TRUEX PROCESS APPLIED TO RADIOACTIVE IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINE

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ABSTRACT

Equal volume batch contact experiments were performed with dissolved, radioactive high-level waste (HLW) calcine and the TRansUranic EXtraction (TRUEX) process solvent. Extraction, scrub, and strip distribution coefficients (D) were obtained for the transuranic (TRU) elements in order to evaluate the efficiency of the TRUEX process in treating this waste. The extraction, scrub, and strip behavior of other elements, such as chromium, zirconium, and technetium, was also observed. A TRU alpha decontamination factor of >10,000 was achieved; after three extraction batch contacts TRU alpha activity was reduced from 1,420 nCi/g to 0.02 nCi/g. Dilute nitric acid was used to scrub extracted acid, zirconium, and iron from the solvent prior to stripping. Dilute 1-hydroxyethane, 1-1, diphosphonic acid (HEDPA) was used as a gross TRU stripping reagent to recover the extracted TRUs. Data from these batch contact experiments were used to develop a counter-current flowsheet for TRU removal using the Generic TRUEX Model (GTM). Process improvements and optimizations of the flowsheet have been evaluated using a non-radioactive dissolved calcine simulant spiked with tracers to obtain additional distribution coefficient data. These data were used in the GTM to refine the flowsheet. The flowsheet was then evaluated using a counter-current 5.5 cm centrifugal contactor pilot plant with a non-radioactive dissolved calcine simulant. The experiments involving radioactive waste provided crucial data for developing a baseline TRUEX process flowsheet which can effectively separate TRU components from ICPP high-level waste.

I. INTRODUCTION

Idaho Chemical Processing Plant (ICPP) high-level waste calcine was generated by the solidification of aqueous spent nuclear fuel reprocessing raffinates at 500 °C in a fluidized bed. There is currently about 3800 m^3 of calcine stored at the ICPP.[1] ICPP calcine can be generally characterized as either aluminum type calcine (generated from aluminum clad fuel) or zirconium type calcine (generated from zirconium clad fuel). Both calcine types contain < 1 wt% of TRU and fission products, primarily due to total fuel element dissolution during reprocessing. The remainder of the calcine composition consists of non-radioactive salts and metal oxides.[2]

A Department of Energy Environmental Impact Statement Record of Decision issued June 1, 1995, selected radionuclide partitioning as the preferred method for radioactive liquid and calcine waste treatment. Separation technologies for radionuclide partitioning are to be evaluated and tested for potential implementation in a future treatment facility. Separated radionuclides would be consolidated, as a high-activity fraction, and immobilized via vitrification. The remaining components are anticipated to be immobilized as a grout and disposed of as a non-TRU low-level waste. A significant HLW glass volume reduction may be achieved by TRU and fission product separation processes. Prior to TRU and

fission product separations, the calcine must first be dissolved in hot (90 °C) 5 M HNO_3 at a calcine weight to acid ratio of 1 kg/10 L while being continuously and aggressively mixed. Typically, >98 wt% of the calcine is dissolved under these conditions.[3] The resulting undissolved solids (UDS) are approximately an order of magnitude higher in TRU activity than the original calcine and are expected to be vitrified with the high-activity fraction.[4] Experimental dissolution data from radioactive zirconium calcine indicates that the build-up of a UDS heel is not likely.[5] Approximately 3000 m^3 of the calcine at the ICPP can be characterized as zirconium type calcine. Zirconium calcines average 18.3 wt% ZrO_2 and are anticipated to be the most challenging to treat with regard to TRU removal because of the significant zirconium content.

The TRUEX Process, as developed by W.W. Schulz, E. P. Horwitz,[6] is being evaluated as a TRU separations process for ICPP high-level waste calcine. Zirconium has historically been problematic in TRU separations flowsheets because of it's tendency to follow the actinides. The extraction of zirconium into the TRUEX solvent can cause physical problems such as third phase formation, interfacial crud, or precipitations, and may extract to such an extent as to suppress actinide extraction. The recovery of zirconium with the actinides may also result in a significant increase in the final HLW glass volume. Three goals that must be met by the TRUEX process used to treat ICPP's zirconium type calcine are: 1) an aqueous raffinate TRU concentration below the 10 nCi/g limit specified in 10 CFR 61.55, 2) minimize the secondary waste volumes, and 3) minimize the final HLW glass volume by reducing inert elements in the high-activity fraction. This paper documents the initial development of a TRUEX process flowsheet for treating ICPP zirconium calcine that satisfies these three goals. Equal volume batch contact experiments with dissolved radioactive calcine were performed to obtain distribution coefficients for baseline flowsheet development using the Generic TRUEX Model (GTM). The high- and low-activity stream compositions predicted by the GTM were used in turn to evaluate the TRU activity in the low-activity fraction and to calculate the impact of inert components in the high-activity fraction on the final HLW glass volume. Iteration between batch contact experiments with a dissolved calcine simulant to obtain distribution coefficient data and GTM predictions was performed until a TRUEX process flowsheet that met the above stated goals was formulated. This flowsheet was tested in a counter-current 5.5 cm centrifugal contactor pilot plant with a dissolved calcine simulant. Each phase of the TRUEX process flowsheet development sequence will be discussed.

II. EXPERIMENTAL

Equal volume batch contacts using 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) and dissolved radioactive zirconium calcine were performed to obtain TRU, Zr, and Tc extraction, scrub and strip distribution coefficients. TRU decontamination factors were determined by contacting an aliquot of the dissolved calcine feed three times with the TRUEX solvent, with fresh solvent being used for each contact. The experimental technique shown in Figure 1 was chosen based on tests performed with radioactive ICPP sodium-bearing waste,[7] as well as laboratory batch contact tests performed with a dissolved zirconium calcine simulant, and used for testing the dissolved radioactive zirconium calcine. Composition of the dissolved calcine feed is shown in Table 1.

Dilute nitric acid (0.075 M HNO_3) was chosen as a potential scrub reagent to remove extracted zirconium from the solvent, while minimizing actinide recycle back to the extraction section. Dilute 1-hydroxyethane-1,1-diphosphonic acid (0.04 M HEDPA) was used as the strip reagent because of it's ability to simultaneously recover all the actinides. A gross actinide strip reagent, such as HEDPA, is desirable for flowsheet simplification.

III. RESULTS AND DISCUSSION

A. Radioactive Calcine Batch Contact Test

Results from the test shown in Figure 1 indicate that >99.99% of the TRU alpha activity was removed from the acidic feed after three contacts (E1, E3, and E4). Distribution coefficients for the actinides and other elements of interest obtained in contacts E1, E3, and E4 are shown in Table 2, which also shows the overall decontamination factors (DF) achieved for these elements in the extraction contacts. The resulting aqueous raffinate solution contained an approximate TRU alpha activity of 0.02 nCi/g, which is well below the limit of 10 nCi/g specified in 10 CFR 61.55 for LLW.

Distribution coefficients obtained from the extraction, scrub, and strip contacts are shown in Table 3. Favorable scrub and strip distribution coefficients were also observed for Am and Pu, indicating the feasibility of recovering these isotopes from the TRUEX solvent with 0.04 M HEDPA in 0.04 M HNO_3. 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 were extracted from the dissolved calcine feed into the TRUEX

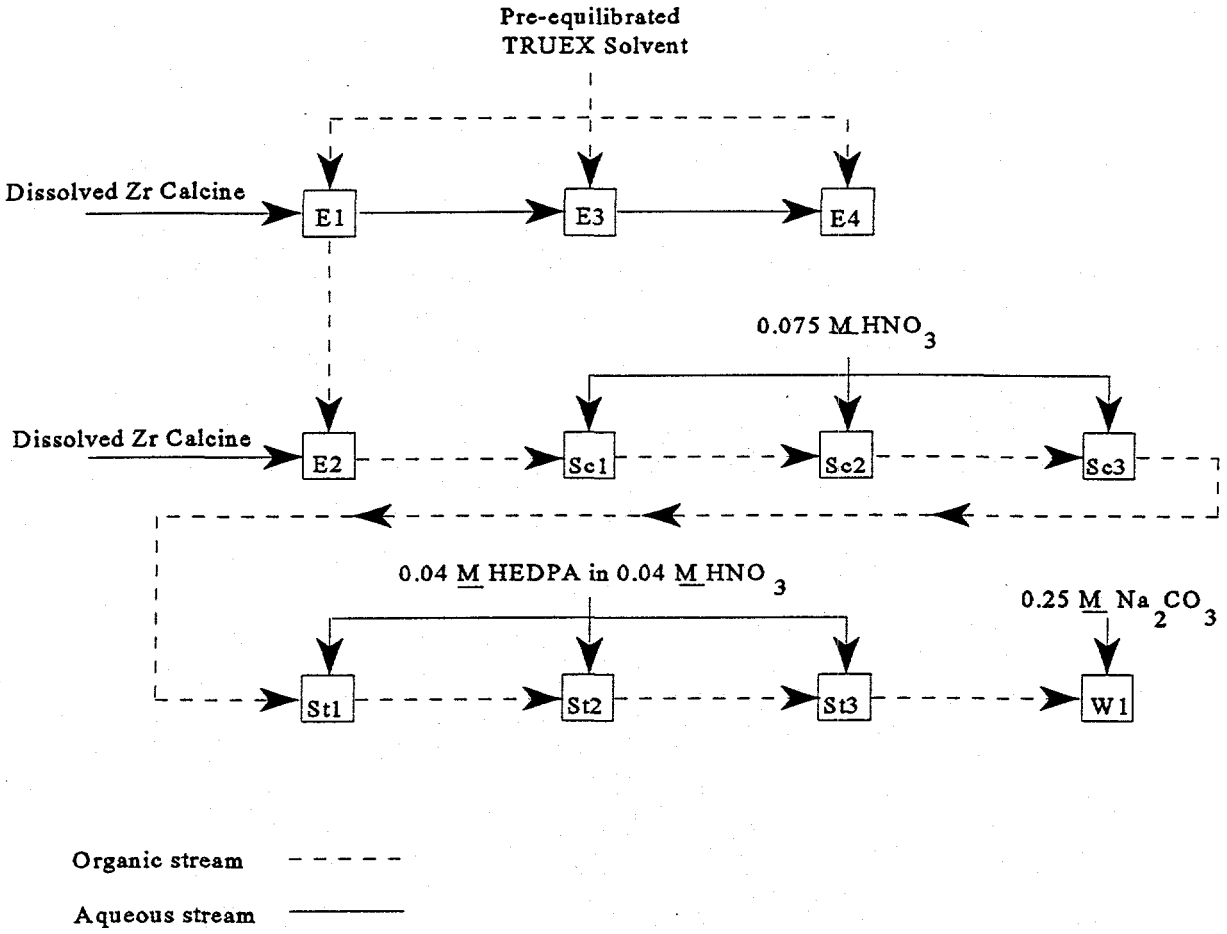

Figure 1: Experimental Method used to Evaluate the TRUEX Solvent on Actual ICPP Dissolved Zirconium Calcine

Table 1: Dissolved Radioactive Calcine Feed Composition

Constituent	M	Radionuclides	d/s/mL
H^+	2.58	Cs-137	8.48E+6
NO_3^-	4.33	Sr-90	1.07E+7
Ca	0.72	Gross α	5.25E+4
Al	0.57	Am-241	4.61E+3
Cr	2.60E-3	Pu-238	4.83E+4
F	0.64	Pu-239	1.86E+3
Fe	0.01	Np-237	20.1
Na	0.2	U	2.69E-3 g/L
Zr	0.066		

Table 2: Extraction Distribution Coefficients and Decontamination Factors Achieved with Radioactive ICPP Dissolved Zirconium Calcine and the TRUEX Solvent

Contact	D_{Cr}	D_{Fe}	D_{Zr}	D_{Tc}	D_{Am}	D_{Np}	D_{Pu}	D_{α}
E1	<< 1	3.7E-1	4.6E+0	2.6E+1	2.6E+0	6.2E+0	1.1E+2	1.3E+2
E3	<< 1	1.4E+0	4.2E+0	2.9E+0	2.6E+1	NA	1.2E+2	3.1E+2
E4	<< 1	1.3E+0	NA	7.1E-1	8.0E+0	NA	1.5E+0	NA
DF	<< 1	7.4	>4.8E+1	1.8E+2	2.0E+2	>7.2E+0	>2.9E+4	>4.4E+4

NA = No activity or no value obtained

Table 3: Extraction, Scrub, and Strip Distribution Coefficients Achieved with Radioactive ICPP Dissolved Zirconium Calcine and the TRUEX Solvent

Contact	D_{Cr}	D_{Fe}	D_{Zr}	D_{Tc}	D_{Am}	D_{Np}	D_{Pu}	D_{α}
E1	<<1	3.7E-1	4.6E+0	2.6E+1	2.6E+0	6.2E+0	1.1E+2	1.3E+2
E2	<<1	2.0E-1	2.4E+0	7.0E+1	2.4E+0	7.4E+0	1.1E+2	5.2E+1
Sc1	NA	1.7E-1	1.8E+0	2.4E+1	2.0E+0	NA	1.3E+1	1.1E+1
Sc2	NA	<1	9.7E-1	6.0E+1	2.0E+0	NA	1.2E+1	1.0E+1
Sc3	NA	<1	1.9E-1	2.2E+1	6.6E+0	NA	2.2E+0	7.0E+0
St1	NA	NA	<1	1.2E+0	5.5E-2	NA	<<1	2.7E-2
St2	NA	NA	<1	2.7E+0	4.3E-1	NA	<<1	8.3E-2
St3	NA	NA	<1	3.5E+0	2.9E-3	NA	<<1	6.3E-2

NA= No activity or no value obtained

solvent. However, >90% of these elements were scrubbed from the solvent using 0.075 M HNO_3, without observing actinide loss.

B. GTM and HLW Volume Evaluation of Proposed Flowsheet

TRU, Zr, Fe, and Cr extraction, scrub, and strip distribution coefficients obtained from the test with radioactive ICPP dissolved zirconium calcine were used in the GTM to evaluate the behavior of these elements under simulated counter-current conditions. Results of the GTM simulation, assuming eight extraction stages (O/A=0.75), four scrub stages (O/A=3), and five strip stages (O/A=1), indicate that the TRU activity in the low-activity fraction (aqueous raffinate) will be approximately 0.45 nCi/g with americium being the major contributor to this activity. The GTM also predicts that 99% of the zirconium in the ICPP dissolved zirconium calcine will report to the high-activity fraction (strip product). The mass of zirconium predicted by the GTM to report to the high-activity fraction in the proposed flowsheet warranted an evaluation of zirconium impact on the final glass volume. Phosphate impact, from the HEDPA strip solution, was also evaluated.

Several assumptions were made with regard to calcine composition, process considerations, and glass formulation to determine the impact of zirconium and phosphate on the final HLW glass volume. Elemental zirconium and phosphorus loadings into the glass were assumed to be 7 wt%, and 1 wt%, respectively. Zirconium and phosphate contributions to the glass volume are not additive.

Zirconium extraction and recovery in the TRUEX flowsheet would result in the production of 1 m^3 of HLW glass for every 1 m^3 of zirconium calcine processed. UDS, resulting from the dissolution of zirconium calcine, also contain zirconium. Zirconium in the UDS is expected to contribute 0.045 m^3 to the final HLW glass volume for every 1 m^3 zirconium calcine processed (assuming 98 wt%

calcine dissolution and a 2 wt% heel build-up). The glass volume from the UDS contribution is anticipated to be the minimum achievable glass volume resulting from the treatment of zirconium calcine. Phosphate from the 0.04 M HEDPA strip solution would result in the production of 0.57 m^3 of HLW glass for every 1 m^3 of zirconium calcine processed.

This same 1 m^3 of zirconium calcine would produce approximately 2 m^3 of HLW glass if no separations processing were performed (assuming 30 wt% calcine loading into the glass). These calculations indicate that: 1) the HLW glass volume is driven by both zirconium and phosphate in the high-activity fraction and, 2) both zirconium and phosphate concentrations in the high-activity fraction must be reduced/eliminated to significantly reduce the final glass volume resulting from the separations process. Table 4 summarizes the contribution of Zr and P to the final waste form volume.

Table 4: Estimated Effects on HLW Glass Volumes from Processing 1 m^3 of Zirconium Calcine

Component	Actual Waste (Baseline) m^3	GTM m^3	Simulant Test m^3
UDS	0.045	0.045	0.045
Zr (TRUEX)	1	0.01	0.35
P (HEDPA)	0.57	0.015	0.015
Radionuclides[1]	0.01	0.01	0.01
Total[2]	1.045	0.055	0.40

1. 1 wt% dry oxide combined TRU/fission product waste loading
2. Zr and P contributions not additive

C. Flowsheet Refinements

Minimizing zirconium and phosphate concentrations in the high-activity fraction was evaluated by performing batch contact tests with the TRUEX solvent and a dissolved zirconium calcine simulant spiked with single isotopes of the actinides or Zr-95.

Scrubbing zirconium with 0.1 M NH_4F in 1.0 M HNO_3 was found to efficiently remove the extracted zirconium from the TRUEX solvent while also minimizing actinide recycle back to the extraction section. Batch contact tests also confirm that efficient actinide stripping can be accomplished with 0.001 M HEDPA.

Actinide and zirconium distribution coefficients obtained from the batch contacts were used in the GTM to model the refined counter-current flowsheet with these scrub and strip solutions. The proposed flowsheet included 8 extraction stages (O/A = 1), 4 scrub stages (O/A = 3) and 4 strip stages (O/A = 1). GTM results are shown in Figure 2. The GTM predicts a gross α activity in the aqueous raffinate of 0.64 nCi/g, which is well below the 10 nCi/g non-TRU waste limit and a Zr concentration of 0.0016 M in the high-activity fraction. GTM results showed that approximately 1 wt% of the zirconium in the feed will report to the high-activity fraction; thus reducing zirconium's contribution to the HLW glass volume from 1 m^3 to 0.01 m^3 (Table 4). This indicates the UDS are the primary zirconium contributor to the glass volume, not the zirconium from the TRUEX process when using 0.1 M NH_4F in 1.0 M HNO_3 as the scrub.

Reducing the HEDPA strip concentration from 0.04 M to 0.001 M would reduce the phosphate contribution to the HLW glass volume from 0.57 m^3 to approximately 0.015 m^3 per m^3 of calcine processed. This modification is expected to eliminate the phosphate contribution to the overall glass volume generated from the treatment of zirconium calcine because the phosphate contribution is less than that of zirconium in the UDS (0.015 m^3 as opposed to 0.045 m^3).

D. Counter-Current Flowsheet Testing

The refined flowsheet was tested in the 5.5 cm centrifugal contactor mockup. Results from this test are shown in Figure 3. Non-radioactive neodymium was used as an Am surrogate in the contactor test, and was spiked into the dissolved zirconium calcine to a concentration of 4.17E-3 M. This concentration was necessary to ensure Nd concentrations were analytically detectable. Americium is expected to be the primary alpha contributor to the low-activity fraction, therefore, if >99.9% of the Am activity is removed, the remaining TRU activity should be negligible.

No flooding problems were encountered during the contactor tests, indicating successful hydraulic performance of the TRUEX solvent. Precipitations and interfacial crud formations were not observed at any contactor stage. Figure 3 shows that approximately 95% of the neodymium was removed from the simulated zirconium calcine feed and approximately 33% of the zirconium reported to the high-activity fraction, which is approximately an order of magnitude more than that predicted by the GTM. The poor Nd removal may have resulted from the combination of zirconium extraction and large neodymium mass in the simulant. Zirconium extraction may have extensively

consumed the CMPO leaving very little "free" CMPO for Nd extraction. Poor Am extraction has not been observed at any juncture in the development process, indicating that americium behavior will be difficult to predict in tests using neodymium (or europium) spiked simulant.

The zirconium concentration in the high-activity fraction was larger than expected but does indicate the viability of selectively scrubbing zirconium from the solvent. The zirconium concentration in the high-activity fraction shown in Figure 3 indicates zirconium from the TRUEX process would be the primary contributor to the final waste form volume (Table 4: 0.35 m^3 of HLW glass per m^3 of calcine processed).

Selectively scrubbing zirconium could be more efficient by optimizing both the fluoride and acid concentrations in the scrub solutions. Minimizing actinide recycle while maximizing zirconium removal would certainly enhance the TRUEX process. Several other options are available for evaluating the reduction of zirconium in the HLW form.

IV. CONCLUSIONS

Results from tests conducted with dissolved radioactive zirconium calcine and subsequent GTM analysis has lead the development of a baseline TRUEX flowsheet for treating ICPP zirconium calcine. A TRUEX flowsheet having 8 extraction stages (O/A = 1), 4 stages of 0.1 M NH_4F in 1.0 M HNO_3 scrub (O/A = 3), and 4 stages of 0.001 M HEDPA in 0.04 M HNO_3 (O/A = 1) to treat dissolved zirconium calcine should result in < 10 nCi/g TRU activity in the aqueous raffinate, and minimize the inert elements in the high-activity fraction. The GTM and subsequent 5.5 cm centrifugal contactor test results show that using 0.1 M NH_4F in 1.0 M HNO_3 to scrub extracted zirconium and using 0.001 M HEDPA to recover the actinides could result in a zirconium calcine HLW glass volume reduction factor between 5 and 36, as opposed to a volume reduction of 2 with the baseline flowsheet. The new baseline flowsheet indicates a significant decrease in the HLW glass volume as compared to that of the original flowsheet, and is recommended for further testing at the ICPP. Optimization of the scrub acid and fluoride concentrations, as well as evaluating the head-end calcine dissolution process, may result in a TRUEX flowsheet capable of achieving a waste reduction factor of 45 (UDS contribution only). Further flowsheet improvements are expected to be tested in 2 cm centrifugal contactors using dissolved radioactive zirconium calcine.

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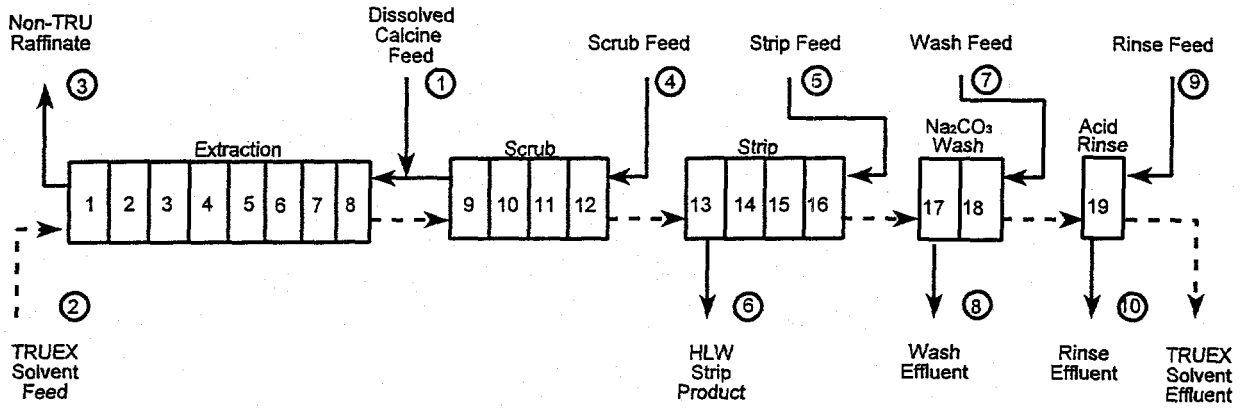
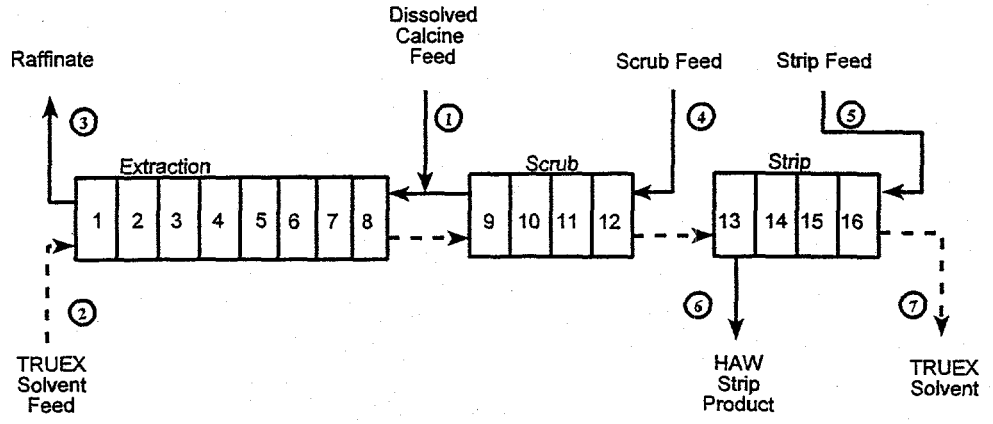


Comp.	Dissolved Calcine Feed 1	TRUEX Solvent Feed 2	Non-TRU Raff. 3	Scrub Feed 4	Strip Feed 5	Strip Product 6	Wash Feed 7	Wash Effluent 8	Rinse Feed 9	Rinse Effluent 10
HNO_3 (M)	3.5		2.9	1.0	0.04				0.10	0.10
HEDPA (M)					0.001	0.001				
NH_4F (M)				0.10						
Na_2CO_3 (M)							0.25	0.25		
Zr (M)	0.21		0.16			0.0016				
Am (nCi/g)	104		0.64			124				
Pu (nCi/g)	1100		1.50E-04			1319		4.3		
U (nCi/g)	0.50		7.27E-08			0.60		0.012		
Np (nCi/g)	0.50		4.70E-07			0.60				
Tc (Ci/m^3)	0.06		0.004			0.0097		0.14		
Relative Flow	1.00	1.00	1.33	0.33	1.00	1.00	0.33	0.33	0.20	0.20

Figure 2. TRUEX Flowsheet Developed Using the Generic TRUEX Model



Component	Dissolved Calcine Feed 1	TRUEX Solvent Feed 2	Non-TRU Raff. 3	Scrub Feed 4	Strip Feed 5	Strip Product 6	TRUEX Solvent 7
HNO_3 M	3.51		2.60	1.00	0.01	0.64	0.02
HEDPA M					0.001	0.001	
NH_4F M				0.1			
Nd M	4.17E-03		1.39E-04			1.44E-03	1.94E-03
Fe M	0.014		9.29E-03			5.37E-04	1.56E-05
Zr M	0.20		0.093			0.067	3.29E-03
Flow (Lpm)	0.40	0.44	0.56	0.16	0.41	0.41	0.44

Figure 3. 5.5 cm Centrifugal Contactor Results