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Actinide Partitioning from Actual ICPP Dissolved Zirconium Calcine Using the TRUEX Solvent

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SUMMARY

The TRansUranic EXtraction process (TRUEX), as developed by E. P. Horwitz and coworkers at Argonne National Laboratory (ANL), is being evaluated as a TRU extraction process for Idaho Chemical Processing Plant (ICPP) wastes. A criteria that must be met during this evaluation, is that the aqueous raffinate must be below the 10 nCi/g limit specified in 10 CFR 61.55. A test was performed where the TRUEX solvent (0.2 M octyl(phenyl)-N-N-diisobutyl-carbamoylmethyl-phosphine oxide (CMPO), and 1.4 M tributylphosphate (TBP) in an Isopar-L diluent) was contacted with actual ICPP dissolved zirconium calcine. Two experimental flowsheets were used to determine TRU decontamination factors, and TRU, Zr, Fe, Cr, and Tc extraction, scrub, and strip distribution coefficients. Results from these two flowsheets show that >99.99% of the TRU alpha activity was removed from the acidic feed after three contacts with the TRUEX solvent (fresh solvent being used for each contact). The resulting aqueous raffinate solution contained an approximate TRU alpha activity of 0.02 nCi/g, which is well below the non-TRU waste limit of 10 nCi/g specified in 10 CFR 61.55. Favorable scrub and strip distribution coefficients were also observed for Am-241, Pu-238, and Pu-239, indicating the feasibility of recovering these isotopes from the TRUEX solvent. A solution of 0.04 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in 0.04 M HNO_3 was used to successfully strip the TRUs from the TRUEX solvent. Physical problems, such as third phase formation, interfacial crud, and precipitation, were not observed in any of the contacts.

Significant amounts of iron and zirconium extracted from the acidic dissolved calcine feed into the TRUEX solvent. However, >90% of these elements were scrubbed from the solvent using 0.075 M HNO_3.

TRU, Zr, Fe, and Cr extraction, scrub, and strip distribution coefficients obtained from the test with actual ICPP dissolved zirconium calcine were used in the Generic TRUEX Model (GTM) to evaluate the behavior of these elements under counter-current conditions. GTM results {eight extraction stages (O/A=0.75), four scrub stages (O/A=3), and five strip stages (O/A=1)} indicate that 99% of the zirconium in the ICPP dissolved zirconium calcine will report to the high-level waste (HLW) fraction (strip product). The GTM also predicts

that the TRU activity in the low-level waste (LLW) fraction (aqueous raffinate) will be approximately 0.45 nCi/g with americium being the major contributor to this activity.

The results of the test using actual ICPP dissolved zirconium calcine, and subsequent GTM evaluation, show the feasibility of removing TRUs from the dissolved zirconium calcine with the TRUEX solvent and the deleterious effects zirconium poses with the ICPP zirconium calcine waste. Test results using actual ICPP zirconium calcine reveal the necessity of preventing zirconium from following the TRUs.

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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 coworkers at Argonne National Laboratory (ANL) [1], is one process being evaluated to separate the actinides from ICPP high-level waste (HLW) calcine generated from the solidification of fuel reprocessing raffinates.

Approximately 3,800 m^3 of HLW calcine is currently stored at the ICPP [2]. The calcine is primarily made-up of inert metal oxides (Al_2O_3, ZrO_2, and CaO) and CaF_2 [3]. Calcium was added to some of the raffinates prior to calcination to inhibit fluoride volatility. Fluoride is present in these raffinates from the dissolution of zirconium fuels. Transuranic (TRU) element and fission product concentrations in the calcine are less than 1 wt% [4]; therefore, a significant volume reduction may be achieved if these radioactive constituents are partitioned from the non-radioactive components of the calcine.

The purpose of this document is to report the results of applying the TRUEX Process to ICPP dissolved calcine. Extraction, scrub, and strip distribution coefficients of the actinides, Fe, Zr, Cr, and Tc were obtained from batch contacts with actual dissolved ICPP zirconium calcine. The experimentally determined distribution coefficients were used in the Generic TRUEX Model (GTM) to simulate counter-current process conditions and to establish the number of stages and flowrates necessary to achieve < 10nCi/g TRU activity in the dissolved calcine raffinate. A lab-scale counter-current test was performed using a dissolved zirconium calcine simulant spiked with Zr-95 and Am-241 to confirm results from a specific set of conditions evaluated by the GTM.

Calcine used in the evaluation of the TRUEX process was generated at the New Waste Calcination Facility (NWCF) in June of 1993. The calcine was generated from a feed blend of 3.5 parts of waste from tank WM-187 and 1 part of waste from WM-185. Tank WM-187 contained raffinates resulting from the dissolution of zirconium fuels and subsequent uranium extraction from the dissolution product. Tank WM-185 contains an incidental waste that is high in sodium. Solutions with significant sodium concentrations are not calcinable directly and must be blended with fuel reprocessing raffinates or non-radioactive aluminum nitrate prior to calcination.

A significant effort has been devoted at the ICPP to develop calcine dissolution flowsheets that result in feeds suitable for aqueous separation processes [5-8]. Suitable calcine solutions are defined as those that: 1) contain the smallest concentration of undissolved solids, 2) are stable with respect to precipitate formation after dissolution and after contact with the extractant, and 3) provide adequate actinide distribution coefficients with no (or a minimal amount) of feed adjustments.

BACKGROUND

McIsaac and co-workers performed actinide separation studies on simulated and actual ICPP nuclear fuel reprocessing waste solutions using dihexyl-N,N-diethylcarbamoylmethylene-phosphonate (CMP) [9]. The actual waste tested by McIsaac and co-workers was a reprocessing raffinate from zirconium fuel. Zirconium fuel reprocessing raffinates are used to generate zirconium calcine; therefore, the actual waste solution tested by McIsaac was similar to the dissolved zirconium calcine feed tested in this study. Single batch contacts of equal organic and aqueous volumes were used to evaluate the behavior of the TRU components from the simulant and actual wastes. McIsaac, et.al., used a solvent containing 30 vol. % CMP with heptane as the diluent. Americium distribution coefficients between 3 and 11 were achieved when actual waste was contacted with the CMP/heptane solvent. It is not known if the D_{Am} decreased as the number of contacts increased. Americium stripping with water proved to be difficult due to CMP impurities. McIsaac purified the CMP according to a procedure suggest by Schulz [10], after which americium was successfully stripped with water. Further tests with the purified CMP solvent and the zirconium raffinate simulant resulted in Pu and Am extraction distribution coefficients of 11.1 and 10.9, respectively. The zirconium extraction distribution coefficient (an element of key interest in this study) of 0.018 was measured from the waste simulant. Testing with the actual reprocessing zirconium waste raffinate resulted in Am-241 and Pu-238 decontamination factors of 95 and 210, respectively, after two contacts with fresh solvent. The final gross α activity in the aqueous raffinate was <5 nCi/mL.

Baker, et al., performed tests with mixer-settlers using actual zirconium fuel reprocessing raffinates and 29% CMP in xylene [11] (a scale-up of the work performed by McIsaac). Baker achieved decontamination factors of 980 and 2700 for Am-241 and Pu-238, respectively, after 8 stages of extraction (O/A = 0.5). It is interesting to note that because of hot cell space limitations, the loaded solvent was not concurrently scrubbed, but rather stored in a holding vessel for scrub and strip contacts using mixer-settlers located outside the hot cell. A white precipitate formed in the loaded solvent prior to scrubbing and stripping contacts. This precipitate was identified as a zirconium complex with CMP impurities. This is a surprising result, since McIsaac [9] reported the $D_{Zr} = 0.018$ in a test with zirconium fuel reprocessing raffinate simulant, indicating that small amounts of extracted zirconium may negatively impact the solvent behavior.

The mixer-settler test was repeated by Baker and co-workers [11], but this time two of the mixer-settler stages in the hot cell were used to concurrently scrub the loaded solvent and the remaining six stages were used for extraction. The solvent was scrubbed with 3 $\underline{M}$ HNO_3 to remove the extracted zirconium. This eliminated the zirconium precipitation. Americium and plutonium decontamination factors of 170 and 2500 were achieved in this test. Greater than 99.98 % of the extracted TRUs were recovered from the solvent using 0.05 $\underline{M}$ $H_2C_2O_4$ in 0.005 $\underline{M}$ HNO_3; however, a white precipitate formed in the first stripping stage after several hours of operation. This precipitate was identified as a rare-earth oxalate. Oxalic acid was recently evaluated at the ICPP as a gross actinide stripping reagent for both CMP and CMPO solvents loaded with a dissolved zirconium calcine simulant. Similar precipitates were observed (unpublished data).

Mincher and co-workers evaluated actinide separation from dissolved ICPP calcines using the TRUEX solvent, 0.1 $\underline{M}$ octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and 1.4 $\underline{M}$ tributylphosphate (TBP) in dodecane [12]. Again, Mincher's work is of value because the dissolved calcine used in his test was similar to the actual ICPP dissolved zirconium calcine used in this study. The dissolved zirconium calcine was contacted three times with equal volumes of fresh TRUEX solvent. Mincher reports that the gross α activity in the dissolved calcine was reduced from 23,300 nCi/g to 0.8 nCi/g after three contacts with the TRUEX solvent. Unfortunately, the extraction behavior of zirconium was not reported nor were scrubbing and stripping contacts performed.

Baker, et al., also performed a detailed bach-contact study using radioisotopes spiked into a simulated ICPP zirconium raffinate solution and the TRUEX solvent (0.1 $\underline{M}$ CMPO and 1.4 $\underline{M}$ TBP in dodecane) [13]. The reported extraction distribution coefficient for zirconium was 0.07. This is a favorable D_{Zr}, and will be used as a comparison for the extraction of zirconium from the dissolved ICPP zirconium calcine used in this test. Again, favorable extraction, scrub, and strip distribution coefficients for the actinides were reported.

EXPERIMENTAL PROCEDURES

Dissolved Zirconium Calcine Feed

Herbst and co-workers developed a method for calcine dissolution in 5 M HNO_3 at an acid volume to calcine weight ratio of 10 mL/g [5]. In addition, the dissolution will occur at >90°C with constant and aggressive mixing. These conditions were applied to dissolve the actual ICPP zirconium calcine with > 95 wt% dissolution being achieved [6]. The resulting feed solution was used to evaluate the TRUEX solvent. Table I provides the chemical composition of the calcine prior to dissolution and the feed solution used in this evaluation.

Table I
Calcine And Feed Characterization

Element	Calcine wt%	TRUEX Feed M
H^+	Not Applicable	2.58
NO_3^{-2}	Not Determined	4.33
Al	19.3	0.72
Ca	22.8	0.57
Cr	0.14	2.60E-3
F	12.2	0.64
Fe	0.56	0.01
K	0.78	0.02
Na	4.58	0.20
Zr	6.02	0.066
Cs-137	2.64E-3	8.48E+6 dps/mL
Sr-90	2.20E-3	1.07E+7 dps/mL
Gross α	Not Determined	5.25E+4 dps/mL
Am-241	4.20E-5	4.61E+3 dps/mL
Pu-238	9.80E-5	4.83E+4 dps/mL
Pu-239	1.03E-3	1.86E3 dps/mL
Np-237	8.30E-4	20.1 dps/mL
U	2.69E-3	2.69E-3 g/L

TRUEX Solvent

The TRUEX solvent used in this test contained 0.2 M CMPO, and 1.4 M TBP in an Isopar-L® diluent. The solvent was prepared by the Quality Control Laboratory at the ICPP. Americium-241 extractions were performed from various concentrations of pure nitric acid solutions prior to using the solvent. The Am-241 extraction distribution coefficients ascertained the CMPO purity and concentration in the solvent [14-15]. Americium distribution coefficients from 0.01 M HNO_3 and 2 M HNO_3 were 0.01 and 20, respectively, indicating the CMPO purity and concentration to be acceptable for use in this test [14].

The solvent was pre-equilibrated with three contacts of 3.5 M HNO_3 prior to contacting the solvent with the calcine feed. Fresh acid was used for each contact. Acid pre-equilibration was performed to minimize/prevent the extraction of acid from the calcine feed, thus reducing perturbations of the extraction distribution coefficients for the elements of interests.

Experimental Flowsheet

A series of extraction, scrub, and strip batch contacts, followed by a single wash contact were performed using the dissolved zirconium calcine feed solution and the TRUEX solvent. An organic-to-aqueous volume ratio of O/A = 1 was maintained in each batch contact. The experimental flowsheet used is shown in Figure 1. Both phases were kept after the first extraction contact for further contacts with either fresh solvent or fresh feed. Contacts E1, E3, and E4 were performed in order to ascertain the TRU decontamination factor from an aliquot of feed after three contacts with fresh TRUEX solvent. Extractions E1 and E2 were performed to measure actinide extraction distribution coefficients and to load the solvent with all the extractable species, including zirconium and iron. This loaded solvent was then scrubbed with 0.075 M HNO_3 and stripped with 0.04 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in 0.04 M HNO_3. Finally, a single wash contact with 0.25 M Na_2CO_3 was performed.

Because of the intense radioactivity of the calcine feed solution, these batch contacts were performed in the heavily shielded hot cell at the ICPP Remote Analytical Laboratory (RAL). Volumes of the non-radioactive TRUEX solvent, scrub and strip solutions were measured outside the hot cell into polyethylene bottles. The bottles were transferred into the hot cell where equal volumes of calcine feed or loaded solvent were added to the contents of the polyethylene bottle. Phase contacts were performed by shaking the bottle with manipulators for three minutes. The two phases were poured from the polyethylene bottle into a glass separatory funnel once phase contacts were complete. Phase disengagement occurred under the influence of gravity. The two phases were allowed to separate for 5 minutes.

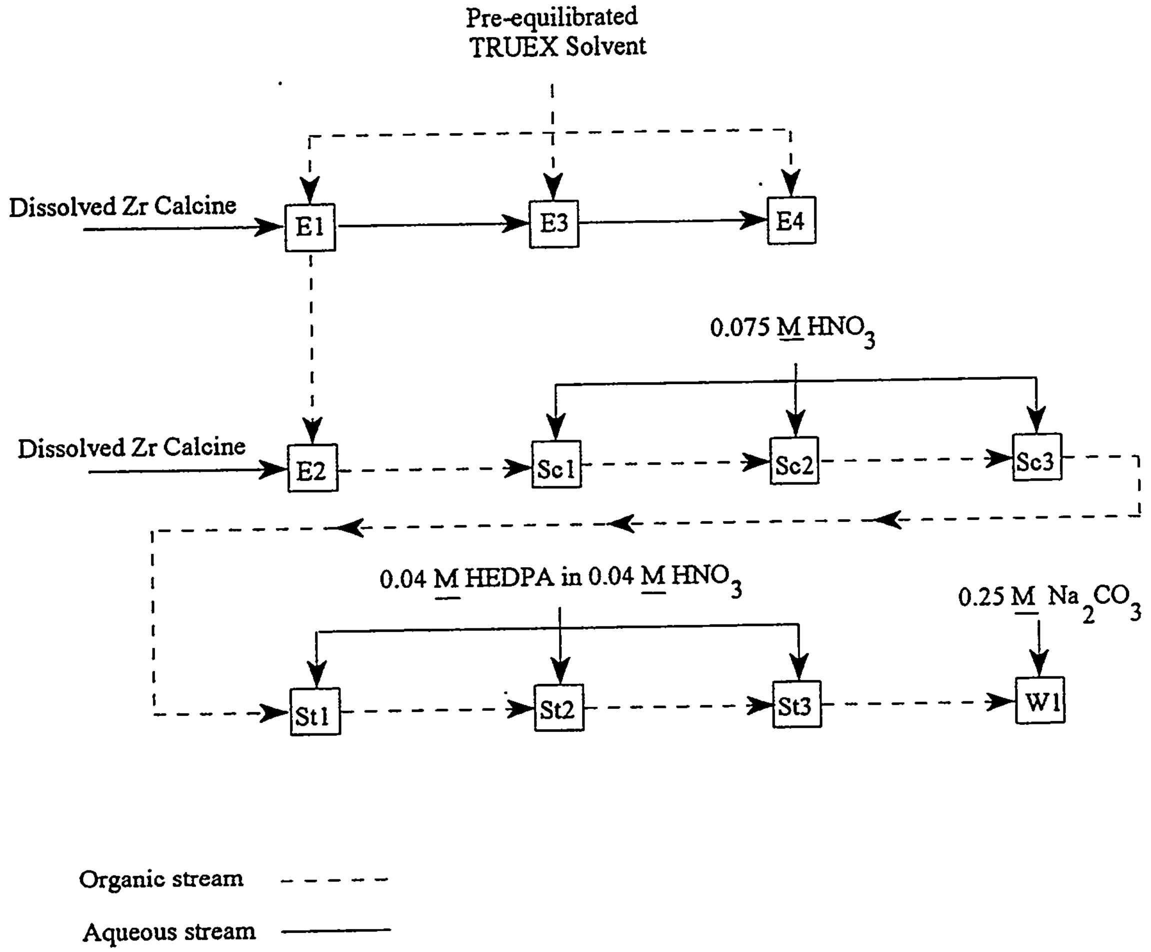

FIGURE 1: Experimental Flowsheet

The aqueous (bottom) phase was drained from the bottom of the separatory funnel into a glass collection vial when phase disengagement was complete. The organic/aqueous interface was not collected; instead, this interface was discarded. To minimize aqueous contamination of the organic phase, additional organic solvent was discarded through the neck of the separatory funnel. The remaining solvent was transferred to a graduated cylinder, where its volume was measured prior to the next contact.

New polyethylene bottles were used in each contact. The separatory funnels and graduated cylinders were replaced following completion of the extraction and scrub contacts. Figure 2 graphical shows the experimental methodology used for the remote contacts.

Counter-Current Batch Contact Test

Counter-current conditions were simulated batchwise with a non-radioactive dissolved zirconium calcine simulant spiked with Am-241 and Zr-95. This simulant is characterized in Table II. Six extraction stages (O/A = 1/3) and four scrub stages (O/A = 3) were performed according to the procedure described by Treybal [16]. Six extraction and scrub cycles were performed to ensure steady-state conditions were approached. Aqueous raffinate and TRUEX product samples were taken at the completion of each cycle. Figure 3 describes the experimental flowsheet used to simulate counter-current conditions.

Table II
Non-Radioactive Dissolved Zirconium Calcine Simulant

Element	M	Element	M	Element	M
H^+	3.4	Ca	0.78	Fe	1.5E-2
NO_3^-	6.4	Cr	5.4E-3	Na	1.2E-2
Al	0.49	F	1.2	Zr	0.23

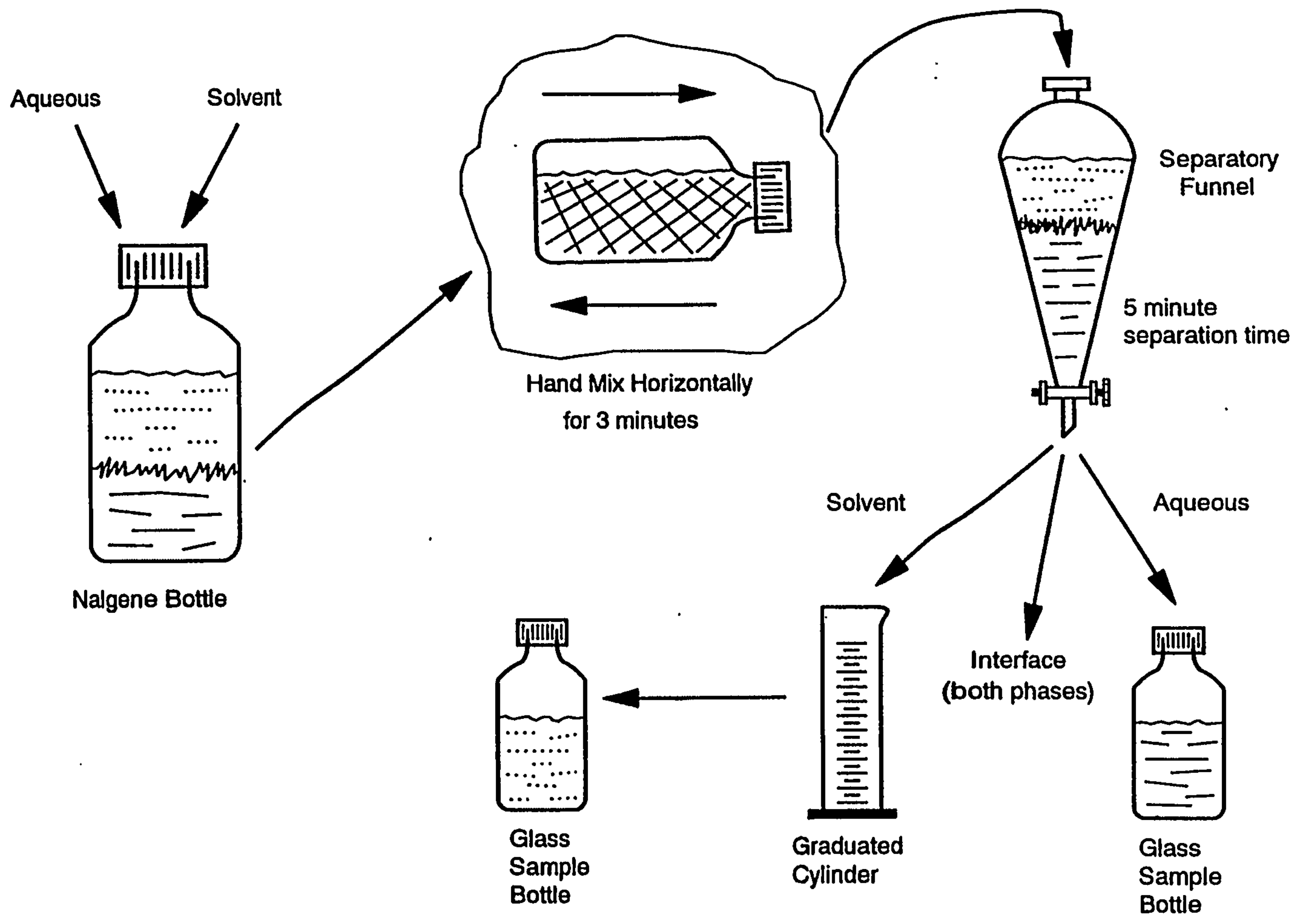

FIGURE 2: Experimental Methodology

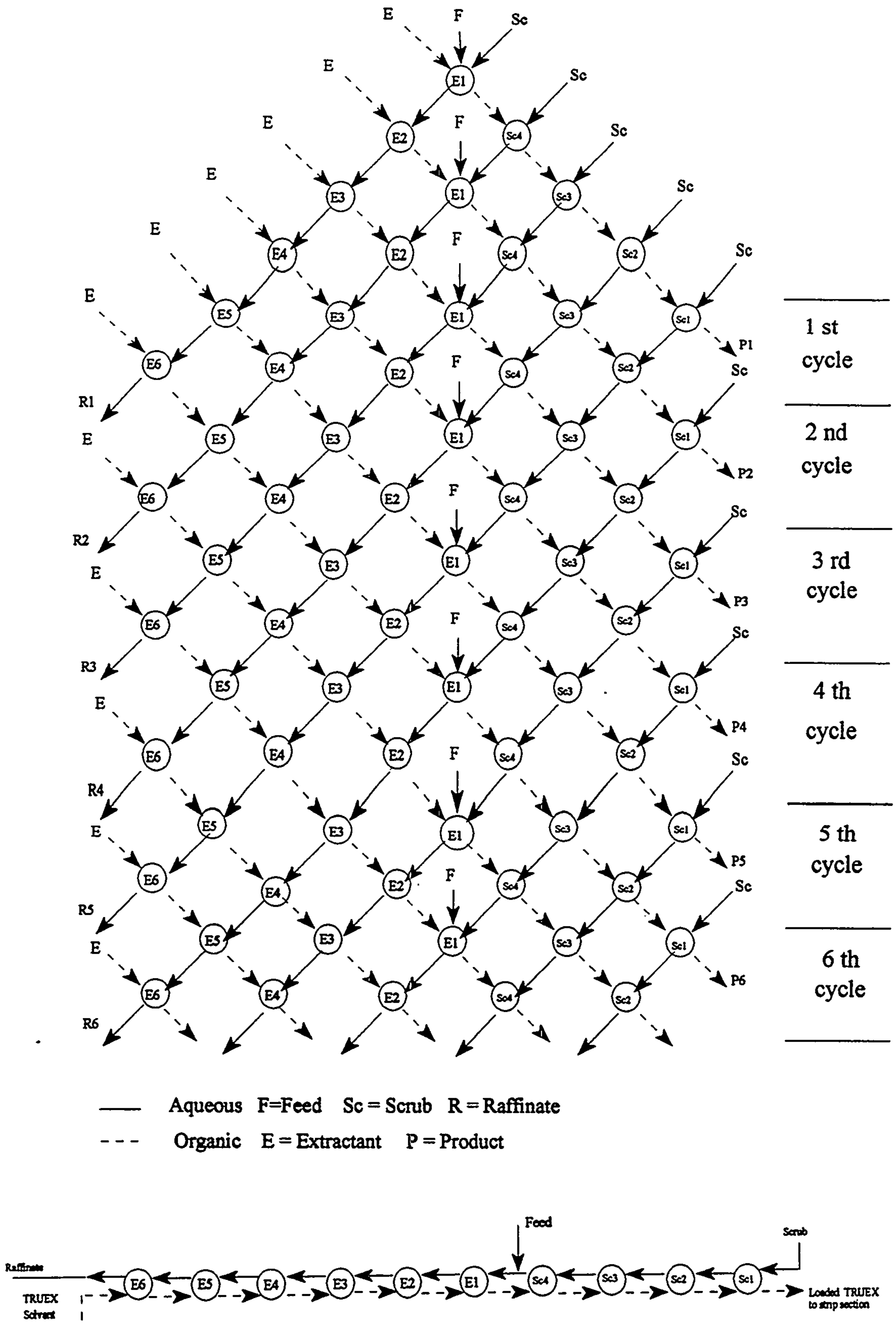

FIGURE 3: Laboratory-Scale Batchwise Counter-Current Flowsheet

Analytical Procedures

The TRUEX solvent was sampled after the E2, E3, E4, and SC3 contacts. Currently, there is no method for directly analyzing the TRUEX solvent. Distribution coefficients obtained from previous tests performed with actual ICPP wastes were determined by calculating the organic phase concentrations from material balances. This led to some erroneous D values, because the small analytical error associated with the aqueous phase analysis is propagated over a series of contacts, resulting in an increasing uncertainty in the calculated organic phase concentration with each successive contact. Indirectly analyzing the contents of the TRUEX solvent by stripping with 0.25 M HEDPA allows for a more direct measurement of the distribution coefficients.

One milliliter of each TRUEX solvent sample was stripped with 5 mL of 0.25 M HEDPA (diluted with water). One mL of the HEDPA strip solution was then pipetted into a 50 mL beaker containing 10 mL of 5 M HNO_3. The solution in the beaker was heated to near boiling then 2 mL of 30% hydrogen peroxide was added to this beaker. Hydrogen peroxide will destroy the HEDPA to CO_2 and H_3PO_4. Heat was applied to accelerate the HEDPA destruction. The solution in the beaker was evaporated to dryness. Ten mL of 5 M HNO_3 was again added to the beaker and the procedure repeated a second and third time. The HEDPA strip solution was analyzed for gross-α, Am-241, Pu-238, Pu-239, Np-237, Zr, Fe, and Cr. Aqueous samples were also taken after each contact for gross-α, Am-241, Pu-238, Pu-237, Np-239, Zr, Fe, and Cr analyses.

Material balances determined from the concentrations of Am-241, Pu-238, Pu-239, Np-239, Zr, Fe, and Cr in the HEDPA and aqueous samples were generally 100% ± 10%, indicating the elements were quantitatively stripped from the 1 mL organic aliquots. A summary of the material balances is located in the Appendix.

Gross α analyses were performed by evaporating a 1 mL aliquot of each sample on a 52 mm stainless steel counting planchet. The planchet was weighed prior to and after sample evaporation to obtained a net weight of the solids after evaporation. The samples were counted by a gas flow proportional counter (Tennelec LB-5100) at a bias of 610 volts. This voltage is within the recombination region for beta emissions to effectively eliminate crosstalk from the beta constituents. A polynomial function of sample weight versus efficiency was used to calculate counting efficiencies for each sample.

Specific actinide activities in the samples were determined by partitioning the actinides with extraction chromatography. TEVA SPEC® and TRU SPEC® columns were sequentially placed and sample aliquots were passed through the columns. Plutonium and neptunium were selectively extracted onto the TEVA SPEC® column by first reducing the sample with ascorbic acid. The sample was then heated to destroy excess ascorbic acid. During heating, plutonium is re-oxidized to the tetravalent oxidation state; however, neptunium remains in the reduced tetravalent state due to the kinetics of re-oxidation. Americium passes through the TEVA SPEC® column and is extracted onto the TRU SPEC® column (along with any Cm^{+3} and UO_2^{+2}). After the columns are rinsed, plutonium and neptunium are removed from the TEVA SPEC® column with 0.5 M HCl while americium is removed from the TRU SPEC® column with 0.025 M HNO_3. Uranium and thorium remain on the respective columns since they are not eluted under these conditions. Following elution, the actinides were co-precipitated from each fraction with NdF_3. The precipitate was then filtered onto a 0.1 μm filter and counted by alpha spectroscopy. NIST Pu-236, Am-243, and Np-239, tracers were added to the sample aliquots prior to these analytical separations to determine chemical yields and account for losses that occurred during isotopic separations. Chemical yields were high in all cases (>80%). The tracer yields were used to calculate the total isotopic activity reported for each sample.

Tc-99 was chemically separated from the aqueous samples and quantified by liquid scintillation (LSC). A rigorous radionuclide separation procedure was performed to prevent erroneous counting results prior to Tc-99 analyses by LSC. Sodium bisulfite was added to the aqueous samples to reduce any radioiodine to I^-. Sodium nitrite was then added to oxidize iodine back to I_2. Samples were taken to dryness to volatilize radioiodine and brought back to volume in 0.1 M HNO_3. The samples were oxidized with hydrogen peroxide and passed through Dowex 50X cation exchange columns to effect a gross Cs/Sr removal following iodine removal. The load fractions from the columns were taken to dryness and brought back to solution in 3 M sulfuric acid. The Tc-99 was extracted from each sulfate solution into 5 mL of pure (100%) TBP. The TBP was pre-equilibrated with 3 M sulfuric acid prior to measuring the 5 mL to negate volume change effects. Four mL of the TBP was pipetted into a liquid scintillation vial after phase separation. The samples were counted on a Packard Tri-Carb 2500 Liquid Scintillation Spectrometer. Activity values were calculated using a curve of counting efficiency vs. quench.

Duplicate aliquots of each sample were analyzed with one of the aliquots spiked with a known amount of Tc-99 tracer. The spiked and non-spiked samples were processed simultaneously for consistency. Chemical yields were then calculated from these spiked samples. All yields were > 85%. These yields were used to account for Tc loss during the analytical separations process and were used to calculate the total technetium activity in each of the non-spiked samples.

Inductive-coupled plasma emission spectroscopy (ICP-ES) was used to determine chromium, iron, and zirconium concentrations.

RESULTS/DISCUSSION

Extraction contacts E1, E3, and E4 were performed by contacting an aliquot of feed three times with fresh TRUEX solvent to obtain actinide decontamination factors. The extraction behavior of technetium, zirconium, iron, and chromium was also evaluated in these contacts. Organic aliquots from E3 and E4 were stripped with 0.25 M HEDPA to obtain actinide and metal concentrations in the TRUEX solvent. Aqueous and organic data from these contacts are shown in Table III.

Table III
Analytical Results From E1, E3, And E4 Contacts

Element	Units	Feed	E1-A	E3-A	E3-O	E4-A	E4-O
Cr	M	2.60E-3	2.60E-3	2.61E-3	<1.0E-3	2.58E-3	<1.0E-3
Fe	M	1.00E-2	7.31E-3	3.11E-3	4.31E-3	1.35E-3	1.70E-3
Zr	M	6.60E-2	1.17E-2	1.96E-3	8.14E-3	<1.4E-3	<1.4E-3
Tc-99	dps/mL	9.75E+2	3.61E+1	9.54E+0	2.81E+1†	5.58E+0	3.96E+0†
Gross α	dps/mL	5.25E+4	3.89E+2	8.83E-1	2.78E+2	<4.90E+0	1.20E+0
Am-241	dps/mL	4.52E+3	1.25E+3	1.87E+1	4.81E+2	2.83E+0	2.27E+1
Np-237	dps/mL	2.17E+1	3.02E+0	<3.07E-1	<2.82E-2	<5.67E-2	<2.31E+0
Pu-238	dps/mL	4.90E+4	4.66E+2	1.67E+0	2.58E+2	6.90E+0	9.99E+0
Pu-239	dps/mL	1.84E+3	2.09E+1	5.06E-1	1.17E+1	2.90E-1	9.31E-1

† = values determined by material balance

Significant masses of iron and zirconium were extracted from the zirconium calcine feed into the TRUEX solvent. Over 85% of the iron and > 98% of the zirconium was extracted after an aliquot of the zirconium calcine feed was contacted three times with fresh TRUEX solvent. Chromium in the dissolved zirconium calcine did not extract into the TRUEX solvent.

The gross α activity decreased from 5.25E+4 dps/mL in the feed to 0.883 dps/mL after two contacts, resulting in >99.99% removal of the α activity from the feed. If the aqueous raffinate density is assumed to be 1 g/mL (a very conservative assumption), the gross α activity in the raffinate stream would be 0.02 nCi/g. This is well below the 10 nCi/g Class A limit specified in 10 CFR 61.55 for non-TRU waste.

The Tc-99 activity decreased from 9.75E+2 dps/mL to 5.58 dps/mL after three contacts with fresh TRUEX solvent. The technetium concentration in the dissolved zirconium calcine feed is below the regulated limit (10 CFR 61.55); however, it may be important to immobilize this element in the HLW glass or glass ceramic waste form. Technetium, as pertechnetate, is very mobile in most environmental settings; therefore, its extraction and recovery with the TRUs is desirable.

Distribution coefficients and decontamination factors measured for contacts E1, E3, and E4 for the inert elements, Tc-99, and the actinides are shown in Table IV.

Table IV
Distribution Coefficients And Decontamination Factors

Element	E1	E3	E4	DF
Cr	<<1	<<1	<<1	<<1
Fe	3.7E-1	1.4E+0	1.3E+0	7.4E+0
Zr	4.6E+0	4.2E+0	ND	>4.8E+1
Tc-99	2.6E+1	2.9E+0	7.1E-1	1.8E+2
Gross α	133	314	ND	4.4E+4
Am-241	2.6E+0	2.6E+1	8.0E+0	2.0E+2
Np-237	6.2E+0	ND	ND	>7.2E+0
Pu-238	1.4E+2	1.5E+2	1.4E+0	>2.9E+4
Pu-239	8.7E+1	2.3E+1	3.2E+0	6.3E+3

ND = Not Determined

The Am-241 extraction distribution coefficient is smaller in the first extraction contact, E1, than in the following two contacts (E3 & E4). This is probably due to the extraction of

Zr into the TRUEX solvent, which may have loaded the solvent and suppressed the extraction of Am-241 in contact E1. The extraction of americium appears to be particularly sensitive to solvent loading. The mass of Zr available for extraction from the feed was smaller in contacts E3 and E4 because of the zirconium mass extracted in E1. The decreased zirconium mass in the feed resulted in less competition between zirconium and Am-241 for free CMPO and enhanced Am-241 extraction into the TRUEX solvent. An increase in D_{Fe} (as Fe^{+3}) from E1 to E4 is also noticed, indicating Zr may have suppressed the extraction of iron as well.

The effects of solvent loading by zirconium are particularly noticeable when the Am and Zr extraction distribution coefficients obtained from this test are compared to those obtained by Baker [13]. Even though Baker used 0.1 M CMPO, as opposed to 0.2 M CMPO used in this test, a larger D_{Am} was reported (6.4 compared to 2.61). The larger D_{Am} reported by Baker was not only obtained using a less concentrated CMPO solvent, it was also obtained from a zirconium raffinate simulant that was lower in acidity (1.2 M), lower in nitrate (1.2 M), and higher in zirconium (0.55 M) than the dissolved zirconium calcine solution used in this study. Baker reports a D_{Zr}= 0.07 from the raffinate simulant. A possible reason for the small D_{Zr} reported by Baker is the extent of zirconium complexing by fluoride in the tested feed. The F/(Al+Zr) molar ratio in the simulant used by Baker was 4.2 respectively, while the F/(Al+Zr) molar ratio in the dissolved ICPP zirconium calcine used in this test was only 0.81.

Increasing the F/(Al+Zr) molar ratio in the dissolved zirconium calcine feed by the addition of fluoride is difficult because of the presence of calcium (0.57 M). The addition of small amounts of fluoride causes undesirable CaF_2 precipitation to occur in the feed. However, it appears from a comparison of Baker's results to those reported here, that lowering the acidity and corresponding nitrate concentrations in the dissolved calcine solutions may not only reduce the zirconium extraction, it may also increase the extraction of americium.

Reducing the acid and nitrate concentrations in the dissolved calcine feed could be accomplished by dilution or dissolving the calcine in a less concentrated nitric acid solution. Decreasing the nitrate concentration may inhibit the extraction of zirconium by simply reducing the salting strength of the feed. Decreasing the salting strength of the feed may also result in decreased TRU extraction, especially for americium. However, the impact of decreasing the salting strength may be partially offset by an increase in the free CMPO concentration available for TRU extraction.

Decreasing the acid concentration of the feed may also inhibit the extraction of zirconium by allowing more fluoride complexing to occur, as shown in Equations 1, 2, and 3.

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \tag{1}$$

$$HF \rightleftharpoons H^+ + F^- \tag{2}$$

$$Zr^{+4} + 4F^- \rightleftharpoons ZrF_4 \tag{3}$$

According to Equations 1 and 2, decreasing the hydrogen ion concentration by lowering the nitric acid concentration will reduce the free HF concentration by shifting the equilibrium of Equation 2 to the right. This will cause an increase in the F^- concentration and provide more fluoride available for zirconium complexing in Equation 3.

Conversely, lowering the nitric acid concentration in these calcine solutions, either by dilution or by simply dissolving the calcine with a more dilute acid solution, may have negative effects. Reducing the nitric acid concentration will increase the volume of dissolved zirconium calcine feed because a larger volume of acid will have to be used to dissolve the calcine. The larger volume of dilute calcine feed may result in feed instabilities and increase the volume of waste to be processed. The impacts of increasing the feed volume to the overall equipment cost of treating the dissolved zirconium calcine and resulting HLW and LLW fractions need to be considered before determining the advantages of a less acidic feed. These cost impacts are beyond the scope of this work.

Extraction distribution coefficients shown in Table IV for Tc-99 decrease with each successive contact. The D_{Tc}= 26 obtained from E1 does seem large; however, D_{Tc} obtained for E3 and E4 (2.94 and 0.71, respectively) are in agreement with those reported by Tse [17] under similar acid and nitrate concentrations. Baker [13] reports a D_{Tc} = 1.3 from the zirconium raffinate simulant. Zirconium has been shown to enhance the extraction of technetium into TBP [18]. The extraction of technetium as a zirconium-pertechnetate-nitrate complex into the TRUEX solvent may explain the large D_{Tc} observed in E1 and the decreasing D_{Tc} trend observed from E1 to E4. The decrease in zirconium concentration from E1 to E4 (Table III) would certainly inhibit Tc extraction if coextraction with Zr was occurring. A technetium decontamination factor of 1.75E+2 was achieved after the dissolved zirconium calcine feed was contacted three times with fresh TRUEX solvent.

The TRUEX solvent from E1 was contacted a second time with fresh dissolved zirconium calcine. Distribution coefficients from the second extraction contact, E2, are shown in Table V. Distribution coefficients from E1 are shown again for comparison. Distribution coefficients determined for E1 (D_{E1}) were calculated by material balance. However, E2 distribution coefficients (D_{E2}) were determined by stripping a 1 mL aliquot of the organic phase, E2-O, with 5 mL of 0.25 M HEDPA and analyzing this strip solution for metal and TRU concentrations.

Table V
Sampled Phase Activities After Extraction Contacts
And Resulting Distribution Coefficients

Element	Units	Feed	E1-A	D_{E1}	E2-A	E2-O	D_{E2}
Cr	M	2.60E-3	2.60E-3	<<1	2.51E-3	<9.6E-4	<<1
Fe	M	1.00E-2	7.31E-3	3.7E-1	1.15E-2	2.33E-3	2.0E-1
Zr	M	6.60E-2	1.17E-2	4.6E+0	3.13E-2	7.54E-2	2.4E+0
Tc-99	dps/mL	9.75E+2	3.61E+1	2.6E+1	2.68E+1	1.89E+3†	7.0E+1
Gross α	dps/mL	5.25E+4	3.89E+2	1.3E+2	2.26E+3	1.19E+5	5.2E+1
Am-241	dps/mL	4.52E+3	1.25E+3	2.6E+0	2.39E+3	5.73E+3	2.4E+0
Np-237	dps/mL	2.17E+1	3.02E+0	6.2E+0	4.78E+0	3.56E+1†	7.4E+0
Pu-238	dps/mL	4.90E+4	4.66E+2	1.0E+2	8.42E+2	9.52E+4	1.1E+2
Pu-239	dps/mL	1.84E+3	20.9	8.7E+1	58.5	3.50E+3	6.0E+1

† = value determined by material balance

Favorable distribution coefficients for Cr and Fe (both <1) were observed in the E1 and E2 extraction contacts. Unfavorable Zr extraction was again observed in E2, where D_{Zr}=

2.41 was obtained. As already mentioned, the extraction of zirconium may have suppressed the extraction distribution coefficient of Am-241. Americium and plutonium distribution coefficients are lower than expected, based on the high acid and nitrate concentrations of the feed and on previous tests performed on other ICPP waste that were similar in acid and nitrate concentrations. Herbst and co-workers [19] achieved $D_{Am} > 20$ from actual ICPP sodium-bearing waste (SBW). The nitrate concentration in the SBW used by Herbst was equivalent to that in the dissolved ICPP calcine waste used in this study, while the acid concentration in the SBW was only slightly lower (1.6 M H^+ as opposed to 3.4 M H^+ in the dissolved calcine).

While the plutonium distribution is also lower than expected, a $D_{Pu} \sim 100$ is acceptable. Baker observed a $D_{Pu}= 72.1$ from the spiked zirconium raffinate simulant into 0.1 M CMPO [13]. Plutonium extraction distribution coefficients reported by Herbst, et al., from actual ICPP sodium-bearing waste were typically greater than 1000 [19]. The zirconium concentration in the SBW used by Herbst was 0.0096 M, resulting in negligible solvent loading and having no impact on TRU extraction. The low D_{Pu} observed by Baker occurred under conditions where very little zirconium extracted ($D_{Zr} = 0.07$). The small D_{Pu} observed from the dissolved zirconium calcine solution used in this test and in the zirconium raffinate used by Baker may also be due to the plutonium oxidation state (Baker's CMPO concentration and diluent also differed which may contribute to the low D_{Pu}).

The oxidation state of plutonium in the dissolved zirconium calcine solution was analytically determined by passing an aliquot of this solution through a TEVA SPEC® column. This column is very specific in extracting the tetravalent actinides from acidic solutions. The eluent was collected for plutonium analysis. The column was then stripped with 0.05 M HCl to recover any extracted tetravalent actinides. The strip solution was also analyzed for plutonium. Results from this test indicate that over 70% of the plutonium in the dissolved zirconium calcine is in the hexavalent oxidation state. The remaining 30% is in the tetravalent oxidation state. Since the extraction distribution coefficient for Pu(VI) is typically lower than that of Pu(IV) into the TRUEX solvent, the suppressed extraction D_{Pu} may be at least partially due to the plutonium oxidation state rather than solely a result of zirconium extraction.

Distribution coefficients for technetium shown in Table IV are again larger than those reported by Baker [13] and Tse [17] under similar acid and nitrate concentrations. Technetium distributions for E1 and E2 are 26 and 70.4, respectively. Even though these large technetium distribution coefficients are desirable, they are certainly contradictory to the expected values. The increase in D_{Tc} from E1 to E2 does indicate a synergistic effect between zirconium (or a combination of other chemical or elemental effects) and technetium is occurring to enhance the extraction of technetium into the TRUEX solvent. Regardless of the mechanism, the large D_{Tc} determined for E1 and E2 is difficult to explain. Further investigation of this phenomena is required, but beyond the scope of this work.

Suppressed TRU extraction distributions shown in Table V may still be acceptable provided that Zr is scrubbed from the TRUEX solvent, thereby, possibly increasing both the free [CMPO] concentration available for TRU extraction and the D_{TRU} in a counter-current process. Three scrub contacts were performed on the loaded solvent using 0.075 M HNO_3. Metal and TRU concentrations and distributions from these scrub contacts are shown in Table VI.

Table VI
Scrub Activities And Distribution Coefficients

Element	Units	SC1-A	D_{SC1}	SC2-A	D_{SC2}	SC3-A	SC3-O	D_{SC3}
Cr	M	<9.58E-4	NA	<9.58E-4	NA	<9.58E-4	No Data	NA
Fe	M	1.14E-1	1.7E-1	<3.20E-4	<1	<3.20E-4	No Data	<1
Zr	M	3.13E-2	1.8E+0	2.93E-2	9.7E-1	2.38E-2	No Data	1.9E-1
Tc-99	dps/mL	7.66E+1	2.4E+1	2.98E+1	6.0E+1	77.2E+1	1.70E+3†	2.2E+1
Gross α	dps/mL	1.03E+4	1.1E+1	9.77E+3	1.0E+1	1.19E+4	8.38E+4	7.0E+0
Am-241	dps/mL	1.93E+3	2.0E+0	1.27E+3	2.0E+0	3.35E+2^{a}	2.19E+3^{b}	6.6E+0
Np-237	dps/mL	<1.26E+1	NA	<1.82E+1	NA	6.96E+1	<1.46E+1	NA
Pu-238	dps/mL	6.54E+3	1.4E+1	6.85E+3	1.2E+1	3.90E+4	8.73E+4	2.2E+0
Pu-239	dps/mL	2.77E+2	1.2E+1	2.81E+2	1.0E+1	1.78E+3	3.08E+3	1.7E+0

NA = Not Applicable
†= value determined by material balance
a. SC3-O = ST1-A + ST2-A + ST3-A + W1-A
b. SC3-A = E2-O - (SC3-O + SC2-A + SC1-A)

Iron was effectively scrubbed from the solvent using 0.075 M HNO_3. A favorably low zirconium distribution coefficient was eventually achieved on the third scrub contact (SC3). The initial scrub acid concentration cannot be decreased from 0.075 M HNO_3 to achieve lower zirconium distributions in the early contacts because unacceptable reflux of the TRUs would occur in the extraction section under counter-current conditions (discussed later). As seen from Table VI, significant plutonium activities were removed from the TRUEX solvent in the third scrub contact. Schulz and Horwitz [20] report a D_{Pu}~ 2.7 for the back extraction of Pu(IV) in ~0.075 M HNO_3 from 0.2 M CMPO and 1.2 M TBP in dodecane (no values were found for Pu(VI) under similar conditions). The $D_{Pu\text{-}238}$= 2.24 and $D_{Pu\text{-}239}$= 1.73 are in good agreement to that reported by Schulz and Horwitz [20]. The D_{Am} = 6.55 determined in SC3 does not agree with that of ~0.8 reported by Schulz and Horwitz [20]; however, D_{Am} observed in SC1 and SC2 agree favorably. D_{Am} for SC3 is likely less than the measured value of 6.55. The equilibrium aqueous acid concentration following the SC3 contact should be very near the 0.075 M HNO_3 (actual analytical result is < 0.14 M HNO_3); D_{Am} at this acid concentration should be < 1 [20]. Neptunium was not detected in the aqueous nor organic scrub samples because of the large dilutions required to reduce the plutonium activities for its analysis.

Scrubbing distribution coefficients for Tc-99 shown in Table VI are much larger than those reported by Tse [17]. Tse reports stripping D_{Tc} = 0.19 for 0.1 M HNO_3 and D_{Tc} =3.21 for 1 M HNO_3. D_{Tc} = 22 was determined for the SC3 contact while the equilibrium acid concentration for this contact was < 0.14 M HNO_3. Again, these large scrub distribution coefficients are desirable and indicate that Tc is not scrubbed with 0.075 M HNO_3. Small Zr distribution coefficients and large D_{Tc} in the scrub contacts does not negate the possible extraction of a zirconium-pertechnetate-nitrate complex. The amount of zirconium remaining in the TRUEX solvent is sufficient for complete technetium complexation.

Stripping distribution coefficients for Cr, Fe, Zr, Tc-99, and the TRUs are shown in Table VII. More gross α activity was stripped in ST1 than was in the analyzed organic from SC3. Both SC3-O and ST1-A were re-analyzed for alpha activity with minimal change in results. Large discrepancies in the activities of the individual actinides were not found between ST1-A and SC3-O; therefore, this discrepancy impacts only the D_α for the ST1 contact. The gross α material balance indicates that the SC3-O analysis is valid and the ST1-

A activity is high. The ST1-A sample may have been contaminated while conducting the test. Favorable actinide stripping distributions were achieved in all three strip contacts using 0.04 M HEDPA in 0.04 M HNO_3, with the majority of the activity being stripped from the TRUEX solvent in the first contact, ST1. The HEDPA/HNO_3 strip solution was chosen because of HEDPA's unique ability to concomitantly strip all the actinides (including uranium) from the TRUEX solvent without forming undesirable precipitates. There is no foreseen need to partition the individual actinides from ICPP wastes; therefore, gross actinide recovery is desirable. Several gross actinide stripping reagents were evaluated (ammonium oxalate, oxalic acid, ketomelonic acid, and tetrahydrofuran-tetracarboxylic acid) as an alternative to HEDPA using a spiked dissolved zirconium calcine simulant. These alternative stripping reagents were either unsuccessful in stripping all the actinides or formed precipitates when contacted with the scrubbed TRUEX solvent.

Table VII
Aqueous Activities And Distribution Coefficients Resulting
From Strip And Wash Contacts

Element	Units	ST1-A	D_{ST1}	ST2-A	D_{ST2}	ST3-A	D_{ST3}	W1-A	D_{W1}
Cr	M	<9.6E-4	ND	<9.6E-4	ND	<9.6E-4	ND	<9.6E-4	ND
Fe	M	<3.2E-4	ND	<3.2E-4	ND	<3.2E-4	ND	<3.2E-4	ND
Zr	M	8.60E-3	<1	<1.3E-3	<1	<1.3E-3	<1	<1.3E-3	<1
Tc-99	dps/mL	7.79E+2	1.2E+0	2.25E+2	2.7E+0	1.55E+2	3.3E+0	No data	ND
Gross α	dps/mL	8.15E+4*	2.7E-2	2.05E+3	8.3E-2	1.60E+2	6.3E-2	1.21E+1	<<1
Am-241	dps/mL	2.08E+3	5.5E-2	8.07E+1	4.3E-1	3.42E+1	2.9E-3	1.22E-1	<<1
Np-237	dps/mL	<1.42E+2	ND	<1.83E+1	ND	<1.73E+1	ND	<2.04E-2	ND
Pu-238	dps/mL	8.95E+4	<<1	1.43E+3	<<1	1.90E+2	<<1	2.33E+0	<<1
Pu-239	dps/mL	3.40E+3	<<1	8.19E+1	<<1	1.93E+1	<<1	1.24E-1	<<1

ND = Not Determined

* Value determined by subtracting the sum of the ST2-A, ST3-A, and W1-A activites from the SC3-O activity. Actual analyically determined gross α activity for ST1-A = 1.26E+5 dps/mL.

Neither interfacial crud nor precipitation problems were observed in any of the strip contacts. This was a concern because of the large mass of zirconium that was extracted from the dissolved calcine feed solution. Even though zirconium scrub distribution coefficients were better than expected, large amounts of zirconium were stripped from the TRUEX solvent in the first strip contact. The strip solution, ST1-A, was found to contain 0.785 g/L Zr and 1.64E-6 g/L of the TRU elements. Based on mass, there is approximately 500,000 times more mass of zirconium in the strip solution than TRUs. It is not known if this amount of zirconium in the HLW stream will impact the final HLW glass or glass-ceramic waste volume to an unacceptable level. The impact of zirconium on the HLW volume is beyond the scope of this work,

HEDPA did not effectively strip Tc-99 from the solvent. In fact, D_{Tc} appear to increase from ST1 to ST3. Unfortunately, there was not enough sample from W1 to analyze for Tc-99; therefore, it is not known if carbonate stripped the remaining technetium from the TRUEX solvent.

GTM RESULTS

The extraction, scrub, and strip distribution coefficients determined during this test were used to evaluate the experimental flowsheet under counter-current conditions with the Generic TRUEX Model (GTM). The TRUEX flowsheet developed for ICPP sodium-bearing waste [21], consisting of five extraction stages (O/A = 1/3), four scrub stages (O/A = 3), and five strip stages (O/A = 1), was initially used to model this flowsheet. GTM results show that 67% of the zirconium in the feed will report to the actinide strip product stream (HLW fraction). The GTM also shows that an Am-241 activity of 34 nCi/mL will be present in the aqueous raffinate stream. The zirconium concentration in the strip product may impact the final HLW glass or glass-ceramic volume to an unacceptable level and the Am-241 activity in the raffinate may preclude the classification of this stream as a Class A low-level waste.

The GTM results were verified by performing a counter-current lab scale test using a dissolved zirconium calcine feed simulant spiked with Zr-95 and Am-241. The feed simulant was similar to the actual ICPP dissolved zirconium calcine feed. Six stages of extraction (O/A = 1/3) and four stages of scrub (O/A = 3) were performed in the lab-scale counter-current test. Six extraction and scrub cycles were performed to ensure steady state conditions were approached. Americium distributions from the sixth cycle of the lab-scale counter-current test are $D_{Am} = 2.9$ in the final (sixth) extraction stage and $D_{Am} = 2.0$ in final (fourth) scrub stage. These distributions agree extremely well with those obtained in the actual ICPP dissolved calcine test (extraction $D_{Am} = 2.4$ and scrub $D_{Am} = 1.9$).

An extraction $D_{Zr} = 0.66$ was obtained in the final (sixth) extraction contact of the sixth cycle, while a $D_{Zr} = 0.87$ was obtained in the final scrub contact of the same cycle. The extraction D_{Zr} is lower than that determined in the actual ICPP dissolved calcine test, but is explainable by comparing the F/(Al + Zr) ratio in the actual and simulated wastes. A F/(Al + Zr) molar ratio of 1.4 was determined in the waste simulant; as already mentioned, a F/(Al + Zr) molar ratio of 0.81 was determined for the actual ICPP dissolved calcine waste. The larger ratio in the simulant would increase the extent of zirconium complexing by fluoride; thus resulting in a reduced extraction D_{Zr}.

No chemical/physical problems, such as third phase formation, precipitation, or interfacial crud were observed during the lab-scale counter-current test. However, when the scrubbed solvent from the fourth scrub stage of the sixth cycle was contacted with an equal volume of 0.04 M HEDPA in 0.04 M HNO_3, a precipitate was observed. This precipitate is believed to be zirconium phosphate.

A series of extraction and scrub flowrates were evaluated by the GTM, again using TRU, Zr, Fe, and Cr distributions obtained from the test using actual ICPP dissolved zirconium calcine, in order to determine the process parameters necessary to achieve <10 nCi/g in the aqueous raffinate. The results from the GTM are shown in Table VIII.

From Table VIII, Run 7 {8 extraction stages (O/A=0.75), four scrub stages (O/A=3), and five strip stages(O/A=1)} is the most appealing because the O/A ratio in the extraction section is minimized while still obtaining an acceptable Am-241 decontamination factor. The projected Am-241 activity of 0.45 nCi/g is well below the Class A limit of 10 nCi/g. This conservative value is deemed necessary since the aqueous non-TRU raffinate will be evaporated and immobilized into a final low-level waste form, resulting in concentration of the TRUs. Significant amounts of zirconium will report to the aqueous strip product regardless of the process conditions (Table VIII). The zirconium phosphate precipitate, observed in the lab-scale counter-current test when the scrubbed solvent was contacted with the 0.04 M HEDPA in 0.04 M HNO_3 solution, will most likely occur with the conditions described in Run 7. However, an extra stripping section using 0.02 M HNO_3 to concomitantly strip Am-241 and Zr prior to the HEDPA strip will potentially alleviate this precipitate. Incorporating a 0.02 M HNO_3 Am/Zr strip may also increase the likelihood of finding an alternative strip reagent to HEDPA. The precipitates observed when using other stripping reagents have been determined to be insoluble zirconium complexes. Removing the zirconium from the solvent prior to stripping with an HEDPA alternative decreases the possibility of precipitation.

The GTM results show that a flowsheet can be developed to reduce the concentration of TRUs in the ICPP dissolved zirconium calcine to below the 10 nCi/g Class A limit. Unfortunately, potentially all of the zirconium in the dissolved calcine feed will report to the aqueous strip product. This zirconium may impact the final HLW volume (glass or glass-ceramic) to such an extent that its recovery with the TRUs must be prohibited by either preventing its extraction (masking) or selectively scrubbing it from the solvent prior to TRU stripping.

Table VIII
GTM Results

	8 Extraction Stages, 4 Scrub Stages, And 5 Strip Stages				
Run #	Extraction O/A	Scrub O/A	Strip O/A	% Feed Zr Reporting To Strip Product	Am-241 Activity In Aqueous Raffinate (nCi/g)
1	0.33	3.0	1.0	70	29.2
2	0.5	3.0	1.0	94	5.87
3	0.5	1.5	1.0	82	5.66
4	0.5	1.25	1.0	72	5.50
5	0.65	3.0	1.0	98	1.21
6	0.65	1.5	1.0	96	1.07
7	0.75	3.0	1.0	99	0.45
8	0.75	1.5	1.0	98	0.36
9	1.0	3.0	1.0	100	0.05
10	1.0	1.5	1.0	100	0.03
	5 Extraction Stages, 4 Scrub Stages, And 5 Strip Stages				
11*	0.33	3.0	1.0	67	33.9
12	0.75	3.0	1.0	97	2.63
13	0.75	1.5	1.0	91	2.13
14	1.0	3.0	1.0	98	0.70
15	1.0	1.5	1.0	97	0.43
16	1.5	3.0	1.0	99	0.09

* Conditions described above

CONCLUSIONS

The TRUEX solvent was evaluated to partition the TRUs from an actual ICPP dissolved calcine acidic feed solution that was high in zirconium. A series of extraction, scrub, strip, and wash batch contacts were performed without the occurrence of third phase, interfacial crud, nor precipitation problems. Favorable actinide decontamination factors were also achieved when an aliquot of the dissolved calcine feed was contacted three times with the TRUEX solvent (fresh solvent being used for each contact). Over 99.99% of the gross α activity was removed from the feed in these three extraction contacts. Unfortunately, over 98% of the zirconium in the feed was also extracted in these three contacts.

Scrub contacts performed on loaded TRUEX solvent indicate favorable Zr distribution coefficients ($D_{Zr} < 1$) were achieved on the second and third batch contacts. Approximately 90% of the extracted zirconium was scrubbed from the TRUEX solvent after three contacts with 0.075 $\underline{M}$ HNO_3. Distribution coefficients for the TRUs were greater than 1 in these scrub contacts.

Extraction and scrub results indicate that Tc-99 will quantitatively extract into the TRUEX solvent and not be scrubbed out with 0.075 $\underline{M}$ HNO_3. Even though these results are extremely favorable, the urge to embrace them must be resisted until further data is obtained to confirm the Tc-99 distribution coefficients.

Modelling results with the GTM indicate approximately 99% of the zirconium will report to the HLW fraction {eight extraction stages (O/A=0.75, four scrub stages (O/A = 3), and five strip stages (O/A = 1)}. Gross α activity in the aqueous raffinate is predicted by the GTM to be 0.45 nCi/g (Am-241 being the major contributor to the aqueous raffinate activity). This is well below the non-TRU Class A limit of 10 nCi/g.

Results from the test with actual ICPP zirconium calcine, and the subsequent GTM evaluation, indicates zirconium extraction significantly suppresses the extraction of americium and that a significant quantity of zirconium will report to the HLW fraction. Preventing zirconium extraction into the TRUEX solvent and/or selectively scrubbing it from the TRUEX solvent would optimize a TRUEX flowsheet for the zirconium calcine feeds.

RECOMMENDATIONS

1. Determine the impact of zirconium on the final HLW glass or glass-ceramic waste volume.

2. Evaluate selective scrubbing of zirconium from the TRUEX solvent to prevent zirconium recovery with the TRUs.

3. Evaluate possible Zr masking agents to prevent the extraction of zirconium into the TRUEX solvent. This may prove difficult to do without forming a precipitate in the feed; but if successful it may not only reduce the amount of zirconium extracted but can also result in increased Am-241 extraction.

4. Evaluate zirconium extraction from zirconium calcine dissolved with less concentrated nitric acid.

5. Evaluate zirconium masking in the aqueous strip product followed by re-contacting the complexed zirconium in the strip product with the TRUEX solvent. Masking the zirconium in the strip product may be less complicated than masking it in the original feed.

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APPENDIX: MATERIAL BALANCE CALCULATIONS

Material Balance Calculations For E1 And E2 Contacts

Element	In	Out	MB
Cr (M)	5.20E-3	5.11E-3	98.3
Fe (M)	2.00E-2	2.11E-3	106
Zr (M)	1.32E-1	1.18E-1	89.7
Tc-99 (dps/mL)	9.75E+2	9.39E+2†	100
Gross α (dps/mL)	1.05E+5	1.22E+5	116
Am-241 (dps/mL)	9.04E+3	9.37E+3	104
Np-237 (dps/mL)	43.4E+1	4.34E+1†	100
Pu-238 (dps/mL)	9.80E+4	9.65E+4	98.5
Pu-239 (dps/mL)	3.68E+3	3.58E+3	97.3

In = Feed Concentration x 2
Out = E1-A + E2-A + E2-O
MB = Out/In x 100
† E2-O concentration determined by Material Balance

Material Balance Calculations For E1, E3 And E4 Contacts

Element	In	Out	MB
Cr (M)	2.60E-3	2.58E-3	99.2
Fe (M)	1.00E-2	1.01E-3	101
Zr (M)	6.60E-2	6.44E-2*	97.6
Tc-99 (dps/mL)	9.75E+2	9.75E+2[1]	100
Gross α (dps/mL)	5.25E+4	5.24E+4	99.8
Am-241 (dps/mL)	4.52E+3	3.78E+3	83.6
Np-237 (dps/mL)	21.7E+1	21.7E+1[2]	100
Pu-238 (dps/mL)	4.90E+4	4.88E+4	99.6
Pu-239 (dps/mL)	1.84E+3	1.83E+3	99.6

In = Feed Concentration
Out = (Feed-E1-A) + E3-O + E4-O + E4-A
MB = Out/In x 100

* E3-A value used to close Material Balance (E4-A and E4-O are less than values)

[1] E3-O and E4-O concentration determined by Material Balance

[2] Out = (Feed - E1-A) + E1-A

Material Balance Calculations For SC1, SC2, And SC3 Contacts

Element	In	Out	MB
Cr (M)	ND	ND	NA
Fe (M)	2.33E-3	1.14E-1	4.89E+3
Zr (M)	7.54E-2	8.44E-2	112
Tc-99 (dps/mL)	1.89E+3[1]	1.89E+3[2]	100
Gross α (dps/mL)	1.19E+5	1.16E+5	97.3
Am-241 (dps/mL)	5.73E+3	5.72E+3[3]	99.8
Np-237 (dps/mL)	ND	ND	NA
Pu-238 (dps/mL)	9.52E+4	1.40E+5	147
Pu-239 (dps/mL)	3.50E+3	5.41E+3	155

In = E2-O Concentration
Out = SC1-A + SC2-A + SC3-A + SC3-O
MB = Out/In x 100
ND = None Detected
NA = Not Applicable
1. E2-O concentration determined by Material Balance
2. SC3-O concentration determined by Material Balance
3. SC3-O = ST1-A + ST2-A + ST3-A + W1-A
3. SC3-A = E2-O - (SC3-O + SC2-A + SC1-A)

Material Balance Calculations For ST1, ST2, ST3 And W1 Contacts

Element	In	Out	MB
Cr (<u>M</u>)	ND	ND	NA
Fe (<u>M</u>)	ND	ND	NA
Zr (<u>M</u>)	ND	8.6E-3	NA
Tc-99 (dps/mL)	1.70E+3[1]	1.70E+3[2]	100
Gross α (dps/mL)	8.38E+4	8.38E+4[3]	100
Am-241 (dps/mL)	2.19E+3[4]	2.19E+3	100
Np-237 (dps/mL)	ND	ND	NA
Pu-238 (dps/mL)	8.73E+4	9.11E+4	104
Pu-239 (dps/mL)	3.08E+3	3.50E+3	114

In = SC3-O
Out = ST1-A + ST2-A + ST3-A + W1-A
MB = Out/In x 100
1. SC3-O concentration determined by Material Balance
2. Out = SC3-O - (ST1-A + ST2-A + ST3-A)
3. ST1-A = SC3-O - (ST2-A + ST3-A + W1-A)
4. SC3-O = ST1-A + ST2-A + ST3-A + W1-A