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INTEGRATED AMP–PAN, TRUEX, AND SREX TESTING. I. EXTENDED FLOWSHEET TESTING FOR SEPARATION OF SURROGATE RADIONUCLIDES FROM SIMULATED ACIDIC TANK WASTE

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ABSTRACT

Three unit operations for the removal of selected fission products, actinides, and Resource Conservation and Recovery Act metals (mercury and lead) were integrated successfully and tested at the Idaho National Engineering and Environmental Laboratory (INEEL) for extended run times with simulated acidic tank waste. The unit operations were ion exchange (IX) for Cs removal, followed by transuranic extraction (TRUEX) for Eu (actinide surrogate), Hg, and Re (Tc surrogate) removal, and subsequent strontium extraction (SREX) for Sr and Pb removal.

Approximately 45 L of simulated acidic tank waste were processed through three IX columns, packed with composite ammonium molybdophosphate–polyacrylonitrile (AMP–PAN) sorbent for Cs removal. The IX system was operated continuously

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for ~34 hr at 22 bed volumes (BV) per hour through the first two columns, each sized at 60 cm^3 BV and operated to 100% breakthrough. The experimental breakthrough data were in excellent agreement with modeling predictions based on data obtained with much smaller (1.5 cm^3) columns. The third column (220 cm^3 BV) was used for polishing and Cs removal after breakthrough of the upstream columns. Cesium removal was >99.83% in the IX system and interference from other species was not observed.

The IX effluent was processed through a TRUEX solvent extraction flowsheet to remove Eu (Am surrogate), Hg, and Re (Tc surrogate) from the simulated waste. The TRUEX flowsheet test was performed using 23 stages of 3.3 cm centrifugal contactors, operated a total of 71.3 hr, and processed ~41 L of the IX effluent using 1.5 L of TRUEX solvent with constant solvent recycle. The TRUEX solvent was recycled through the flowsheet an estimated 17 times. Greater than 99.999% of the Eu, 96.3% of the Hg, and 56% of the Re were extracted from the simulated feed and recovered in the strip and wash streams. Over the course of the test, there was no detectable build-up of any components in the TRUEX solvent.

The raffinate from the TRUEX test was processed subsequently through a SREX solvent extraction flowsheet to remove Sr, Pb, and Re (Tc surrogate) from the simulated waste. The SREX flowsheet test was performed using the same centrifugal contactors used in the TRUEX test after reconfiguration and the addition of three stages. Approximately 51 L of TRUEX raffinate was processed through the system during 77.9 hr of continuous operation with 1.5 L of SREX solvent and continuous solvent recycle. The SREX solvent was recycled through the system an estimated 45 times without measurable build-up of any components in the solvent. Approximately 99.9% of the Sr, >99.89% of the Pb, and >96.4% of the Re were extracted from the aqueous feed to the SREX flowsheet and recovered in the strip and wash sections.

INTRODUCTION

Waste treatment processes for the removal of radionuclides from acidic wastes are being developed worldwide in countries such as the United States, Britain, France, Japan, China, and Russia (1–4) with the primary goal of reducing the volume of high-level waste requiring disposal. The Idaho National Engineering and Environmental Laboratory (INEEL) previously reprocessed spent nuclear fuel to recover enriched uranium. The radioactive raffinate streams from reprocessing were stored and subsequently solidified at 500°C in a fluidized bed calciner. Calcination converted the liquid wastes into a granular, free-flowing solid (calcine).

A secondary acidic aqueous waste, typically high in Na, was generated during equipment decontamination between processing campaigns and from solvent cleanup activities. Currently, over five million liters of the secondary liquid waste are stored in underground, concrete enclosed stainless steel tanks at INEEL. This liquid waste is not directly amenable to calcination due to its high sodium content, which causes agglomeration of the fluidized bed. Historically, the high sodium secondary wastes were blended with reprocessing raffinates; however, blending is no longer possible since all raffinate solutions have been calcined. The remaining inventory of tank wastes can be calcined if blended with nonradioactive aluminum nitrate, which reduces calciner throughput and increases calcine volume. Reduced throughput may prevent meeting the deadline (2012) for emptying the tank farm, as agreed upon by Department of Energy (DOE), the State of Idaho, and the Environmental Protection Agency (EPA).

Separation processes are being evaluated for treating the INEEL wastes, including acidic solutions of re-dissolved calcine, for final disposition. The large volume of calcine drives the economics of the separation processes, since the tank wastes are a small fraction of the total waste volume stored at INEEL. The goal of the separations processes is to remove fission products and actinides from the liquid wastes so the bulk of the treated waste meets Nuclear Regulatory Commission Class A low-level waste (LLW) requirements as defined by 10 Code of Federal Regulations 61.55. It is anticipated that the low-activity waste (LAW) raffinate stream resulting from the separation unit operations would be grouted for near surface disposal. The remaining high-activity fractions containing transuranic (TRU) and fission products would be vitrified and disposed as high-activity waste (HAW) glass. The economic benefit of separation processes is a significant reduction in HAW glass, which has substantial disposal costs.

One treatment alternative under consideration for the INEEL tank wastes has been termed the "full separation" option. This option consists of three integrated separation unit operations intended to remove collectively the major radionuclides and, as an unintentional benefit of process chemistry, certain Resource Conservation and Recovery Act (RCRA) metals are also removed from INEEL waste solutions. These unit operations include ion exchange (IX) using ammonium molybdophosphate (AMP)–polyacrylonitrile (PAN) composite sorbent (referred to as AMP–PAN) to remove cesium; the Transuranic Extraction (TRUEX) process to remove the actinides, mercury, and technetium; and the Strontium Extraction (SREX) process to remove Sr, Pb, and Tc.

Ammonium molybdophosphate is a well-known inorganic cesium precipitant in acidic media, but due to small particle size, is not alone suitable for use in columns as an IX medium. Recently, Czech scientists have developed an engineered form of AMP by forming a composite of AMP and PAN (5,6). Numerous experiments at the Czech Technical University and INEEL using simulated and actual tank waste and solutions of dissolved calcine have demonstrated that AMP–PAN has a high capacity and selectivity for cesium from these acidic waste solutions (7–9). Elution of Cs and regeneration/reuse of the sorbent is possible, but requires the use of concentrated ammonium salts, which have undesirable material handling or safety characteristics. Ammonium molybdophosphate is readily dissolved from the PAN support with caustic solutions (8,10), which may provide a convenient means to separate the organic substrate (PAN) from the Cs laden inorganic (AMP) for subsequent processing.

The TRUEX process, developed by Horwitz et al., is the most mature actinide separation technology for INEEL acidic tank waste (11). The active extractant in the TRUEX process solvent is octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO). Tributylphosphate (TBP) is added to the solvent as a phase modifier to prevent third phase formation. Isopar L®, a paraffinic hydrocarbon, is used as the diluent. The TRUEX process has demonstrated effective removal of actinides from INEEL wastes to well below the 10 nCi/g NRC Class A LLW TRU requirements (11,12). Previous testing also indicates the TRUEX solvent effectively removes mercury from tank waste and the sodium carbonate wash cycle back extracts mercury from the solvent (13,14).

The SREX process, developed by Horwitz et al. (15,16), has been shown to remove Sr, Pb, and Tc from INEEL tank waste (17). The active extractant used in the SREX solvent is 4′,4′(5′)-di-(*tert*-butyldicyclohexo)-18-crown-6 (DtBuCH18C6). Tributylphosphate is added as a phase modifier and the diluent is Isopar L, as used in the TRUEX solvent. The SREX flowsheet performance has been demonstrated previously at INEEL using both actual and simulated wastes (12–17).

It is anticipated that the HAW resulting from the full separation process would be vitrified and disposed of as a glass waste form in a deep geological repository. A goal of separation options for the treatment of radioactive waste is to reduce significantly the quantity of HAW glass generated if such treatment options are to be economically feasible.

Grouting of the LAW fraction is the anticipated method for disposal in an approved near-surface landfill. Potential disposal routes for the LAW would likely require a "performance grout," which meets performance measures of strength and leaching characteristics for RCRA constituents and radionuclides and the NRC Class A LLW criteria for ^{137}Cs, ^{90}Sr, and transuranic alpha activity. It is estimated that 0.21 L of LAW grout would be generated per 1.0 L of LAW (18). Initial material balance calculations indicate that there are approximately 5 L of LAW produced per liter of tank waste treated with the full separations process. Therefore, another goal of the separations flowsheet for treatment of INEEL tank waste is to reduce the activity in the LAW raffinate to less than 105% of the NRC Class A LLW limits in order for the resulting grout to meet these limits. On the basis of the radionuclide content in INEEL acidic wastes and potential grout formulations, removal efficiencies of 97.3% for Cs-137, 99.9% for Sr-90, and 99.1% for TRU elements in the raffinate from separation flowsheets are necessary to ensure that the NRC Class A requirement is met in the LAW waste.

OBJECTIVES

The overall objective of this work was to evaluate the performance of an integrated full separations flowsheet for the treatment of simulated tank waste over an extended period of operation. The specific objectives are as follows.

- Integrating the three unit operations (IX–TRUEX–SREX) performed in series to evaluate and/or confirm the behavior of targeted species and numerous waste matrix components in the integrated flowsheet.
- Increasing the scale of the IX columns over those used in earlier tests to evaluate the associated effect on cesium removal and obtain complete breakthrough curves for two of the AMP–PAN columns. Effluent Cs concentrations were to be maintained at low values using a third, polishing column in series with the first two columns.
- Extending the run times used in the solvent extraction flowsheets to identify potential problems with recycle of the TRUEX and SREX organic solvents occurring from solvent degradation or long term build-up of materials in the organic phases.
- Evaluating the feasibility and testing optimal conditions under which the TRUEX flowsheet could be used for mercury removal from the simulated tank waste and stripping of the extracted Hg in the carbonate wash stream.
- Evaluating the effect of any residual Hg in the TRUEX process raffinate on the SREX process.
- Evaluating the feasibility and conditions for lead removal and stripping in the SREX flowsheet.

EXPERIMENTAL

Ammonium Molybdophosphate–Polyacrylonitrile Ion Exchange Columns

Three borosilicate glass columns and accessories were obtained from the ACE Glass Company (Vineland, NJ) for AMP–PAN testing. All columns were of 2.54 cm inside diameter. The first two columns were filled with AMP–PAN to a bed height of 11.8 cm [60 cm^3 bed volume (BV)] and the third column was filled to a bed height of 43.4 cm (220 cm^3 BV). The columns were operated in series and sized such that the first two would reach complete Cs breakthrough, while the third column functioned as a polishing column to remove the Cs following the breakthrough of the upstream columns. Sintered glass frits (2.54 cm outer diameter) were inserted at the top and bottom of the columns to prevent AMP–PAN from escaping through or plugging the column outlet during testing. Hollow Teflon® plugs were placed in the threaded ends of the columns to support the glass frit and provide the means to attach necessary valves and tubing to the glass columns. Three-way valves were attached to the bottom of the columns to allow for sample collection during operation. Pressure gauges were placed on inlet and outlet lines to monitor differential pressure of the columns. Simulated waste was pumped from the feed vessel to the columns using a valveless metering pump.

The AMP–PAN sorbent was procured from the Czech Technical Institute, Prague, Czech Republic, and used as received (wet). The first two columns were filled with AMP–PAN/SF (0.3–0.6 mm particle diameter) and the third column was filled with an older batch of AMP–PAN material (0.4–0.85 mm particle diameter). The SF designator denotes that the AMP–PAN was dried after formation, improving mechanical properties, then rehydrated, while the AMP–PAN without the SF designator was stored in solution since production. The AMP–PAN/SF sorbent is composed of 85.7 wt% AMP and 14.3 wt% PAN.

Transuranic Extraction/Strontium Extraction Solvent Extraction

Solvent extraction testing was performed in 3.3 cm centrifugal contactors designed and fabricated in Moscow, Russia by the Research and Development Institute of Construction Technology (NIKIMT). The contactor set-up consists of twenty-six stages, feed and receiving vessels and pumps with associated controllers. Each stage operates independently allowing numerous configurations. Solutions are fed to the contactors using valveless metering pumps.

The composition of the TRUEX solvent was 0.2 M CMPO and 1.4 M TBP in Isopar L, a branched chain paraffinic hydrocarbon. Several weeks prior to the TRUEX flowsheet test, the entire volume of TRUEX solvent (2 L) was washed with 0.25 M Na_2CO_3 followed by acid rinsing with 0.1 M HNO_3 in the 3.3 cm centrifugal contactors. The solvent cleanup consisted of three carbonate wash stages [organic-to-aqueous $(O/A) = 5$] and two acid rinse stages $(O/A = 3)$. The purity and composition of the washed TRUEX solvent were tested subsequently by determination of the extraction distributions of Am-241 at various HNO_3 concentrations, a procedure previously developed as a quality control measure for the TRUEX solvent (19).

The composition of the SREX solvent was 0.15 *M* 4′,4′(5′)-di-(*tert*-butylcyclohexo)-18-crown-6 and 1.5 *M* TBP in Isopar L. The crown ether (Eichrom Industries, Darien, IL) was used as received. Several days prior to the SREX test, the entire volume of SREX solvent (2 L) was washed with 0.25 *M* Na_2CO_3 followed by acid rinsing with 3.0 *M* HNO_3 in the centrifugal contactors. The solvent cleanup utilized two carbonate wash stages (O/A = 5) and four acid rinse stages (O/A = 2). The Sr distribution of the solvent was confirmed based on the extraction of Sr-85 from 3 *M* HNO_3, a previously developed quality control measure for the SREX solvent. The Sr distribution from 3 *M* HNO_3 was $D_{Sr} \geq 4$, indicating the extraction properties were acceptable for use in the SREX flowsheet test.

Simulated Tank Waste Composition

Approximately 50 L of simulated tank waste were prepared from stock chemical reagents. The simulated waste was prepared to represent the average composition of actual tank waste currently stored at INEEL. Compositions of the actual and simulated waste solutions are presented in Table 1. Nonradioactive europium was added as a surrogate for americium to evaluate the performance of the TRUEX process with respect to actinide behavior. Stable cesium and strontium were added to increase their respective concentrations in the feed providing better analytical results to calculate removal data for IX and SREX unit operations more accurately. The simulated waste used in these tests was prepared, allowed to settle overnight, and partially filtered the next day. The solution was allowed to stand overnight and the entire volume was re-filtered the following day.

Flowsheet Configuration

The flowsheet used in the integrated testing is shown in Fig. 1. The AMP–PAN IX system was placed first in the series since early cesium removal (primary γ-emitter) could result in a potential reduction of shielding requirements for the downstream operations. Using the as-received tank wastes, the IX columns would process minimal waste volumes for Cs removal, i.e., placing the IX columns downstream of the TRUEX and/or SREX process would require larger volumes of waste be processed through the IX system due to scrub dilution in the solvent extraction flowsheets. The TRUEX flowsheet was ordered second in the integrated flowsheet, primarily due to consideration of mercury interactions in SREX. The TRUEX process effectively removes mercury from the tank waste through extraction and subsequent stripping in the carbonate wash stream. The SREX process solvent also effectively extracts mercury from the tank wastes; however, there is currently no known method to re-extract Hg from the SREX

Table 1. Composition of Actual and Simulated Idaho National Engineering and Environmental Laboratory (INEEL) Tank Waste

Element	Average Tank Composition (*M*)	Composition of Simulated Waste (*M*)	Composition of Simulated Waste (mg/L)	Element	Average Tank Composition (*M*)	Composition of Simulated Waste (*M*)	Composition of Simulated Waste (mg/L)
Acid	1.97	1.55	—	NO_3	5.92	—	N/A[a]
Al	0.63	0.54	1.41×10^4	Ni	0.002	0.002	107.6
B	0.016	0.018	194.7	Pb	0.002	0.001	191.7
Ca	0.046	0.045	1797	PO_4	0.016	N/A	N/A
Cl	0.034	0.041	1450	Sr	1.35×10^{-5}	0.001	86.85
Cs	2.89×10^{-5}	0.001	130	SO_4	0.051	N/A	N/A
Cr	0.004	0.005	247.3	Zr	0.006	0.0014	130.7
F	0.067	0.259	4930	Eu	—	0.0070	1067
Fe	0.022	0.023	1282	Re	—	0.0036	667.4
Hg	0.0016	0.0020	395	Ba	5.65×10^{-5}	0.00011	15.00
K	0.19	0.118	4600	Ag	2.25×10^{-5}	4.12×10^{-5}	4.446
Mn	0.013	0.008	426.2	Se	2.56×10^{-5}	2.87×10^{-5}	2.266
Mo	6.55×10^{-4}	0.0012	119.5	Ru	3.01×10^{-5}	1.94×10^{-5}	1.966
Na	1.82	1.24	2.84×10^4	Rh	—	$<1.00 \times 10^{-6}$	<0.10
Cl/Hg (molar)	21.3	20.8	—	Pd	4.75×10^{-6}	$<6.31 \times 10^{-7}$	<0.07

[a] N/A = not analyzed.

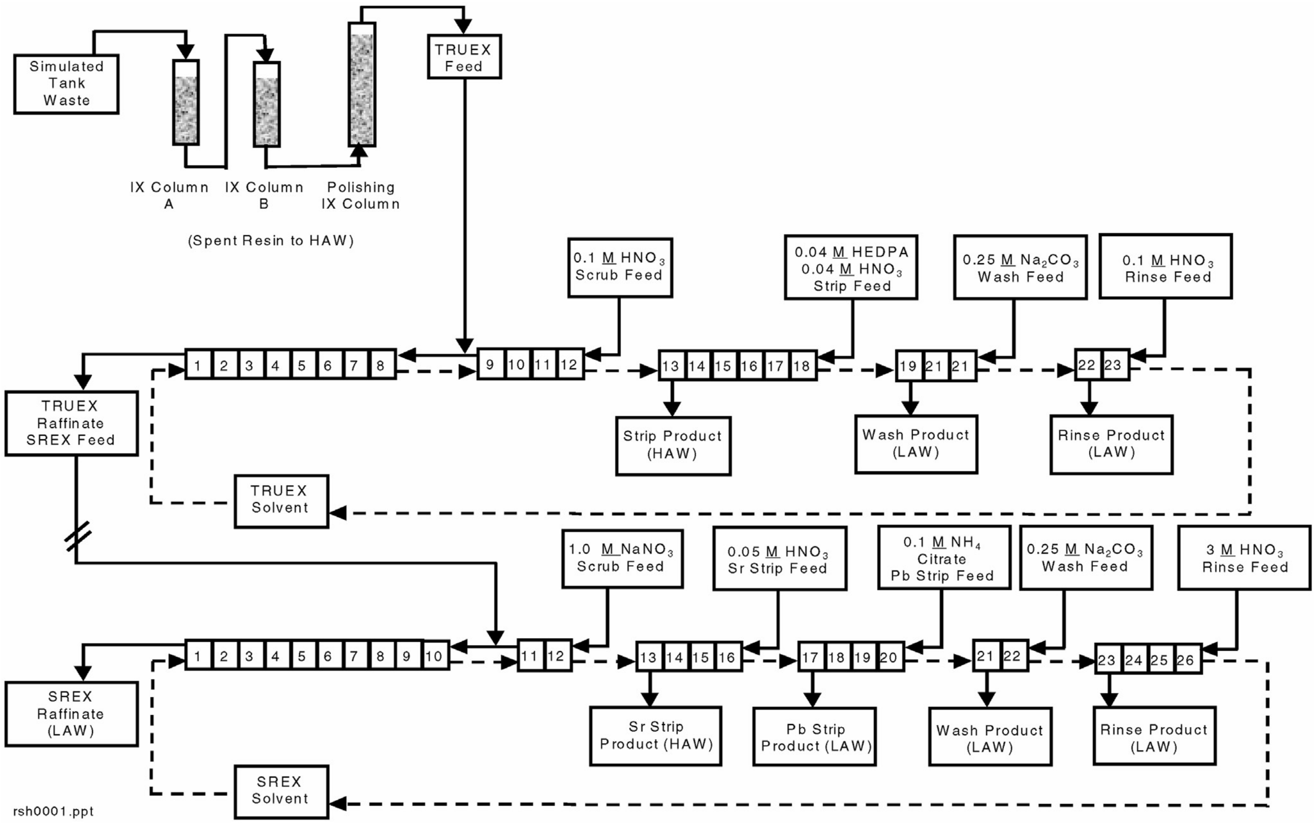

Figure 1. Integrated flowsheet for testing with simulated tank waste.

process solvent. Consequently, mercury is extracted from the waste in the SREX process and is built up in the solvent, ultimately degrading the process efficiency with regard to Sr removal. This potential problem is overcome largely by placing the TRUEX process in front of the SREX process and extracting the Hg prior to SREX processing. Experimental work is continuing to elucidate further the SREX/Hg interaction. Once Hg stripping from the SREX process is viable, it may be advantageous to order the solvent extraction processes in the reverse (SREX then TRUEX) from the standpoint of a further reduction in shielding requirements for the TRUEX portion of the integrated flowsheet.

The flowsheet in Fig. 1 was not optimized with respect to impacts on LAW and HAW immobilization. Rather, the conditions tested were those known to work with regard to separation flowsheet performance. Notable, nonoptimal conditions employed in the tests include the 1-hydroxyethane 1,1-diphosphonic acid (HEDPA) concentration in the TRUEX strip and the use of ammonium citrate in the SREX Pb strip. The 0.04 *M* HEDPA concentration used in the TRUEX strip feed is a factor of 4–10 times too high from the standpoint of final HAW volume since phosphate significantly impacts waste loading in borosilicate glass. It is also anticipated that citrate would have deleterious effects on LAW grouting operations since it inhibits solidification. Further development efforts in these areas (at a minimum) are required to optimize the separation processes with regard to the overall flowsheet.

RESULTS AND DISCUSSION

Cesium Ion Exchange

The duration of the cesium IX test was ~34 hr and ~45 L of simulated tank waste was processed. The flowrate through the system was ~22 BV/hour, based on the first two columns, for the duration of the test. Initially the columns were configured for up flow. Small voids were observed in the first two columns upon starting the feed pump with minor fluidization of the AMP–PAN in the voids. The system was shut down and the first and second columns were re-configured for down flow to eliminate the voids observed in the bed. The final polishing column was left in an up flow configuration.

Effluent samples for Cs analysis were taken hourly from columns A and B for the first 15 hr of operation, followed by samples at 3 hr intervals for 9 hr. Subsequent samples were taken every 5 hr until the end of the IX test. Cesium breakthrough results are shown in Fig. 2, where the ratio of cesium concentration in the column effluent (C) divided by the cesium concentration in the feed (Co) is plotted vs. BV of solution processed. A second-order kinetic equation (7) was used to predict cesium effluent concentration as a function of the feed volume

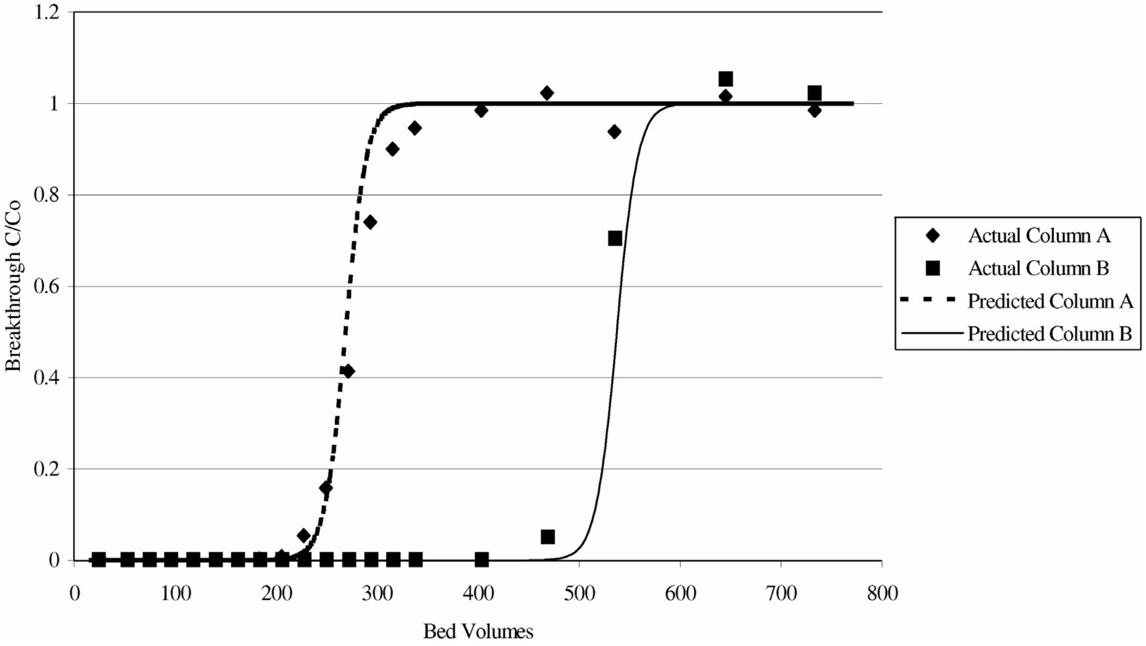

Figure 2. Cesium breakthrough curves for the AMP–PAN IX columns A and B. (Feed 130 mg/L Cs, 60 mL bed volume per column, 1.32 L/hr flowrate).

processed. Using the cesium concentration in the feed (130 mg/L) and referring to an AMP–PAN isotherm previously obtained (7), a maximum equilibrium cesium capacity of approximately 64 mg Cs per gram AMP was calculated. Using the mass transfer coefficient derived from AMP–PAN testing in 1.5 cm^3 columns, breakthrough curves for the two 60 cm^3 columns were predicted (7). The predicted breakthrough curves are also shown in Fig. 2 and indicate excellent agreement with the experimental data. Scale-up of the AMP–PAN IX process from 1.5 to 60 cm^3 columns was predicted accurately using the kinetic model, even though cesium feed concentrations varied by greater than an order of magnitude between the different column tests.

Fifty-percent cesium breakthrough was observed at approximately 280 BV for column A and 525 BV for column B. It is important to note that complete cesium breakthrough of column A occurred before 1% cesium breakthrough occurred in column B. This is significant since it indicates complete loading of the first column, in a two-column series arrangement, can be realized while maintaining the desired Cs removal, thus minimizing the total amount of sorbent that is required.

Total dynamic capacity was calculated by numerical integration for the total volume of feed processed. The dynamic capacity is shown in Table 2 at 50 and 100% breakthrough for each column. Dynamic capacities at 100% breakthrough agree well with the AMP–PAN equilibrium isotherm, indicating that the sorbent is at or very near equilibrium. Dynamic capacities at 50% breakthrough are very close to the equilibrium isotherm capacity, indicating that nearly all of the AMP–PAN sorption capacity can be realized.

Breakthrough data were not obtained for the third, polishing column. However, a composite sample of the effluent from the IX test indicated a Cs concentration of 0.219 mg/L. This represents a cumulative breakthrough of $C/\mathrm{Co} = 0.168\%$, or an overall removal efficiency of 99.83%. Previous IX testing performed at the INEEL with simulated tank waste indicated that some simulant components may interfere with the atomic absorption analysis of cesium and result in a bias toward higher cesium concentrations than actual (20). Analytical results of this test show cesium concentrations in the Column A effluent range 0.15–0.16 mg/L for 0–160 BV, and in the Column B effluent range

Table 2. Dynamic Capacities (DC) of Ammonium Molybdophosphate–Polyacrylonitrile (AMP–PAN) Columns

	DC at 50% Breakthrough mg Cs/g AMP–PAN	DC at 100% Breakthrough mg Cs/g AMP–PAN
Column A	62.2	64.0
Column B	63.1	64.0

Table 3. Percent Removal of Various Components During the Ammonium Molybdophosphate–Polyacrylonitrile (AMP–PAN) Ion Exchange Test

Component	Simulated Waste (IX Feed) (mg/L)	IX Effluent (Transuranic Extraction Feed) (mg/L)	Percentage Removed
Cs	130	<0.219	>99.83
Ag	4.45	0.048	98.91
Re	667	659	1.3
Ba	15.0	14.7	2.1
Cr	247	238	3.6
F	4930	4490	8.9
Ni	108	104	3.5
Zr	131	117	11

0.19–0.3 mg/L for 0–400 BV. Due to the high affinity AMP–PAN has for cesium, it is highly unlikely that this level of cesium passed through both columns early in the test. Since the exact cesium analytical bias is unknown, the results are reported as >99.83%, which is sufficient to reduce the ^{137}Cs activity in a grout waste form to well below the NRC Class A LLW limit.

The percentages of matrix components removed from the simulated feed solution by the AMP–PAN columns are listed in Table 3. Rhenium, barium, chromium, fluorine, and nickel were all essentially not sorbed on the AMP–PAN. The small removal efficiencies shown in Table 3 are all within the uncertainty associated with the analytical methods. Zirconium results are inconclusive, the removal efficiency shown in Table 3 corresponds to the upper limit of analytical uncertainty, indicating that Zr was either not sorbed, or a small amount (<10%) of Zr was sorbed. The validity of the high Ag removal efficiency is also uncertain. Silver nitrate was added to the initial IX feed and the feed had been filtered prior to entering the IX columns. It is possible that Ag precipitated in the feed vessel, as opposed to quantitative removal by the AMP–PAN. Further testing is needed to determine if Ag is indeed sorbed by the AMP–PAN.

Transuranic Extraction Flowsheet

The TRUEX test was operated 71.3 hr and processed 40.1 L of simulated feed. Note that the initial portion of the TRUEX test operated simultaneously with the Cs IX test, and continued after completion of the IX run.

During the course of the run, flooding was never observed in any of the effluent streams. At several points during the run, the contactors and feed pumps were simultaneously, momentarily shut down (<5 min), and stage 13 in the strip section and stage 19 in the carbonate wash section were opened and inspected for precipitates. Precipitates were never observed in the strip stage. During visual inspection of the stage 19 contactor after approximately 4 hr of operation, a slight band of rust/orange colored precipitate was observed on the exterior of the contactor rotor. The solution in the contactor indicated no visible signs of precipitates. On the basis of previous experience, the precipitate was HgO, which could be potentially eliminated by increasing the carbonate feed flowrate, thus decreasing the O/A and the mercury concentration in the carbonate wash section. The decision was made to continue the run under the initial conditions to determine if the precipitation problem would worsen or was an artifact of startup. The stages were rechecked several more times and the HgO precipitate on stage 19 appeared slightly worse. At ~20 hr into the run, the carbonate wash feed flowrate was increased slightly from 7.9 to 8.3 mL/min. The rotor was inspected several more times without noticeable difference in the amount of HgO deposited on the rotor. At ~40 hr into the run, the carbonate flowrate was increased again from 8.3 to 9.3 mL/min to determine if the HgO on the rotor would re-dissolve. This flowrate was maintained for the duration of the run with no discernable, visual difference in the amount of HgO present on the rotor. Aside from the slight HgO precipitation, other problems were not encountered during the test.

Product and feed flowrates were determined by measurement of the effluent stream volumes and calculation from feed tank depletion and product tank filling rates. The different methods of determining flowrates were used to establish a time-weighted average for each flowrate during the course of the run. The actual and target flowrates, as well as organic-to-aqueous (O/A) phase ratios are listed in Table 4. The average carbonate flow rate reported reflects adjustment of the flows in the carbonate wash section. The actual flowrates shown in Table 4 are comparable to the target values and were used for all subsequent calculations. On the basis the initial volume of 1500 mL of TRUEX solvent, a run time of 71.3 hr, and the organic flowrate of 6.04 mL/min, the solvent recycled through the centrifugal contactors a calculated 17.2 times.

Approach to Steady State

The primary species of interest for evaluating TRUEX flowsheet characteristics were Eu, Fe, Re, and Hg. Samples of the aqueous raffinate and strip product were taken every half-hour for the first 3 hr for Eu, Fe, and Re analyses to determine when steady-state conditions were achieved. Additionally, mercury analyses were performed on the aqueous raffinate samples to evaluate

Table 4. Flowrates and Organic-to-Aqueous (O/A) Ratios for the Transuranic Extraction (TRUEX) Flowsheet Test

		Flowrate (mL/min)		O/A Ratio		
Section	Phase	Desired	Actual	Desired	Actual	Total Flow (mL/min)
All	Organic	6	6.04	—	—	—
Extraction	Aqueous	14	13.23	0.43	0.46	19.27
Scrub	Aqueous	4	3.85	1.5	1.57	9.89
Strip	Aqueous	8	8.64	0.75	0.70	14.68
Carbonate wash	Aqueous	8	8.65	0.75	0.70	14.69
Acid rinse	Aqueous	1	0.97	6.0	6.2	7.01

the steady-state conditions. Beginning at 5 hr into the run, samples of the aqueous raffinate, strip, carbonate wash, acid rinse, and organic products were taken at 5 hr intervals for analysis of Eu, Fe, Re, and Hg.

The concentrations of Fe, Re, and Hg in the aqueous raffinate indicated that the extraction section was operating at steady state, with regard to each of these elements, within the first 5 hr of testing. The concentrations of Eu, Fe, and Re in the strip product indicated that the stripping section was operating at steady-state conditions, with regard to these elements, within the first 5 hr of the experiment. The time to reach steady state is predominately a function of contactor size and flowrates. The total volumetric capacity (organic plus aqueous) of the 3.3 cm contactors is 25 L/hr. On the basis of the flowrates chosen for this test, the volumetric throughputs were 1.156 L/hr (19.27 mL/min) in the extraction section and 0.88 L/hr in the strip section. Had the throughputs used in the test been closer to the maximum capacity of the contactors, the time required to achieve steady state would have been substantially less, probably within the first 30–60 min of operation.

Time-wise concentrations of Hg and Re in the carbonate wash product indicated that the carbonate wash section was never actually operating at steady-state conditions with regard to Hg. This is understandable due to precipitation of HgO in the wash stages and also due to the manual increase in carbonate feed flowrate in an effort to prevent this precipitation. Whether the steady-state operation was actually achieved with regard to Re was also questionable.

Time-wise concentrations of Hg and Fe in the organic product stream, as it exited from the acid rinse section, indicated that Hg (0.4–0.6 mg/L) and Fe (1.6–1.9 mg/L) were not increasing in the solvent as a function of time. Averages of 1.7 mg/L Al, 3.8 mg/L B, 7.7 mg/L Ca, 0.06 mg/L Cr, 0.6 mg/L K, 1.5 mg/L Mo,

Table 5. Primary Components and Parameters of the Composite Product Samples

Component	Aqueous Feed	Aqueous Raffinate	Strip Product	Carbonate Wash	Acid Rinse	TRUEX Organic[a]	Material Balance[b]
Eu (mg/L)	1066	<0.01	1382	4.41	0.034	0.04	
% per stream	—	<0.001	105.8	0.38	—	0.002	106%
Fe (mg/L)	1297	867.1	2.84	0.16	3.21	2.05	
% per stream	—	94.32	0.18	0.01	0.03	0.1	94.50%
Re (mg/L)	658.5	203.8	289.4	136.7	0.72	<0.08	
% per stream	—	43.66	35.83	19.16	0.01	<0.01	98.70%
Hg (mg/L)	422	11.1	1.12	314	0.28	<0.05	
% per stream	—	3.71	0.22	68.68	0.01	<0.01	72.60%
Final volume[c] (L)	—	54.7	32.8	36.6	3.92	0.69	—
Flow (mL/min)	9.38	13.23	7.64	8.65	0.97	6.04	—

[a] Organic composition not included in the material balance since solvent was recycled.
[b] Calculated as a percentage of out/in.
[c] Does not account for samples removed during the course of the experiment or the volume remaining in the stages after shutdown.

Table 6. Measured Stagewise Distribution Coefficients from the TRUEX Test

Section	Stage #	Eu	Fe	Re	Hg
Extraction	1	—	0.75	0.78	0.59
	2	—	0.92	0.67	0.51
	3	—	0.94	0.68	0.47
	4	—	0.96	0.65	0.50
	5	>36	0.93	0.73	0.72
	6	>35	0.92	0.76	0.82
	7	>31	0.92	0.80	1.3
	8	25	0.69	0.81	1.3
Scrub	9	14	0.12	2.4	7.7
	10	12	0.06	5.3	16
	11	7.6	0.03	12	31
	12	3.8	0.04	19	34
Strip	13	0.02	—	2.0	520
	14	<0.01	—	1.2	133
	15	<0.35	—	1.1	1000
	16	—	—	1.0	1250
	17	—	—	1.0	1360
	18	—	—	1.0	1150
Carbonate wash	19	—	—	0.06	0.004
	20	—	—	0.06	9.4
	21	—	—	<0.4	23
Acid rinse	22	—	—	—	0.9
	23	—	—	—	0.6

7.4 mg/L Na, and 2.6 mg/L Zr were detected in the organic product samples at 20, 40, and 60 hr. The results for these elements were consistent in the three different samples. The data clearly indicated none of the matrix components was building up in the solvent.

Composite Product Concentrations and Stagewise Distribution Coefficients

Important information from the extended flowsheet test included the composition of all final products from the TRUEX run. Composite samples of the product solutions were taken at the end of the test, and are anticipated to be representative of the products that would be expected in full scale, continuous operation. Concentrations of the primary metals of concern, e.g., Eu, Fe, Re, and Hg, and the percentage of each component in the various composite products are indicated in Table 5. Average flowrates for the duration of the test, final total volumes, and the material balances for these components are also indicated. The stagewise distribution coefficients for these species were also measured for each stage after shutdown and are shown in Table 6.

The data in Table 5 indicate >99.999% of the Eu (Am surrogate) was extracted from the feed. Note that if Am-241 is removed from the actual wastes, the remaining actinides will also be removed since Am is the most difficult to extract (i.e., Am has a lower distribution coefficient than most actinides). The material balance of 106% for Eu is acceptable, with most of the discrepancy attributed to the strip product sample. The distribution coefficients were very high for stages 5 through 8 in the extraction section. The distribution coefficients indicate an excessive number of stages for Eu extraction; however, the required number of extraction stages was based on Hg removal (*vide infra*). The Eu distribution coefficients were large enough in the scrub section ($D_{\mathrm{Eu}} > 4$) to ensure very little Eu scrubbing. All of the extracted Eu was recovered in the strip product (106% of the Eu in the feed), consistent with the low Eu distribution coefficients measured in the strip section ($D_{\mathrm{Eu}} \leq 0.35$). Distribution coefficients in the carbonate wash section could not be evaluated since Eu was below detection limits; a small amount of the Eu was detected in the carbonate wash product (4.41 mg/L, or 0.38%). The results indicate the effectiveness of the TRUEX process for actinide removal and recovery from INEEL tank wastes. With this high actinide removal efficiency, the LAW grout will be well below the 10 nCi/g NRC Class A LLW limits.

The distribution data in Table 6 indicate that some iron extracted since $D_{\mathrm{Fe}} \sim 0.9$ in the extraction section, and was scrubbed effectively based on a $D_{\mathrm{Fe}} < 0.1$ in the scrub section. The iron concentration in the organic phase exiting the scrub section was low, 2.3 mg/L, and the distribution data were meaningless for stages13 through 23. The distribution data are consistent with the results in Table 5, which indicate most of the Fe in the feed (94.3%) exited with the aqueous raffinate.

Rhenium was added to the simulated feed (as perrhenate, $\mathrm{ReO_4^-}$) as a surrogate for technetium (as pertechnetate, $\mathrm{TcO_4^-}$). The results in Table 5 indicate that approximately 56% of the Re was extracted from the simulated waste. This is consistent with the distribution coefficients in Table 6, which indicates D_{Re} was 0.65–0.81 in the extraction section and $D_{\mathrm{Re}} > 2.4$ in the scrub section. Approximately 36% of the Re was stripped with the HEDPA solution, consistent with the strip $D_{\mathrm{Re}} \sim 1$. Roughly 19% of the Re exited with the carbonate wash stream, which was very effective at removing Re from the TRUEX solvent, as indicated by the D_{Re} of 0.06 to <0.4 in the carbonate wash stages. The material balance for Re was very good at 98.7%.

It should be noted that the tank wastes currently stored at INEEL are below the limits of concern for Tc in Class A grout. However, since pertechnetate is extremely mobile in the environment, it is desirable to understand the behavior of this species for any treatment option.

One of the goals in the TRUEX portion of the integrated test was to determine the efficiency of Hg removal from the simulated waste. To this end, the flowsheet was modified from previous tests to include more extraction stages and higher flowrates in the carbonate wash section to recover as much of the mercury as possible from the wastes. Mercury removal is important from the aspect that it is a RCRA regulated metal present in significant quantities in the tank wastes. Use of the TRUEX process to partition Hg into a relatively clean (low metals and radionuclide content) stream is viewed as an advantage if Hg must be removed ultimately and dispositioned in accord with RCRA regulations. Furthermore, mercury complicates the SREX process.

Data from the composite samples indicate 96.3% of the Hg was extracted from the feed, which is consistent with the extraction section mercury distribution ratios of ~ 1. Very little of the Hg was scrubbed from the solvent as manifest from the available scrub section distributions of $D_{\mathrm{Hg}} > 8$. The HEDPA strip solution was also ineffective at stripping Hg from the solvent, with distribution ratios of $D_{\mathrm{Hg}} > 100$ in the strip section. A mere 0.22% of the mercury exited with the strip product. Table 5 indicates that 68.7% of the mercury exited with the carbonate wash product. The overall material balance of mercury was quite low at 72.6%, consistent with the precipitation of HgO encountered in the carbonate wash section.

In general, the TRUEX portion of the flowsheet indicated relatively good Hg removal from the simulated tank waste. Further work is required to enhance mercury removal, if necessary, and to eliminate the precipitation of Hg in the carbonate wash section. Several more extraction stages and/or a slight modification in the extraction section O/A could be used to enhance the Hg extraction. Likewise, the O/A in the carbonate wash section could be altered to eliminate the HgO precipitation.

Samples of the composite products were also analyzed for a variety of matrix components, both micro and macro constituents in the simulated tank waste, to evaluate or confirm further their behavior in the TRUEX 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 7. The only elements extracted to any measurable extent were Mo, Ru, Zr, and perhaps Rh and Cl. Less than 1% of the remaining elements (Al, Ag, B, Ca, Cr, K, Mn, Na, Ni, Pb, Se, Sr, and F) were extracted from the feed. The percentage of Ag, Rh, F, and Cl extracted from the feed is relatively uncertain since the material balances for these species were typically very poor or marginal, at 190% for Ag, 220% for Rh, 144% for F, and 89% for Cl.

Table 7. Percentage of Matrix Components in the Composite Products

Stream	Al	Ag	B	Ba	Ca	Cr	K
Aqueous raffinate	98.56 (99.98)[a]	190.1 (100)	96.95 (100)	103.1 (99.97)	100.0 (99.92)	100.8 (99.96)	95.49 (99.97)
Strip product	<0.0004 (0)	<49.6 (0)	<0.03 (0)	<0.06 (0)	0.006 (0.006)	0.010 (0.010)	0.001 (0.002)
Carbonate wash	0.001 (0.001)	<56.2 (0)	<0.03 (0)	<0.17 (0)	0.050 (0.050)	0.011 (0.011)	0.002 (0.002)
Acid rinse	0.022 (0.023)	<6.30 (0)	<0.04 (0)	0.03 (0.03)	0.021 (0.021)	0.024 (0.024)	0.021 (0.022)
Organic product	0.012	<200	<1.6	<0.23	0.26	0.014	0.002
Mass balance[b]	98.6	190	96.95	103.2	100.1	100.9	95.52

Stream	Mn	Mo	Na	Ni	Pb	Rh	Ru
Aqueous raffinate	98.09 (99.98)	3.30 (3.35)	94.99 (99.98)	103.4 (99.89)	92.68 (99.50)	173.7 (78.94)	89.43 (91.61)
Strip product	<0.002 (0)	93.86 (95.27)	0.003 (0.003)	0.033 (0.032)	0.29 (0.31)	46.34 (21.06)	<3.49 (0)
Carbonate wash	<0.002 (0)	1.28 (1.30)	0 (0)	0.060 (0.058)	0.17 (0.18)	<47.6 (0)	8.19 (8.39)
Acid rinse	0.023 (0.023)	0.082 (0.083)	0.013 (0.014)	0.024 (0.024)	0.022 (0.023)	<5.34 (0)	<0.44 (0)
Organic product	<0.01	0.6	0.02	<0.1	0.13	<170	<14
Mass balance[b]	98.12	98.52	95.01	104	93.16	220	97.6

Stream	Se	Sr	Zr	F	Cl
Aqueous raffinate	98.75 (100)	96.84 (99.98)	71.49 (71.43)	143.3 (99.86)	80.20 (90.10)
Strip product	<4.59 (0)	<0.01 (0)	28.46 (28.43)	0.203 (0.142)	<0.94 (0)
Carbonate wash	<5.19 (0)	<0.01 (0)	0.133 (0.133)	<0.06 (0)	8.82 (9.90)
Acid rinse	<0.58 (0)	0.021 (0.022)	0.011 (0.011)	<0.01 (0)	<0.12 (0)
Organic product	<19	<0.04	0.63	<0.2	<3.7
Mass balance[b]	98.75	96.86	100.1	144	89.0

[a] Normalized percentages for a 100% material balance.

[b] 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. Normalized organic percentages are not reported.

The strip product contained most of the extracted Mo and Zr, indicating the HEDPA was effective at stripping these components from the TRUEX solvent. It also appears that the extracted Rh was quantitatively removed from the solvent by the HEDPA strip solution. It should be noted that the Rh results are uncertain based on the extremely poor material balance of 220%.

The carbonate wash section was effective at stripping Cl and Ru from the TRUEX solvent. The chloride present in the carbonate wash product is not surprising since Hg is known to extract into the TRUEX product as $HgCl_2$ (13). Confirmation of this phenomenon is reinforced when observing the measured concentrations of Cl and Hg in the carbonate wash product, based on the composite samples. The concentration of Hg in the wash product was analytically determined to be 314 mg/L or 0.00157 *M* Hg. Likewise, the chloride concentration was measured to be 147 mg/L or 0.00415 *M* Cl. The molar ratio of Cl to Hg in the carbonate wash is therefore 2.65, slightly higher, but consistent with the molar ratio of 2 for the $HgCl_2$ compound. Assuming the mercury was extracted into the solvent as $HgCl_2$ and completely stripped in the carbonate wash, the excess chloride (above the molar ratio of 2) in the wash product may be an indirect measure of the amount of mercury lost to precipitation of HgO. An estimated 3.71 g of Hg was lost as precipitated HgO in the carbonate wash section over the course of the experiment, corresponding to 22.1% of the mercury in the feed. Including this mass in the overall Hg material balance leads to a respectable 94.7% overall mass balance for mercury.

Strontium Extraction Flowsheet

The SREX test was operated a cumulative of 77.9 hr and processed 50.97 L of the TRUEX raffinate. The SREX portion of the integrated test was performed approximately 5 weeks after completing the TRUEX test since the centrifugal contactors had to be reconfigured and hydrodynamically tested before the SREX test.

During the course of the run, flooding or precipitation was never observed in any of the effluent streams. The test proceeded for the entire 78 hr duration without stopping the contactors or shutting down solution flows.

Product and feed flowrates were determined by periodic measurement of the effluent streams and calculation from feed tank depletion and product tank filling rates. The different methods of determining flowrates were used to establish a time-weighted average for the flowrate of each stream. The actual and target flowrates, as well as organic-to-aqueous (O/A) phase ratios are listed in Table 8. The actual flowrates shown in Table 8 are in excellent agreement with the target values and were used for all subsequent calculations.

Table 8. Flowrates and Organic-to-Aqueous (O/A) Ratios for the Strontium Extraction (SREX) Flowsheet Test

Section	Phase	Flowrate (mL/min)		O/A Ratio		Total Flow (mL/min)
		Target	Actual	Target	Actual	
All	Organic	14.7	14.6	—	—	—
Extraction	Aqueous	14.7	14.5	1.0	1.0	29.2
Scrub	Aqueous	3.67	3.60	4.0	4.06	18.2
Sr strip	Aqueous	29.3	30.4	0.5	0.48	45.0
Pb strip	Aqueous	14.7	14.2	1.0	1.03	28.8
Carbonate wash	Aqueous	2.93	2.73	5.0	5.34	17.3
Acid rinse	Aqueous	7.34	6.63	2.0	2.2	21.2

Based on the 1500-mL initial volume of SREX solvent, a run time of 77.9 hr, and an organic flowrate of 14.6 mL/min, the organic was recycled through the centrifugal contactors a calculated 45.5 times.

Approach to Steady State

The primary species of interest for evaluating flowsheet characteristics were Sr, Pb, and K. Samples of the aqueous raffinate, Pb strip, and Sr strip products were taken every half-hour for the first 3 hr to determine when the steady-state conditions were achieved. Beginning at 5 hr into the run, samples of the aqueous raffinate, Sr strip, Pb strip, carbonate wash, acid rinse, and organic products were taken at 5-hr intervals.

The concentrations of Sr and K in the aqueous raffinate indicated that the extraction section was operating at steady state with regard to these components within the first 5 hr of testing. The concentrations of K, Sr, and Pb in the Sr strip product and the K and Pb concentrations in the Pb strip product indicated that both the Sr and Pb stripping sections were operating at steady-state conditions within the first 5 hr of the experiment. The concentrations of K and Pb in the carbonate wash product indicated that the wash section was operating at steady-state conditions within the first 5–10 hr of the experiment. The concentration of K in the rinse product was very low (<0.1 mg/L), making it difficult to evaluate the steady-state operation in the rinse section. Potassium and Na were the only elements consistently present above analytical detection limits in the organic product. There was no evidence of K or Na build up in the organic product as a function of time based on the analytical results.

Composite Product Concentrations and Stagewise Distribution Coefficients

Important information from the extended flowsheet test includes the composition of all final products from the SREX run. Composite samples of the product solutions were anticipated to be representative of the products that would be expected in full scale, continuous operation. Concentrations in the composite products of the primary metals of concern, e.g., Sr, K, Pb, and Hg, and the percentage of each component in the various streams, are shown in Table 9. Average flowrates for the duration of the test, final total volumes, and the material balances for these components are also indicated. The stagewise distribution coefficients for these species were also measured for numerous stages after shutdown and are shown in Table 10.

Based on the data in Table 9, 99.86% of the strontium was removed from the feed. It is estimated that approximately 99.9% Sr removal is required to meet the NRC Class A LLW requirement in the final grouted waste for the INEEL tank wastes. Thus, the Sr removal obtained in this test is marginally acceptable to meet this requirement. Note that due to the analytical limitations for stable Sr in the simulated waste feed used in this experiment, the amount of Sr in the feed to the SREX process (63.9 mg/L) is substantially higher than anticipated in the actual tank wastes (~1.5 mg/L). Most of the stable Sr in actual wastes is “tramp” Sr from chemical additions during processing. Strontium removal is consistent with the extraction distribution coefficients of $D_{Sr} = 2.3$ to 3.2 measured in the extraction stages for the test (refer to Table 10). The only scrub stage distribution measured (stage 11) was $D_{Sr} = 1.56$, and is low enough to indicate a fraction of the extracted Sr will have scrubbed and recycled to the extraction section. The scrub section conditions could be improved by altering the $NaNO_3$ concentration in the scrub feed or the scrub feed flowrate to minimize Sr recycle to the extraction section. All of the extracted Sr, 100.8%, was recovered in the Sr strip section, indicating this section was very effective for Sr recovery. This result is consistent with the Sr distribution coefficient of $D_{Sr} = 0.125$ measured on the first Sr strip stage (stage 13). Strontium distributions could not be obtained for any of the stages past 13 since the concentrations were below the analytical detection limits. The material balance for Sr, based on the composite samples, was excellent at 101%.

Lead is a RCRA regulated metal, present in significant quantities (~320 mg/L) in INEEL tank wastes. The SREX process is capable of removing Pb from the tank waste for subsequent disposal. The data in Table 9 indicate

Table 9. Primary Components and Parameters of the Composite Product Samples

Component	Aqueous Feed	Aqueous Raffinate	Sr Strip Product	Pb Strip Product	Carbonate Wash	Acid Rinse	SREX Organic[a]	Material Balance[b]
Sr (mg/L)	63.9	0.067	23.1	<0.013	<0.013	<0.013	<0.126	
% per stream	—	0.14	100.8	<0.026	<0.005	<0.012	<0.26	101%
Pb (mg/L)	128.5	<0.11	7.62	91.9	0.6	<0.11	<1.07	
% per stream	—	<0.11	16.5	93.2	0.12	<0.051	<1.12	110%
K (mg/L)	3520	2430	123	1.07	0.19	0.13	12.4	
% per stream	—	92.2	9.74	0.04	0.001	0.002	0.47	101.9%
Hg (mg/L)	11.1	0.425	0.008	3.04	6.33	0.14	1.92	
% per stream	—	5.11	0.201	35.7	14.3	0.77	23.2	56.10%
Final volume[c] (L)	—	68.1	142.1	66.5	12.8	31	0.42	—
Flow (mL/min)	10.9	14.5	30.4	14.2	2.73	6.63	14.6	—

[a] Organic composition not included in the material balance since solvent was recycled.

[b] Calculated as a percentage of out/in.

[c] Does not account for samples removed during the course of the experiment or the volume remaining in the stages after shutdown.

Table 10. Measured Stagewise Distribution Coefficients from the Strontium Extraction Test

Section	Stage #	Sr	Pb	K
Extraction	1	3.23	13.3	0.22
	3	2.38	10.5	0.22
	5	2.32	7.10	0.27
	7	2.26	7.72	0.27
	9	2.37	7.63	0.29
	10	2.28	99.6	0.28
Scrub	11	1.56	115	0.23
Sr strip	13	0.125	35.3	0.093
	16	—	3.73	409
Pb strip	17	—	0.017	8.70
	20	—	3.53	3.53
Carbonate wash	21	—	2.73	60.3
	22	—	2.37	23.9
Acid rinse	23	—	20.2	78.7
	26	—	8.51	104

>99.89% of the Pb in the SREX feed was extracted. This is consistent with the Pb distribution coefficients of $D_{\mathrm{Pb}} = 7.6$ to 100 measured in the extraction stages. The measured scrub distribution of $D_{\mathrm{Pb}} = 115$ on stage 11 indicates lead was not scrubbed from the SREX solvent. A fraction of the extracted Pb, 16.5%, was recovered with the Sr strip product and the balance, 93.2%, was recovered with the Pb strip product. The overall material balance for Pb was marginal at 110%, indicating the fraction of Pb reporting to the Sr strip and/or Pb strip product streams may be high, and/or slight errors in the Pb feed analysis or flowrate. The SREX flowsheet was extremely effective at removing Pb from the simulated tank waste. Optimization of the flowrates and/or compositions for the Sr and Pb strip feed streams is anticipated to result in the complete recovery of lead in the Pb strip product.

It is known that the SREX process has a slight affinity for the extraction of potassium from the tank waste matrix. Potassium is a bulk matrix component present in INEEL tank wastes at ~7.5 g/L. It is desirable to minimize the mass of inert matrix components, including K, that report to the high-activity streams, thereby minimizing the final volume of HAW. The data in Table 9 indicate 7.8% of the K in the SREX feed was removed, which is consistent with the distribution coefficients measured for the extraction section of $D_{\mathrm{K}} = 0.22$ to 0.29. The primary function of the scrub section is to remove extracted K and recycle it back to the extraction section. Much of the K was scrubbed based on the stage 11 distribution coefficient of $D_K = 0.23$. The Sr strip section effectively recovered virtually all of the extracted potassium. The overall material balance for potassium was excellent at 102%. Optimization of the scrub section could reduce the amount of K reporting to the Sr strip product stream.

One of the major concerns with the SREX process is the extraction of mercury, which currently cannot be stripped very effectively from the solvent. Approximately 95% of the residual Hg in the TRUEX raffinate was removed in the SREX process. Approximately 50% of the extracted Hg was recovered in the Pb strip and carbonate wash products. The material balance for Hg (not including the solvent, which was recycled) was particularly poor at 56.1%. The poor material balance could be attributed to continuous mercury build up in the solvent. The organic phase mercury concentration of 1.92 mg/L could be erroneously low due to poor Hg stripping by the 0.1 *M* ammonium citrate used to prepare the organic samples for analysis. Mercury build up in the SREX solvent should not pose problems at the low concentrations remaining in the TRUEX raffinate and entering the SREX extraction section. With some removal in the solvent wash section (~50% in this test), Hg should build up to a steady-state value in the SREX solvent. Recent calculations indicate that the mercury could potentially build up in the solvent to ~63% of that in the SREX feed (or ~7 mg/L Hg in the solvent during this test) at steady state (21).

The fractionation of numerous other matrix components as analyzed in the composite samples is summarized in Table 11. On the basis of the *normalized* percentages in the raffinate samples, less than 1% of the Al, B, Ca, Cr, Fe, Mn, Ni, Zr, and F were removed in the SREX flowsheet. These results are consistent with previous SREX flowsheet tests, and indicate Al, B, Ca, Cr, Fe, Mn, and Ni are essentially inextractable by the SREX solvent (17). In prior testing (17), >81.6% of the Zr was extracted and recovered in the Sr strip product, using a 2.0 *M* HNO_3 scrub solution. It is postulated that the 1.0 *M* $NaNO_3$ scrub solution used in this test effectively scrubbed Zr back to the extraction section. Unfortunately, stage wise Zr distributions were not determined to confirm this hypothesis.

Based on the chemical similarity of barium and strontium, Ba is expected to extract in the SREX process. Table 11 indicates that 63.2% of the Ba in the simulated feed was removed in the SREX test and recovered in the Sr strip product. This result is consistent with those in previous flowsheet tests where 63.6% of the Ba in actual tank waste was removed and recovered in the Sr strip product (17). Due to the similarity of Ba and Sr, it is unlikely that a substantially better separation between the two could be achieved through flowsheet optimization.

The results in Table 11 indicate that approximately 3% of the Mo in the simulated feed was removed in the SREX process and recovered in the Sr strip product. Analyses for Mo in the SREX process have not been performed previously for INEEL tank wastes.

Table 11. Percentage of Other Matrix Components in the Composite Products

Stream	Al	B	Ba	Ca	Cr	Fe	Mn
Aqueous raffinate	95.55 (99.995)[a]	91.92 (99.72)	36.50 (35.79)	87.08 (99.95)	90.58 (99.96)	97.18 (99.96)	92.74 (99.98)
Sr strip product	<0.002 (<0.002)	<0.15 (<0.16)	65.23 (63.96)	<0.01 (<0.02)	<0.01 (<0.02)	<0.01 (<0.01)	<0.01 (<0.01)
Pb strip product	<0.001 (<0.0010	<0.07 (<0.07)	<0.13 (<0.13)	<0.01 (<0.01)	0.013 (0.014)	0.0130.013	<0.01 (<0.01)
Carbonate wash	<0.001 (<0.001)	<0.01 (<0.01)	0.064 (0.063)	0.021 (0.024)	<0.001 (<0.001)	0.004 (0.004)	<0.001 (<0.001)
Acid rinse	0.001 (0.001)	<0.03 (<0.03)	<0.06 (<0.06)	<0.003 (<0.004)	0.008 (0.008)	0.013 (0.014)	0.003 (0.003)
Organic Product	<0.01 (<0.011)	<0.7 (<0.76)	<1.31 (<1.29)	<0.07 (<0.08)	0.066 (0.073)	0.049 (0.050)	<0.06 (<0.06)
Mass Balance[b]	<95.56	<92.2	<102.0	<87.13	<90.62	<97.22	<92.76

Stream	Mo	Na	Ni	Re	Zr	F	Cl
Aqueous raffinate	97.73 (95.56)[a]	84.54 (92.0)	91.27 (99.78)	3.59 (3.58)	92.69 (99.16)	65.57 (99.51)	102.7 (91.33)
Sr strip product	3.10 (3.03)	0.467 (0.508)	<0.11 (<0.12)	92.37 (92.02)	<0.13 (<0.14)	<0.18 (<0.27)	<5.63 (<5.01)
Pb strip product	<0.87 (<0.85)	0.001 (0.001)	<0.05 (<0.06)	3.38 (3.37)	<0.06 (<0.06)	<0.08 (<0.12)	<2.63 (<2.34)
Carbonate wash	<0.17 (<0.16)	6.86 (7.47)	<0.01 (<0.01)	0.58 (0.58)	0.567 (0.607)	<0.03 (<0.04)	<0.25 (<0.23)
Acid rinse	<0.41 (<0.40)	0.024 (0.026)	0.037 (0.040)	0.45 (0.45)	<0.03 (<0.03)	<0.04 (<0.06)	<1.23 (<1.09)
Organic product	<8.94 (<8.74)	0.017 (0.019)	<0.52 (<0.57)	0.18 (0.18)	<0.62 (<0.66)	<0.84 (<1.3)	<27.1 (<24.1)
Mass Balance[b]	<102.3	91.89	<91.47	100.4	<99.47	<65.9	<112.4

[a] Normalized percentages for a 100% material balance.

[b] 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. Normalized organic percentages are not reported.

Rhenium was added to the simulated waste as perrhenate to function as a surrogate for technetium (as pertechnetate). Rhenium was extracted effectively, with 96.4% of the Re in the SREX feed being removed. Much of the removed Re, 92.4% of the total, was recovered in the Sr strip product and 3.4% of the total Re reported to the Pb strip product.

CONCLUSIONS

Three unit operations for the removal of fission products, actinides, and RCRA metals (mercury and lead) were integrated successfully and tested for extended run times with simulated INEEL acidic tank waste. The integrated unit operations performed effectively without deleterious effects to the individual unit operations from coupling the systems together. Furthermore, accumulation of components was not observed in any of the unit operations.

The Cs removal was >99.83% in the AMP–PAN IX system and interference from other species was not observed. The experimental breakthrough data were in excellent agreement with modeling predictions based on data obtained with much smaller (1.5 cm^3) columns, lending confidence to column scale-up predictions. The dynamic capacities calculated for the two 60 cm^3 columns (operated to 100% breakthrough) were in excellent agreement with the equilibrium capacity, indicating virtually all of the Cs removal capacity of the sorbent can be realized.

The effluent from the IX system was processed through a TRUEX solvent extraction flowsheet to remove europium (americium surrogate), mercury, and rhenium (technetium surrogate) from the simulated waste. The TRUEX solvent was recycled through the flowsheet an estimated 17.2 times without detectable degradation of process performance from acid hydrolysis, component build-up, or changes in solvent composition. Greater than 99.999% of the Eu, 96.3% of the Hg, and 56% of the Re were removed from the simulated feed, these components were recovered effectively in the strip and wash streams. Although the HEDPA concentration in the strip solution for this test was very effective at recovering these elements, its use has a major impact on the final HAW glass volume. The HEDPA concentration must be reduced substantially or eliminated in future optimization efforts to reduce the final HAW glass volume. It is estimated that >22.1% of the Hg was lost as an HgO precipitate in the carbonate wash section. Precipitate formation in the contactors is unacceptable and future efforts must define conditions to prevent the mercury precipitation.

The raffinate from the TRUEX test was subsequently processed through a SREX solvent extraction flowsheet to remove strontium and lead from the simulated waste. The SREX solvent was recycled through the system an estimated 45.5 times without measurable build-up of matrix components in the solvent. Approximately 99.9% of the Sr, >99.89% of the Pb, and >96.4% of the Re were removed from the aqueous feed to the SREX flowsheet and recovered in the strip and wash sections. Operational problems such as flooding and precipitation were not encountered during the SREX test.

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