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COUNTERCURRENT FLOWSHEET TESTING OF THE
TRUEX PROCESS WITH ICPP CALCINE

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ABSTRACT

Calcine was generated at the Idaho Chemical Processing Plant over several decades as a method of solidifying numerous raffinates and wastes from spent nuclear fuel reprocessing for convenient interim storage. Unfortunately, the bulk of the calcine is inert, with radionuclides comprising less than 1 weight percent of the total calcine mass. The bulk of the calcine currently stored at the ICPP was produced from wastes generated during reprocessing of zirconium clad fuels. Consequently, this material contains varying, but large quantities of zirconium oxide. Currently, separations options are being considered for acidic solutions of dissolved ICPP calcines to minimize high level waste volumes and economic penalties perceived for final disposal of these wastes. The actinide separation process being emphasized for the dissolved calcine solutions is the TRUEX process. Substantial problems have been encountered during TRUEX flowsheet development efforts for dissolved zirconium calcine simulant due to the high concentrations and subsequent extraction of zirconium from the feed. Alteration of the calcine dissolution parameters has resulted in the development of a successful TRUEX/Zr calcine baseline flowsheet. This flowsheet has been tested using 22 stages of a 2.0 centimeter diameter centrifugal contactor pilot plant using simulated dissolved Zr calcine solution. With this flowsheet, a removal efficiency of >96.0% was obtained for ^{241}Am (analytical detection limits were reached). Less than 0.25% of the ^{95}Zr exited with the high-level waste strip product.

I. INTRODUCTION

The Transuranic Extraction (TRUEX) process, as developed by W. W. Schulz, E. P. Horwitz and coworkers at Argonne National Laboratory,^{1,2} is being evaluated as a transuranic (TRU) extraction process for Idaho Chemical Processing Plant (ICPP) wastes. Aqueous raffinates resulting from the TRU separation process will also be treated for fission product removal. The treated wastes resulting from the TRU and fission product separation processes are anticipated to be grouted and disposed as non-TRU low-level wastes (LLW). The resulting fractions containing the TRUs and fission products will be vitrified and disposed as high-level wastes (HLW).

HLW calcine is one of the ICPP wastes being evaluated for TRU removal by the TRUEX process. Calcine is generated by the solidification of aqueous fuel reprocessing raffinates at 500 °C in a fluidized bed. There is currently approximately 4,000 m³ of calcine at the ICPP.³ ICPP calcine can be characterized as either aluminum type calcine (generated from aluminum fuel reprocessing raffinates) or zirconium type calcine (generated from zirconium fuel reprocessing raffinates). Both calcine types are <1 wt% in TRU and fission product content.⁴ Therefore, a significant HLW glass volume reduction may be achieved by TRU and fission product separation processes.

The calcine must first be dissolved in nitric acid prior to the removal of TRUs and fission products. The currently developed dissolution flowsheet calls for

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Figure 1. Flowsheet for the Testing of the TRUEX Process with Dissolved ICPP Calcine

dissolving the calcine in hot ($>90^{\circ}\text{C}$) 3.0 M HNO_3 at a calcine weight to acid volume ratio of $1\text{ kg}/10\text{ L}$, and the dissolution must occur under vigorous and constant mixing. Complete calcine dissolution is not accomplished; however, dissolution studies performed with actual zirconium (and aluminum) calcine indicate the volume of undissolved solids (UDS) remaining after dissolution will be small⁵ ($<2\text{ vol\%}$ of the total volume), and that these solids will require disposal with the HLW.⁶

Approximately $3,000\text{ m}^3$ of the calcine at the ICPP can be characterized as zirconium type calcine. Zirconium calcines average $18.3\text{ wt\% ZrO}_2$ and are anticipated to be the most challenging to treat with regards to TRU removal because of the large zirconium content. Zirconium has historically been problematic in TRU separation flowsheets because of its tendency to follow the actinides. The extraction of zirconium into the TRUEX solvent can cause physical phenomena to occur, such as third phase formation, interfacial crud, or precipitates. The recovery of zirconium with the TRUs may also result in a significant increase in the final HLW glass volume.

Phosphate is also present in the TRUEX high-activity fraction and comes from the use of 1-hydroxyethane 1,1-diphosphonic acid (HEDPA) as a gross actinide stripping reagent. Phosphate tends to inhibit homogeneous glass forms; therefore, most glasses can tolerate only small phosphate waste loading. 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.

Two goals that must be met by the TRUEX process used to treat ICPP zirconium calcine are: 1) an aqueous raffinate TRU concentration below the NRC Class A LLW limit of 10 nCi/g specified in $10\text{ CFR } 61.55$, and 2) minimizing the final HLW glass volume by reducing the inert elements in the HLW fraction. Extensive laboratory testing was performed in order to recommend a TRUEX flowsheet that would meet these two goals.⁷

This paper reports the results from TRUEX flowsheet testing performed with a dissolved calcine simulant in a 2-cm centrifugal contactor pilot plant. The centrifugal contactors are located in the Remote Analytical Laboratory hot cell at the ICPP, allowing easy and effective use of radioactive tracers in the test. The flowsheet evaluated in this experiment was recommended from laboratory tests and previous flowsheet testing.⁸

II. EXPERIMENTAL PROCEDURE

The dissolved calcine feed used in this test was prepared by dissolving pilot plant zirconium calcine under the baseline dissolution conditions of 10 L of 3 M HNO_3 per kg of calcine at near boiling temperature ($T \geq 90^{\circ}\text{C}$) for 60 minutes with constant, vigorous mechanical stirring. Since the pilot plant calcine contains the macro constituents, but no radioactive materials, it provides a representative simulant for the matrix components in actual zirconium calcines. To evaluate the fate of the actinides and zirconium in the proposed flowsheet, the dissolved calcine feed was spiked with ^{241}Am and ^{95}Zr

radioisotopes. Finally, the feed was reduced by the addition of micro quantities of hydrogen peroxide to reduce Cr from the extractable +6 oxidation state to the inextractable +3 state. The composition of the resulting dissolved calcine solution is given in Table 1.

Table 1. Composition of Dissolved Calcine Feed.

Component	Dissolved Calcine	Component	Dissolved Calcine
Acid (M)	1.27	F (M)	0.94
Al (M)	0.43	Na(M)	0.0091
B (M)	0.067	NO ₃ (M)	3.0
Ca (M)	0.65	Pb (M)	<1.9E-6
Ce (M)	3.2E-04	SO ₄ (M)	0.050
Cl (M)	<0.088	Zr (M)	0.13
Cr (M)	0.0048	²⁴¹ Am (dps/mL)	327
Fe (M)	0.010	⁹⁵ Zr (dps/mL)	204

The TRUEX flowsheet tested is shown in Figure 1. The flowsheet consisted of six stages of extraction at an O/A = 0.5, four stages of 0.1 M NH₄F in 0.7 M HNO₃ scrub at an O/A = 1, six stages of 0.04 M HEDPA strip at an O/A = 1, two stages of 0.25 M Na₂CO₃ wash at an O/A = 5, and two stages of 0.1 M HNO₃ rinse at an O/A = 10. Prior to performing this flowsheet testing, testing was performed using a similar flowsheet to the one shown in Figure 1.⁸ However, with the previous testing a scrub feed composition of 0.3 M NH₄F in 0.2 M HNO₃ at a flowrate of 7.5 mL/min was used. With this flowsheet test the solubility of CeF₃ was exceeded in the scrub section resulting in a Ce and Am precipitate forming in the scrub section. As a result of this previous testing, the flowsheet shown in Figure 1 was developed.

Flowsheet testing was performed as follows. The contactor rotors were started at 3,600 rpm. All aqueous feed flows were started except for the spiked simulated waste feed. A solution of 1.1 M HNO₃ was used as initial aqueous feed. When aqueous solution exited each of the sections, solvent feed flow was initiated. When solvent filled each of the contactor stages, spiked simulated waste feed was initiated. At intervals of 30, 60, 90, and 140 minutes after the start of spiked feed, samples of each of the effluent streams were taken. The contactors were then shutdown by simultaneously stopping the contactor motors and the feed pumps. With this type of shutdown the solution in each contactor stage remains approximately at steady state conditions. Individual

contactor stages were then drained, re-equilibrated, separated, and submitted for analysis so that distribution coefficients could be determined.

III. RESULTS AND DISCUSSION

A. Contactor Operation

Actual solution flowrates were calculated from feed tank depletion rates and are compared to the desired flowrates in Table 2. Flooding or third phase formation was not observed during testing. Also, precipitate formation was not observed during testing, specifically in the scrub section where previous flowsheet testing resulted in a CeF₃ precipitate.

B. Approach to Steady State

Samples of the aqueous raffinate and strip product streams were taken at intervals of 30, 60, 90, and 140 minutes after the start of spiked feed. The activity of

Table 2. Flowrates for TRUEX Flowsheet Testing.

Section	Phase	Flowrate (mL/min)	
		Desired	Actual
All	Org.	6.0	5.7
Extraction	Aq.	14.0	13.7
Scrub	Aq.	4.0	4.0
Strip	Aq.	6.0	5.7
Na ₂ CO ₃ Wash	Aq.	6.0	6.1
Acid Rinse	Aq.	1.0	1.1

Figure 2. ²⁴¹Am Approach to Steady State (Strip Product)

Figure 3. ^{95}Zr Approach to Steady State (Raffinate)

^{241}Am in the strip product and ^{95}Zr in the aqueous raffinate as a function of time is given in Figures 2 and 3. Steady state was reached within 90 minutes for ^{241}Am in the strip product and within 30 minutes for ^{95}Zr in the raffinate. The activities of ^{241}Am in the raffinate and ^{95}Zr in the strip product were below detection limits so the approach to steady state could not be evaluated for these conditions.

C. Concentrations at Shutdown

Results from the flowsheet test are shown in Tables 3 and 4. Table 3 lists the percentages of ^{241}Am and ^{95}Zr in each of the effluent streams and Table 4 lists the distribution coefficients for ^{241}Am , ^{95}Zr , and H^+ in several of the stages.

^{241}Am was effectively extracted and stripped from the TRUEX solvent. A removal efficiency of $>96.4\%$ was obtained. It should be noted that the analytical detection limit for ^{241}Am was reached after only two of the six extraction stages so the actual removal efficiency could not be determined. However, the distribution coefficient for ^{241}Am in the extraction section was 24.6. With this distribution coefficient for the six stages of extraction, a removal efficiency of $>99.99\%$ is anticipated. The scrub distribution coefficients for ^{241}Am ranged from 16 to 26 resulting in very little ^{241}Am being scrubbed from the TRUEX solvent. The ^{241}Am was effectively stripped from the TRUEX solvent with a distribution coefficient of 0.05 on the first strip stage. The overall material balance for ^{241}Am was good (120%) indicating that the CeF_3 solubility was not exceeded during this testing and, therefore, did not result in the formation of a precipitate.

Table 3. Percentages of ^{241}Am and ^{95}Zr in Each of the Effluent Streams.

Stream	^{241}Am	^{95}Zr
Aqueous Raffinate	$<3.6\%$	101.5%
Strip Product	119.8%	$<0.24\%$
Na_2CO_3 Effluent	$<0.25\%$	$<0.06\%$
Rinse Effluent	$<0.12\%$	$<0.02\%$
Solvent Effluent	$<1.2\%$	$<0.2\%$
Mass Balance	120%	102%

Table 4. Distribution Coefficients for ^{241}Am , ^{95}Zr , and H^+

Stage	$D_{\text{Am-241}}$	$D_{\text{Zr-95}}$	D_{H^+}
Extraction	1	---	0.60
	3	>1.6	0.59
	5	>15.1	0.63
	6	24.6	0.57
	7	16.6	0.84
	8	16.0	0.79
Scrub	9	20.6	0.58
	10	26.3	0.15
	11	24.2	<0.21
	12	18.6	---
	13	0.05	---
Strip	14	<0.29	0.17

The distribution coefficients for ^{95}Zr in the extraction section were 0.6 resulting in a significant amount of ^{95}Zr extracted into the TRUEX solvent (39%). The 0.1 M NH_4F scrub was effective in scrubbing this extracted ^{95}Zr from the solvent, resulting in $<0.24\%$ of the ^{95}Zr exiting with the HLW strip product. Distribution coefficients for ^{95}Zr in the scrub section steadily dropped from 0.84 on the first scrub stage to 0.15 on the fourth scrub stage.

Analytical results for other elements of interest, such as Fe, Ce, and Cr, have not been obtained for this flowsheet test. However, based on analytical results from previous flowsheet testing, it is expected that approximately 0.4% of the Fe, 0.2% of the Cr and $>99\%$ of the Ce is extracted and exits with the strip product with this flowsheet.

CONCLUSIONS

A preliminary flowsheet has been developed for the removal of actinides from simulated dissolved ICPP zirconium calcine. This flowsheet, as shown in Figure 1, effectively extracted the actinides from the simulated waste while minimizing the quantity of Zr in the HLW strip product (<0.24%). Precipitate formation and/or flooding were not observed while performing the flowsheet test.

FUTURE DIRECTION

The following activities are planned to complete the development of the TRUEX process for the treatment of ICPP dissolved calcine. 1) Optimize the composition and flowrate of the NH_4F scrub feed solution in order to minimize the effects of corrosion and volume increase in the aqueous raffinate, 2) Evaluate other solutions to scrub Zr from the TRUEX solvent such as the use of citrate as a scrub solution and/or feed complexant, 3) Perform flowsheet testing with actual dissolved ICPP calcines, and 4) Develop flowsheets for the treatment of other ICPP calcine types such as aluminum calcine.

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