloudy.

Both batches of TRUEX-CCl_4 process solvent became cloudy on standing overnight and appeared to have a small quantity of precipitate near the surface. The precipitate was easily removed by filtration through Wattman #1 Qualitative filter paper or a small silica gel (Porasil™-B) column; however, the cloudiness reappeared on standing overnight a second time. The two batches of solvent were combined and diluted with 200 mL of CCl_4 to restore the CMPO and TBP concentrations to 0.25 and 0.75M, respectively. (The amount of CCl_4 required was determined by measuring D_{Am} at 2M HNO_3.) After diluting with CCl_4, the process solvent was divided equally between two 2-L glass bottles. About 100 mL of water was added to each bottle as a barrier to lessen the evaporative loss of CCl_4. The TRUEX process solvent still appeared cloudy, but began to clarify after small quantities of 4M HNO_3 were added to the water layer and manually mixed. Once the pH of the water layer reached ∿2 to 3, the solvent became clear. The solvent was stored in this condition for the demonstration run.

The extraction properties of a sample of the resin-purified TRUEX process solvent were tested in a simulated batch extraction of ^{241}Am from synthetic PFP waste, which was followed by two consecutive scrub contacts and three consecutive strip contacts. This was done to ensure that the process solvent gave the proper D_{Am} values in each stage of the process. In addition, the disengagement times of the purified TRUEX solvent were measured using 0.25M Na_2CO_3. The D_{Am} values obtained with the resin-treated TRUEX-CCl_4 process solvent used for the hot test run are listed in Table A-4. These values are experimentally identical with D_{Am} values measured using freshly crystallized CMPO [HORWITZ-1985A,B].

Table A-4. Batch D_{Am} Values for Consecutive Extraction, Scrub, and Strip Operations for Resin-Treated TRUEX-CCl_4 Process Solvent[a]

Batch Operation	D_{Am}
Extraction[b]	18
Scrub 1	8.2
Scrub 2	6.4
Strip 1[c]	0.96
Strip 2[c]	0.15
Strip 3[c]	0.098

[a]Measured at 25°C with the same phase ratio as used in the demonstration.

[b]Synthetic PFP waste solution with no addition of scrub solution.

[c]Americium strip solution (0.05M HNO_3).

6. Worksheet Calculations

The worksheet calculations presented in this section were made following the procedure given by Leonard [LEONARD]. The electronic worksheet used was DIGICALC, as implemented on a VAX computer. The work discussed here is for one component, americium. The concentrations for the other components of the reference flowsheet (Table III-2) were calculated in a similar fashion. In some cases, the results were extrapolated from those for other components; in such a case, the concentration in Table III-2 is simply shown as being less than a given value. Calculations were first made using the expected D_{Am} values; then the measured values; and finally, the corrected values. In the last two instances, the calculations were done both with and without solvent recycle.

a. Expected Coefficients

A summary of worksheet calculations using the expected values of the americium distribution coefficients given in Table III-1 is listed in Table A-5 as Case A. The temperatures shown are those at which the distribution coefficients were measured. When solvent recycle is indicated in the table, the organic effluent (FP) is assumed to be immediately recycled to the organic feed port (DX). When this is the case, the DX concentration is determined as part of the worksheet calculations.

To get the worksheet results for the six cases summarized in Table A-5, the americium concentration was calculated as a function of stage number and time. Computer listings of these americium concentrations for Case A are given in Tables A-6 and A-7 for the aqueous (x_i) and organic (y_i) phases, respectively, where i is the stage number. Because of the computational technique, each americium concentration in each column is calculated

Table A-5. Effect of Americium Distribution Coefficients on the Calculated Americium Concentration in the Effluents of the Reference Flowsheet at Steady-State Conditions[a]

Parameter	Case A	Case B	Case C	Case D	Case E	Case F
Temperature, °C	30	25	25	25	25	25
Solvent Recycle	Yes	Yes	No	No	No	Yes
Americium Concentration (input data except as noted), 10^{-6}M:						
DF	6.0	6.0	5.81	5.81	5.81	5.81
DX	1.25E-4[b]	0.170[b]	0	0	0	0.028[b]
Americium Distribution Coefficient Type:						
Extraction	Expected	Measured	Measured	Corrected	Corrected	Corrected
Scrub & Strips	Expected	Measured	Measured	Measured	Corrected	Corrected
Americium Distribution Coefficient Values:						
Stage 1	16	31	31	23.7	23.7	23.7
Stage 2	16	29	29	22.9	22.9	22.9
Stage 3	17	27	27	21.7	21.7	21.7
Stage 4	17	35	35	26.7	26.7	26.7
Stage 5	17	32	32	24.9	24.9	24.9
Stage 6	8.8	17	17	17	12.5	12.5
Stage 7	6.5	15	15	15	11.0	11.0
Stage 8	0.87	4	4	4	2.9	2.9
Stage 9	0.13	0.69	0.69	0.69	0.51	0.51
Stage 10	0.11	0.3	0.3	0.3	0.22	0.22
Stage 11	0.11	0.3	0.3	0.3	0.22	0.22
Stage 12	0.1	0.31	0.31	0.31	0.23	0.23
Stage 13	0.1	0.25	0.25	0.25	0.184	0.184
Stage 14	0.1	0.2	0.2	0.2	0.174	0.174
Americium Concentration (calculated values), 10^{-6}M:						
DW	8.8E-4	5.5E-3	4.2E-5	1.43E-4	1.44E-4	1.33E-3
EW	16.0	13.8	13.2	13.2	14.7	14.7
FW	0.039	4.4	4.2	4.2	1.59	1.59
FP	1.25E-4	0.170	0.155	0.163	0.028	0.028

[a]Flow rates and stage numbers are as shown in Fig. III-1. No americium in feed streams DS, EF, and FF, as shown in Fig. III-1.

[b]Calculated value.

Table A-6. Americium Concentration in the Aqueous Phase of the Contactor Stages for Case A

Approx. Time, min	Aqueous Phase Concentration (x_i) of Americium in Stage (i), 10^{-6} M														
	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	x_{12}	x_{13}	x_{14}
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	8.000E-01	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	1.200E-01	8.000E-01	1.489E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1.5	0.000E+00	0.000E+00	1.800E-02	1.200E-01	9.268E-01	1.489E+00	1.918E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	0.000E+00	2.842E-03	1.800E-02	1.543E-01	9.268E-01	1.795E+00	1.918E+00	6.665E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2.5	4.488E-04	2.842E-03	2.542E-02	1.543E-01	9.611E-01	1.795E+00	2.312E+00	6.665E+00	5.132E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3	4.488E-04	4.392E-03	2.542E-02	1.658E-01	9.611E-01	1.873E+00	2.312E+00	1.078E+01	5.132E+00	6.010E-01	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3.5	6.935E-04	4.392E-03	2.838E-02	1.658E-01	9.721E-01	1.873E+00	2.412E+00	1.078E+01	8.831E+00	6.010E-01	5.956E-02	0.000E+00	0.000E+00	0.000E+00
4	6.935E-04	5.065E-03	2.838E-02	1.699E-01	9.721E-01	1.897E+00	2.412E+00	1.311E+01	8.831E+00	1.088E+00	5.956E-02	1.092E-02	0.000E+00	0.000E+00
4.5	7.997E-04	5.065E-03	2.954E-02	1.699E-01	9.761E-01	1.897E+00	2.444E+00	1.311E+01	1.105E+01	1.088E+00	1.078E-01	1.092E-02	1.820E-03	0.000E+00
5	7.997E-04	5.338E-03	2.954E-02	1.715E-01	9.761E-01	1.906E+00	2.444E+00	1.441E+01	1.105E+01	1.392E+00	1.078E-01	2.128E-02	1.820E-03	3.033E-04
5.5	8.445E-04	5.338E-03	3.000E-02	1.715E-01	9.776E-01	1.906E+00	2.455E+00	1.441E+01	1.232E+01	1.392E+00	1.379E-01	2.128E-02	3.800E-03	3.033E-04
6	8.445E-04	5.448E-03	3.000E-02	1.721E-01	9.776E-01	1.909E+00	2.455E+00	1.512E+01	1.232E+01	1.567E+00	1.379E-01	2.845E-02	3.800E-03	6.333E-04
6.5	8.635E-04	5.448E-03	3.018E-02	1.721E-01	9.781E-01	1.909E+00	2.459E+00	1.512E+01	1.303E+01	1.567E+00	1.553E-01	2.845E-02	5.270E-03	6.333E-04
7	8.635E-04	5.492E-03	3.018E-02	1.724E-01	9.781E-01	1.910E+00	2.459E+00	1.551E+01	1.303E+01	1.666E+00	1.553E-01	3.287E-02	5.270E-03	8.783E-04
7.5	8.718E-04	5.492E-03	3.025E-02	1.724E-01	9.784E-01	1.910E+00	2.460E+00	1.551E+01	1.342E+01	1.666E+00	1.651E-01	3.287E-02	6.210E-03	8.783E-04
8	8.718E-04	5.510E-03	3.025E-02	1.725E-01	9.784E-01	1.911E+00	2.460E+00	1.573E+01	1.342E+01	1.720E+00	1.651E-01	3.544E-02	6.210E-03	1.035E-03
8.5	8.755E-04	5.510E-03	3.028E-02	1.725E-01	9.784E-01	1.911E+00	2.461E+00	1.573E+01	1.363E+01	1.720E+00	1.705E-01	3.544E-02	6.769E-03	1.035E-03
9	8.755E-04	5.518E-03	3.028E-02	1.725E-01	9.784E-01	1.911E+00	2.461E+00	1.584E+01	1.363E+01	1.750E+00	1.705E-01	3.689E-02	6.769E-03	1.128E-03
9.5	8.772E-04	5.518E-03	3.029E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.584E+01	1.375E+01	1.750E+00	1.734E-01	3.689E-02	7.089E-03	1.128E-03
10	8.772E-04	5.521E-03	3.029E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.591E+01	1.375E+01	1.766E+00	1.734E-01	3.770E-02	7.089E-03	1.182E-03
10.5	8.780E-04	5.521E-03	3.029E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.591E+01	1.381E+01	1.766E+00	1.750E-01	3.770E-02	7.268E-03	1.182E-03
11	8.780E-04	5.523E-03	3.029E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.594E+01	1.381E+01	1.775E+00	1.750E-01	3.814E-02	7.268E-03	1.211E-03
11.5	8.784E-04	5.523E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.594E+01	1.384E+01	1.775E+00	1.759E-01	3.814E-02	7.367E-03	1.211E-03
12	8.784E-04	5.523E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.596E+01	1.384E+01	1.780E+00	1.759E-01	3.839E-02	7.367E-03	1.228E-03
12.5	8.786E-04	5.523E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.596E+01	1.386E+01	1.780E+00	1.764E-01	3.839E-02	7.421E-03	1.228E-03
13	8.786E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.386E+01	1.782E+00	1.764E-01	3.852E-02	7.421E-03	1.237E-03
13.5	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.387E+01	1.782E+00	1.766E-01	3.852E-02	7.450E-03	1.237E-03
14	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.387E+01	1.784E+00	1.766E-01	3.859E-02	7.450E-03	1.242E-03
14.5	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.388E+01	1.784E+00	1.767E-01	3.859E-02	7.466E-03	1.242E-03
15	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.388E+01	1.784E+00	1.767E-01	3.863E-02	7.466E-03	1.244E-03
15.5	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.597E+01	1.388E+01	1.784E+00	1.768E-01	3.863E-02	7.474E-03	1.244E-03
16	8.787E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.768E-01	3.865E-02	7.474E-03	1.246E-03
16.5	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.865E-02	7.479E-03	1.246E-03
17	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.866E-02	7.479E-03	1.247E-03
17.5	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.866E-02	7.482E-03	1.247E-03
18	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.866E-02	7.482E-03	1.247E-03
18.5	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.866E-02	7.483E-03	1.247E-03
19	8.788E-04	5.524E-03	3.030E-02	1.725E-01	9.785E-01	1.911E+00	2.461E+00	1.598E+01	1.388E+01	1.785E+00	1.769E-01	3.867E-02	7.483E-03	1.247E-03

Table A-7. Americium Concentration in the Organic Phase of the Contactor Stages for Case A

Approx. Time, min	Organic Phase Concentration (y_i) of Americium in Stage (i), 10^{-6} M													
	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_{10}	y_{11}	y_{12}	y_{13}	y_{14}
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	1.360E+01	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	2.040E+00	1.360E+01	1.310E+01	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1.5	0.000E+00	0.000E+00	3.060E-01	2.040E+00	1.576E+01	1.310E+01	1.246E+01	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	0.000E+00	4.547E-02	3.060E-01	2.623E+00	1.576E+01	1.580E+01	1.246E+01	5.799E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2.5	7.180E-03	4.547E-02	4.322E-01	2.623E+00	1.634E+01	1.580E+01	1.503E+01	5.799E+00	6.671E-01	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3	7.180E-03	7.027E-02	4.322E-01	2.818E+00	1.634E+01	1.648E+01	1.503E+01	9.378E+00	6.671E-01	6.611E-02	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3.5	1.110E-02	7.027E-02	4.825E-01	2.818E+00	1.653E+01	1.648E+01	1.568E+01	9.378E+00	1.146E+00	6.611E-02	6.552E-03	0.000E+00	0.000E+00	0.000E+00
4	1.110E-02	8.104E-02	4.825E-01	2.889E+00	1.653E+01	1.670E+01	1.568E+01	1.140E+01	1.148E+00	1.197E-01	6.552E-03	1.092E-03	0.000E+00	0.000E+00
4.5	1.280E-02	8.104E-02	5.022E-01	2.889E+00	1.659E+01	1.670E+01	1.588E+01	1.140E+01	1.437E+00	1.197E-01	1.186E-02	1.092E-03	1.820E-04	0.000E+00
5	1.280E-02	8.541E-02	5.022E-01	2.916E+00	1.659E+01	1.677E+01	1.588E+01	1.253E+01	1.437E+00	1.531E-01	1.186E-02	2.128E-03	1.820E-04	3.033E-05
5.5	1.351E-02	8.541E-02	5.100E-01	2.916E+00	1.662E+01	1.677E+01	1.595E+01	1.253E+01	1.602E+00	1.531E-01	1.517E-02	2.128E-03	3.800E-04	3.033E-05
6	1.351E-02	8.716E-02	5.100E-01	2.926E+00	1.662E+01	1.680E+01	1.595E+01	1.316E+01	1.602E+00	1.724E-01	1.517E-02	2.845E-03	3.800E-04	6.333E-05
6.5	1.382E-02	8.716E-02	5.130E-01	2.926E+00	1.663E+01	1.680E+01	1.598E+01	1.316E+01	1.694E+00	1.724E-01	1.709E-02	2.845E-03	5.270E-04	6.333E-05
7	1.382E-02	8.787E-02	5.130E-01	2.930E+00	1.663E+01	1.681E+01	1.598E+01	1.350E+01	1.694E+00	1.832E-01	1.709E-02	3.287E-03	5.270E-04	8.783E-05
7.5	1.395E-02	8.787E-02	5.142E-01	2.930E+00	1.663E+01	1.681E+01	1.599E+01	1.350E+01	1.744E+00	1.832E-01	1.816E-02	3.287E-03	6.210E-04	8.783E-05
8	1.395E-02	8.817E-02	5.142E-01	2.932E+00	1.663E+01	1.682E+01	1.599E+01	1.368E+01	1.744E+00	1.892E-01	1.816E-02	3.544E-03	6.210E-04	1.035E-04
8.5	1.401E-02	8.817E-02	5.147E-01	2.932E+00	1.663E+01	1.682E+01	1.599E+01	1.368E+01	1.772E+00	1.892E-01	1.875E-02	3.544E-03	6.769E-04	1.035E-04
9	1.401E-02	8.829E-02	5.147E-01	2.933E+00	1.663E+01	1.682E+01	1.599E+01	1.378E+01	1.772E+00	1.925E-01	1.875E-02	3.689E-03	6.769E-04	1.128E-04
9.5	1.404E-02	8.829E-02	5.149E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.378E+01	1.787E+00	1.925E-01	1.908E-02	3.689E-03	7.089E-04	1.128E-04
10	1.404E-02	8.834E-02	5.149E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.384E+01	1.787E+00	1.943E-01	1.908E-02	3.770E-03	7.089E-04	1.182E-04
10.5	1.405E-02	8.834E-02	5.150E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.384E+01	1.795E+00	1.943E-01	1.925E-02	3.770E-03	7.268E-04	1.182E-04
11	1.405E-02	8.836E-02	5.150E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.387E+01	1.795E+00	1.952E-01	1.925E-02	3.814E-03	7.268E-04	1.211E-04
11.5	1.405E-02	8.836E-02	5.150E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.387E+01	1.799E+00	1.952E-01	1.935E-02	3.814E-03	7.367E-04	1.211E-04
12	1.405E-02	8.837E-02	5.150E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.388E+01	1.799E+00	1.958E-01	1.935E-02	3.839E-03	7.367E-04	1.228E-04
12.5	1.406E-02	8.837E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.388E+01	1.802E+00	1.958E-01	1.940E-02	3.839E-03	7.421E-04	1.228E-04
13	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.389E+01	1.802E+00	1.960E-01	1.940E-02	3.852E-03	7.421E-04	1.237E-04
13.5	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.389E+01	1.803E+00	1.960E-01	1.943E-02	3.852E-03	7.450E-04	1.237E-04
14	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.803E+00	1.962E-01	1.943E-02	3.859E-03	7.450E-04	1.242E-04
14.5	1.405E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.962E-01	1.944E-02	3.859E-03	7.466E-04	1.242E-04
15	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.944E-02	3.863E-03	7.466E-04	1.244E-04
15.5	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.945E-02	3.863E-03	7.474E-04	1.244E-04
16	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.945E-02	3.865E-03	7.474E-04	1.246E-04
16.5	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.945E-02	3.865E-03	7.479E-04	1.246E-04
17	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.945E-02	3.866E-03	7.479E-04	1.247E-04
17.5	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.946E-02	3.866E-03	7.482E-04	1.247E-04
18	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.804E+00	1.963E-01	1.946E-02	3.866E-03	7.482E-04	1.247E-04
18.5	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.805E+00	1.963E-01	1.946E-02	3.866E-03	7.483E-04	1.247E-04
19	1.406E-02	8.838E-02	5.151E-01	2.933E+00	1.663E+01	1.682E+01	1.600E+01	1.390E+01	1.805E+00	1.964E-01	1.946E-02	3.867E-03	7.483E-04	1.247E-04

twice. This happens because two rows represent a complete time cycle, based on the interaction between adjacent stages. Each row represents the average time that a phase stays in one stage, that is, the stage residence time. The calculation assumes that the stage residence time is the same for both phases. In actual practice, contactors usually deviate from this assumed condition; thus, the approach-to-steady-state values calculated by this procedure will b only an approximation to the actual situation. However, the steady-state values given by the calculation will be correct. The organic phase volume in each stage is 50 to 75 mL; thus, based on the organic phase flow rate of 150 mL/min, the stage residence time is 20 to 30 seconds. The aqueous phase volume in each stage is 25 to 50 mL; thus, based on the various aqueous flow rates of 50 to 450 mL/min (the higher flow rates are associated with the higher stage volumes of the aqueous phase), the stage residence time is 7 to 30 seconds. Thus, each row of calculated results shown in Tables A-6 and A-7 represents a process time of 30 seconds or less, and the 38 rows shown represent a total process time of 19 minutes or less. A review of Tables A-6 and A-7 on this basis, shows that stage 14 is the last to reach steady-state conditions. Even this stage is within 99% of its steady-state americium concentration within 14 minutes. Based on these calculations, the total time for the demonstration run was set at 20 minutes, with the collection of the last samples to start 18 minutes into the run.

Because of evaporative losses of the CCl_4, the actual distribution coefficients during the demonstration run were not the expected values used in these calculations. Additional calculations were done to show that, with more appropriate values for the americium distribution coefficients in the demonstration run, the electronic worksheet closely predicts the observed concentration of americium in each effluent.

b. Measured Coefficients

After the demonstration run was completed, the americium distribution coefficients were measured for each stage at 25°C. Using these higher values for the Am distribution coefficient, the above calculations for the expected coefficients were repeated. Note in Table A-5 that the average value for the measured americium distribution coefficients in the extraction section, stages 1-5, is 30.7 (Case B), compared with 16.6 for the expected coefficients (Case A). A key result in the new calculation is the much higher americium concentration than that observed in the aqueous raffinate (DW). This is the result of the immediate recycle of the solvent in the calculations. As discussed in the body of the report and shown by the fairly constant values for the aqueous raffinate, essentially no americium was recycled with the solvent during the demonstration run.

To reflect the fact that almost no americium was recycled in the demonstration run, the worksheet was modified so that all solvent fed to the contactor had no americium in it. The results of this calculation are summarized at Case C in Table A-5. Note that the americium concentration in the DW effluent is now two orders of magnitude lower than it was in the recycle case (Case B). In fact, the americium concentration in the DW effluent is now lower by a factor of four than the observed concentration during the demonstration run. To address this problem, it is necessary to correct the values of the americium distribution coefficients, as is discussed in the main body of the report.

c. Corrected Coefficients

When the extraction/scrub sections of the contactor were analyzed, it was found that a small drop in the extraction efficiency from 100% to 97.26% would explain the observed difference in the calculated americium concentration in the DW effluent and the observed value. This lower extraction efficiency gives the effective distribution coefficients, shown as Case D in Table A-5, and the appropriate value for the americium concentration in the DW effluent. (Note also that the average value for the corrected americium distribution coefficients in the extraction section is 23.9.) As discussed in the main body of the report, these corrected or effective distribution coefficients include any deviations of extraction efficiency from 100% (as much as 2.74%), as well as americium distribution coefficients that are lower because of a CMPO concentration lower than 0.3M in the solvent or because of a temperature effect.

Further analysis is required to determine how much of the correction to the distribution coefficients for the extraction section is due to some loss in extraction efficiency and how much is due to the distribution coefficients actually being lower. This further analysis is possible by looking at the scrub and strip sections, stages 6-14, of Case D. Any deviation of the extraction efficiency from 100% in the scrub and strip sections would result in a higher americium concentration in the solvent effluent (FP) than that predicted by Case D. Lower americium distribution coefficients in these sections would result in a lower americium concentration in the FP effluent than that predicted by Case D. The measured americium concentration in FP is about six times lower than the value predicted by Case D; thus, it would appear that the controlling factor is a lower value for the americium distribution coefficients throughout the contactor. For the extraction section, the average corrected americium distribution coefficient is made 0.778 times that of the measured coefficient, to produce the required americium concentration in the DW raffinate.

In the scrub and strip sections, the correction factor is 0.735. When this factor is used, the worksheet calculation gives the americium concentration in the organic effluent (FP) observed at 18 minutes into the run. The results of this calculation, summarized as Case E in Table A-5, show the steady-state value for the americium in the FP effluent, which is slightly higher than the concentration observed at 18 minutes into the run. Because of the third-power dependence of the americium distribution coefficient on the CMPO concentration, this suggests that CMPO concentration is slightly lower than the 0.30M value seen in the stage liquid samples (taken after the test and used to measure the distribution coefficients). The CMPO concentration during the run was measured in FP effluent samples to be between 0.27 and 0.28M. This would make the ratio of the corrected americium distribution coefficients to the measured values lie between 0.729 and 0.813, which is just what was observed. Thus, the problem in analyzing the data seems to be due, in part, to a loss of CCl_4 from the solvent after the test. The solvent and the lighter aqueous phase, which covers the solvent and so minimizes evaporation, were not removed from the contactor stages until the day after the test. The samples of the effluent streams were sealed as soon as they were taken and bagged out of the glove box the day of the test. Thus, all the correction in the americium distribution coefficients seems to be due to the solvent concentration; the contactor stage efficiency was not measurably

different from 100%. Also, because the two phases stayed in the contactor overnight between the cold and hot runs, there might have been solvent losses to account for those seen on the following day. This would put the initial CMPO concentration in the solvent at about 0.25M, the actual initial value. Thus, based on this analysis, an overnight loss, not greater than the expected evaporative loss during the test, would appear to be the most likely explanation for the CCl_4 losses. Further tests to clarify this point are needed.

Detailed listings of the americium concentrations as a function of stage number and time for the aqueous and organic phases when the corrected americium distribution coefficients for all stages (Case E) are used are given in Tables A-8 and A-9, respectively. These listings show how, with the higher americium distribution coefficients in the strip sections of the contactor, the americium concentration in these stages approaches steady state more slowly than was the case when the expected americium distribution coefficients were used. As with Case A, the first 38 lines of data in Tables A-8 and A-9 correspond roughly to the first 19 minutes of the run. In addition, 20 lines, which correspond roughly to a 10-minute interval between 44 and 54 minutes into the run, are included to show that the americium concentrations calculated with the corrected distribution coefficients do approach a steady-state value, even in the strip sections. The calculations also show that, as observed in the stage liquid samples, the americium concentrations are high in the first stages of the first strip section. It is these high americium concentrations that caused the strip sections of the 14-stage contactor to take so long to reach steady-state conditions.

One final question remains. What would have happened to the americium concentration in the DW effluent had the demonstration run continued to operate with the same corrected americium distribution coefficients until complete solvent recycle with the americium had been established? This scenario was calculated with the worksheet and the results are summarized as Case F on Table A-5. If steady-state operation with complete solvent recycle had been realized, the americium concentration in the DW effluent would have been higher than in Case E, but the solidified DW waste still would have contained less than 10 nCi/g of TRU waste.

7. Preparation of Synthetic PFP Waste

Table A-10 shows the quantities of reagents used to prepare 20 L of the synthetic PFP waste solution used in the reported studies. The requisite amounts of uranium (3×10^{-6} M), plutonium (3×10^{-5} M), and americium (6×10^{-6} M) were added to the feed solution 18 hours before the hot run began. Distribution ratios of americium and plutonium were measured in batch experiments by spiking the synthetic PFP waste solution with tracer quantities of ^{241}Am and ^{239}Pu from nitric acid stock solutions.

8. Preparation of TRUEX-CCl_4 Process Solvent

The CMPO used in this study was obtained from M&T Chemicals, Inc., Rahway, NJ. Gas chromatographic analysis showed the material to be ~97% CMPO and to contain essentially the same level of contaminants as previously purchased samples of this compound [VANDEGRIFT-1984]. The crystalline solid had a slight yellowish color. Because the solid contained black specks, the CMPO was dissolved in CCl_4 and filtered before preparation of the TRUEX-CCl_4 solvent. The TBP and CCl_4 were industrial-grade chemicals.

Table A-8. Americium Concentration in the Aqueous Phase of the Contactor Stages for Case E

Approx. Time, min	Aqueous Phase Concentration (x_i) of Americium in Stage (i), 10^{-6} M						
	x_1	x_2	x_3	x_4	x_5	x_6	x_7
0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	5.553E-01	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	5.609E-02	5.553E-01	1.078E+00	0.000E+00
1.5	0.000E+00	0.000E+00	6.813E-03	5.609E-02	6.219E-01	1.078E+00	1.186E+00
2	0.000E+00	7.891E-04	6.813E-03	6.779E-02	6.219E-01	1.238E+00	1.186E+00
2.5	8.867E-05	7.891E-04	8.966E-03	6.779E-02	6.350E-01	1.238E+00	1.362E+00
3	8.867E-05	1.120E-03	8.966E-03	7.069E-02	6.350E-01	1.268E+00	1.362E+00
3.5	1.258E-04	1.120E-03	9.624E-03	7.069E-02	6.381E-01	1.268E+00	1.395E+00
4	1.258E-04	1.230E-03	9.624E-03	7.149E-02	6.381E-01	1.275E+00	1.395E+00
4.5	1.382E-04	1.230E-03	9.823E-03	7.149E-02	6.390E-01	1.275E+00	1.402E+00
5	1.382E-04	1.264E-03	9.823E-03	7.172E-02	6.390E-01	1.277E+00	1.402E+00
5.5	1.420E-04	1.264E-03	9.883E-03	7.172E-02	6.392E-01	1.277E+00	1.404E+00
6	1.420E-04	1.275E-03	9.883E-03	7.179E-02	6.392E-01	1.277E+00	1.404E+00
6.5	1.432E-04	1.275E-03	9.901E-03	7.179E-02	6.393E-01	1.277E+00	1.405E+00
7	1.432E-04	1.278E-03	9.901E-03	7.181E-02	6.393E-01	1.277E+00	1.405E+00
7.5	1.436E-04	1.278E-03	9.906E-03	7.181E-02	6.393E-01	1.277E+00	1.405E+00
8	1.436E-04	1.279E-03	9.906E-03	7.181E-02	6.393E-01	1.277E+00	1.405E+00
8.5	1.437E-04	1.279E-03	9.908E-03	7.181E-02	6.393E-01	1.277E+00	1.405E+00
9	1.437E-04	1.279E-03	9.908E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
9.5	1.437E-04	1.279E-03	9.908E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
10	1.437E-04	1.279E-03	9.908E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
10.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
11	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
11.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
12	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
12.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
13	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
13.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
14	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
14.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
15	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
15.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
16	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
16.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
17	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
17.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
18	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
18.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
19	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
44.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
45	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
45.6	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
46	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
46.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
47	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
47.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
48	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
48.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
49	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
49.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
50	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
50.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
51	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
51.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
52	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
52.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
53	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
53.5	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00
54	1.437E-04	1.279E-03	9.909E-03	7.182E-02	6.393E-01	1.277E+00	1.405E+00

Table A-8. (contd)

Approx. Time, min	Aqueous Phase Concentration (x_i) of Americium in Stage (i), 10^{-6} M						
	x_8	x_9	x_{10}	x_{11}	x_{12}	x_{13}	x_{14}
0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	3.318E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2.5	3.318E+00	6.472E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3	5.453E+00	6.472E+00	2.689E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3.5	5.453E+00	1.242E+01	2.689E+00	4.859E-01	0.000E+00	0.000E+00	0.000E+00
4	7.056E+00	1.242E+01	5.560E+00	4.859E-01	1.472E-01	0.000E+00	0.000E+00
4.5	7.056E+00	1.745E+01	5.560E+00	1.004E+00	1.472E-01	4.905E-02	0.000E+00
5	8.354E+00	1.745E+01	8.075E+00	1.004E+00	3.380E-01	4.905E-02	1.393E-02
5.5	8.354E+00	2.165E+01	8.075E+00	1.459E+00	3.380E-01	1.228E-01	1.393E-02
6	9.426E+00	2.165E+01	1.019E+01	1.459E+00	5.263E-01	1.228E-01	3.488E-02
6.5	9.426E+00	2.515E+01	1.019E+01	1.841E+00	5.263E-01	2.009E-01	3.488E-02
7	1.031E+01	2.515E+01	1.196E+01	1.841E+00	6.959E-01	2.009E-01	5.706E-02
7.5	1.031E+01	2.806E+01	1.196E+01	2.161E+00	6.959E-01	2.736E-01	5.706E-02
8	1.105E+01	2.806E+01	1.343E+01	2.161E+00	8.425E-01	2.736E-01	7.771E-02
8.5	1.105E+01	3.047E+01	1.343E+01	2.426E+00	8.425E-01	3.376E-01	7.771E-02
9	1.167E+01	3.047E+01	1.465E+01	2.426E+00	9.669E-01	3.376E-01	9.587E-02
9.5	1.167E+01	3.248E+01	1.465E+01	2.647E+00	9.669E-01	3.923E-01	9.587E-02
10	1.217E+01	3.248E+01	1.566E+01	2.647E+00	1.071E+00	3.923E-01	1.114E-01
10.5	1.217E+01	3.414E+01	1.566E+01	2.830E+00	1.071E+00	4.385E-01	1.114E-01
11	1.260E+01	3.414E+01	1.651E+01	2.830E+00	1.158E+00	4.385E-01	1.245E-01
11.5	1.260E+01	3.553E+01	1.651E+01	2.982E+00	1.158E+00	4.771E-01	1.245E-01
12	1.295E+01	3.553E+01	1.721E+01	2.982E+00	1.231E+00	4.771E-01	1.355E-01
12.5	1.295E+01	3.668E+01	1.721E+01	3.108E+00	1.231E+00	5.093E-01	1.355E-01
13	1.324E+01	3.668E+01	1.779E+01	3.108E+00	1.292E+00	5.093E-01	1.447E-01
13.5	1.324E+01	3.763E+01	1.779E+01	3.213E+00	1.292E+00	5.362E-01	1.447E-01
14	1.348E+01	3.763E+01	1.827E+01	3.213E+00	1.342E+00	5.362E-01	1.523E-01
14.5	1.348E+01	3.842E+01	1.827E+01	3.301E+00	1.342E+00	5.585E-01	1.523E-01
15	1.368E+01	3.842E+01	1.867E+01	3.301E+00	1.384E+00	5.585E-01	1.586E-01
15.5	1.368E+01	3.908E+01	1.867E+01	3.373E+00	1.384E+00	5.770E-01	1.586E-01
16	1.385E+01	3.908E+01	1.900E+01	3.373E+00	1.418E+00	5.770E-01	1.639E-01
16.5	1.385E+01	3.963E+01	1.900E+01	3.433E+00	1.418E+00	5.924E-01	1.639E-01
17	1.399E+01	3.963E+01	1.928E+01	3.433E+00	1.447E+00	5.924E-01	1.683E-01
17.5	1.399E+01	4.008E+01	1.928E+01	3.483E+00	1.447E+00	6.052E-01	1.683E-01
18	1.411E+01	4.008E+01	1.951E+01	3.483E+00	1.471E+00	6.052E-01	1.719E-01
18.5	1.411E+01	4.046E+01	1.951E+01	3.525E+00	1.471E+00	6.159E-01	1.719E-01
19	1.420E+01	4.046E+01	1.970E+01	3.525E+00	1.491E+00	6.159E-01	1.749E-01
44.5	1.467E+01	4.229E+01	2.062E+01	3.726E+00	1.587E+00	6.675E-01	1.895E-01
45	1.467E+01	4.229E+01	2.063E+01	3.726E+00	1.587E+00	6.675E-01	1.896E-01
45.5	1.467E+01	4.230E+01	2.063E+01	3.726E+00	1.587E+00	6.676E-01	1.896E-01
46	1.467E+01	4.230E+01	2.063E+01	3.726E+00	1.588E+00	6.676E-01	1.896E-01
46.5	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.677E-01	1.896E-01
47	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.677E-01	1.896E-01
47.5	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.677E-01	1.896E-01
48	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.677E-01	1.896E-01
48.5	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.678E-01	1.896E-01
49	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.678E-01	1.897E-01
49.5	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.678E-01	1.897E-01
50	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.678E-01	1.897E-01
50.5	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.679E-01	1.897E-01
51	1.467E+01	4.230E+01	2.063E+01	3.727E+00	1.588E+00	6.679E-01	1.897E-01
51.5	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01
52	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01
52.5	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01
53	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01
53.5	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01
54	1.467E+01	4.231E+01	2.063E+01	3.728E+00	1.588E+00	6.679E-01	1.897E-01

Table A-9. Americium Concentration in the Organic Phase of the Contactor Stages for Case E

Approx. Time, min	Organic Phase Concentration (y_i) of Americium in Stage (i), 10^{-6} M						
	y_1	y_2	y_3	y_4	y_5	y_6	y_7
0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	1.383E+01	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	1.498E+00	1.383E+01	1.347E+01	0.000E+00
1.5	0.000E+00	0.000E+00	1.478E-01	1.498E+00	1.548E+01	1.347E+01	1.307E+01
2	0.000E+00	1.807E-02	1.478E-01	1.810E+00	1.548E+01	1.547E+01	1.307E+01
2.5	2.101E-03	1.807E-02	1.946E-01	1.810E+00	1.581E+01	1.547E+01	1.501E+01
3	2.101E-03	2.564E-02	1.946E-01	1.887E+00	1.581E+01	1.584E+01	1.501E+01
3.5	2.981E-03	2.564E-02	2.088E-01	1.887E+00	1.589E+01	1.584E+01	1.538E+01
4	2.981E-03	2.815E-02	2.088E-01	1.909E+00	1.589E+01	1.593E+01	1.538E+01
4.5	3.275E-03	2.816E-02	2.132E-01	1.909E+00	1.591E+01	1.593E+01	1.546E+01
5	3.275E-03	2.895E-02	2.132E-01	1.915E+00	1.591E+01	1.595E+01	1.546E+01
5.5	3.367E-03	2.895E-02	2.145E-01	1.915E+00	1.592E+01	1.595E+01	1.548E+01
6	3.367E-03	2.919E-02	2.145E-01	1.917E+00	1.592E+01	1.596E+01	1.548E+01
6.5	3.394E-03	2.919E-02	2.148E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
7	3.394E-03	2.926E-02	2.148E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
7.5	3.403E-03	2.926E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
8	3.403E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
8.5	3.405E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
9	3.405E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
9.5	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
10	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
10.5	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
11	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
11.5	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
12	3.406E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
12.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
13	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
13.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
14	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
14.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
15	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
15.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
16	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
16.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
17	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
17.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
18	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
18.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
19	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
44.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
45	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
45.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
46	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
46.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
47	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
47.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
48	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
48.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
49	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
49.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
50	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
50.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
51	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
51.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
52	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
52.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
53	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
53.5	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01
54	3.407E-03	2.929E-02	2.150E-01	1.917E+00	1.592E+01	1.596E+01	1.549E+01

Table A-9. (contd)

Approx. Time, min	Organic Phase Concentration (y_i) of Americium in Stage (i), 10^{-6}M						
	y_8	y_9	y_{10}	y_{11}	y_{12}	y_{13}	y_{14}
0	0	0	0	0	0	0	0
0.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1.5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2	9.755E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
2.5	9.755E+00	3.282E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3	1.603E+01	3.282E+00	5.930E-01	0.000E+00	0.000E+00	0.000E+00	0.000E+00
3.5	1.603E+01	6.300E+00	5.930E-01	1.071E-01	0.000E+00	0.000E+00	0.000E+00
4	2.074E+01	6.300E+00	1.226E+00	1.071E-01	3.354E-02	0.000E+00	0.000E+00
4.5	2.074E+01	8.851E+00	1.226E+00	2.215E-01	3.354E-02	9.013E-03	0.000E+00
5	2.456E+01	8.851E+00	1.781E+00	2.215E-01	7.701E-02	9.013E-03	2.048E-03
5.5	2.456E+01	1.098E+01	1.781E+00	3.217E-01	7.701E-02	2.257E-02	2.048E-03
6	2.771E+01	1.098E+01	2.248E+00	3.217E-01	1.199E-01	2.257E-02	5.127E-03
6.5	2.771E+01	1.275E+01	2.248E+00	4.061E-01	1.199E-01	3.692E-02	5.127E-03
7	3.033E+01	1.275E+01	2.637E+00	4.061E-01	1.586E-01	3.692E-02	8.387E-03
7.5	3.033E+01	1.423E+01	2.637E+00	4.764E-01	1.586E-01	5.028E-02	8.387E-03
[illegible]	3.250E+01	1.423E+01	2.961E+00	4.764E-01	1.920E-01	5.028E-02	1.142E-02
8.5	3.250E+01	1.545E+01	2.961E+00	5.349E-01	1.920E-01	6.203E-02	1.142E-02
9	3.430E+01	1.545E+01	3.230E+00	5.349E-01	2.203E-01	6.203E-02	1.409E-02
9.5	3.430E+01	1.647E+01	3.230E+00	5.836E-01	2.203E-01	7.208E-02	1.409E-02
10	3.579E+01	1.647E+01	3.454E+00	5.836E-01	2.441E-01	7.208E-02	1.638E-02
10.5	3.579E+01	1.732E+01	3.454E+00	6.240E-01	2.441E-01	8.057E-02	1.638E-02
11	3.704E+01	1.732E+01	3.639E+00	6.240E-01	2.640E-01	8.057E-02	1.830E-02
11.5	3.704E+01	1.802E+01	3.639E+00	6.575E-01	2.640E-01	8.767E-02	1.830E-02
12	3.807E+01	1.802E+01	3.794E+00	6.575E-01	2.805E-01	8.767E-02	1.992E-02
12.5	3.807E+01	1.860E+01	3.794E+00	6.854E-01	2.805E-01	9.359E-02	1.992E-02
13	3.893E+01	1.860E+01	3.922E+00	6.854E-01	2.943E-01	9.359E-02	2.126E-02
13.5	3.893E+01	1.908E+01	3.922E+00	7.085E-01	2.943E-01	9.852E-02	2.126E-02
14	3.964E+01	1.908E+01	4.028E+00	7.085E-01	3.057E-01	9.852E-02	2.238E-02
14.5	3.964E+01	1.949E+01	4.028E+00	7.278E-01	3.057E-01	1.026E-01	2.238E-02
15	4.023E+01	1.949E+01	4.117E+00	7.278E-01	3.152E-01	1.026E-01	2.332E-02
15.5	4.023E+01	1.982E+01	4.117E+00	7.437E-01	3.152E-01	1.060E-01	2.332E-02
16	4.072E+01	1.982E+01	4.190E+00	7.437E-01	3.231E-01	1.060E-01	2.409E-02
16.5	4.072E+01	2.010E+01	4.190E+00	7.570E-01	3.231E-01	1.089E-01	2.409E-02
17	4.113E+01	2.010E+01	4.251E+00	7.570E-01	3.297E-01	1.089E-01	2.473E-02
17.5	4.113E+01	2.033E+01	4.251E+00	7.680E-01	3.297E-01	1.112E-01	2.473E-02
18	4.147E+01	2.033E+01	4.302E+00	7.680E-01	3.352E-01	1.112E-01	2.527E-02
18.5	4.147E+01	2.052E+01	4.302E+00	7.772E-01	3.352E-01	1.132E-01	2.527E-02
19	4.175E+01	2.052E+01	4.344E+00	7.772E-01	3.397E-01	1.132E-01	2.571E-02
44.5	4.312E+01	2.145E+01	4.548E+00	8.216E-01	3.616E-01	1.227E-01	2.786E-02
45	4.312E+01	2.145E+01	4.548E+00	8.216E-01	3.617E-01	1.227E-01	2.787E-02
45.5	4.312E+01	2.145E+01	4.548E+00	8.217E-01	3.617E-01	1.227E-01	2.787E-02
46	4.312E+01	2.145E+01	4.548E+00	8.217E-01	3.617E-01	1.227E-01	2.787E-02
46.5	4.312E+01	2.145E+01	4.548E+00	8.217E-01	3.617E-01	1.227E-01	2.787E-02
47	4.312E+01	2.145E+01	4.549E+00	8.217E-01	3.617E-01	1.227E-01	2.787E-02
47.5	4.312E+01	2.145E+01	4.549E+00	8.218E-01	3.617E-01	1.227E-01	2.787E-02
48	4.312E+01	2.145E+01	4.549E+00	8.218E-01	3.618E-01	1.227E-01	2.788E-02
48.5	4.312E+01	2.145E+01	4.549E+00	8.218E-01	3.618E-01	1.227E-01	2.788E-02
49	4.313E+01	2.145E+01	4.549E+00	8.218E-01	3.618E-01	1.227E-01	2.788E-02
49.5	4.313E+01	2.145E+01	4.549E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
50	4.313E+01	2.145E+01	4.549E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
50.5	4.313E+01	2.145E+01	4.549E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
51	4.313E+01	2.145E+01	4.549E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
51.5	4.313E+01	2.146E+01	4.549E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
52	4.313E+01	2.146E+01	4.550E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
52.5	4.313E+01	2.146E+01	4.550E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
53	4.313E+01	2.146E+01	4.550E+00	8.219E-01	3.618E-01	1.227E-01	2.788E-02
53.5	4.313E+01	2.146E+01	4.550E+00	8.220E-01	3.618E-01	1.227E-01	2.788E-02
54	4.313E+01	2.146E+01	4.550E+00	8.220E-01	3.619E-01	1.227E-01	2.786E-02

Table A-10. Preparation of Simulated Nonradioactive PFP Waste Solution

Constituent	Form	Formula Weight, g	Concentration M	Concentration g/20 L	$[NO_3^-]$ Added, M	Other Constituent Added (Concentration, M)	Amount Added, mg/L	Measured Results,[a] mg/L
HNO_3	Concentrated Solution	15.6M	1.5×10^0 (1.41 added)	1.808[b]	1.41	$H^+(1.41)$	-	-
Be	Be	9.01	7×10^{-5}	0.0126	-	$H^+(1.4\times10^{-4})$	6.45×10^{-1}	7×10^{-1}
Na	Na_2SO_4	142.0	1.34×10^{-2}	19.03	-	$SO_4^{2-}(6.7\times10^{-3})$	-	-
	$NaNO_3$	85.0	2.66×10^{-2}	45.22	0.0266	-	-	-
			4.00×10^{-2}	-	-	-	9.20×10^2	9.3×10^2
Mg	$Mg(NO_3)_2\cdot6H_2O$	256.41	6×10^{-2}	307.69	0.12	-	1.46×10^3	1.54×10^3
Al	$Al(NO_3)_3\cdot9H_2O$	375.13	4.3×10^{-1}	3226	1.29	-	1.16×10^4	1.20×10^4
K	KNO_3	101.1	3×10^{-3}	6.07	0.003	-	1.14×10^2	1.4×10^0[c]
Ca	$Ca(NO_3)_2\cdot2H_2O$	236.16	6×10^{-2}	283.39	0.12	-	2.40×10^3	2.3×10^3
Cr	$Cr(NO_3)_3\cdot9H_2O$	400.18	4×10^{-4}	3.20	0.0012	-	2.08×10^1	2.0×10^1
Mn	$MnSO_4\cdot H_2O$	169.02	3×10^{-3}	10.14	-	$SO_4^{2-}(3\times10^{-3})$	1.65×10^2	1.75×10^1
Fe	$Fe(NO_3)_3\cdot9H_2O$	404.0	3×10^{-2}	242.46	0.09	-	1.69×10^3	1.71×10^3
Ni	$Ni(NO_3)_2\cdot6H_2O$	290.82	4×10^{-4}	2.33	0.0008	-	2.35×10^1	2.1×10^1
Cu	$CuSO_4\cdot5H_2O$	249.68	3×10^{-4}	1.50	-	$SO_4^{2-}(6\times10^{-4})$	1.50×10^1	2.0×10^1
Zn	$Zn(NO_3)_2\cdot6H_2O$	297.5	6×10^{-4}	3.57	0.0012	-	3.92×10^1	4.0×10^1
Pb	$Pb(NO_3)_2$	331.23	5×10^{-4}	3.31	0.001	-	1.04×10^2	9.6×10^1
F^-	Conc. HF soln	28.3M	9×10^{-2}	63.6[d]	-	$H^+(0.09)$	-	-
SO_4^{2-}	Na_2SO_4 $CuSO_4\cdot5H_2O$ $Mn SO_4\cdot H_2O$	-	1×10^{-2}	-	-	Listed above as the metal-ion salts	-	-
NO_3^-	-	-	3.06×10^0	-	-	Listed above as the metal-ion salts	-	-

[a]Inductively coupled plasma/atomic emission spectroscopic analyses were performed with an error of 3 to 10%.
[b]Liters per 20 liters.
[c]Estimated error is greater than 10%.
[d]Milliliters per 20 liters.

REFERENCES FOR APPENDIX A

GOANKAR

A. G. Goankar and R. D. Neuman, The Effect of Wettability of Wilhelmy Plate and Du Noiiy Ring on Interfacial Tension Measurements in Solvent Extraction Systems, J. Colloid Interface Sci. 98, 112 (1984).

HORWITZ-1985A

E. P. Horwitz, K. A. Martin, H. Diamond, and R. Chiarizia, unpublished data, Chemistry Division, Argonne National Laboratory (1985).

HORWITZ-1985B

E. P. Horwitz and W. W. Schulz, Solvent Extraction and Recovery of the Transuranic Elements from Waste Solutions Using the TRUEX Process, Proceedings of the International Meeting on Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle, AERE Harwell, United Kingdom, September 3-6, 1985, Ellis Harwood Limited, Market Cross House, West Sussex, England (1985).

LEONARD

R. A. Leonard, Use of Electronic Worksheets for Calculation of Stagewise Solvent Extraction Processes, accepted for presentation at the Fourth Symposium on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1985.

VANDEGRIFT

G. F. Vandegrift, R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. J. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, Transuranic Decontamination of Nitric Acid Solutions by the TRUEX Solvent Extraction Process - Preliminary Development Studies, Argonne National Laboratory, ANL-84-45 (1984).

WEAST

R. C. Weast (ed.), CRC Handbook of Chemistry and Physics, 65th ed., CRC Press, Inc., Boca Raton, FL (1984).

ZUIDEMA

H. H. Zuidema and G. W. Waters, Ring Method for the Determination of Interfacial Tension, Ind. Eng. Chem. 13, 312 (1941).

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