# FLOWSHEET TESTING OF THE UNIVERSAL SOLVENT EXTRACTION PROCESS FOR THE SIMULTANEOUS SEPARATION OF CESIUM, STRONTIUM, AND THE ACTINIDES FROM DISSOLVED INEEL CALCINE

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## ABSTRACT

The Universal Solvent Extraction (UNEX) process is being developed for the simultaneous separation of Cs, Sr, and the actinides from dissolved high-level waste (HLW) calcine as part of a collaborative effort between the Idaho National Engineering and Environmental Laboratory (INEEL) and the Khlopin Radium Institute (KRI) with the goal of minimizing the high-activity waste volume to be disposed in a deep geological repository. Flowsheet testing was performed using dissolved pilot plant calcine (non-radioactive) and 26 stages of 3.3-cm diameter centrifugal contactors. The UNEX solvent utilized for testing consisted of 0.08 M chlorinated cobalt dicarbollide for the extraction of Cs, 0.35 vol. % polyethylene glycol-400 (PEG-400) for the extraction of Sr, and 0.01 M diphenyl-N,N-dibutylcarbamoyl phosphine oxide ($Ph_2Bu_2CMPO$) for the extraction of the actinides. The diluent for the UNEX process consisted of phenyltrifluoromethyl sulfone (FS-13). With this testing, removal efficiencies of 99.95%, >99.999%, >98.3%, and >99.6% were obtained for Cs, Sr, Nd (Am surrogate), and Ce (Am surrogate), respectively. This is sufficient to reduce the activities of $^{137}Cs$, $^{90}Sr$, and the actinides to below NRC Class A LLW requirements in a grout waste form. Significant amounts of the Ba (99.7%), K (48%), Mo (19%), and Fe (10%), were also removed from the feed with the universal solvent extraction flowsheet. Operational problems such as flooding or precipitate formation were not observed during testing.

## INTRODUCTION

The Idaho National Engineering and Environmental Laboratory (INEEL) previously reprocessed spent nuclear fuel to recover fissionable uranium. The radioactive raffinates from the uranium recovery processes were converted to granular solids (calcine) in a high temperature (500 $^{o}$C) fluidized bed. Currently, there are 4,071 $m^3$ of calcine temporarily stored at the INEEL. The calcine can be characterized as either aluminum type calcine (generated from aluminum clad fuel reprocessing raffinates) or zirconium type calcine (generated from zirconium clad fuel reprocessing raffinates). Both calcine types are <1 wt % in transuranic (TRU) and fission product content. High-level waste (HLW) calcine at the INEEL must be removed from existing bins and put in a form suitable for disposal by 2035 as part of an agreement with the State of Idaho. Separation processes are being developed for pretreatment of the waste prior to any stabilization process, such as vitrification, being performed. The aqueous raffinate resulting from the separation processes would be grouted and disposed of as low-level waste (LLW). The resulting fraction containing the transuranic elements (TRU) and fission products would be vitrified and disposed of as HLW glass. The primary benefit of the radionuclide partitioning option is a significant HLW glass volume reduction.

One separation process being developed at the INEEL for the treatment of dissolved calcine is the Universal Solvent Extraction (UNEX) process. The UNEX process can be used to simultaneously separate the Cs, Sr, and actinides from dissolved INEEL high-level waste (HLW) calcine. The UNEX process separates and recovers the Cs, Sr, and actinides with one cycle of solvent extraction, as opposed to two or more unit operations, which are typically required to achieve the same separation.

The UNEX process is being developed as a collaborative effort between the INEEL and the Khlopin Radium Institute in St. Petersburg, Russia. Previous testing to support development of the UNEX process has primarily been focused on the treatment of acidic INEEL tank waste (1-5). UNEX flowsheets have been demonstrated using simulated and actual tank waste solutions at the Khlopin Radium Institute and the INEEL. More recently, the UNEX process is being developed for the treatment of dissolved INEEL calcine. The results of flowsheet testing performed using dissolved pilot plant calcine (non-radioactive) and 26 stages of 3.3-cm diameter centrifugal contactors are presented.

## EQUIPMENT DESCRIPTION

Flowsheet testing was performed using 26 stages of 3.3-cm diameter centrifugal contactors. The contactor setup consists of the contactor stages, reagent feed and receiving vessels, and feed pumps with associated controllers. The 3.3-cm centrifugal contactor mockup is pictured in Figure 1.

The 3.3-cm contactors were designed and fabricated in Moscow, Russia by the Research and Development Institute of Construction Technology (NIKIMT). Table I lists the operating specifications of the contactors. A total of 26 contactors were obtained from NIKIMT for testing purposes. Each stage can be operated independently allowing numerous combinations for changing flowsheet configurations.

Solutions are fed to the contactors using valveless metering pumps with controllers. Flow rates were adjusted by controlling pump speed using a ten-turn potentiometer or by manual adjustment of the piston stroke length and/or a combination of the two. Once solutions enter the contactors, flow through the equipment is by gravity, i.e., the solutions in the contactors are not under pressure. The product solutions from the contactors drain by gravity to the product vessels.

Heat tape was wrapped around the strip section centrifugal contactors in order to operate the strip section at an elevated temperature. The temperature of the solution in these contactors was maintained at approximately 60 ºC by monitoring the temperature of the solution in the stages and adjusting the current to the heat tape as necessary. In addition, the strip feed solution was heated to approximately 60 ºC by pumping the solution through a heating coil submerged in a heated water bath. Solvent exiting the strip section was cooled prior to recycle to the extraction section by pumping the solvent through a cooling coil submerged in an ice water bath.

Fig. 1. 3.3-cm centrifugal contactor pilot plant.

Table I. Operating specifications for the 3.3 cm contactors.

| | |
|---|---|
| Size | 3.3-cm rotor diameter |
| Mixing Chamber Volume | 22 mL |
| Separating Chamber Volume | 32 mL |
| Overall Dimensions:<br>Length<br>Width<br>Height | <br>105 mm (4.13 in)<br>132 mm (5.2 in)<br>286 mm (11.26 in) |
| Volumetric Capacity | 25 L/hr (for the system TBP-kerosene/2 M $HNO_3$) |
| Mass | 5 kg per stage (includes electric motor) |
| Motor | 160-180 volt, 50-60 Hz, 0.04 kW (Russian Design) |
| RPM | 2700 rpm (slightly adjustable) |
| Material of construction | 12X18H10T stainless steel (Russian designation) |
| Inlet and outlet ports | 3/8 in. o.d. tubing |
| Configuration | Single stage units, which can be configured as desired. Stages connected using U-tubes. |

The 3.3 cm centrifugal contactors do not have provisions for sampling aqueous or organic streams exiting from individual stages. Aqueous raffinate, aqueous strip, and solvent recycle streams were sampled by periodically routing the solution draining to the appropriate receiving vessel into a sample bottle.

## METHODOLOGY/EXPERIMENTAL PROCEDURE

### Dissolved Pilot Plant Calcine Feed

Run #74 pilot plant calcine was selected as the representative zirconium calcine for use in development testing. The compositions of solid and dissolved Run #74 pilot plant calcine are listed in Table II. At first glance, the Run #74 calcine appears to be significantly different than the actual material. Actual Zr calcine types are varied and the composition may best be represented as a range of values. However, the Run #74 calcine is anticipated to represent a "worst case" Zr content, which is important since it is indeed the Zr which provides the major impediment to the UNEX process. The ideology is that if the UNEX flowsheet can be developed to meet the current performance criteria with respect to Run #74 calcine, it will likely be readily adaptable to all compositions of radioactive Zr calcine types. Ultimately, the UNEX flowsheet must be tested on dissolved samples of actual radioactive calcines.

The baseline dissolution procedure for zirconium calcines calls for 10 L of 3 M $HNO_3$ per 1 kg calcine at near boiling (~100°C) temperatures for a minimum of 60 minutes. This procedure was used for dissolving the pilot plant calcine to prepare the aqueous feed for development efforts herein reported. The acid concentration of the resulting dissolved calcine solution is typically 1.1 to 1.2 M, and the solution has a density of $\rho = 1.2$ g/mL. The resulting dissolved pilot plant calcine was diluted by 20% with 0.1 M HF to reduce the concentration of metals and complex the Zr, Fe, and Mo, thus preventing the loading of the actinide extractant in the UNEX solvent. Loading of the solvent with metals will reduce the extraction of actinides.

### Solvent Composition

The UNEX process solvent used in this testing is a "universal extraction mixture" which was developed to remove all of the radionuclides of concern, both fission product and actinides, in a single solvent extraction unit operation. The solvent is designed to be the heavy phase, i.e., it has a specific gravity greater than the aqueous solutions. The target solvent composition was 0.08 M chlorinated cobalt dicarbollide, 0.35 vol.% polyethylene glycol-400 (PEG-400), and 0.01 M diphenyl-N,N-dibutylcarbamoyl phosphine oxide ($Ph_2Bu_2CMPO$) in a diluent consisting of phenyltrifluoromethyl sulfone (FS-13). The solvent was continually recycled during the testing. Approximately one liter of UNEX solvent, which was continuously recycled during a recent UNEX test with simulated SBW (66 hours of continuous operation), was adjusted and used for this testing.

Table II. Compositions of Run #74 calcine and dissolver product.

| Element | Wt % in Run #74 Calcine Before Dissolution [a] | Dissolved Run #74 Calcine Concentration with HF dilution (M) |
|---|---|---|
| Al | 11.2 | 0.33 |
| B | 1.1 | --- |
| Ca | 25.0 | 0.49 |
| Ce | 0.1 | 2.6E-04 |
| Cr | 0.4 | 4.0E-03 |
| Cs | 0.5 | 2.8E-03 |
| Fe | 0.1 | 9.1E-03 |
| K | <0.1 | 6.7E-04 |
| Mo | --- | 3.4E-06 |
| Na | 0.4 | 0.010 |
| Ni | 0.1 | 1.3E-03 |
| Pb | <0.1 | <4.8E-07 |
| Sr | 0.7 | 5.8E-03 |
| Zr | 16.6 | 0.12 |
| $Cl^-$ | <0.2 | 4.5E-04 |
| $F^-$ | 17.4 | 0.42 |
| $H^+$ | --- | 1.14 |
| $NO_3^-$ | <0.1 | --- |
| $SO_4^{-2}$ | 5.4 | --- |
| Density g/cm$^3$ | --- | 1.2 |

[a] Remainder of mass balance is oxygen

## Flowsheet Configuration and Testing

Based on the results of universal solvent development studies performed at the KRI and the INEEL, a flowsheet was developed and recommended for countercurrent flowsheet testing in the 3.3-cm diameter centrifugal contactors. This flowsheet, as shown in Figure 2, consists of thirteen stages of extraction at an organic to aqueous phase ratio (O/A) of 1.0, two stages of scrub (0.1 M HF and 0.017 M $Al(NO_3)_3$ in 0.033 M $HNO_3$) at an O/A of 6.0, ten stages of strip (110 g/L guanidine carbonate, 20 g/L diethylene triamine pentaacetic acid, DTPA) at an O/A of 2.0, and one stage of strip (20 g/L guanidine carbonate, 40 g/L DTPA) at an O/A of 4.0.

The flowsheet testing was performed as follows. Each of the centrifugal contactors were filled with approximately 40 mL of process solution. A 1.1 M $HNO_3$ solution was used for the stages in the extraction section. The centrifugal contactor heat tape (strip section) was turned on. The centrifugal contactor motors were then started at 2,740 rpm. Solvent flow was established. When solvent began exiting contactor stage 1, aqueous solution flows were established. New effluent containers were then placed in service and time T=0 was established. The process then continued to operate with recycle of the solvent. The contactor heat tape was periodically

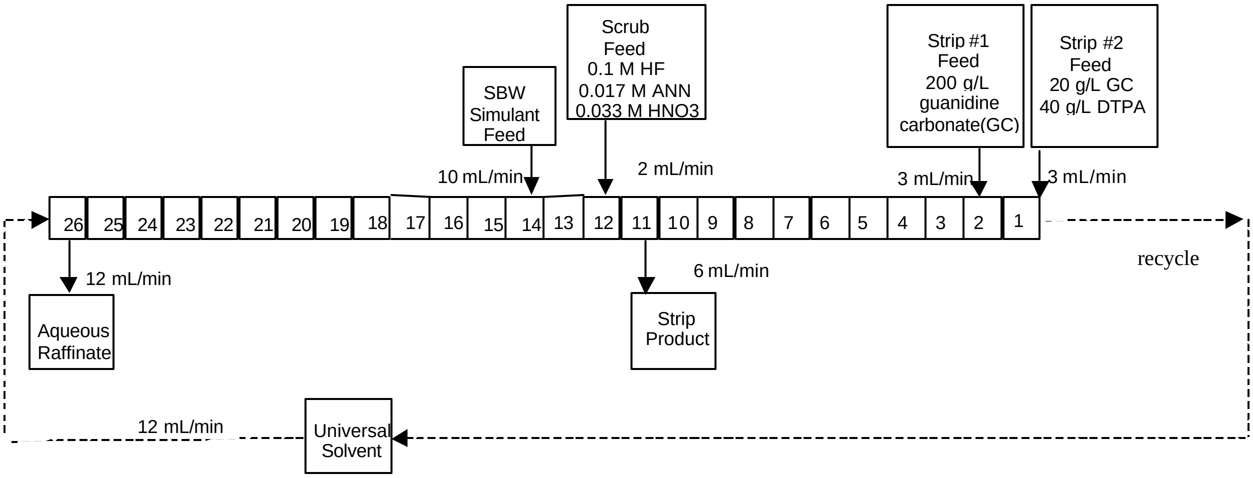

Fig. 2. Flowsheet for testing of the UNEX process.

adjusted throughout the test to maintain temperature in the strip section at approximately 60 ºC. Samples were then taken from each of the effluent streams every 30 minutes for five hours. The contactors were then shut down by simultaneously stopping the contactor motors and feed pumps. Each stage remains approximately at steady-state operating conditions with this type of shutdown. This allowed aqueous and organic samples to be taken from each stage and, therefore, distribution coefficients to be determined for any of the 26 stages.

## RESULTS AND DISCUSSION

### Contactor Operation

Actual solution flowrates for the duration of the test were calculated from feed tank depletion rates and are compared to the desired flowrates in Table III. Desired and actual flowrates compare very well for each of the feed streams. Slight flooding was observed in the strip product stream. Based upon the total volume of solvent collected in the strip product vessel at the completion of the test, it was determined that <0.56% carryover of solvent occurred in the strip product stream. Precipitate formation was not observed in any of the samples taken during operation or in the contactors after shutdown.

The centrifugal contactors in the strip section were heated to approximately 60 ºC by using heat tape wrapped around the stages. In addition, the strip #1 feed solution was heated to 60 ºC through the use of a hot water bath. Temperatures of the solution in several of the strip stages were monitored. Temperatures were maintained between 50 ºC and 60 ºC throughout the test.

### Composition of Effluents

The primary species of interest for evaluating UNEX flowsheet characteristics were Cs, Sr, Nd (Am surrogate), and Ce (Am surrogate). Samples of the aqueous raffinate, strip product, and

Table III. Flowrates and O/A ratios for the extended flowsheet testing with simulated waste.

|  |  | Flowrate (mL/min) |  | O/A Ratio |  | Total Flow |
|---|---|---|---|---|---|---|
| Section | Phase | Desired | Actual | Desired | Actual | (mL/min) |
| All | Org. | 12.0 | 12.3 | --- | --- | --- |
| Extraction | Aq. | 12.0 | 13.0 | 1.0 | 0.95 | 25.3 |
| Scrub | Aq. | 2.0 | 1.9 | 6.0 | 6.5 | 14.2 |
| Strip #1 | Aq. | 6.0 | 5.8 | 2.0 | 2.1 | 18.1 |
| Strip #2 | Aq. | 3.0 | 3.0 | 4.0 | 4.1 | 15.3 |

solvent effluent were taken every 30 minutes until shutdown at 300 minutes of operation. Cs, Sr, Nd, and Ce analyses were performed on each of these samples. In addition, samples of the aqueous raffinate, strip product, and solvent effluent were taken immediately prior to shutdown for analysis of Cs, Sr, Nd, Ce, Al, Ba, Ca, Cr, Fe, K, Na, Mn, Mo, Ni, and Zr. Concentrations of the metals and the percentage of each component in the various effluent streams are indicated in Table IV. The stagewise distribution coefficients for several of these metals were also calculated for each stage after shutdown and are presented in Table V.

As shown in Table IV, 99.95% Cs removal was obtained. This removal efficiency is expected to be greater than the required removal efficiency necessary to reduce the activity of $^{137}$Cs in the dissolved Zr type calcine to below the NRC Class A LLW requirement of 1.0 Ci/m$^3$ in a grout waste form. Distribution coefficients for Cs ranged from 0.82 to 3.3 in the extraction section. For comparison purposes, many of the aqueous and organic stage samples taken at the completion of the test were spiked with $^{137}$Cs, re-equilibrated, and the two phases analyzed to determine distribution coefficients. The resulting $^{137}$Cs distribution coefficients are also presented in Table V. The distribution coefficients obtained for $^{137}$Cs were very comparable to the stable Cs distribution coefficients. Additionally, distribution coefficients were obtained for $^{137}$Cs on several of the extraction stages (22 – 26) for which stable Cs distribution coefficients were not obtained due to analytical detection limits. The distribution coefficients for $^{137}$Cs decreased steadily from the feed stage (stage 14) to the raffinate stage (stage 26). This is likely due to the fact that the recycled solvent contains entrained guanidine carbonate, which adversely impacts Cs distribution coefficients. As the solvent moves through the extraction section, the entrained guanidine carbonate is washed from the solvent by the acidic waste solution, which results in the Cs distribution coefficients increasing from stage to stage. Most of the increase in Cs distribution coefficients occurs within the first five stages indicating guanidine is primarily washed out of the solvent by stage 21. The Cs distribution coefficients in the scrub section ranged from 87 to 127 indicating that very little of the Cs was scrubbed from the solvent. Greater than 99.98% of the extracted Cs was removed from the solvent in the strip section ($D_{Cs}$ ˜ 0.2).

As shown in Table IV, >99.999% Sr removal was obtained. This removal efficiencies is expected to be greater than the required removal efficiency necessary to reduce the activity of $^{90}$Sr in the average dissolved Zr type calcine to below the NRC Class A LLW requirement of 0.04 Ci/m$^3$ in a grout waste form. Distribution coefficients for Sr ranged from 1.6 to 3.5 in the

Table IV. Percentage of metals in the effluent streams.

| Stream | Cs | Sr | Ce | Nd | Al |
|---|---|---|---|---|---|
| Aq. Raffinate | 0.05% | <0.001% | <0.34% | <1.7% | 96.1% |
| Strip Product | 73.2% | 89.9% | 83.3% | 94.4% | 0.05% |
| Solvent Effluent | <0.02% | 0.07% | <3.1% | <3.3% | 0.04% |
| Mass Balance [a] | 73.3% | 89.9% | 83.3% | 94.4% | 96.1% |
| Stream | Ba | Ca | Cr | Fe | K |
| Aq. Raffinate | <0.28% | 90.7% | 98.0% | 86.1% | 49.4% |
| Strip Product | 96.0% | 2.4% | 0.14% | 8.9% | 43.2% |
| Solvent Effluent | <2.6% | 0.17% | 0.45% | 2.1% | <142% |
| Mass Balance [a] | 96.0% | 93.1% | 98.1% | 95.0% | 92.6% |
| Stream | Na | Mn | Mo | Ni | Zr |
| Aq. Raffinate | 93.3% | 93.3% | 98.3% | 98.2% | 97.0% |
| Strip Product | 3.1% | 2.8% | 18.7% | 1.1% | 1.6% |
| Solvent Effluent | <40.3% | 6.9% | <41.8% | <0.7% | 0.01% |
| Mass Balance [a] | 96.4% | 96.1% | 117.0% | 99.3% | 98.6% |

[a] Material balance based on sample analysis, calculated as out/in*100%. Organic product was not included in the material balance since the organic was recycled. Concentrations which are below the detection limit are assumed to be 0% for purposes of calculating the material balance.

extraction section. The Sr distribution coefficients in the scrub section ranged from 464 to 2514 indicating very little of the Sr was scrubbed from the solvent. Greater than 99.94% of the extracted Sr was removed from the solvent in the strip section $D_{Sr}$ ˜ 0.002. For comparison purposes, the aqueous and organic stage samples taken at the completion of the test were spiked with $^{85}$Sr, re-equilibrated, and the two phases analyzed to determine distribution coefficients. The resulting $^{85}$Sr distribution coefficients are also presented in Table V. The $^{85}$Sr distribution coefficients were very comparable to the stable Sr distribution coefficients on all stages.

Cerium and neodymium, present in the dissolved calcine solution, were used as surrogates to evaluate the expected behavior of Am in the surrogate calcine solution. As shown in Table IV, >99.6% Ce removal and >98.3% Nd removal was obtained with this flowsheet test. Actual removal efficiencies were not obtained since the concentration of Ce and Nd reached analytical detection limits after nine and six stages of extraction, respectively. The extraction distribution coefficients for Ce ranged from 1.1 to 2.1 and the extraction distribution coefficients for Nd ranged from 1.7 to >14. Scrub distribution coefficients were high for both Ce and Nd, indicating very little of these components was scrubbed from the solvent. The extracted Ce and Nd were effectively stripped from the solvent ($D_{Ce}$ and $D_{Nd}$ ˜ <0.02).

The behavior of Ce and Nd can be used to estimate the removal efficiency of $^{241}$Am; however, no surrogates are present which will emulate the behavior of Pu. Typically, Pu distribution coefficients are much greater than Am distribution coefficients and higher removal efficiencies can be expected for Pu. To confirm this, laboratory testing with solutions from this flowsheet test and Pu tracers were performed to estimate the Pu distribution coefficients and, therefore, what TRU removal efficiency could be expected. The aqueous and organic stage samples taken at the completion of the test were spiked with $^{239}$Pu or $^{241}$Am,

Table V. Measured stagewise distribution coefficients from the UNEX testing.

| Section | Stage # | Cs | $^{137}$Cs | Sr | $^{85}$Sr | Nd | Ce | $^{239}$Pu | $^{241}$Am | Ca | Fe | Zr | K | Na |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Strip #2 | 1 | --- | 0.72 | --- | 16.8 | --- | --- | --- | 0.22 | --- | --- | --- | --- | --- |
| Strip #1 | 2 | --- | 0.24 | --- | <0.0003 | --- | --- | --- | <0.003 | --- | --- | --- | --- | --- |
| | 3 | <0.94 | 0.23 | --- | <0.0003 | --- | --- | --- | <0.002 | --- | --- | --- | --- | --- |
| | 4 | <0.14 | 0.23 | --- | <0.0003 | --- | --- | --- | <0.002 | --- | --- | --- | --- | --- |
| | 5 | <0.03 | 0.24 | --- | <0.0003 | --- | --- | --- | <0.003 | --- | --- | --- | --- | --- |
| | 6 | 0.16 | 0.24 | --- | <0.0003 | --- | --- | --- | <0.003 | --- | --- | --- | --- | --- |
| | 7 | 0.11 | 0.24 | --- | <0.0003 | --- | <6.9 | --- | <0.002 | --- | --- | 0.1 | --- | --- |
| | 8 | 0.22 | 0.23 | --- | <0.0003 | <1.0 | <1.5 | --- | <0.002 | --- | --- | 0.040 | --- | --- |
| | 9 | 0.22 | 0.22 | --- | <0.0003 | 0.27 | <0.22 | --- | <0.002 | --- | --- | 0.013 | --- | --- |
| | 10 | 0.21 | 0.22 | 0.002 | <0.0003 | 0.017 | <0.02 | --- | <0.003 | --- | --- | 0.003 | --- | --- |
| | 11 | 0.22 | 0.23 | --- | 0.001 | <0.02 | <0.02 | --- | <0.003 | --- | --- | 0.003 | -- | --- |
| Scrub | 12 | 127 | 54.7 | 2514 | 456 | 105 | >246 | --- | >304 | 38.2 | 277 | 0.16 | --- | 10.2 |
| | 13 | 87 | --- | 464 | --- | 81.0 | >239 | 631.4 | --- | 6.8 | 869 | 0.20 | --- | 11.5 |
| Extraction | 14 | 1.8 | 4.3 | 1.6 | 1.8 | 2.5 | 1.9 | --- | 1.4 | 0.028 | 0.12 | 0.044 | 3.8 | 0.49 |
| | 15 | 3.3 | --- | 2.1 | --- | 1.7 | 2.1 | 40.1 | --- | 0.030 | 0.12 | 0.045 | 3.7 | 0.48 |
| | 16 | 2.9 | 3.7 | 2.8 | 3.3 | 3.1 | 2.1 | --- | 1.3 | 0.037 | 0.12 | 0.047 | 3.6 | 0.50 |
| | 17 | 2.7 | --- | 3.2 | --- | 2.1 | 2.0 | 39.7 | --- | 0.037 | 0.10 | 0.048 | 3.4 | 0.50 |
| | 18 | 2.0 | 3.0 | 3.5 | 4.0 | 4.2 | 2.0 | --- | 1.7 | 0.034 | 0.09 | 0.047 | 4.1 | 0.40 |
| | 19 | 0.82 | 3.1 | 3.4 | 4.1 | >14.1 | 1.1 | --- | 1.8 | 0.039 | 0.15 | 0.051 | 4.5 | 0.42 |
| | 20 | --- | 3.0 | 3.0 | 4.2 | >5.4 | <3.6 | --- | 2.1 | 0.041 | 0.10 | 0.055 | 4.5 | 0.40 |
| | 21 | --- | 3.2 | 1.6 | 4.8 | >5.9 | <6.3 | --- | 2.8 | 0.035 | 0.092 | 0.051 | 5.2 | 0.39 |
| | 22 | --- | --- | --- | --- | >5.7 | --- | 102.5 | --- | 0.037 | 0.074 | 0.050 | 5.1 | 0.39 |
| | 23 | --- | 2.3 | --- | 4.0 | >7.5 | --- | --- | 3.2 | 0.036 | 0.057 | 0.051 | 4.5 | 0.38 |
| | 24 | --- | 2.0 | --- | 3.9 | >7.4 | --- | --- | 4.0 | 0.037 | 0.04 | 0.055 | 5.8 | 0.3 |
| | 25 | --- | 1.4 | --- | 3.9 | >6.7 | --- | --- | 5.1 | 0.036 | 0.03 | 0.053 | 5.8 | 0.35 |
| | 26 | --- | 0.60 | --- | 3.6 | >5.6 | --- | --- | 13.8 | 0.035 | --- | 0.048 | 4.9 | 0.39 |

[a] Distribution coefficients of the metals are not shown for many strip stages since the metal concentrations on these strip stages approached analytical detection limits after only a few stages of stripping. Also, trace concentrations of metals (Sr, Na, Ca, K, Fe) have been detected in the freshly prepared strip feed solutions, thus further effecting detection limits.

re-equilibrated, and the two phases analyzed to determine distribution coefficients. The resulting $^{239}$Pu and $^{241}$Am distribution coefficients are presented in Table V. It should be noted that the $^{239}$Pu was added to the stage samples as Pu(IV). It is believed that the Pu in the SBW is also primarily present as Pu(IV). The $^{241}$Am distribution coefficients are in good agreement with the distribution coefficients obtained for Ce and Nd. The $^{239}$Pu distribution coefficients in the extraction section ranged from 40 to 102. The extraction and scrub Pu distribution coefficients were used in conjunction with the Generic TRUEX Model (GTM) to estimate the Pu removal efficiency, which would be obtained with these distribution coefficients and the flowsheet tested. The GTM predicts 99.98% Am removal and >99.999% Pu removal would be obtained assuming 90% stage efficiency. With these removal efficiencies, the TRU activity should be well below the 100 nCi/g non-TRU limit.

The samples of the products were also analyzed for a variety of matrix metals, both micro and macro constituents in the simulated tank waste, to evaluate or further confirm their behavior in the UNEX process. The results for these constituents, expressed in terms of percentage of each element in the different product streams relative to the feed composition, are listed in Table IV. Distribution coefficients for several of the elements are listed in Table V. Of these metals, Ba was nearly completely extracted from the feed. In addition, significant amounts of Fe, K, and Mo were extracted and exited with the strip product (>5%).

## CONCLUSIONS

Flowsheet testing of the UNEX process was successfully completed using dissolved pilot plant calcine (Zr type calcine). With this flowsheet test, removal efficiencies of 99.95%, >99.999%, >99.6%, and >98.3% were obtained for Cs, Sr, Ce, and Nd, respectively. Barium was nearly completely extracted from the feed (>99.7% removal). Significant amounts of Fe, K, and Mo were also extracted and exited with the strip product (>5%). Flooding and/or precipitate formation were not observed with this flowsheet test. Based on the results of this flowsheet test, it appears that the UNEX process is a viable process for the treatment of INEEL dissolved calcine.

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