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INTEGRATED AMP–PAN, TRUEX, AND SREX TESTING. II. FLOWSHEET TESTING FOR SEPARATION OF RADIONUCLIDES FROM ACTUAL ACIDIC RADIOACTIVE WASTE

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ABSTRACT

Three separation processes for the removal of selected fission products, actinides, and Resource Conservation and Recovery Act metals (mercury and lead) have been integrated successfully and tested using actual acidic radioactive waste at the Idaho National Engineering and Environmental Laboratory (INEEL). The separation processes integrated were ion exchange for ^{137}Cs removal, followed by TRUEX solvent extraction for actinide, Hg, and ^{99}Tc removal, and subsequent SREX solvent extraction for ^{90}Sr and Pb removal. A flowsheet comprising these three processes is being developed at the INEEL to reduce the activity of acidic tank waste to allow disposal, after immobilization, as an NRC Class A LLW.

Approximately 1350 mL of actual INEEL tank waste was first processed through an ion exchange column for selective Cs

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removal. The column was packed with a composite ammonium molybdophosphate–polyacrylonitrile (AMP–PAN) sorbent. The ion-exchange system was operated at 26 bed volumes per hour and was sized at a bed volume of 2 cm^3. A ^{137}Cs removal of 99.95% was obtained in the ion exchange system without notable interference from other species.

The effluent from the ion-exchange (IX) system was stored and subsequently processed several weeks later through a TRUEX solvent extraction flowsheet to separate actinides, Hg, and ^{99}Tc from the tank waste. The TRUEX flowsheet test was performed utilizing 23 stages of 2.0-cm diameter centrifugal contactors. Removal efficiencies of 99.2%, 94.7%, and 63% were obtained for total alpha, Hg, and ^{99}Tc, respectively. Operational problems such as flooding and/or precipitate formation were not observed during the TRUEX flowsheet test.

The raffinate from the TRUEX test was stored and subsequently processed several weeks later through a SREX solvent extraction flowsheet to separate ^{90}Sr and Pb, from the tank waste. The SREX flowsheet test was performed using the same centrifugal contactors used in the TRUEX test after reconfiguration. Approximately 99.997% of the ^{90}Sr and 98% of the Pb were extracted with the SREX flowsheet and recovered in the strip and wash sections. In addition, approximately 93% of the remaining alpha activity was extracted and recovered in the strip section. Operational problems such as flooding and/or precipitation formation were not observed during the SREX test.

INTRODUCTION

The Idaho National Engineering and Environmental Laboratory (INEEL) is currently storing approximately five million liters of acidic radioactive liquid waste. An aggressive development effort has been underway since 1993 to evaluate technologies for processing and immobilizing these tank wastes (1). One of the proposed treatment methods for the tank waste is to separate the radionuclides from the bulk waste components via solvent extraction and/or ion exchange technologies (2). Separation of the radionuclides from the bulk waste components is anticipated to reduce significantly disposal costs of the waste by reducing the volume of high-activity waste (HAW) requiring disposal in a geological repository. The bulk of the waste could then be disposed off as a low-activity waste (LAW) grout. As a part of this development effort, an integrated flowsheet consisting of AMP–PAN ion exchange for Cs removal, TRUEX solvent extraction for actinide removal, and SREX solvent extraction for Sr removal has been developed and recently tested using surrogate waste solutions (1). As a continuation of this work, a similar flowsheet was tested using actual tank waste solution and 24 stages of 2-cm diameter centrifugal contactors installed in a shielded cell facility. The results of this flowsheet testing with actual tank waste are presented in this report.

EQUIPMENT DESCRIPTION

AMP–PAN IX Column

A single IX column with a 9.5 mm diameter and 28 mm height bed section was used for AMP–PAN testing. The bed section was constructed of plexiglass to allow visual inspection of the bed material during operation and the end sections were constructed of stainless steel. The column contained approximately 2.0 cm^3 of sorbent and was configured for downward flow. Actual tank waste was pumped from a high-density polyethylene (HDPE) feed bottle to the column using a valveless metering pump. Column effluent samples were collected approximately every hour in HDPE sample bottles.

TRUEX/SREX Solvent Extraction

The TRUEX and SREX portions of the flowsheet demonstration were performed using 2-cm diameter centrifugal contactors installed in a shielded hot cell facility. The equipment consisted of 24 stages of 2-cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, and an air purge system for the contactor bearings. The aqueous and organic feed pumps and feed vessels were located inside the shielded cell. The scrub, strip and wash feed pumps, and feed vessels were located outside the cell. All of the feed pump controllers were located outside the cell. Non-radioactive solutions used for the flowsheet testing were pumped to the centrifugal contactors through penetrations in the cell wall.

The centrifugal contactors were designed and fabricated by Argonne National Laboratory. They were designed specifically for operation of the TRUEX process with INEEL tank waste. The contactors were modified at the INEEL for remote installation and operation in the shielded hot cell facility. A description of the centrifugal contactors is provided in Table 1.

Table 1. Description of the 2-cm Centrifugal Contactors

Size	2-cm Rotor Diameter
Motor	115 V, 60 Hz Bodine model 710
RPM	3,600 rpm (not adjustable)
Material of construction	304 L stainless steel
Inlet and outlet ports	3/8-in. o.d. tubing
Configuration	Single stage units—configured as desired

METHODOLOGY/EXPERIMENTAL PROCEDURE

Tank Waste Feed Composition

Approximately 1350 mL of actual INEEL acidic tank waste were used as feed solution for the integrated flowsheet testing. Volume limits imposed by Federal and State Treatability Study regulations precluded the use of a larger volume of waste for this testing. The composition of the tank waste used for this testing is shown in Table 2. Chemical feed adjustments were not made prior to performing the integrated demonstration. The feed solution was first filtered through a 0.45-μm filter.

Flowsheet Configuration

On the basis of the results of previous integrated flowsheet testing with simulated tank waste (1), a similar flowsheet was proposed for integrated testing

Table 2. Tank Waste Feed Composition

Component	Concentration	Component	Concentration
Acid (M)	1.35	K (M)	0.17
Al (M)	0.26	Ni (M)	0.001
B (M)	0.018	Na (M)	1.44
Ba (M)	8.2×10^{-6}	NO_3 (M)	3.5
Ca (M)	0.069	Zr (M)	0.0085
Cr (M)	0.0041	α (nCi/g)	313
Cs (M)	4.3×10^{-5}	^{241}Am (nCi/g)	40
F (M)	0.32	^{137}Cs (Ci/m^3)	91
Fe (M)	0.017	^{238}Pu (nCi/g)	350
Pb (M)	0.0015	^{239}Pu (nCi/g)	43
Hg (M)	0.0052	^{99}Tc (Ci/m^3)	0.036
Mo (M)	0.00023	^{90}Sr (Ci/m^3)	91

with actual tank waste as indicated in Fig. 1. Due to the limited volume of actual waste available for testing, it was impractical to test multiple IX columns in series. Therefore, only one IX column was used in this testing as compared with three IX columns used in the previous testing with simulant.

The proposed disposal routes of the product streams (LAW or HAW) are indicated in Fig. 1. The compositions of the input streams to the solvent extraction flowsheets are also shown.

The TRUEX portion of the integrated flowsheet, as shown in Fig. 1, consists of eight stages of extraction at an organic to aqueous phase ratio (O/A) of 0.46, four stages of scrub (0.1 *M* HNO_3) at an O/A of 1.5, six stages of strip (0.04 *M* HEDPA in 0.04 *M* HNO_3) at an O/A of 0.8, three stages of solvent wash (0.25 *M* Na_2CO_3) at an O/A of 0.6, and two stages of acid rinse (0.1 *M* HNO_3) at an O/A of 5.75.

The SREX portion of the integrated flowsheet, as shown in Fig. 1, consists of ten stages of extraction at an organic to aqueous phase ratio (O/A) of 1.0, two stages of scrub (1.0 *M* $NaNO_3$) at an O/A of 4.0, four stages of Sr strip (0.05 *M* HNO_3) at an O/A of 0.5, four stages of Pb strip (0.1 *M* ammonium citrate) at an O/A of 1.0, and two stages of solvent wash (0.25 *M* Na_2CO_3) at an O/A of 5.0. The acidification portion of the flowsheet was not included in this testing due to a limited number of cell penetrations available for the feed solutions.

Startup and operation of the centrifugal contactor equipment proceeded as follows: The centrifugal contactor motors were started at 3600 rpm. Aqueous solution flows were established in the contactors; a startup solution consisting of 1.5 *M* HNO_3, 0.56 *M* $Al(NO_3)_3$, and 1.2 *M* $NaNO_3$ was used in place of the tank waste during this period. The solvent flow was started after aqueous flows were established. When the solvent was observed exiting the final section of the flowsheet, the actual tank waste (raffinate from the previous process) was started in place of the startup solution, marking time zero for the test. The process then continued to operate with recycle of the solvent (TRUEX flowsheet only). Samples of the raffinate, strip product, wash effluent, rinse effluent, and solvent effluent were taken 30, 60, 90, 120, 150, and 170 min after the start of actual waste feed. 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 stages.

AMP–PAN Sorbent

The AMP–PAN sorbent material was procured from Dr. Ferdinand Šebesta of the Czech Technical University and used as received (wet). The

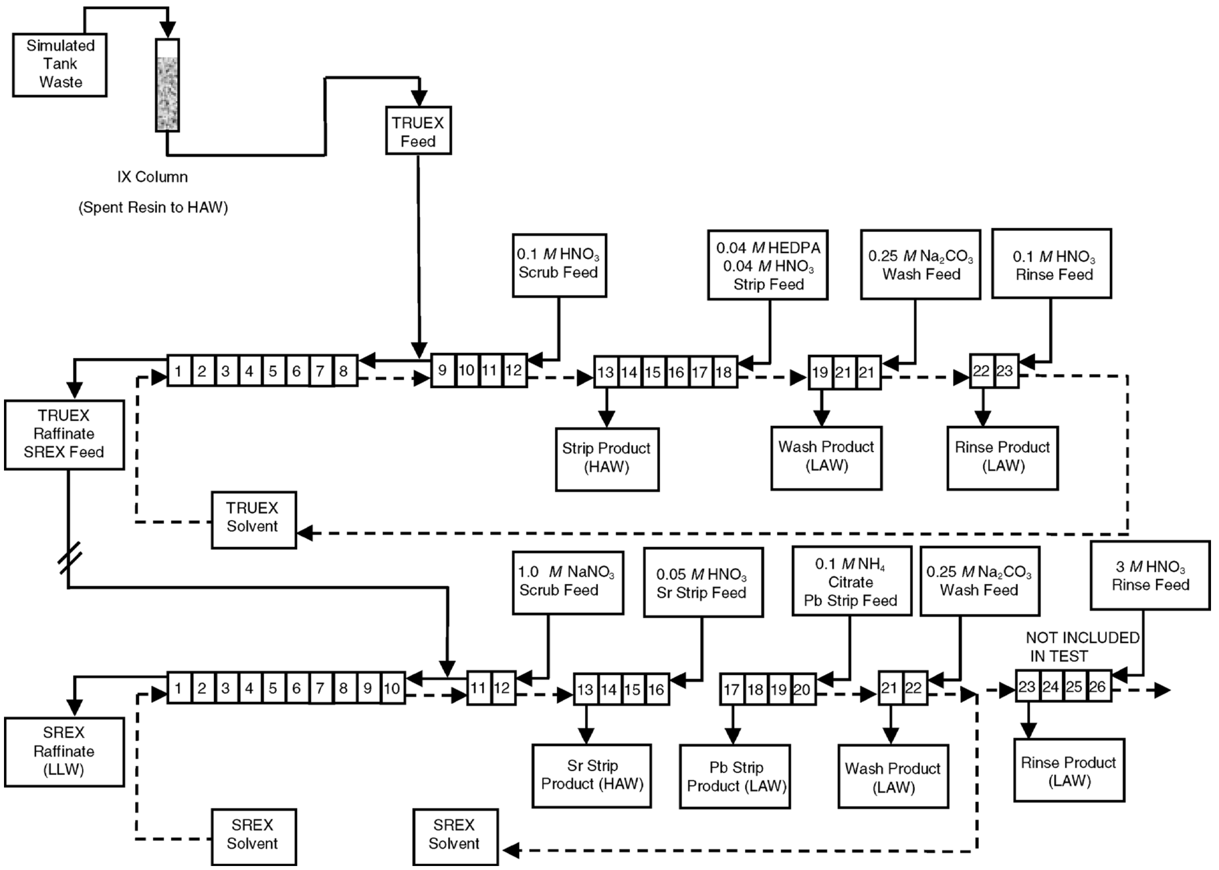

Figure 1. Integrated flowsheet for demonstration with actual tank waste.

column was filled with AMP–PAN/SF (< 0.3 mm particle diameter) and lightly tapped several times to settle the sorbent and eliminate potential voids in the bed. The SF designator denotes that the AMP–PAN was dried after formation, improving mechanical properties, then rehydrated. The AMP–PAN/SF sorbent is composed of 85.7 wt% AMP and 14.3 wt% PAN.

TRUEX Solvent

The composition of the TRUEX solvent used in the testing was 0.2 *M* CMPO and 1.4 *M* tributyl phosphate (TBP) in Isopar L®, a branched chain paraffinic hydrocarbon. The CMPO was obtained from Elf Atochem North America (Philadelphia, PA), the TBP from Fischer Scientific (Fairlawn, NJ), and the Isopar L® from Exxon Chemical (Fairfax, VA). All were used as received. The solvent had been used previously for flowsheet development studies in the 3.3-cm Centrifugal Contactor Pilot Plant (1). It had been recycled 17 times as part of this previous testing of the TRUEX flowsheet with surrogate waste. Several days prior to its use in this flowsheet test, the solvent was washed with 0.25 *M* Na_2CO_3, twice at an $O/A = 1$, followed by acid rinsing with 0.1 *M* HNO_3, once at an $O/A = 1$.

SREX Solvent

The SREX solvent composition used in the testing was 0.15 *M* 4′,4′(5′)-di-(tert-butyldicyclohexo)-18-crown-6 and 1.5 *M* TBP in Isopar-L. The solvent had been used previously for flowsheet development studies in the 3.3-cm Centrifugal Contactor Pilot Plant (1). It had been recycled 45 times as part of this previous testing of the SREX flowsheet with surrogate waste. The crown ether extractant was obtained from Eichrom Industries, Darien IL and was used as received. Approximately one week prior to its use in this flowsheet test, the solvent was washed with 0.25 *M* Na_2CO_3, once at an $O/A = 1$, followed by acidification with 3.0 *M* HNO_3, twice at an $O/A = 1$. With this pre-equilibration, the HNO_3 concentration of the SREX solvent feed was approximately 1.0 *M*. Pre-equilibration of the solvent prevents the extraction of HNO_3 from the acidic waste, which would result in lower ^{90}Sr distribution coefficients in the extraction section.

Analytical

Analysis of ^{137}Cs in the IX samples was performed using High Purity Germanium Gamma Spectroscopy (HPGE). Alpha spectroscopy was used for Am and Pu analyses. Total alpha and ^{90}Sr analyses were performed using gas-flow proportional counting. Inductively Coupled Plasma Emission Spectroscopy (ICP–ES) was used for Al, B, Ba, Ca, Cr, Fe, Mn, Ni, and Pb analyses. Sodium and potassium analyses were performed using Atomic Absorption Spectroscopy. Mercury analyses were performed using fluorescence spectroscopy. Samples of the TRUEX or SREX solvents could not be analyzed directly. Consequently, the organic samples from the TRUEX test were stripped with 0.25 *M* HEDPA in 0.05 *M* HNO_3 at an O/A ratio of 0.2 to quantitatively strip all metals with the exception of Hg and a portion of the ^{99}Tc into an aqueous solution. The resulting aqueous phase was analyzed for all metals except Hg. The organic phase, after contact with the HEDPA strip solution, was contacted with 0.25 *M* Na_2CO_3 at an O/A of 0.2 to strip Hg and the remaining ^{99}Tc from the organic phase. The carbonate samples were analyzed for Hg and ^{99}Tc. Analyses of the SREX organic samples were performed similarly by stripping of the SREX solvent with 0.1 *M* ammonium citrate at an O/A of 0.2. The citrate stripping procedure was conducted twice on each organic sample and the two aqueous fractions combined for analysis.

RESULTS AND DISCUSSION

Cesium Ion Exchange

The ion exchange test ran for ~25.5 hr and processed ~1350 mL of actual tank waste through one AMP–PAN loaded column. The flow rate through the system was 0.88 mL/min (26.3 bed volumes/hr) for the duration of the test. Operational problems were not encountered during the Cs IX run.

Samples of the effluent from the ion exchange column were taken approximately every 60 min. Figure 2 displays the ^{137}Cs breakthrough curve for the ion exchange test. Approximately 0.2% breakthrough was reached at the time of shutdown (700 bed volumes). The ^{137}Cs activity in the tank waste was reduced from 3.35×10^6 dps/mL in the tank waste to 1.56×10^3 dps/mL in the composite effluent (TRUEX feed). This corresponds to an overall ^{137}Cs removal efficiency of 99.95%, which is sufficient to reduce the ^{137}Cs activity in a grout waste form to well below the NRC Class A LLW limit based on the assumption that 1.05 L of grout would be generated per 1.0 L of tank waste processed (1).

TRUEX Solvent Extraction

The TRUEX solvent extraction portion of the test was designed to separate predominately the actinides and mercury from the tank waste. The TRUEX flowsheet for this testing is shown in Fig. 1. The TRUEX process was initially operated using the effluent from the Cs ion exchange test. During this TRUEX

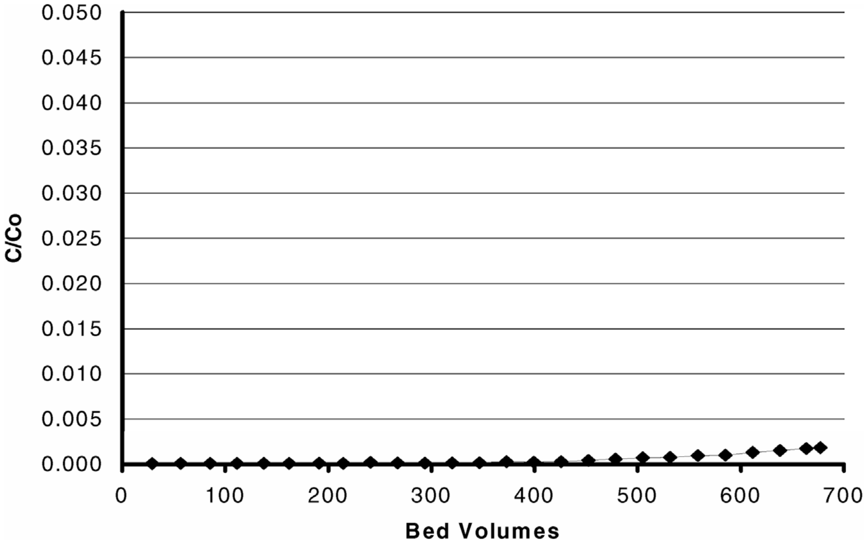

Figure 2. ^{137}Cs breakthrough curve for processing actual tank waste through AMP-PAN sorbent.

flowsheet test, feed of the solvent to the contactors stopped shortly (35–85 min) after processing of the ion exchange effluent began, due to the feed line inadvertently being pulled above the solvent feed level by a manipulator during sampling activities. Eighty-five minutes after the start of feed solution, the contactors were shutdown and the remaining feed solution was combined with the raffinate collected to that point, sampled, and used as feed for a second TRUEX test. The raffinate solution was reworked into the remaining feed solution since the loss of solvent flow resulted in contamination of the raffinate with actinides. In addition, the amount of the remaining ion exchange effluent feed solution was not enough to allow a second flowsheet test to be performed using only it as feed.

The resulting feed solution for the second flowsheet test was not impacted greatly by the rework of the raffinate into the feed. The total alpha (extractable species) activity in the feed for the second test (1.01×10^4 dps/mL) represents approximately a 40% dilution as compared to the alpha activity in the ion exchange effluent (1.75×10^4 dps/mL). For the non-extractable species, the feed concentration for the second test represented only approximately a 15% dilution as compared to the concentration of the ion exchange effluent. The nitric acid concentration was anticipated to decrease by approximately 15% since the extracted nitric acid is subsequently scrubbed from the solvent. Analytical results obtained for the reworked feed solution were used for all subsequent material balance and removal efficiency calculations.

During the course of operation, flooding and/or precipitate formation were not observed in any of the effluent streams. After shutdown, precipitate was not observed in any of the contactor stages including the solvent wash stages where HgO precipitate formation has been observed in previous tests where the O/A ratio was higher (1).

The percentages of total alpha, ^{241}Am, ^{238}Pu, ^{239}Pu, ^{90}Sr, ^{99}Tc, Al, Ba, B, Ca, Cr, Fe, Hg, K, Mn, Na, Ni, and Pb, in each of the effluent streams and the overall material balance for each component are given in Tables 3 and 4. For the radioactive components, the material balance is based upon the activity in each of the effluent streams immediately prior to shutdown. The sample volume collected for these effluent streams was expended when performing radionuclide analyses; therefore, analytical results were not obtained for the non-radioactive components in the effluent streams immediately prior to shutdown. Instead, composite samples of each of the effluent streams (obtained by sampling the effluent containers at completion of the test) were analyzed in order to determine the quantities of these non-radioactive components in each of the effluent streams and to calculate an overall material balance. The overall material balances for the non-radioactive components (except Na and Al) are expected to be below 100% due to dilution of the effluent vessels from startup solutions. A feed surrogate containing 1.9 M HNO_3, 1.6 M $NaNO_3$, and 0.6 M $Al(NO_3)_3$ was used during startup; therefore, dilution of Na and Al in the raffinate during startup was not expected. Indeed, as shown in Table 4, the overall material balances for the non-radioactive components (excluding Na and Al) are considerably lower than 100%, ranging from 76 to 92%. Distribution coefficients were measured for total alpha, ^{241}Am, ^{238}Pu, ^{239}Pu, Hg, and Fe on various stages. The resulting distribution coefficients are given in Table 5. A discussion of the behavior of each component in the TRUEX flowsheet follows.

Table 3. Percent of Radionuclides in the TRUEX Effluent Streams

Effluent	Alpha (%)	^{241}Am (%)	^{238}Pu (%)	^{239}Pu (%)	^{99}Tc (%)	^{90}Sr (%)
Raffinate	0.79	0.051	0.10	0.25	37.0	89.9
Strip	94.4	90.3	85.3	93.5	69.0	0.13
Wash	0.003	0.0002	0.002	0.002	18.8	<0.0001
Rinse	—	—	—	—	—	—
Solvent	0.002	0.007	0.003	0.001	0.19	<0.0004
Material balance	95.2	90.3	85.4	93.8	124.9	90.0

Table 4. Percent of Metals in the TRUEX Effluent Streams

Effluent	Al	Ba	B	Ca	Cr	Fe
Raffinate	92.5	83.3	84.6	92.5	86.6	77.6
Strip	<0.01	<2.7	<1.8	<0.08	<0.2	<0.02
Wash	—	—	—	—	—	—
Rinse	—	—	—	—	—	—
Solvent	—	—	—	—	—	—
Material balance	92.5	83.3	84.6	92.5	86.6	77.6
Effluent	Hg	Mn	Na	Ni	K	Pb
Raffinate	5.3	85.7	94.6	86.3	87.5	77.1
Strip	0.11	<0.01	13.5	<1.1	0.5	<0.7
Wash	71.2	—	—	—	—	—
Rinse	—	—	0.03	—	—	—
Solvent	0.08	—	—	—	—	—
Material balance	76.6	85.7	108.1	86.3	88.0	77.1

Table 5. Distribution Coefficients from the TRUEX Flowsheet Demonstration

Stage		Alpha	$D_{Am\text{-}241}$	$D_{Pu\text{-}238}$	$D_{Pu\text{-}239}$	$D_{Tc\text{-}99}$
Extraction	1	3.3	—	—	—	1.6
	2	10.2	17.8	991	—	2.5
	4	—	19.2	4375	—	2.6
	6	67.9	—	—	—	2.7
	8	648	208.5	1.67×10^{4}	—	2.0
Scrub	9	52.4	—	—	—	5.8
	12	10.9	—	—	—	11.2
Strip	13	2.2×10^{-4}	0.002	1.6×10^{-4}	2.6×10^{-4}	—
	14	2.3×10^{-4}	0.004	0.001	6.6×10^{-4}	—
	16	1.1×10^{-3}	0.001	0.001	2.1×10^{-4}	—
	18	4.1×10^{-3}	—	0.004	8.9×10^{-3}	—
Wash	19	0.025	—	—	—	0.45
	20	0.18	—	—	—	0.43
	21	0.29	—	—	—	0.97
Rinse	22	0.70	—	—	—	0.54

Actinides

The total alpha activity was reduced from 1.01×10^4 dps/mL in the feed to 56.9 dps/mL (1.2 nCi/g) in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 99.2%. Further alpha decontamination also occurs in the SREX portion of the flowsheet (*vide infra*).

Contributors to total alpha activity in the WM-185 waste include Am, Pu, U, and Np. Analytical data were obtained individually for Am and Pu, but not U and Np since the feed activities of these components are very low (approximately 1.6 nCi/g for Np and 0.64 nCi/g for U) and would be well below the NRC Class A LLW requirements in a final grout waste form even without separation. Removal efficiencies of 99.95, 99.9, and 99.8% were obtained for ^{241}Am, ^{238}Pu, and ^{239}Pu, respectively. The slight differences in the results for ^{238}Pu and ^{239}Pu, as shown in Tables 3 and 5, are attributed to analytical uncertainty. The extraction distribution coefficients for Pu (991 to 1.7×10^4) are much greater than for Am (18 to 209) so a higher removal efficiency was expected for Pu. However, the ^{241}Am, ^{238}Pu, and ^{239}Pu activities in the raffinate are very small and likely will be impacted by residual contamination from previous flowsheet testing. The ^{238}Pu activity (0.85 dps/mL) and ^{239}Pu activity (0.16 dps/mL) in the composite sample of the raffinate were significantly lower than in the raffinate sample taken prior to shutdown (5.7 dps/mL for ^{238}Pu and 1.6 dps/mL for ^{239}Pu). On the basis of the composite raffinate sample, removal efficiencies of 99.98% were obtained for ^{238}Pu and ^{239}Pu. The ^{241}Am activity in the composite sample (0.29 dps/mL) was comparable to the activity of the raffinate prior to shutdown (0.65 dps/mL). In the strip section, 99.99, 99.97, and 99.99% of the total alpha, ^{241}Am, and ^{238}Pu, respectively, were recovered from the solvent. These results indicate the effectiveness of the TRUEX process for actinide removal/recovery from the acidic tank wastes currently stored at the INEEL. With the high removal efficiency obtained for the actinides, and the assumption that 1.05 L of grout would be generated per 1.0 L of tank waste processed (1), a LAW grout would be well below the 10 nCi/g NRC Class A LLW limit for TRU.

Technetium

The activity of ^{99}Tc was reduced from 1.01×10^3 dps/mL in the feed to 265 dps/mL in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 63%. Extraction distribution coefficients ranged from 1.6 to 2.7. Strip data obtained for ^{99}Tc are unclear and contradictory. Approximately 70% of the extracted ^{99}Tc exited with the strip product and the remaining 30% exited with the wash effluent. Previous TRUEX testing with actual tank waste indicates that ^{99}Tc is primarily stripped in the wash section

(74%) (3). The overall material balance for ^{99}Tc was high (125%) suggesting the analytical result for the strip product solution may be too high. The ^{99}Tc activity in the stage 13 aqueous sample at shutdown, which should be approximately equal to the activity of the strip product immediately prior to shutdown, was a factor of nine lower than the activity of the strip product. On the basis of the stage 13 aqueous activity, 25% of the extracted ^{99}Tc exited with the strip product and 75% exited with the wash effluent. It is important to note that the ^{99}Tc activities in INEEL tank wastes are very low and are anticipated to be below the NRC Class A LLW limit of 0.3 Ci/m^3 in a final grout waste form. Technetium removal is of concern due to its mobility, as TcO_4^-, in the environment. It is therefore advantageous to understand the behavior of this species for any treatment option.

Mercury

One of the goals in the TRUEX portion of the integrated test was to determine the efficiency of Hg removal from the tank waste. Mercury removal is important from the aspect that it is a Resource Conservation and Recovery Act (RCRA) regulated metal present in significant quantities in the tank waste. 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 ultimately be separated and dispositioned in accord with RCRA regulations. Further, Hg is extracted in the SREX process but cannot currently be effectively stripped from the SREX solvent. Consequently, if Hg was not removed in the TRUEX portion of the flowsheet, it would tend to build up in the SREX solvent and could eventually completely load the extractant, impacting Sr extraction.

With the flowsheet tested, 95% of the Hg was extracted from the tank waste. The extracted Hg was effectively stripped from the solvent in the sodium carbonate wash section. Only 0.1% of the Hg exited with the HAW strip product. Extraction of 95% of the Hg is an improvement over previous flowsheet testing with actual tank waste in which only 74% was extracted (3). It should be noted that Hg precipitate was not observed in the centrifugal contactors in the wash section of the flowsheet. In the TRUEX portion of the integrated test with simulated waste, HgO precipitate formed on the contactor rotors in the wash section. For this test with actual tank waste, the O/A in the wash section was increased from 0.70 to 0.60 to prevent the Hg from precipitating.

Other Matrix Components

The behavior of Al, Ba, B, Ca, Cr, Fe, Mn, Na, Ni, K, and Pb was evaluated for the TRUEX flowsheet. Of these components, only Na has a significant concentration in the strip product solution. Numerous data on the behavior of Na with the TRUEX process indicate that Na is not extracted from INEEL tank waste by the TRUEX solvent (3,4). The overall material balance for Na was high (108%), indicating analytical error or contamination of the sample may account for the significant amount of Na (13.5%) in the strip product.

Iron is known to extract from INEEL tank waste with the TRUEX process based on previous flowsheet testing ($D_{\mathrm{Fe}} = 0.8$) (3). The dilute nitric acid scrub section in the flowsheet scrubs the Fe from the TRUEX solvent thus minimizing the amount of Fe in the HAW strip product. The scrub section was very effective in removing the extracted Fe from the TRUEX solvent with $<0.02\%$ exiting with the strip product.

SREX Solvent Extraction

The SREX solvent extraction portion of the test was designed to separate the ^{90}Sr and Pb from the tank waste. The SREX flowsheet for this testing is presented in Figure 1. The SREX process was operated using the raffinate from the TRUEX flowsheet testing described previously. Note that the SREX portion of the integrated test was performed approximately two months after completing the TRUEX test because the centrifugal contactors had to be reconfigured and decontaminated before the SREX test.

During the course of operation, flooding and/or precipitate formation were not observed in any of the effluent streams. After shutdown, precipitate was not observed in any of the contactor stages.

The percentages of ^{90}Sr, total alpha, Al, Ba, B, Ca, Cr, Fe, Hg, K, Mo, Mn, Na, Ni, and Pb in each of the effluent streams and the overall material balance for each component are given in Tables 6 and 7. For the radioactive components, the

Table 6. Percent of Radionuclides in the SREX Effluent Streams at Shutdown

Effluent	^{90}Sr (%)	Alpha (%)
Raffinate	0.003	6.9
Sr strip product	101.3	91.5
Pb strip product	6.7×10^{-5}	4.9
Wash effluent	3.0×10^{-5}	5.0
Solvent effluent	Bdl[a]	0.14
Material balance	101.3	108.4

[a] Below detection limit.

Table 7. Percent of Metals in the SREX Effluent Streams

Effluent	Al (%)	Ba (%)	B (%)	Ca (%)	Cr (%)	Fe (%)	Hg (%)
Raffinate	107.4	18.7	116.6	102.2	106.3	113.6	12.8
Sr Strip	0.027	96.8	<2.3	<0.07	<0.28	0.096	<6.3
Pb Strip	<0.006	<1.3	<1.1	<0.03	<0.13	0.056	4.9
Wash	0.001	0.37	<0.2	0.042	0.063	0.013	0.091
Solvent	<0.06	<13.1	<10.9	0.34	<1.4	0.24	82
Material Balance	107.4	115.9	116.6	102.5	106.4	113.9	99.8
Effluent	Mn	Mo	Na	Ni	K	Pb	
Raffinate	115.4	120.2	109.1	105.7	592	2.1	
Sr Strip	0.026	<28	2.1	<1.4	16.4	21.6	
Pb Strip	0.005	<13	8×10^{-4};	<0.63	0.037	87.4	
Wash	<0.001	<2.6	—	<0.13	0.004	<0.076	
Solvent	<0.04	<134	0.53	<6.5	0.002	<3.8	
Material alance	115.4	120.2	111.7	105.7	608	111.1	

Table 8. Distribution Coefficients from the SREX Flowsheet Demonstration

Stage		$D_{Sr\text{-}90}$	D_{Pb}
Extraction	1	7.7	—
	2	5.7	—
	4	6.7	—
	6	6.4	—
	9	4.6	—
	10	4.6	24
Scrub	11	3.0	100
	12	2.0	145
Sr Strip	13	0.001	37
	14	0.07	185
	16	0.0001	9.4
Pb Strip	17	0.17	<0.4
	18	0.01	<4.2
	20	0.006	

material balance is based upon the activity in each of the effluent streams immediately prior to shutdown. The sample volume collected for these effluent streams was expended when performing these analyses; therefore, analytical results were not obtained for the non-radioactive components in the effluent streams immediately prior to shutdown. The composite samples of each of the effluent streams (obtained by sampling the effluent containers at completion of the test) were analyzed in order to determine the quantities of these components in each of the effluent streams and to calculate an overall material balance. The effluent vessels were emptied 15 min after the start of the TRUEX raffinate feed solution in order to prevent dilution of the contents with any startup solution. Distribution coefficients were measured for ^{90}Sr and Pb on various stages. The resulting distribution coefficients are given in Table 8. A discussion of the behavior of each component in the SREX flowsheet follows.

Strontium

The ^{90}Sr activity was reduced from 1.93×10^6 dps/mL in the TRUEX raffinate feed to 47.6 dps/mL (0.0013 Ci/m^3) in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 99.997% which is sufficient to reduce the ^{90}Sr activity in a grout waste form to well below the NRC

Class A LLW limit based on the assumption that 1.05 L of grout would be generated per 1.0 L of tank waste processed (1). The extracted ^{90}Sr was effectively stripped from the SREX solvent in the Sr strip section (solvent ^{90}Sr activity reduced to 2.1 dps/mL). With this high ^{90}Sr stripping efficiency, the SREX solvent can be recycled to the extraction section without impacting the 99.997% removal efficiency obtained.

Distribution coefficients for ^{90}Sr ranged from 4.6 to 7.7 in the extraction section and from 2.0 to 3.0 in the scrub section. These distribution coefficients were used in conjunction with the Generic TRUEX Model (GTM) to estimate the centrifugal contactor stage efficiency in the extraction section. The stage efficiency is a variable parameter in the GTM, iterations at different efficiencies are performed until the actual, and modeled aqueous phase activities on the various stages coincide. The data indicate that the extraction section was operating at 80% stage efficiency during the SREX test. This relatively low stage efficiency is routinely observed in small-scale centrifugal contactors and can be explained as follows (5). In small-scale contactors, such as the 2.0-cm contactors used for this testing, surface tension forces can be greater than the fluid momentum. This results in the liquid entering the annular mixing zone in discrete slugs of liquid. These slugs of liquid can have a volume that is on the same order of magnitude as that in the mixing zone of the 2-cm contactor. Thus, one liquid can pass through the mixing zone without contacting much liquid of the other phase and vice versa. As a result, even though the actual stage efficiency is close to 100%, the apparent stage efficiency is significantly lower. For full-scale centrifugal contactors, flow is continuous and stage efficiencies close to 100% are expected. The operation of this SREX flowsheet using full-scale contactors is expected to result in a ^{90}Sr removal efficiency which is even greater than the excellent result obtained in this test.

Total Alpha

The active extractant in the PUREX process, which was developed to separate Pu and U from dissolved nuclear fuels, is TBP. The SREX solvent also contains TBP as a phase modifier. As a result, the SREX solvent is effective in extracting Pu and U from INEEL tank waste. Americium, which is in the +3 valence state, is not extracted by the TBP in the SREX solvent. Therefore, it is expected that the SREX process would further reduce the activity of U and Pu, and thus the total alpha activity, of the tank waste. Indeed, the total alpha activity was reduced from 47.2 dps/mL in the TRUEX raffinate feed to 2.4 dps/mL in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 93%. Combined with the removal efficiency of 99.2% obtained with the TRUEX portion of the integrated flowsheet testing, an overall removal efficiency resulting from TRUEX and SREX processing of 99.97% was obtained for the total alpha activity. The extracted alpha activity was primarily stripped in the Sr strip section, with approximately 10% exiting in the Pb strip and wash effluents.

Lead

Lead is a RCRA regulated metal, present in significant quantities (~310 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 7 indicate 98% of the Pb in the SREX feed was extracted in the process. It is interesting to note that the Pb concentration in the aqueous phase of the extraction stages decreased from 147 mg/L in the SREX feed to 4.3 mg/L in the aqueous phase exiting stage 10 (one stage of extraction). On the remaining nine stages of extraction, the Pb concentration remained approximately the same (2.6–3.7 mg/L). These data suggest, (1) that the contactors may have had residual Pb contamination from previous testing, (2) trace concentrations of Pb may have been present in the stock chemicals used to dilute the samples for analysis, and/or (3) inextractable Pb complexes are formed in the tank waste. Results from recent integrated testing with simulated INEEL tank waste resulted in Pb distribution coefficients ranging from 7.1 to 99.6 on all extraction stages and an overall removal efficiency >99.89%. While further study would be required to determine why this discrepancy exists, little benefit can be seen in having the capability to separate greater than 98% of the Pb from INEEL tank waste. In actuality, there are no requirements for the separation of Pb from INEEL tank waste. A significant fraction of the extracted Pb was recovered with the Sr strip product (21.6%) and the balance was recovered with the Pb strip product. Overall, >97.3% of the extracted Pb was recovered in the two strip sections.

Potassium

It is known that the SREX process has a slight affinity for the extraction of potassium from the INEEL 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 7 indicate 16.4% of the K in the SREX feed was separated. It should be noted that the overall material balance for K was 608% likely due to an error in the raffinate sample analysis. The amount of K recovered in the Sr strip product, 16.4%, is consistent with recent testing of the same integrated flowsheet using simulated waste in which 7.8% of the K was recovered in the Sr strip product. Optimization of the scrub section may be possible to reduce the amount of K reporting to the Sr strip product stream.

Mercury

One of the major concerns of the SREX process is the extraction of mercury, which currently cannot be stripped effectively from the solvent. Processing of the INEEL waste with the TRUEX process prior to the SREX process resulted in a 95% reduction in the concentration of Hg in the feed to SREX. With the SREX flowsheet, 87.2% of the remaining Hg was extracted into the SREX solvent. Less than 15% of this extracted Hg was recovered in the strip and carbonate wash products. Based upon a 100% material balance it is expected that the Hg concentration in the solvent effluent was approximately 15 mg/L. Mercury build up in the SREX solvent should not pose problems due to the low Hg concentration remaining in the TRUEX raffinate (SREX feed). With some removal in the strip and solvent wash sections, Hg should build up to a steady state value in the SREX solvent. On the basis of the modeling of the experimental results, it is estimated that the concentration of Hg will build up in the SREX solvent to approximately 19 mg/L at steady state conditions. This is not expected to have a deleterious effect on the SREX process efficiency.

Other Matrix Components

The behavior of Al, Ba, B, Ca, Cr, Fe, Mn, Mo, Na, and Ni was also evaluated for the SREX flowsheet. Analytical detection limits in the effluent streams, which in many cases are highly relative to the concentration of the components in the feed, were reached for several of the components. As a result, it is difficult to determine if some of the elements were extracted in significant quantities. It is apparent that very little (<3%) of the Al, B, Ca, Cr, Fe, Mn, Na, and Ni were extracted. A significant quantity of Ba (81%) was extracted and recovered in the Sr strip product. The extraction of Mo is not as clear. The material balance for Mo indicates 120% of the Mo remained in the raffinate. However, analytical detection limits on the effluent samples are quite high (<44% extracted) so the amount of Mo in these streams is unknown. In previous SREX flowsheet testing Mo analyses were not requested, so data for comparison are not available. However, the 120% material balance for Mo in the raffinate suggests that Mo is not extracted in significant quantities.

Table 9. Summary of Removal Efficiencies from Integrated Testing

Component	Removal Efficiency (%)
^{137}Cs	99.95
^{90}Sr	99.997
Total alpha	99.97
Hg	99.6
Pb	97.9

CONCLUSIONS

The AMP–PAN ion exchange, TRUEX solvent extraction, and SREX solvent extraction, were successfully integrated at the INEEL for the treatment of actual acidic tank waste. Physical problems, such as flooding and/or precipitate formation, were not observed during solvent extraction operation. The overall removal efficiencies obtained for the integrated testing are summarized in Table 9. With these removal efficiencies, the activity of the resulting raffinate and a final grout waste form are expected to be well below NRC Class A LLW requirements.

Mercury was effectively separated from the tank waste with the TRUEX process (95% removal efficiency). The SREX solvent extracted nearly all of the remaining Hg. At this time, an effective stripping reagent for the removal of Hg from the SREX solvent has not been identified. With the TRUEX process preceding the SREX process, the buildup of Hg in the SREX solvent is not a concern since the quantity of Hg in the feed to the SREX process is very low (24 mg/L). It should be noted that Fe was extracted by the TRUEX solvent but was effectively scrubbed, resulting in $<0.02\%$ of the Fe in the HAW strip product. Lead was effectively separated, and the majority selectively stripped into a LAW stream, with the SREX portion of the integrated testing. The only other elements determined to be extracted to a significant extent by the SREX solvent were Ba and K.

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