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**Idaho
National
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Laboratory**

**Elimination of Phosphate and
Zirconium in the High-Activity Fraction
Resulting From TRUEX Partitioning of
ICPP Zirconium Calcines**

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Lockheed-Martin Idaho Technologies Company

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ABSTRACT

Laboratory testing was undertaken with the aim of developing a TRUEX flowsheet that would efficiently remove actinides from solutions of dissolved zirconium calcine and minimize the glass volume produced from the ensuing high-activity fraction. A TRUEX flowsheet is recommended for testing in the 2-cm centrifugal contactor pilot-plant based on the results from this testing. These laboratory tests show that zirconium recovery in the high activity fraction is minimized by scrubbing with an optimized NH_4F concentration of 0.2 M. This NH_4F concentration in the scrub allowed the HEDPA strip concentration to be reduced from 0.04 M to 0.004 M because HEDPA is not consumed by zirconium. Complete TRU stripping was also achieved in these laboratory tests with 0.004 M HEDPA. Data from the small-scale laboratory batch contact tests were used in the Generic TRUEX Model (GTM) to evaluate the proposed flowsheet under counter-current conditions. GTM results indicate the raffinate will meet the Class A non-TRU limit of $< 10 \text{ nCi/g}$ in six extraction stages ($\text{O/A} = 1$), and quantitative actinide recovery will be achieved with the 0.004 M HEDPA in six strip stages ($\text{O/A} = 1$). Only 6.6 % of the initial zirconium concentration is anticipated to be recovered with the actinides, indicating the four scrub stages ($\text{O/A} = 3$) efficiently removes zirconium from the TRUEX solvent. In addition to recommending an improved TRUEX flowsheet for testing in the 2-cm centrifugal contactor pilot-plant, this work has shown that small reductions in zirconium extraction drastically improves flowsheet performance. These small changes in zirconium extraction can be accomplished by modifying the calcine dissolution parameters. Therefore, further calcine dissolution testing followed by TRUEX testing with the resulting feed solutions is also recommended.

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INTRODUCTION

Actinide separation processes are being evaluated at the Idaho Chemical Processing Plant (ICPP) to minimize the volume of high-level radioactive waste requiring disposal in a geological repository. The TRansUranic Extraction (TRUEX) process, developed by Horwitz and Schulz [1-2], is one process being evaluated for treating ICPP wastes.

Approximately 3,800 m³ of high-level waste (HLW) calcine is currently stored at the ICPP [3]. ICPP calcine can generally be classified as either aluminum or zirconium type calcine which was generated from fuel reprocessing raffinates in a fluidized bed operated at 500°C. Zirconium type calcine constitutes approximately 3,000 m³ of the total ICPP inventory. The zirconium calcine primarily contains non-radioactive metal oxides (Al₂O₃, ZrO₂, and CaO) and CaF₂ [4]. Calcium was added to zirconium raffinates prior to calcination to inhibit fluoride volatility and subsequent equipment corrosion. Transuranic (TRU) and fission product concentrations in the calcine is less than 1 wt% [5]; therefore, a significant high-level waste volume reduction may be achieved if the radioactive constituents in the calcine can be partitioned from the non-radioactive components.

Direct vitrification of the current 3000 m³ of zirconium calcine would generate approximately 6200 m³ of high-level waste glass [6]. Separating the TRUs and fission products from this calcine using the initial TRUEX flowsheet [6] would result in an estimated 3000 m³ of glass. The primary contributors to this volume being zirconium and phosphate. Zirconium has historically been problematic throughout the nuclear industry, especially in actinide solvent extraction processes. The undesired extraction of zirconium by either the active extractant, diluent, and/or phase modifier (all components of the solvent) can result in 1) suppressed actinide decontamination factors, 2) a second organic phase, 3) interfacial crud, 4) increased high-level waste volumes, and 5) increased operation costs. The extraction of zirconium and use of reagents containing phosphates in actinide separation processes are problematic because these two constituents will increase the high-level waste glass volume requiring disposal. Therefore, the glass volume could be reduced even further if the TRUEX flowsheet could be modified so that both zirconium and phosphate concentrations in the high activity fraction are reduced or eliminated.

The purpose of this document is to report the results of investigating modifications to the TRUEX flowsheet to process ICPP dissolved zirconium calcine. The objective of this work was to reduce or eliminate the amount of phosphate and zirconium in the product strip stream. Options examined for accomplishing this objective were adjustment of calcine dissolution parameters, adjustment of solution resulting from calcine dissolution, alternative scrub stream compositions, and alternative strip stream chemicals. Extensive laboratory testing was undertaken to reduce or eliminate zirconium and phosphate concentrations in the strip product because of the impact these constituents may have on the high-level waste glass volume. The emphasis of this laboratory work was aimed at developing a TRU separations process that would result in a high activity fraction containing minimal amounts of inert material.

BACKGROUND

The TRUEX process was developed to reduce the TRU concentration in waste solutions having a wide range of nitric acid, salt, and fission product concentrations [1]. The typical TRUEX solvent contains 0.1-0.3 M CMPO, 1.4 M tributyl phosphate (TBP) in a normal paraffinic hydrocarbon (NPH). The generic TRUEX process is shown in Figure 1. The extraction section was initially designed to remove the TRUs to < 100 nCi/g in the waste solutions. Practically all the TRUs are extracted into the solvent without any oxidation state adjustments. Rare earths and some Tc will also extract. Oxalic acid was used to scrub Zr and Mo from the solvent and the stripping sequence was established to selectively partition the TRU elements. Dilute nitric acid is used to strip Am from Pu and Np. The rare earth elements and Tc will also strip with americium. Dilute HF and nitric acid is then used to strip Pu and Np. Solvent clean-up is performed with a macroporous anion exchange material to remove CMPO impurities (dialkylphosphinic acid and alkyl(phenyl)phosphinic acid). A Na_2CO_3 PUREX type clean-up process can be employed once these impurities are removed.

Figure 1. Generic TRUEX flowsheet.

The large concentration of zirconium relative to that of the actinides in solutions of dissolved zirconium calcine results in copious amounts of zirconium extracting into the solvent

(even with small extraction distribution coefficients, D_{Zr}) due to the law of mass action. Zirconium extraction has traditionally been inhibited by the use of masking agents which form inextractable complexes with zirconium. The use of zirconium masking agents in processing ICPP dissolved zirconium calcines has been shown to have deleterious effects due to the large amount of calcium also present in these solutions. Calcium forms undesirable precipitates with these masking agents, even when micro-amounts of the masking reagent are added.

Small-scale batch contacts were performed in the laboratory to formulate a baseline flowsheet for treating solutions of dissolved zirconium calcine, made from Run 74 pilot plant calcine [7]. Large extraction distribution coefficients for the actinides were obtained in these batch contacts; however, significant zirconium extraction was also observed. Dilute ammonium fluoride in medium strength nitric acid was found to selectively scrub zirconium while minimizing actinide recycle. Phosphate in the TRUEX high-activity fraction (strip stream) comes from the use of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) as a gross actinide stripping reagent in the strip solution. Phosphate tends to inhibit homogeneous glass forms; therefore, most glasses can tolerate only small phosphate waste loadings. Dilute HEDPA was used as a gross actinide stripping reagent because simultaneous recovery of the actinides is desirable for flowsheet simplification and high-activity waste fraction aqueous volume reduction. Distribution data from these tests are shown in Table 1.

Table 1. Batch contact distribution data for baseline flowsheet development.

Contact	D_{Zr}	D_U	D_{Am}	D_{Pu}
E1	0.749	329	4.70	124
E2	0.679	390	2.80	123
E3	0.674	404	2.23	122
0.1 M NH_4F in 1.0 M HNO_3 Scrub				
Sc1	0.656	277	10.2	67.6
Sc2	0.131	319	19.6	69.6
Sc3	<<1	132	17.8	15.4
0.04 M HEDPA in 0.04 M HNO_3 Strip				
St1	NA	0.0425	0.119	0.064
St2	NA	0.0097	<<1	0.027
St3	NA	<<0.1	NA	0.434

NA = No activity detected in either phase (detection limit ~ 0.1 dps/mL)

Zirconium distribution coefficients in the scrub contacts were less than 1.0 while those for the actinides were greater than 1.0, indicating zirconium will be efficiently scrubbed from the solvent with a minimal amount of actinide recycle. However, the extraction of zirconium (and perhaps nitric acid) suppressed americium extraction. The third extraction contact D_{Am} of 2.23 was much lower than expected. As a comparison, a D_{Am} of greater than 20 was achieved during batch contacts with actual ICPP sodium-bearing waste (SBW) [7,8]. The nitrate concentrations between dissolved calcine and SBW are practically the same, 5.17 M NO_3^- for the SBW as

opposed to 6.0 M NO_3^- in dissolved zirconium calcine; therefore, the americium extraction distribution coefficient was expected to be similar between these two wastes, rather than differing by an order of magnitude. The acid concentration, as HNO_3 , in the dissolved calcine is approximately twice that of the SBW, which may have caused excessive acid extraction, as well as assisted zirconium extraction; thereby reducing the extraction of americium by consuming most of the CMPO.

Attempts were made to reduce the HEDPA concentration early in the development process. Batch contacts were performed with dissolved calcine spiked with either Zr-95, Am-241, U-233, Pu-238, or Tc-99. Ammonium fluoride ($0.1 \text{ M NH}_4\text{F}$ in 1.0 M HNO_3) was used to scrub zirconium but 0.001 M HEDPA was used to strip the actinides. Extraction and scrub distribution coefficients obtained from these contacts closely compare to those shown in Table 1, and will not be shown here. Strip distribution coefficients obtained for Zr, Am, U, Pu, and Tc are shown in Table 2.

Table 2. Strip distribution coefficients obtained with 0.001 M HEDPA.

Contact	Zr	Am	U	Pu	Tc
St1	0.84	3.47	6.51	0.76	6.45
St2	1.00	0.15	0.25	0.17	11.2
St3	0.38	$6.77\text{E-}4$	0.01	0.05	6.56

Distribution coefficient data shown in Table 2 indicate 0.001 M HEDPA will efficiently remove Am, U, and Pu and therefore, may be used to recover the actinides from the TRUEX solvent. Data shown in Table 2 also suggest that the amount of zirconium reporting to the high activity fraction may be reduced by increasing the strip acid concentration to that of St2. $D_{\text{Zr}} \sim 1$ were obtained in St2 while actinide distribution coefficients were approximately 0.2.

A second flowsheet for treating ICPP dissolved zirconium calcine was proposed, based on the results shown in Tables 1 and 2. This flowsheet used $0.1 \text{ M NH}_4\text{F}$ in 1.0 M HNO_3 to scrub zirconium and used 0.001 M HEDPA to strip the actinides. This flowsheet, shown in Figure 2, was tested in the 5.5 cm centrifugal contactors. Data from the 5.5 cm centrifugal contactor test show that substantial zirconium recovery occurred in the strip product (approximately 34% of the zirconium) [9] and a precipitate also occurred in the strip product which was analytically determined to be zirconium phosphate. This detailed laboratory investigation regarding zirconium extraction and scrubbing, as well as, alternative HEDPA strip reagents was initiated as a result of this pilot plant test.

Laboratory testing focused on three options for preventing zirconium recovery with the actinides, all of which may have a direct impact on reducing or eliminating the HEDPA strip concentration. The first option for preventing Zr recovery with the actinides may be to change the calcine dissolution parameters. Reducing the nitrate feed concentration may be the best and

easiest change. Nitrate drives the extraction of zirconium and acid in accord with the following reactions:

Large amounts of CMPO, the active extractant in the TRUEX solvent, are consumed by the extraction of zirconium and acid. The extraction of both components may explain the small extraction distribution coefficients consistently obtained for americium. Decreasing the initial nitric acid concentration used to dissolve zirconium calcine may reduce the extraction of zirconium and nitric acid, thereby, increasing the "free" CMPO available for americium extraction.

Another benefit to reducing the initial HNO_3 concentration used to dissolve calcine may be zirconium polymerization. Zirconium tends to polymerize as the zirconium concentration increases and as the nitric acid concentration decreases. Polymerized zirconium species are poorly extracted by most solvents. The zirconium concentration in solutions of dissolved zirconium calcine can be increased by increasing the amount of calcine dissolved per unit volume of acid. Increasing the mass of calcine dissolved per unit volume of acid will also increase acid consumption, resulting in a final lower concentration of feed acid.

Figure 2. 5.5 cm centrifugal contactor test.

Care must be taken when changing the dissolution process to ensure copious amounts of undissolved solids do not remain which will require disposal to the high-activity fraction. Feed stability must not be compromised either. Optimizing the dissolution parameters around the extraction of americium and zirconium should be performed none-the-less.

The second option for preventing zirconium recovery with the actinides was to evaluate the effectiveness of various masking agents that would prevent zirconium extraction. The third option was to find a more efficient method of scrubbing zirconium which would also enable the use of dilute (0.001 M) HEDPA or an alternative strip reagent. Poor zirconium scrubbing observed in the 5.5-cm centrifugal contactor pilot-plant test (Figure 2) could be enhanced by increasing 1) scrub flow, 2) number of scrub stages, or 3) the ammonium fluoride concentration.

EXPERIMENTAL

Batch Contact Test Methodology

Equal volume batch contacts were performed in the laboratory using both non-radioactive, and traced, dissolved zirconium calcine feed simulants. The feed simulant was prepared from calcine generated in the 30-cm calciner pilot-plant and is designated as Run 74 calcine. The composition of the Run 74 calcine feed is shown in Table 3 [10]. Weight percent concentrations, shown in Table 3, were determined from direct analysis of the calcine, while molar concentrations were determined from direct analysis of the dissolved calcine solution. This calcine feed was generated from the baseline dissolution parameters of: 1) an initial HNO_3 concentration equal to 5 M, 2) 1 gram of calcine dissolved per 10 mLs acid, 3) a 30 minute dissolution time, and 4) a dissolution temperature of 90°C. Radioactive tracers of the actinides or zirconium were spiked into the Run 74 feed at least 48 hours before the feed was to be used. The feed was also reduced with hydrogen peroxide, 100 μ l of 30% H_2O_2 per 30 mLs of Run 74 feed, 24 hours before use in order to reduce the extractable Cr^{+6} to the less-extractable Cr^{+3} . Early TRUEX work performed with unreduced dissolved Run 74 calcine showed Cr^{+6} extraction to cause third phase formation, and severe interfacial crud. The results/impacts of Cr^{+6} extraction are discussed later in this document.

The TRUEX solvent was pre-equilibrated prior to use by contacting a given volume of the solvent three times with non-spiked reduced Run 74 calcine or with 3.4 M HNO_3 . Nitric acid was used to pre-equilibrate the solvent if zirconium was being evaluated in order to prevent the equilibration of zirconium with the solvent. Scrub solution was added to the feed in some cases to simulate a counter-current feed-scrub mixture. This practice was not generally performed; therefore, it will be clearly stated when scrub was added to the feed.

Cross-current type flowsheets, like the one shown in Figure 3, were performed in the laboratory to evaluate and optimize the scrub and strip solutions. Three extraction, scrub, and strip contacts were performed. Wash contacts with 0.25 M Na_2CO_3 were occasionally performed to ensure the absence of interfacial crud and precipitates.

Distribution coefficients were determined directly by radiochemically analyzing both phases. Neptunium-239, Am-241 and, Zr-95 analyses were performed by gamma spectroscopy, while Pu-239 analysis were performed by Liquid Scintillation Counting. All radiochemical analyses were done by the ICPP Radiochemistry Group. The distribution coefficients were determined simply by:

$$D_x = \frac{\text{Activity } X_{\text{Org.}}}{\text{Activity } X_{\text{Aq.}}}$$

Table 3. Dissolved Run 74 feed composition.

Element	wt % in calcine before dissolution ¹	Feed concentration <i>M</i>
Al	11.2	4.2E-1
B	1.1	6.8E-2
Ca	25.0	6.5E-1
Ce	0.1	4.0E-4
Cr	0.4	5.7E-3
Cs	0.5	4.7E-3
Fe	0.1	1.3E-2
K	<0.1	6.0E-4
Mo	ND	1.8E-4
Na	0.4	8.5E-3
Ni	0.1	1.7E-3
Pb	<0.1	<1.9E-6
Sr	0.7	8.1E-3
Zr	16.6	2.1E-1
Cl ⁻	<0.2	<8.8E-2
F ⁻	17.4	8.9E-1
H ⁺	NA	3.5
NO ₃ ⁻	<0.1	6.0
PO ₄ ⁻³	ND	ND
SO ₄ ⁻²	5.4	5.0E-2
density g/mL	NA	1.2

NA = Not Applicable

ND = Not Determined

¹ = Remainder of mass balance is oxygen

Figure 3. Batch contact cross-current experimental flowsheet.

Material balance calculations were determined from gamma spectroscopy results and were typically $100 \pm 10\%$.

Methodology Used to Reduce/Eliminate Zr in Strip Stream

Adjusting Calcine Dissolution Parameters. The calcine dissolution experiments were performed to determine the effect of zirconium and nitric acid concentrations on the extraction distribution coefficients of americium and zirconium. Zirconium and americium extraction distribution coefficients were also evaluated as a function of feed acid and zirconium concentrations, which were varied by changing some of the calcine dissolution parameters. Experiments were performed by varying either the initial acid concentration and dissolving 1 gram of calcine per 10 mLs of acid or by varying the calcine weight dissolved in 10 mLs of 5 M HNO_3 . The dissolution apparatus shown in Figure 4 was used for these experiments.

Five grams of calcine, made-up from 4 grams calcine product plus 1 gram calcine fines, were dissolved in different nitric acid concentrations. Five calcine feeds were prepared using a calcine weight to acid volume ratio of 1 gram calcine per 10 mLs acid. A sixth feed was prepared by dissolving 2.5 grams of calcine in 50 mLs of 5.0 M HNO_3 (0.5 grams calcine per 10 mLs of acid). All calcines (5.0 grams total calcine weight) were dissolved in a 50 mLs (total volume) of hot acid for thirty minutes using the dissolution apparatus shown in Figure 4. The feeds were filtered through a 0.45 micron filter before contact with the TRUEX solvent. No undissolved solids (UDS) measurements were obtained from any of these dissolutions. The initial nitric acid concentrations and equilibrium feed compositions are shown in Table 4.

Table 4. Feed compositions from changing initial HNO_3 concentration.

Feed	Initial HNO_3	H^+ M	Zr M	Al M	Ca M	F M	F/(Al+Zr)
#1	2.5 M	0.949	0.099	0.353	0.554	0.911	2.02
#2	3.0 M	1.450	0.121	0.353	0.585	0.955	2.01
#3	3.5 M	1.773	0.138	0.365	0.581	0.966	1.92
#4	4.0 M	2.193	0.149	0.380	0.591	0.963	1.82
#5	4.5 M	2.815	0.173	0.407	0.633	1.025	1.77
#6 ^a	5.0 M	4.011	0.096	0.194	0.310	0.524	1.80

a = 2.5 grams of calcine in 50 mLs of acid

The TRUEX solvent was pre-equilibrated with nitric acid having the same concentration as the feed to be contacted with the solvent. This ensured zirconium and americium distribution coefficients would be obtained under fairly constant nitric acid concentrations. Each TRUEX solvent was contacted three times with the feed.

Figure 4. Calcine dissolution set-up.

Dissolving various weights of Run 74 zirconium calcine in 5.0 M HNO₃ (each > 1.0 g/10 mL) allows for increasing the zirconium concentration while also decreasing the H⁺ concentration after dissolution. Total calcine weights (4 parts product to 1 part fines) of 1.25 g, 1.50 g, 1.75 g, 2.00 g, 2.50 g, and 3.0 g were dissolved per 10 mLs of 5.0 M HNO₃. Each experiment was performed with 100 mLs of acid and the appropriate calcine weight. The solutions were well mixed during dissolution and heated to >90 °C for 30 minutes. The acid was brought to temperature before calcine addition. Each solution was filtered through a 0.45 micron filter after cooling to remove the undissolved solids. Undissolved solids were measured after some tests, but these were typically not measured since the extent of calcine dissolution was not a part of this work. The HNO₃ concentration after dissolution may be similar to those obtained by varying the initial acid concentration, but the total nitrate concentration in these tests will be constant. Therefore, increasing the calcine mass dissolved in a constant volume and concentration of nitric acid, has the effect of consuming more HNO₃, which will result in a lower equilibrium H⁺ concentration, but these solutions maintain a high NO₃⁻ concentration necessary for americium extraction.

A total of 11 feeds were prepared using the dissolution system shown in Figure 4. Feeds #1-#7 were prepared in 100 mLs of 5 M HNO₃ and a 30 minute dissolution time. Feeds #8 and #9 were prepared using ~ 4.0 M HNO₃ and dissolution times of 30 minutes and 5 hours, while feeds #10 and #11 used ~ 3.0 M HNO₃ and dissolution times of 30 minutes and 5 hours. All dissolutions occurred at > 90°C and constant mixing. Table 5 summarizes the dissolution conditions for each feed and Table 6 contains each feed's chemical description.

Table 5. Dissolution conditions used to generate calcine feeds by increasing calcine mass.

Feed	Initial HNO ₃ <i>M</i>	Total Calcine Wt (g)	Dissolution Time	Final HNO ₃ <i>M</i>
#1 (Control)	5.0	10.0	30 min	3.32
#2	5.0	12.5	30 min	2.90
#3	5.0	15.0	30 min	2.52
#4	5.0	17.5	30 min	2.18
#5	5.0	20.0	30 min	1.89
#6	5.0	25.0	30 min	1.22
#7	5.0	30.0	30 min	0.73
#8	4.2	15.0	30 min	1.55
#9	4.1	15.0	5 hours	1.06
#10	3.1	15.0	30 min	0.64
#11	3.1	15.0	5 hours	0.46

Table 6. Chemical composition of feeds produced by increasing calcine mass.

Feed	B M	Ca M	Zr M	Al M	F M	F/(Al+Zr)
#1	0.059	0.454	0.122	0.284	0.94	2.31
#2	0.074	0.721	0.187	0.446	1.17	1.84
#3	0.093	0.646	0.158	0.440	1.36	2.27
#4	0.133	1.227	0.287	0.845	1.47	1.30
#5	0.116	1.031	0.237	0.782	1.59	1.56
#6	0.238	1.647	0.325	1.269	1.88	1.18
#7	0.173	1.989	0.349	1.624	2.04	1.03
#8	0.112	0.823	0.174	0.567	1.29	1.74
#9	0.120	0.992	0.237	0.616	1.41	1.65
#10	0.089	0.749	0.128	0.570	1.20	1.72
#11	0.099	0.801	0.139	0.554	1.34	1.93

Each feed shown in Table 6 was contacted three times with the TRUEX solvent that was previously pre-equilibrated with a nitric acid solution having the same molarity as the feed. Each feed was reduced with H_2O_2 and spiked with Zr-95 and Am-241 prior to contacting with the TRUEX solvent.

Feed Adjustments. Dissolved Run 74 calcine does have a substantial fluoride concentration ($\sim 0.6 M$), but the extent of zirconium complexing by fluoride is uncertain because of the presence of aluminum and boron which compete with zirconium for fluoride. Ascorbic acid, H_2A was evaluated as a zirconium complexing (masking) agent. Zirconium, iron, and chromium extraction was evaluated from three Run 74 feeds: ascorbic acid was not added to Feed #1 (this feed was used as a control), Feed #2 was adjusted to 0.3 g/L H_2A , and Feed #3 was adjusted to 10 g/L H_2A . Each feed was contacted four times with the TRUEX solvent; fresh feed being used for every contact, so that the solvent would become heavily loaded with the extractable species.

Several other zirconium complexing agents were evaluated by a single contact of the TRUEX solvent with the adjusted Run 74 calcine. Ascorbic acid was again evaluated, but at a much larger concentration. Citric acid (CA) and diethylenetriaminepentaacetic acid (DTPA) were evaluated because of their ability to complex with zirconium while at the same time not forming insoluble complexes with other components in the feed. These complexing agents were added to the feed as solids to minimize dilution effects. Enough mass of each complexant was added so that the final concentration of each was 0.1 M in the feed. This concentration was large enough to see the effects of these complexants on zirconium extraction but low enough to prevent unwanted precipitates in the feed.

Ketomalonic acid ($\text{H}_2\text{C}_3\text{O}_5$) was evaluated as a zirconium complexing agent by adjusting Run 74 calcine to 0.005 M malonate, $\text{C}_3\text{O}_5^{2-}$. Precipitation occurred when the feed was adjusted to $> 0.005 M$ malonate. The ability of ketomalonic acid to complex zirconium at this concentration was indirectly evaluated by measuring americium's extraction distribution coefficient. D_{Am} was expected to increase if D_{Zr} decreased. Ketomalonic acid adjusted feed was contacted three times with the TRUEX solvent; fresh feed being used for each contact.

Oxalic acid was also evaluated as a zirconium complexing agent. Oxalate is known to form soluble complexes with zirconium. Run 74 feed was diluted 50% with 0.02 M $\text{H}_2\text{C}_2\text{O}_4$ in 4.0 M HNO_3 resulting in a final $\text{H}_2\text{C}_2\text{O}_4$ feed concentration of 0.01 M. Zr-95 and Am-241 were spiked into the oxalate adjusted feed and the feed was allowed to equilibrate for 24 hours. This feed was contacted three times with the TRUEX solvent; fresh feed being used for each contact. Feed stability tests were conducted with solutions of Run 74 calcine to determine the extent of oxalate addition before a precipitate occurred. Various stock solutions of oxalic acid, and ammonium oxalate were prepared in 4.0 M HNO_3 . Five mLs of each stock solution were added to 5 mLs of dissolved Run 74 calcine (50% dilution). These adjusted feeds were monitored over time for the occurrence of a precipitation.

Fluoride was evaluated as a zirconium complexing agent by spiking small volumes of concentrated HF into 50 mLs of Run 74 dissolved calcine. HF was added until specific F/(Zr + Al) molar ratios were achieved. The HF adjusted feeds sat for five days prior to contacting four times with the TRUEX solvent; fresh feed being used for each contact.

Fluoride was also added to the feed in the form of ammonium fluoride, NH_4F . A solution of 1.0 M NH_4F was prepared and used to adjust the total fluoride concentration in the feed. A total of five feeds were prepared. These feeds are described in Table 7. Each feed was allowed to equilibrate for seven days. A precipitate occurred in Feed #5 after the equilibration period which precluded its testing. Each feed was spiked with Zr-95 and Am-241 then contacted three times with the TRUEX solvent that had been pre-equilibrated with 3.5 M HNO_3 . Fresh adjusted feed was used for each contact.

Table 7. Run 74 calcine adjusted with 1.0 M NH_4F .

Feed	Feed Vol. mL	NH_4F Vol. mL	Total Vol. mL	F M	Zr M	Al M	F/(Zr+Al)
#1	9.9	0.1	10	0.89	0.21	0.42	1.4
#2	9.5	0.5	10	0.90	0.20	0.40	1.5
#3	9.0	1.0	10	0.91	0.19	0.38	1.6
#4	8.0	2.0	10	0.92	0.17	0.34	1.8
#5	7.5	2.5	10	0.92	0.16	0.31	2.0

Zr = 0.21 M

Al = 0.42 M

F = 0.89 M

Solid ammonium fluoride was added to Run 74 dissolved calcine so that D_{Zr} and D_{Am} measurements could be repeated. The purpose of adding solid ammonium fluoride was to evaluate the effect of dilution on D_{Zr} and D_{Am} . Adjusted feed compositions are shown in Table 8. The F/(Zr + Al) molar ratios shown in Table 8 are not identical to those shown in Table 7 because the [Zr] and [Al] were not diluted significantly by the addition of solid NH_4F . Distribution data were also obtained by adding concentrated HF to 50 mLs of dissolved Run 74

calcine. Small volumes of HF were added, thus minimizing the effects of dilution on the zirconium distribution coefficient.

Table 8. Run 74 calcine adjusted feed make-up with solid NH_4F .

Feed	Feed Vol. mL	NH_4F wt. mg	Total Vol. mL	Total F <i>M</i>	F/(Zr+Al)
#1	15	5.550	15	0.90	1.4
#2	15	27.75	15	0.94	1.5
#3	15	55.50	15	0.99	1.6
#4	15	83.25	15	1.04	1.65

Run 74 calcine was also diluted with water and 3.5 *M* HNO_3 to determine the effects of zirconium dilution only (3.5 *M* HNO_3) and zirconium, acid, and nitrate dilutions (water). Run 74 to diluent dilution ratios of 8:1, 4:1, 4:2, and 4:4 were prepared and contacted three times with the TRUEX solvent.

Scrub Adjustments. D_{Zr} as a function of scrub acid concentration was determined by contacting the TRUEX solvent three times with Zr-95 spiked Run 74 calcine. The solvent was divided into five equal portions and contacted three times with either 0.01 *M*, 0.50 *M*, 1.5 *M*, 2.0 *M*, or 5.0 *M* HNO_3 . In a separate experiment, 0.02 *M* HNO_3 was evaluated by contacting the zirconium loaded TRUEX solvent nine times with this scrub solution. The purpose of these tests was to ascertain the ability of nitric acid to remove extracted zirconium without causing significant americium recycle.

The ability to scrub zirconium with dilute nitric acid was further evaluated using TRUEX solvents that were 0.25 *M* and 0.3 *M* in CMPO (as opposed to 0.2 *M* CMPO). The purpose of these tests was to ascertain the effect of increased CMPO concentration on extraction D_{Am} , while also determining if a larger spread between scrub D_{Zr} and D_{Am} can be obtained in dilute HNO_3 by changing the CMPO concentration. Run 74 calcine was spiked with Am-241 and Zr-95 and was contacted with the 0.25 *M* and 0.30 *M* CMPO TRUEX solvent three times. Again, fresh feed was used for each contact. The 0.25 *M* CMPO solvent was divided into three equal volume aliquots which were scrubbed with 0.055 *M*, 0.09 *M*, or 0.13 *M* HNO_3 . The 0.30 *M* solvent was scrubbed with 0.075 *M* HNO_3 only.

Optimizing the scrub fluoride concentration was performed in order to maximize zirconium removal while minimizing that of americium. Four scrub solutions were prepared, all being 1.0 *M* in HNO_3 , but having NH_4F concentrations of 0.075, 0.050, 0.025, or 0.01 *M*, respectively. The TRUEX solvent was loaded with zirconium and americium by contacting it with Run 74 spiked calcine that was also adjusted to 0.2 *M* NH_4F . Solid NH_4F was used to adjust the feed to minimize feed dilution. The loaded solvent was split into four equal volume fractions after contact with the adjusted spiked feed, then contacted three times with the appropriate scrub solution.

Sodium fluoride and hydrofluoric acid were also evaluated as zirconium scrub reagents. Both reagents were evaluated at 0.1 M in 1.0 M HNO₃. The feed was adjusted to 0.2 M fluoride using solid NH₄F, just as in the previous tests. The feed was also spiked with Zr-95 and Am-241. The TRUEX solvent was contacted three times with the adjusted spiked feed, then split into two equal volume fractions. Each fraction was contacted three times with either 0.1 M NaF in 1.0 M HNO₃ or 0.1 M HF in 1.0 M HNO₃.

A series of non-radioactive batch contacts were performed using 0.1 M NH₄F scrub adjusted feed and O/As that would be used in a counter-current test. One part scrub was added to every four parts feed to account for scrub flow into the feed. The purpose of these contacts was to verify the absence or presence of a precipitate in the flowsheet before it was recommended and tested in one of the centrifugal contactor pilot-plants. Extraction, scrub, strip, and wash O/A ratios of 0.75, 3, 1, and 5 were used. The strip solution being 0.02 M HNO₃ and the wash solution being 0.25 M Na₂CO₃. Distribution coefficients were not measured for this test.

A batch contact test was performed to determine the optimum NH₄F concentration for a scrub O/A = 3. Reduced, but non-scrub adjusted, plutonium spiked feed was contacted with the TRUEX solvent (O/A=0.75). The loaded solvent was then contacted with either 0.25 M, 0.20 M, or 0.15 M NH₄F. The scrubbed solvent was also contacted three times with 0.02 M HNO₃ (O/A=1) followed by two contacts with 0.25 M Na₂CO₃ (O/A=5). A second (repeat) experiment was conducted by adding the NH₄F scrub solution to the feed in order to simulate more realistic conditions; i.e. scrub flow back into the feed during counter-current operation. Two scrub O/A ratios (3 and 2) were evaluated in this test and two NH₄F concentrations were tested (0.20 M and 0.15 M NH₄F). The feed was adjusted with the appropriate scrub volume and concentration prior to contacting with the TRUEX solvent. Plutonium was stripped from the solvent with 0.02 M HNO₃.

Methodology Used to Reduce/Eliminate PO₄³⁻ in Strip Stream

Alternative Strip Reagents. Strip solutions containing 1, 5, 10, and 20 wt% hydrogen peroxide (H₂O₂) or ascorbic acid (H₂A) in 0.02 M HNO₃ were contacted with the TRUEX solvent that had been first contacted three times with spiked Run 74 feed, and scrubbed with 0.1 M NH₄F in 1.0 M HNO₃. In addition, stripping control experiments were performed using 0.02 M HNO₃ that contained no reductant. Two wash contacts with 0.25 M Na₂CO₃ were performed after the three strip contacts. The purpose of the wash contacts was to determine the presence of interfacial crud, or precipitates, neither of which were observed during the wash contacts or at any point during testing.

The TRUEX solvent was contacted three times with calcine feed adjusted with 0.2 M NH₄F scrub (1 part scrub to 4 parts feed). Extraction O/A = 0.75 was used for these contacts. The loaded TRUEX solvent was then contacted three times with 0.2 M NH₄F in 1.0 M HNO₃ scrub at an O/A = 3. The scrubbed solvent was then stripped with either: 0.001 M HF in 0.02 M HNO₃, 10% H₂O₂ in 0.02 M HNO₃, 0.01 M oxalic acid in 0.02 M HNO₃, 10% ascorbic acid in 0.02 M HNO₃, 0.0025 M Na₂CO₃, or 0.001 M HEDPA in 0.02 M HNO₃. Two wash contacts with

0.25 M Na_2CO_3 followed the strip contacts. The purpose of these non-radioactive contacts was to determine the presence of precipitates or crud with the various strip solutions. If precipitates or crud were observed, that strip solution would not be tested with traced feed.

Oxalic acid was evaluated by contacting scrub adjusted feed (spiked with plutonium) three times with the TRUEX solvent (O/A = 0.75). The TRUEX solvent was scrubbed with three contacts of 0.2 M NH_4F in 1.0 M HNO_3 (O/A = 3). The scrubbed solvent was then split into three equal volume fractions and contacted with either 0.1 M, 0.05 M, or 0.01 M oxalic acid. Two 0.25 M Na_2CO_3 wash contacts were to be performed after the strip contacts.

Reducing HEDPA Concentration. Tests were conducted with 0.004 M HEDPA, as opposed to 0.04 M HEDPA. Plutonium was spiked into reduced Run 74 calcine, and contacted with the TRUEX solvent. The solvent was scrubbed with 0.2 M NH_4F then contacted three times with the 0.004 M HEDPA.

RESULTS /DISCUSSION

Eliminating/Reducing Zirconium in the High-Activity Fraction

Changing Calcine Dissolution Parameters. The current calcine dissolution parameters call for 1 kg of calcine to be dissolved in 10 liters of hot 5.0 M HNO₃ while being constantly and vigorously mixed [10]. D_{Zr} and D_{Am} were measured from solutions of dissolved calcines that were generated by changing one of two calcine dissolution parameters: the initial acid concentration, or the calcine weight to acid volume ratio. D_{Zr} and D_{Am} data shown in Table 9 were obtained from calcine dissolved in different initial HNO₃ concentrations.

Table 9. D_{Zr} and D_{Am} from calcine dissolved in different HNO₃ solutions.

Feed ¹	1 st Extraction		2 nd Extraction		3 rd Extraction	
	D _{Zr}	D _{Am}	D _{Zr}	D _{Am}	D _{Zr}	D _{Am}
#1	0.59	39.6	0.54	30.4	0.55	27.9
#2	0.56	27.3	0.50	19.3	0.49	17.2
#3	0.63	21.4	0.58	15.4	0.55	13.3
#4	0.66	17.0	0.51	10.3	0.62	9.83
#5	0.74	11.4	0.67	7.44	0.66	6.30
#6	1.37	13.4	1.07	7.15	1.04	5.81

1. Refer to Table 4 on page 9 for feed compositions

Zirconium distribution values in Table 9 increased with increasing initial nitric acid concentration (Table 4), while D_{Am} decreases as D_{Zr} increases. Tremendous gains can be made in americium extraction by small changes in the initial acid concentration according to Table 9. Table 9 also reveals how a small D_{Zr} decrease causes a substantial increase in D_{Am}.

The remaining UDS must be considered when recommending changes in the calcine dissolution flowsheet. Very little UDS remained in feed #6, where the mass of calcine dissolved in 50 mLs of HNO₃ was decreased by 50 wt%, which indicates that the vast majority (>99%) of the calcine is soluble in nitric acid. The calcine dissolution kinetics also slows as the acid is consumed. Therefore, longer dissolution times may be required to dissolve the calcine without increasing the undissolved solids. Calcine dissolution as a function of dissolution time in each of these acid concentrations should be revisited because the data in Table 9 indicate that significant progress can be made in reducing zirconium extraction and increasing americium extraction by making small changes in the initial nitric acid concentration. These feeds were stable over a two week time period (the time of testing and analyzing), and all but feed #1 were stable for one month.

Increasing the calcine mass may also provide another benefit not afforded by simply decreasing the initial acid concentration. Zirconium is known to polymerize [11]. The degree of zirconium polymerization is dependent on the acid and zirconium concentrations [11]. Favorable

zirconium polymerization conditions occur when the acid concentration is less than 3 M HNO₃ and when the zirconium concentration increases. Both these conditions are met when the calcine mass dissolved is increased, provided the acid concentration and volume are not changed.

Batch contact tests were conducted on the eleven feeds prepared by varying the calcine mass to acid volume ratio (Table 5). D_{Zr} and D_{Am} values obtained for each feed from three extraction contacts are shown in Table 10. D_{Am} in feeds #1-#7 indicate americium extraction increases with increasing calcine mass dissolved in a constant acid volume (100 mLs) and concentration (5 M). A decrease in zirconium extraction also correlates with increased calcine mass dissolved, except in feeds #6 and #7, where large D_{Zr} were obtained. Interestingly, D_{Am} in feeds #6 and #7 did not decrease with the D_{Zr} increase. The cause of this interesting behavior may be attributed to zirconium precipitation in these two feeds. Large amounts of a zirconium precipitate may have decreased the aqueous zirconium concentration to where Zr extraction did not consume "all" the CMPO; thereby causing a significant increase in D_{Am} . However, feed composition data shown in Table 6 contradict a zirconium precipitate in feeds #6 and #7. Feed #6 is 0.325 M in zirconium, while feed #7 is 0.349 M Zr, both these concentrations are larger than those shown for feeds #1-#5. The feeds were heated prior to analysis in order to re-dissolve the precipitate. Therefore, the analytical results shown in Table 6 are from feeds containing "no" precipitates. The same contradictory D_{Zr}/D_{Am} trend is also seen in contacts with feeds #8-#11. The zirconium concentrations in these feeds are approximately half of those in feeds #6 and #7, and is supporting data to the loss of zirconium in feeds #6 and #7 through precipitation.

Table 10. D_{Zr} and D_{Am} using feeds generated by increasing the calcine mass.

Feed ¹	1 st Extraction		2 nd Extraction		3 rd Extraction	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
#1	0.917	8.29	0.746	4.11	0.726	3.51
#2	0.723	7.93	0.673	4.35	0.644	3.55
#3	0.706	8.50	0.646	4.39	0.624	3.71
#4	0.794	10.4	0.645	4.90	0.586	3.77
#5	0.735	10.9	0.621	5.17	0.589	3.98
#6	1.15	19.8	0.872	8.05	0.840	5.75
#7	2.41	44.0	1.22	12.7	1.22	8.99
#8	0.919	45.9	0.776	26.5	0.674	22.1
#9	0.609	16.9	0.566	11.5	0.545	9.20
#10	1.32	59.3	1.00	31.4	0.905	25.9
#11	0.770	21.1	0.649	10.6	0.537	8.27

1. Refer to Table 6 on page 12 for feed compositions

Feeds #8 - #11 were generated to ascertain the likelihood of achieving >90 wt% dissolution in more dilute HNO₃ solutions by simply increasing the dissolution time. UDS measurements were obtained from these dissolutions. The percent dissolution increased from 87.1 wt% in feed #8 to 94.4 wt% in feed #9, and from 80 wt% in feed #10 to 85 wt% in feed #11.

These data suggest that the percent calcine dissolution will not be compromised when the initial acid concentration is decreased provided the dissolution time is increased.

All but feeds #1 and #2 developed a precipitate shortly after cooling, indicating feed stability to be a problem when drastically increasing the calcine mass. Feeds #7, #10, and #11 were heavily precipitated, while the other feeds contained only small amounts of precipitated solids. These precipitates were analyzed by X-ray diffraction spectroscopy (XRDS) and were determined to contain primarily S, O, F, Ca, and Zr, i.e. CaSO_4 , ZrSO_4 , CaF_2 , and ZrF_4 .

Comparing the distribution coefficient data shown in Table 10 to those shown in Table 9 indicates that simply decreasing the initial nitric acid concentration, without increasing the calcine mass dissolved, has more of an impact on decreasing the extraction of zirconium, and increasing that of americium. In addition, feed stability is not difficult to maintain when the acid concentration is decreased, while feed stability is virtually non-existent when the calcine mass is increased.

Feed Adjustments. Ascorbic acid, H_2A , was evaluated as a chromium reductant in solutions of Run 74 calcine by measuring the chromium extraction distribution coefficient. The extraction distribution coefficient of iron was also measured since H_2A will reduce iron. H_2A is a possible chelating agent, in addition to a strong and fast reducing agent; therefore, its use as a zirconium complexing agent was also evaluated by measuring the extraction distribution coefficient of zirconium. Data from these contacts are shown in Table 11. Distribution measurements from a non- H_2A adjusted feed were run as a control.

A slight increase in D_{Zr} is noticed between the control and the feed containing 10 g/L H_2A , indicating ascorbic acid does not form inextractable zirconium complexes (if significant Zr complexing was occurring, D_{Zr} would have decreased with increasing H_2A concentration). A substantial density increase in the TRUEX solvent contacted with the unadjusted feed was also noticed, which is indicative of solvent loading with zirconium and chromium. The TRUEX solvent from these contacts contained 0.09 M Zr and 0.004 M Cr after the fourth contact with the dissolved calcine. Recent CMPO/Zr stoichiometry studies performed at the ICPP show that 2 moles of CMPO are consumed for every mole of zirconium extracted [unpublished data]. The CMPO stoichiometry for Cr is not known. TBP is known to extract zirconium, but if the majority of the zirconium is complexed with CMPO, as much as 0.18 M CMPO could be consumed by the extracted zirconium; thus leaving only 0.02 M CMPO available for the extraction of acid ($\sim 1.0 \text{ M HNO}_3$ in the TRUEX solvent after the fourth contact), Cr, Fe, and the actinides. Solvent loading, by these inert components, leaves very little CMPO available for actinide extraction, and explains the physical problems (third phase formation and interfacial crud) sometimes observed with the TRUEX solvent when the feed is not chemically reduced. Solvent loading by these inert components also explains suppressed actinide extraction.

Solvent loading by zirconium was experimentally verified by preparing a TRUEX solution containing 0.3 M CMPO, as opposed to 0.2 M CMPO. Zirconium distribution coefficients for the three extraction contacts were 4.84, 2.83, and 2.33 respectively, while $D_{\text{Am}} \sim 4$ was observed in the final contact. Comparing D_{Zr} and D_{Am} values between the 0.3 M and 0.2 M

CMPO solvents (Table 1) shows a factor of 4 increase in D_{Zr} while D_{Am} increased slightly. These data suggest the majority of zirconium is extractable (uncomplexed), and the primary reason for the low zirconium distribution coefficient is the excess of zirconium compared to CMPO.

Iron extraction coefficients shown in Table 11 seem to increase as the ascorbic acid concentration increases. Ascorbic acid should reduce Fe(III) to the less extractable Fe(II). The reason for the increase in D_{Fe} with increasing H_2A is unknown.

Table 11. Zirconium, iron, and chromium extraction into the TRUEX solvent from Run 74 feeds adjusted with ascorbic acid.

Extraction Contact	D_{Zr}	D_{Fe}	D_{Cr}	Solvent Density (0.868) ¹
Feed #1 (No H_2A)				
#1	0.573	0.063	0.27	0.915
#2	0.635	0.058	0.62	0.926
#3	0.616	0.056	0.94	0.928
#4	0.606	0.057	1.13	No Data
Feed #2 (0.3 g/L H_2A)				
#1	0.621	0.103	0.110	No Data
#2	0.563	0.092	0.258	No Data
#3	0.660	0.094	0.477	No Data
#4	0.651	0.090	0.402	No Data
Feed #3 (10 g/L H_2A)				
#1	0.608	0.064	0.014	No Data
#2	0.767	0.149	0.052	No Data
#3	0.655	0.134	0.168	No Data
#4	0.825	0.245	0.352	No Data

¹ density of fresh solvent prior to contact

Ascorbic acid was re-evaluated by increasing its concentration to 17 g/L (0.1 M) in the feed. Various other complexing agents were also evaluated at the same molar concentration. A sample of feed was also diluted 50 vol% with water ($[H^+] = 3.9 M$), while another feed sample was diluted with nitric acid. Zirconium distribution coefficients from a single contact performed with these adjusted feeds are shown in Table 12.

Like ascorbic acid, citric acid and diethylenetriaminepentaacetic acid did not prevent zirconium extraction. Diluting the acid, nitrate, zirconium, and other constituents in the feed by 50% with water did not appear to reduce zirconium extraction either, but this does decrease the overall mass of zirconium in the solvent (discussed later). The zirconium distribution coefficient also increased when the nitric acid concentration in the feed is increased from 3.9 M to 4.67 M.

Table 12. Inhibiting zirconium extraction with feed dilution, acid adjustment, and complexing agents.

Feed Adjustment	D_{Zr}
50% Feed Dilution with Water	0.642
Feed Adjusted to 4.67 M HNO_3	0.933
Feed Adjusted to 0.1 M H_2A	0.674
Feed Adjusted to 0.1 M CA	0.686
Feed Adjusted to 0.1 M DTPA	0.696

H_2A = ascorbic acid

CA = citric acid

DTPA = diethylenetriaminepentaacidic acid

Ketomalonic acid ($H_2C_3O_5$) was evaluated as a zirconium complexing agent by adjusting Run 74 calcine to 0.005 M malonate, $C_3O_5^{2-}$. Precipitation, most likely CaC_3O_5 , occurred when the feed was adjusted to > 0.005 M malonate. The ability of ketomalonic acid to complex zirconium at this concentration was indirectly evaluated by measuring americium extraction distribution coefficients. D_{Am} was expected to increase if D_{Zr} decreased. D_{Am} for the three contacts were 4.17, 2.11, and 1.54, respectively. No improvement in D_{Am} was observed between the adjusted and unadjusted feeds; therefore, the use of ketomalonic acid as a zirconium complexing agent was abandoned.

Results from extraction contacts performed with feed adjusted by a 50 vol% dilution with 0.02 M $H_2C_2O_4$ in 4 M HNO_3 are shown in Table 13. Feed not adjusted with oxalic acid was also contacted with the TRUEX solvent as a control experiment.

D_{Zr} data shown in Table 13 indicate little effect of oxalate complexing on zirconium, because D_{Zr} in the adjusted feed are larger than those in the unadjusted feed. The extraction of Am also increased with zirconium in the adjusted feed. The increase in zirconium distribution coefficient is not all that surprising when the fundamental distribution coefficient expression is considered:

$$D_{Zr} = \frac{[Zr]_{org}}{[Zr]_{aq}}$$

The distribution expression shown above is a function of concentration and temperature, $f(C,T)$, and D usually increases when the initial aqueous concentration decreases. The distribution coefficient can also be defined by the equilibrium expression. The equilibrium expression for the extraction of Am into the TRUEX solvent is defined by the following reaction:

therefore,

$$D_{Am} = K[NO_3^-]_{aq}^3 [CMPO]_{org}^2$$

D_{Am} is very dependent on the equilibrium NO_3^- and CMPO concentrations. The NO_3^- concentration was virtually the same between the adjusted and unadjusted feeds, but the "free" CMPO concentration in those contacts must have been larger than with the unadjusted feed. An increase in the free CMPO concentration would occur in the adjusted feed because it was diluted by 50%; therefore, there was less zirconium mass in the TRUEX solvent in those contacts with adjusted feed resulting in less CMPO consumption by zirconium.

Table 13. D_{Zr} and D_{Am} obtained from Run 74 dissolved calcine adjusted with $H_2C_2O_4$ compared to D_{Zr} and D_{Am} obtained from unadjusted Run 74 dissolved calcine.

Contact #	D_{Zr}	D_{Am}
$H_2C_2O_4$ Adjusted Feed		
1	0.739	11.3
2	0.830	5.87
3	0.818	4.34
Unadjusted Feed		
1	0.661	6.69
2	0.675	2.22
3	0.692	1.51

Data shown in Table 13 suggest that simple feed dilution may be one means of reducing the amount of zirconium extracted into the TRUEX solvent. In addition, diluting the feed may cause an increase in D_{Am} which may be required if poor actinide decontamination factors occur in the TRUEX process when treating solutions of dissolved calcine.

A possible reason for the apparent ineffectiveness of oxalate in decreasing D_{Zr} may have been due to an inadequate oxalate concentration in the feed. Feed stability tests were conducted by diluting (50 vol%) Run 74 calcine with various oxalate solutions prepared in 4 M HNO_3 to determine the extent of oxalate addition before a precipitate occurred. Results from these tests are shown in Table 14.

Table 14. Feed stability tests with oxalic acid and ammonium oxalate.

$C_2O_4^{2-}$ Feed Concentration M	Solids from $(NH_4)_2C_2O_4$	Solids from $H_2C_2O_4$
0.0050	No solids after two days	No solids after two days
0.0125	Solids after two days	Solids after two days
0.0250	Solids within hours	Solids within hours
0.0500	Solids within hours	Solids within hours
0.125	Solids within hours	Solids within hours

Feed stability problems occurred quickly after the oxalate concentration in the feed exceeded 0.0125 M. The unwanted precipitate may be calcium oxalate. Calcium is problematic in these solutions because it acts as a "buffer". The calcium concentration in the feed is much larger than 0.0125 M; therefore, most (if not all) the oxalate is prevented from complexing with zirconium because it precipitates with calcium. Specifically, copious amounts of oxalate would be required for zirconium complexing because enough oxalate would have to be added in order for the calcium concentration to be drastically reduced by the process of precipitation. Data in Table 14 also show no advantage to ammonium oxalate over oxalic acid. The feed used to generate distribution data shown in Table 13 was adjusted to 0.01 M H₂C₂O₄ and the data in Table 14 indicate feed stability problems at 0.0125 M; therefore, little reduction in D_{Zr} is expected when the feed is adjusted to > 0.01 M oxalate.

Fluoride was evaluated as a zirconium complexing agent by spiking small volumes of concentrated HF into 50 mLs of Run 74 dissolved calcine until specific F/(Zr + Al) molar ratios were achieved. Table 15 shows the F/(Zr + Al) molar ratios tested, qualitative feed stability results, and D_{Zr} data.

Table 15. D_{Zr} from Run 74 feeds adjusted with HF.

Feed	F/(Zr+Al) (Molar)	ppt after 5 days	Extraction Contact #			
			#1 D _{Zr}	#2 D _{Zr}	#3 D _{Zr}	#4 D _{Zr}
Unadjusted	1.5	none	0.661	0.675	0.692	No Data
#1	1.75	none	0.52	0.57	0.54	0.53
#2	2.0	intermediate	0.80	1.15	1.19	4.17
#3	3.0	heavy	6.71	9.69	15.0	16.9
#4	3.5	heavy	28.0	79.3	108	70.6

Feed stability problems occurred in the feed when the total fluoride concentration was increased from 1.0 M in the unadjusted feed to 1.37 M in Feed #2. Calcium fluoride is believed to be the unwanted precipitate. D_{Zr} increases as the initial F/(Zr + Al) molar ratio increases. Initial F/(Zr + Al) molar ratio being that ratio not accounting for fluoride loss by a CaF₂ precipitate. The F/(Zr + Al) molar ratio shown in Table 15 is not the equilibrium ratio for those feeds where a precipitate occurred. The D_{Zr} increase may have been caused by a decrease in zirconium concentration; provided zirconium co-precipitated with calcium.

The effects of calcium "buffering" in dissolved zirconium calcine are again noticed in Table 15. Feeds are stable until the solubility of CaF₂ is exceeded. When the CaF₂ solubility product is exceeded by the addition of fluoride, a CaF₂ precipitate will occur until the concentrations of calcium and/or fluoride have decreased to below the solubility product:

$$K_{sp} = [Ca^{+2}][F^-]^2 = 3.9 \times 10^{-11}$$

The precipitate will continue to occur as long as fluoride is added to the solution until practically all of the calcium has been precipitated. At this point, additional zirconium complexing by fluoride may occur.

Fluoride was also added to the feed in the form of ammonium fluoride, NH_4F . D_{Zr} and D_{Am} data from these contacts are shown in Table 16.

Table 16. D_{Zr} and D_{Am} from NH_4F adjusted feed.

Feed	1 st Contact		2 nd Contact		3 rd Contact	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
#1	0.836	4.87	0.753	2.41	0.628	1.88
#2	0.711	5.66	0.677	3.04	0.608	2.47
#3	0.652	7.28	0.580	4.00	0.584	3.38
#4	0.564	10.9	0.493	7.02	0.479	6.39

Distribution data shown in Table 16 clearly show an increase in D_{Am} and a decrease in D_{Zr} as more NH_4F was added to the feed. Feed #1 in Table 15 was adjusted to a $\text{F}/(\text{Zr} + \text{Al})$ molar ratio of 1.75 using HF, while feeds #3 and #4 in Table 16 were adjusted to 1.6 and 1.8, respectively, with NH_4F (Table 7). D_{Zr} data shown in Table 15 for feed #1 are comparable to the D_{Zr} data for feeds #3 and #4 shown in Table 16. This comparison suggests that either HF or NH_4F will efficiently complex zirconium but the amount of fluoride added to the feed must be carefully monitored. For the particular calcine used in these tests, a precipitate occurred if the $\text{F}/(\text{Zr} + \text{Al})$ molar ratio exceeded 1.75 (Table 15).

Fluoride addition by either HF or ammonium fluoride will successfully decrease zirconium extraction and at the same time increase D_{Am} . The reason ammonium fluoride works as well as HF is it completely dissociates in strongly acidic solutions to form HF according to the following reaction:

Protonated fluoride, HF, is a weak acid; therefore, it does not strongly dissociate.

The difference in available fluoride for zirconium complexing between HF and ammonium fluoride is negligible, since ammonium fluoride generates HF anyway.

Solid ammonium fluoride was added to Run 74 dissolved calcine for the purpose of evaluating the effects of dilution on D_{Zr} and D_{Am} (Table 8). These data are shown in Table 17.

Table 17. D_{Zr} and D_{Am} from feed adjusted with solid NH_4F .

Feed	1 st Contact		2 nd Contact		3 rd Contact	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
#1	0.732	6.03	0.676	2.91	0.657	2.57
#2	0.726	7.06	0.680	3.33	0.618	2.90
#3	0.673	7.09	0.631	3.68	0.611	3.21
#4	0.627	8.22	0.585	4.27	0.554	3.50

Excellent D_{Zr} and D_{Am} agreement was obtained between Feeds #1, #2, and #3 of Table 16 and Feeds #1, #2, and #3 of Table 17. The $F/(Zr + Al)$ molar ratio of Feed #4 in Table 17 is 1.65, which falls between the $F/(Zr + Al)$ molar ratios of Feeds #3 and #4 in Table 16. D_{Zr} and D_{Am} for each contact using this feed (Feed #4 in Table 17) also fall between the Feed #3 and #4 zirconium and americium distribution coefficients shown in Table 16. Distribution data shown in Table 17 also show D_{Am} increases as D_{Zr} decreases, and suggest that solid NH_4F could be added to dissolved zirconium calcines up to a $F/(Zr + Al)$ molar ratio of 1.7 (Table 15) without causing a feed precipitation nor a substantial increase in the feed volume. Distribution data shown in Tables 16 and 17 also indicate that fluoride can be added to the same $F/(Zr + Al)$ molar ratio of 1.7 to decrease zirconium extraction while significantly increasing americium extraction.

Run 74 calcine was also diluted with water and 3.5 $M HNO_3$ to determine the effects of zirconium dilution only (3.5 $M HNO_3$) and zirconium, acid, and nitrate dilutions (water). D_{Zr} and D_{Am} results from the water and 3.5 $M HNO_3$ diluted feeds are shown in Tables 18 and 19.

Distribution data shown in Tables 18 and 19 indicate that simple dilution is another means of decreasing the amount of zirconium extracting with the actinides and improving actinide extraction. D_{Zr} and D_{Am} did not change significantly between diluents, indicating even water diluted feeds have enough "salting" strength to favor americium extraction. Comparing distribution data in these two tables would also indicate that HNO_3 extraction has little effect on americium extraction since D_{Am} between the two diluents are practically identical.

Table 18. D_{Zr} and D_{Am} from water diluted Run 74 calcine.

Run 74:Water Volume Ratio	1 st Contact		2 nd Contact		3 rd Contact	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
8:1	0.74	6.75	0.70	3.55	0.65	3.00
4:1	0.84	8.75	0.65	5.21	0.65	4.44
4:2	0.76	13.0	0.64	8.56	0.61	7.69
4:4	0.66	18.3	0.63	14.0	0.62	13.3

Table 19. D_{Zr} and D_{Am} from 3.5 M HNO_3 diluted Run 74 calcine.

Run 74:Acid Volume Ratio	1 st Contact		2 nd Contact		3 rd Contact	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
8:1	0.77	6.04	0.84	3.11	0.61	2.66
4:1	0.36	8.54	0.40	4.65	0.57	3.93
4:2	0.74	12.8	0.63	8.76	0.64	7.62
4:4	0.54	19.5	0.62	15.1	0.62	13.0

Selectively Scrubbing Zirconium. Another means of preventing zirconium recovery with the actinides is to selectively scrub it from the TRUEX solvent. This is less appealing than preventing its extraction because scrubbing may not improve (increase) americium extraction. Scrubbing zirconium from the solvent may satisfy the goal of reducing its concentration in the high-activity fraction, which will be significant, provided the waste is decontaminated below Class A TRU requirements. Dilute nitric acid, aluminum nitrate, and fluoride in various forms were evaluated as selective zirconium scrubbing agents.

Scrub D_{Zr} data as a function of scrub HNO_3 concentration are listed in Table 20. The ability to scrub zirconium from the TRUEX solvent using nitric acid without stripping americium would appear to be difficult, if not impossible, according to the data shown in this table. Americium has been shown to have a distribution coefficient of approximately one in 0.2 M HNO_3 [12], which is very close to D_{Zr} in 0.2 M HNO_3 . Zirconium does strip in very dilute nitric acid (0.01 M HNO_3) but so does americium [12].

Table 20. D_{Zr} as a function of HNO_3 concentration..

HNO_3 M	1 st Scrub Contact	2 nd Scrub Contact	3 rd Scrub Contact
0.01	1.43	0.970	0.146
0.2 ^a	1.47	1.64	1.15
0.5	1.57	2.45	3.07
1.5	1.64	3.32	4.60
2.0	1.86	3.44	5.55
5.0	2.51	5.57	8.57

a: D_{Zr} = 1.9 after 8 scrub contacts, and no Zr-95 activity detected in the aqueous phase in the 9th contact.

Americium and zirconium extraction and scrub distribution coefficients for 0.2 and 0.3 M CMPO solvents scrubbed with various HNO_3 solutions are shown in Tables 21 and 22. D_{Zr} comparison between Tables 21 and 22 show a significant zirconium extraction increase in the 0.3 M CMPO TRUEX solvent. D_{Zr} for the 0.2, 0.25, and, 0.3 M CMPO TRUEX solvents are approximately 0.6, 0.8, and 2.3, respectively. The large increase between the 0.25 and 0.3 M solvents is probably due to overcoming the effects of solvent loading. Increasing the CMPO

concentration does seem to improve the extraction of americium, although this improvement is small. Scrubbing zirconium, without stripping americium, does appear to be possible in both 0.25 and 0.3 *M* CMPO solvents, provided the scrub acid concentration is between 0.05 and 0.09 *M* HNO₃. *D*_{Zr} in the final scrub contacts with both solvents were less than one, while *D*_{Am} were greater than 2 in these same contacts.

Table 21. Extraction and scrub *D*_{Zr} and *D*_{Am} data using 0.25 *M* CMPO in the TRUEX solvent.

Contact	<i>D</i> _{Zr}	<i>D</i> _{Am}
1 st Extraction	0.85	10.1
2 nd Extraction	0.81	3.75
3 rd Extraction	0.83	2.85
0.055 <i>M</i> HNO ₃		
1 st Scrub	1.78	3.90
2 nd Scrub	1.60	3.56
3 rd Scrub	0.43	2.46
0.09 <i>M</i> HNO ₃		
1 st Scrub	1.69	4.19
2 nd Scrub	1.86	3.88
3 rd Scrub	0.73	2.98
0.134 <i>M</i> HNO ₃		
1 st Scrub	1.73	4.32
2 nd Scrub	2.08	3.97
3 rd Scrub	1.15	3.45

Table 22. *D*_{Zr} and *D*_{Am} using 0.30 *M* CMPO and 0.075 *M* HNO₃ scrub.

Contact	<i>D</i> _{Zr}	<i>D</i> _{Am}
1 st Extraction	4.84	Not Determined
2 nd Extraction	2.83	7.00
3 rd Extraction	2.33	4.07
1 st Scrub	2.53	4.44
2 nd Scrub	1.84	5.44
3 rd Scrub	0.814	4.22

An actual dissolved calcine waste batch experiment was performed using 0.075 *M* HNO₃ to scrub zirconium from 0.2 *M* TRUEX solvent [13]. The solvent and scrub compositions chosen for this test were based on the data shown in Tables 20, 21, and 22. Scrub results from this batch contact test indicate that zirconium could be scrubbed from the solvent without americium (*D*_{Zr} = 0.19, and *D*_{Am} = 2.0). These scrub distribution coefficients were used in the Generic TRUEX Model (GTM) to calculate the efficiency of this scrub solution under counter current conditions. GTM results showed that 67% of the feed zirconium would report to the high-level fraction, and that americium decontamination was very poor [13]. These results were

confirmed by performing a laboratory scale batchwise counter current test [13] and a 5.5 cm centrifugal contactor pilot plant test [9]. A zirconium phosphate precipitate was also observed in both these tests when the HEDPA strip solution was contacted with the scrubbed solvent. This precipitate occurred because of poor zirconium scrubbing. Scrubbing zirconium with nitric acid was abandoned, based on these results.

Fluoride was chosen as a good candidate for selectively scrubbing zirconium from the TRUEX solvent because it is known to form soluble species with zirconium. Fluoride also forms complexes with the lanthanides and actinides. These complexes are not desirable since they may prevent the extraction of these elements. Non-extractable actinide species may prevent the Class A TRU waste criteria from being met. Therefore, optimizing the fluoride concentration in the scrub was considered essential.

D_{Zr} and D_{Am} as a function of NH_4F scrub concentration are shown in Table 23. Comparing D_{Zr} and D_{Am} scrub distribution coefficients in Tables 1 and 23 indicates that 0.1 M NH_4F in 1.0 M HNO_3 efficiently removes zirconium without compromising americium decontamination ($D_{Am} \sim 18$).

Table 23. D_{Zr} and D_{Am} using various NH_4F concentrations in 1.0 M HNO_3 .

Contact	D_{Zr}	D_{Am}
1st Extraction	0.56	7.23
2nd Extraction	0.51	4.18
3rd Extraction	0.51	3.46
0.075 M NH_4F		
1st Scrub	0.64	11.6
2nd Scrub	0.19	17.8
3rd Scrub	0.37	18.4
0.050 M NH_4F		
1st Scrub	0.85	9.03
2nd Scrub	0.50	15.1
3rd Scrub	0.18	18.7
0.025 M NH_4F		
1st Scrub	1.17	7.25
2nd Scrub	1.31	11.7
3rd Scrub	0.71	15.2
0.010 M NH_4F		
1st Scrub	1.41	5.97
2nd Scrub	2.17	8.42
3rd Scrub	2.12	10.9

Extraction and scrub distribution coefficients using 0.1 M NaF or HF are listed in Table 24. Comparing D_{Zr} and D_{Am} results in Tables 1, and 24 indicates the source of fluoride to be of insignificance

Table 24. Scrub D_{Zr} and D_{Am} using 0.1 M NaF or HF in 1.0 M HNO_3 .

Contact	D_{Zr}	D_{Am}
1 st Extraction	0.57	7.04
2 nd Extraction	0.53	4.03
3 rd Extraction	0.51	3.41
0.1 M HF		
1 st Scrub	0.43	12.9
2 nd Scrub	0.06	17.6
3 rd Scrub	ND	16.4
0.1 M NaF		
1 st Scrub	0.46	13.8
2 nd Scrub	0.06	18.3
3 rd Scrub	ND	16.7

ND = not determined due to lack of activity in both phases

A series of non-radioactive batch contacts were performed using 0.1 M NH_4F scrub adjusted feed and O/As that would be used in a counter-current flowsheet. The purpose of these contacts was to verify the absence or presence of a precipitate in the flowsheet before it was recommended and tested in one of the centrifugal contactor pilot-plants.

Precipitates were not observed during any of the extraction, scrub, or strip contacts. However, a white precipitate occurred in both sodium carbonate wash contacts. This precipitate is presumed to be zirconium oxide, and indicates potential problems in the flowsheet. The wash precipitate could be eliminated by increasing the scrub flow, increasing the number of scrub stages, or by further optimization of the NH_4F concentration using the anticipated scrub O/A. The later option was chosen. A scrub concentration of 0.25 M NH_4F in 1.0 M HNO_3 was found to alleviate the precipitate in the wash contacts.

The extraction, scrub, and strip distribution coefficients for zirconium, americium, and plutonium were re-determined using the new scrub concentration. The spiked feeds were adjusted with one part 0.25 M NH_4F for every three parts feed. Three equal volume extraction, scrub (0.25 M NH_4F in 1.0 M HNO_3), and strip (0.02 M HNO_3) contacts were performed. Distribution data are shown in Table 25.

Small amounts of interfacial crud were observed in the second and third scrub contacts. Data in Table 25 would indicate the crud to contain some plutonium, since D_{Pu} in those contacts are less than one and the material balance did show significant plutonium loss. The crud was not observed during scrub contacts when an O/A = 3 was used in the non-radioactive tests. Americium was not scrubbed from the solvent, while zirconium was removed after the second scrub contact. These data suggests the scrub fluoride concentration must be optimized around the scrub O/A. Plutonium distribution coefficients obtained as a function of NH_4F concentration and at a scrub O/A = 3 are shown in the Table 26.

Table 25. D_{Zr} , D_{Am} , and D_{Pu} using 0.25 M NH_4F scrub solution.

Contact	D_{Zr}	D_{Am}	D_{Pu}
1 st Extraction	0.67	12.1	1044
2 nd Extraction	0.63	7.90	1081
3 rd Extraction	0.62	6.14	1088
1 st Scrub	0.032	19.5	43.1
2 nd Scrub	<<0.4	12.6	0.62
3 rd Scrub	ND	7.5	0.09
1 st Strip	ND	1.11	3.69
2 nd Strip	ND	0.16	1.13
3 rd Strip	ND	0.25	0.82

ND = not determined because no activity in either phase

Table 26. NH_4F scrub concentration optimization by evaluating plutonium scrub distribution coefficients.

Contact	NH_4F Concentration (Scrub O/A = 3)		
	0.25 M	0.20 M	0.15 M
Sc1	226	227	197
Sc2	123	155	93
Sc3	12	38	16.7
St1	8.3	24.8	8.4
St2	1.7 ^a	4.9 ^a	1.4
St3	0.47 ^a	8.6 ^a	0.47
W1	0.001	0.001	0.01
W2	0.31	0.39	0.14

^a = poor material balance indicating loss of plutonium

Poor material balances obtained in strip contacts St2 and St3 with the 0.25 M and 0.20 M NH_4F are of concern. Inefficient scrubbing, which resulted in the formation of an insoluble species, may have caused the precipitate in the dilute nitric acid strip solution. Regardless of the chemical composition of the precipitate, inefficient scrubbing is believed to be the cause.

Plutonium scrub and strip distribution coefficients obtained from feed adjusted with NH_4F and using two different scrub O/As and two NH_4F scrub ratios were measured and are shown in Table 27. Dilute HNO_3 was used to strip plutonium. Data shown in Table 27 indicate better zirconium scrubbing since no physical problems were observed in the strip section (an indirect analysis of scrub efficiency). These data also suggest that the operating envelope for scrubbing zirconium will be very narrow. This is not a favorable situation when considering the diversity in the feed zirconium concentration that is expected between feed batches. Plutonium strip data shown in Table 27 also suggest poor plutonium stripping with 0.02 M HNO_3 . A plutonium strip distribution coefficient of 0.65 in St3 is not small enough for complete plutonium recovery with the anticipated number of strip stages (6). The strip solution had to be re-

evaluated based on the strip D_{pu} shown in Table 27 for the 0.20 M NH_4F scrub ($O/A=3$). Strip solutions were initially evaluated by performing the experimental flowsheet mentioned above with non-traced simulant.

Table 27. Plutonium scrub and strip distribution coefficients from scrub adjusted feed.

Contact	O/A=3	O/A=2	O/A=2
	0.20 M NH_4F	0.20 M NH_4F	0.15 M NH_4F
Sc1	200	256	197
Sc2	130	26.3	93
Sc3	34.7	3.82	16.7
St1	19.3	2.06	8.4
St2	3.2	0.35	1.4
St3	0.65	1.67 ^a	0.47
W1	0.01	0.011	0.01
W2	0.25	0.28	0.14

a = poor material balance obtained

Eliminating/Reducing Phosphate in the High-Activity Fraction

Alternative Strip Reagents. Various strip solutions were evaluated in attempt to eliminate crud from occurring during stripping. Results from these contacts are descriptively shown in Table 28. Data shown in Table 28 indicate oxalic acid and dilute HEDPA can be used without causing interfacial crud or precipitates in the strip or wash contacts. Additional tracer tests with americium and plutonium spiked scrub adjusted feeds were performed to further evaluate the use of oxalic acid and dilute HEDPA strip reagents.

Plutonium strip distribution coefficients as a function of oxalic acid concentration are shown in Table 29. Data shown in Table 29 indicate that oxalic acid will be difficult to use as a plutonium stripping reagent without causing a precipitate in the strip solution. The occurrence of a precipitate was unexpected since tests performed with a non-spiked calcine had shown the strip contacts to be free of any precipitation.

These contacts were repeated with non-spiked calcine feed using 0.1 M oxalic acid in order to obtain the precipitate for analysis. In addition, reproducing the solids occurrence with non-spiked feed would eliminate contaminants in the plutonium tracer solution causing the precipitate. Solids were observed and collected in the cold contacts and analyzed by X-ray diffraction (XRD) spectroscopy. XRD analyses show the precipitate to be cerium oxalate, indicating lanthanides may pose a problem in the dissolved calcine flowsheet.

Table 28. Re-evaluation of alternative strip solutions from non-traced feeds by observing precipitate and crud formation in the strip and wash contacts.

Reagent	Results
0.001 M HF 0.02 M HNO ₃	Clear in the strip contacts; white precipitate in the 1 st wash contact
10% H ₂ O ₂ in 0.02 M HNO ₃	Clear in the strip contacts; white interfacial crud in the 1 st wash contact
0.01 M oxalic acid in 0.02 M HNO ₃	Clear in the strip and wash contacts
10% ascorbic acid in 0.02 M HNO ₃	Amber colored interfacial crud in the strip contacts; white interfacial crud in the 1 st wash contact
0.0025 M Na ₂ CO ₃ [†]	Heavy precipitate in the 1 st strip contact; wash contacts not performed
0.004 M HEDPA in 0.02 M HNO ₃	Clear strip and wash contacts

† = strip contacts with 0.0025 M Na₂CO₃ followed three strip contacts with 0.02 M HNO₃

Table 29. Plutonium strip distribution coefficients using various concentrations of oxalic acid. (All oxalic acid solutions were prepared in 0.02 M HNO₃)

Contact	0.1 M Oxalic Acid	0.05 M Oxalic Acid	0.01 M Oxalic Acid
St1	0.197	0.806	5.463
St2	0.268 ^a	0.780 ^a	0.107
St3	0.477	0.299	0.564 ^a
W1	Not performed	Not performed	0.046
W2	Not performed	Not performed	0.350

^a = white precipitate observed in these contacts resulting in poor plutonium material balance.

Tests were conducted to evaluate non-HEDPA strip solutions. Reductive stripping is a viable option since the primary actinide components in the calcine are americium and plutonium. Uranium is present in this waste in appreciable quantities but can be dealt with by other means if the need arises, i.e., uranium can be removed in the Na₂CO₃ wash section. Americium is removed efficiently from the TRUEX solvent with dilute nitric acid, while plutonium can also be stripped from the TRUEX solvent with dilute nitric acid if it is first reduced to Pu⁺³. Several innocuous reagents are available for plutonium reduction. Hydrogen peroxide and ascorbic acid were chosen for evaluation in this work because these compounds are easily destroyed and will not contribute to the final HLW volume.

Plutonium distribution coefficients using strip solutions varying in H₂O₂ and H₂A concentrations are shown in Table 30. Data in Table 30 show that little change in plutonium strip distribution values occurred as the H₂O₂ or H₂A concentrations were increased. Strip contact #3 values are virtually the same for all contacts, including the contact performed with the

0.02 M HNO₃ containing no reductant. All distribution coefficients decrease from strip contact #1 to strip contact #3, regardless of the strip solution, because of the removal of acid from the solvent in the first two contacts. Data in Table 30 were surprising because plutonium was not expected to strip in dilute nitric acid containing no reductant, and D_{Pu} was expected to decrease as the reductant concentration increased. Distribution data for the 0.25 M Na₂CO₃ are not shown or discussed. Analytical data from the wash contacts are not very interesting since most, if not all, the activity was stripped from the TRUEX solvent prior to contact with sodium carbonate. The data shown in Table 30 indicate phosphate elimination is possible and warrants further discussion to explain these unexpected results.

Dilute nitric acid will not strip Pu⁺⁴ or Pu⁺⁶ from the TRUEX solvent, but will strip Pu⁺³; therefore, the D_{Pu} observed in strip #3, where no reductant was used, was unexpected. Run 74 dissolved calcine feed was adjusted with hydrogen peroxide prior to contact with the TRUEX solvent in order to reduce hexavalent chromium to trivalent chromium. Hydrogen peroxide will reduce Pu⁺⁴ to Pu⁺³ [14], where it may have somehow remained in the trivalent oxidation state once reduced, and extract into the TRUEX solvent as Pu(NO₃)₃. But the extraction distribution coefficient of Pu⁺³ should be similar to that of Am⁺³ [15]. Extraction data in Table 1 show that D_{Pu} is much greater than D_{Am} which seems contradictory to the suggestion of plutonium extracting as Pu⁺³.

Table 30. D_{Pu} using various H₂O₂ and H₂A concentrations.

Strip Solution	Strip Contact Number		
	1	2	3
No Reductant	6.75	1.03	0.26
1 wt% H ₂ O ₂	5.35	1.18	0.17
1 wt% H ₂ A	5.31	0.96	0.12
5 wt% H ₂ O ₂	4.32	0.40	0.19
5 wt% H ₂ A	5.76	0.99	0.13
10 wt% H ₂ O ₂	3.84	0.44	0.29
10 wt% H ₂ A	1.38	0.83	0.031
20 wt% H ₂ O ₂	4.77	No Data	No Data
20 wt% H ₂ A	7.79	1.33	0.15

A more likely explanation of the data shown in Table 30 is the extraction of a fluoride species from the feed or from ammonium fluoride in the scrub section. The extracted fluoride may then react with plutonium in the strip section causing plutonium to be stripped from the solvent. GTM modeling shows that $D_{Pu} \ll 1$ is achieved with fluoride concentrations as low as 0.001 M in the strip solution. Therefore, very small amounts of fluoride in the strip product stream will significantly reduce D_{Pu} .

Figure 5. Plutonium strip distribution coefficients using various hydrogen peroxide solutions.

Reducing HEDPA Concentration. Precipitates were not observed when plutonium or americium spiked calcine feeds were tested with 0.004 M HEDPA (Table 28). Contacts, performed exactly as in the oxalic acid strip test, were performed with Am and Pu spiked feeds. Americium and plutonium extraction, scrub, strip, and wash distribution coefficients are shown in Table 31.

Complete americium and plutonium stripping was achieved with 0.004 M HEDPA in 0.02 M HNO₃ without observing any interfacial crud or precipitation. Larger than expected americium extraction distribution coefficients were also observed, indicating a big advantage to the small amount of complexing (or dilution) caused by scrub addition to the feed. In addition, all of the plutonium was stripped in the first strip contact, St1, therefore, the plutonium distribution coefficients obtained in St2, and St3, are meaningless since hardly any plutonium remained in the solvent. This result suggests that the HEDPA concentration could be further reduced. Material balances for plutonium and americium were 100% $\pm$ 10%.

Figure 6. Plutonium strip distribution coefficients using various ascorbic acid solutions.

A TRUEX flowsheet for removing the actinides from solutions of dissolved calcine was recommended based on the results shown in Table 31. This flowsheet recommends the use of 0.2 M NH_4F in 1.0 M HNO_3 at an O/A = 3 to scrub and complex extracted zirconium from the TRUEX solvent. The actinides (plutonium and americium) will then be stripped from the scrub solvent with 0.004 M HEDPA in 0.02 M HNO_3 at an O/A = 1.

Table 31. Americium and plutonium extraction, scrub, strip, and wash distribution coefficients using 0.004 M HEDPA in 0.02 M HNO₃ as the strip reagent.

Contact	D _{Am}	D _{Pu}
E1	7.46	124 ^a
E2	6.78	123 ^a
E3	6.91	122 ^a
Sc1	13.0	200 ^b
Sc2	20.1	130 ^b
Sc3	22.6	34.7 ^b
St1	3.68	0.016
St2	0.17	0.100
St3	0.043	0.406
W1	No activity in phases	No activity in phases
W2	No activity in phases	No activity in phases

a = plutonium extraction distribution coefficients taken from Table 1.

b = plutonium scrub distribution coefficients taken from Table 25.

CONCLUSIONS

- Selective zirconium scrubbing can be accomplished with ammonium fluoride in 1.0 *M* HNO_3 . The optimized ammonium fluoride concentration, which maximizes zirconium scrubbing and minimizes actinide scrubbing is 0.2 *M* when the scrub O/A = 3. Minimal impact to the high-activity glass volume from zirconium is expected with this scrub solution.
- The optimized NH_4F scrub concentration is dependent on the scrub O/A.
- Larger than expected americium extraction distribution coefficients from feeds complexed with this ammonium fluoride concentration indicate that <10 nCi/g TRU activity will be easily achieved.
- Gross actinide stripping can be accomplished with 0.004 *M* HEDPA. HEDPA will also reduce the probability of a precipitate occurring in the strip and wash sections of a counter-current process. Minimal impact to the high-level waste glass volume is also expected with 0.004 *M* HEDPA.
- Lanthanide extraction may cause flowsheet problems. Specifically, cerium may form an insoluble precipitate in the strip solution.
- Changing the calcine dissolution parameters may also increase americium extraction and minimize zirconium extraction into the TRUEX solvent. Decreasing the initial acid concentration used to dissolve the calcine does have a greater impact than increasing the mass of calcine dissolved in 5 *M* HNO_3 .
- Feed stability problems are likely in solutions of dissolved calcine when the mass of calcine is increased above 1 kg/10 L HNO_3 .
- Feed stability problems are not as likely in solutions of dissolved calcine when the initial acid concentration is between 2.5 and 5.0 *M*.

RECOMMENDED FLOWSHEET

The distribution coefficients in Table 32 were used in conjunction with the Generic TRUEX Model (GTM) to develop a TRUEX flowsheet for the separation of actinides from dissolved ICPP calcine. The resulting flowsheet, shown in Figure 4, consists of six stages of extraction at an $O/A = 0.75$, four stages of $0.2\text{ M NH}_4\text{F}$ in 1.0 M HNO_3 scrub at an $O/A = 3$, six stages of 0.004 M HEDPA strip at an $O/A = 1$, two stages of $0.25\text{ M Na}_2\text{CO}_3$ wash at an $O/A = 5$, and two stages of 0.1 M HNO_3 rinse at an $O/A = 10$. With this flowsheet, the GTM predicts the actinide activity will be reduced to 3.1 nCi/g , which is below the NRC Class A LLW requirement of 10 nCi/g for TRU. Also, only 6.7% of the Zr is extracted and exits with the HAW strip product. It is recommended that this flowsheet be used as a baseline flowsheet for future testing with simulated and actual dissolved calcine solutions in the 2-cm centrifugal contactors.

Figure 7. TRUEX flowsheet for the treatment of dissolved calcine.

Table 32. Stream concentrations in the TRUEX treatment of dissolved calcine.

Component	Dissolved Calcine Feed 1	TRUEX Solvent Feed 2	LAW Raff. 3	Scrub Feed 4	Strip Feed 5	Strip Product 6	Na ₂ CO ₃ Feed 7	Na ₂ CO ₃ Effluent 8	Acid Rinse Feed 9	Acid Rinse Effluent 10	TRUEX Solvent Effluent 11
H ⁺ (M)	3.5	---	2.6	1.0	0.01	---	---	---	0.1	---	---
HEDPA (M)	---	---	---	---	0.004	0.004	---	---	---	---	---
NH ₄ F (M)	---	---	0.05	0.2	---	---	---	---	---	---	---
Na ₂ CO ₃ (M)	---	---	---	---	---	---	0.25	0.25	---	---	---
CMPO (M)	---	0.2	---	---	---	---	---	---	---	---	0.2
Al (M)	0.42	---	0.32	---	---	---	---	---	---	---	---
B (M)	0.068	---	0.05	---	---	---	---	---	---	---	---
Ca (M)	0.65	---	0.49	---	---	---	---	---	---	---	---
Ce (M)	4.0E-04	---	1.2E-05	---	---	3.8E-04	---	---	---	---	---
Fe (M)	0.013	---	0.01	---	---	---	---	---	---	---	---
Zr (M)	0.21	---	0.15	---	---	0.014	---	---	---	---	---
Pu (nCi/g)	1130	---	4.1E-05	---	---	1280	---	---	---	---	---
Am (nCi/g)	103	---	3.1	---	---	113	---	---	---	---	---
Relative Flowrate	1.0	1.0	1.33	0.33	1.0	1.0	0.2	0.2	0.1	0.1	1.0

Evaluating the TRUEX flowsheet from feeds generated by decreasing the initial acid concentration used to dissolve calcine is also recommended. This will require a coordinated effort between calcine dissolution development and TRUEX development. Increased process efficiency, and a more problem free flowsheet may be obtained if the acid concentration is decreased from 5.0 M HNO₃. The impact of the dissolution changes on the undissolved solids, dissolution time, heel build-up, etc., must also be evaluated to obtain an overall process impact on changing the dissolution parameters.

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