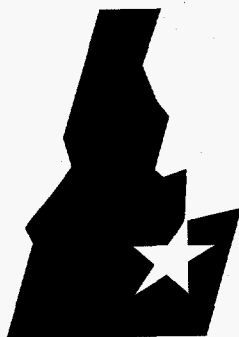


November 1996



**Idaho
National
Engineering
Laboratory**

Development and Testing of a SREX Flowsheet for the Partitioning of Strontium and Lead from Simulated ICPP Sodium-Bearing Waste

**J. D. Law
D. J. Wood**

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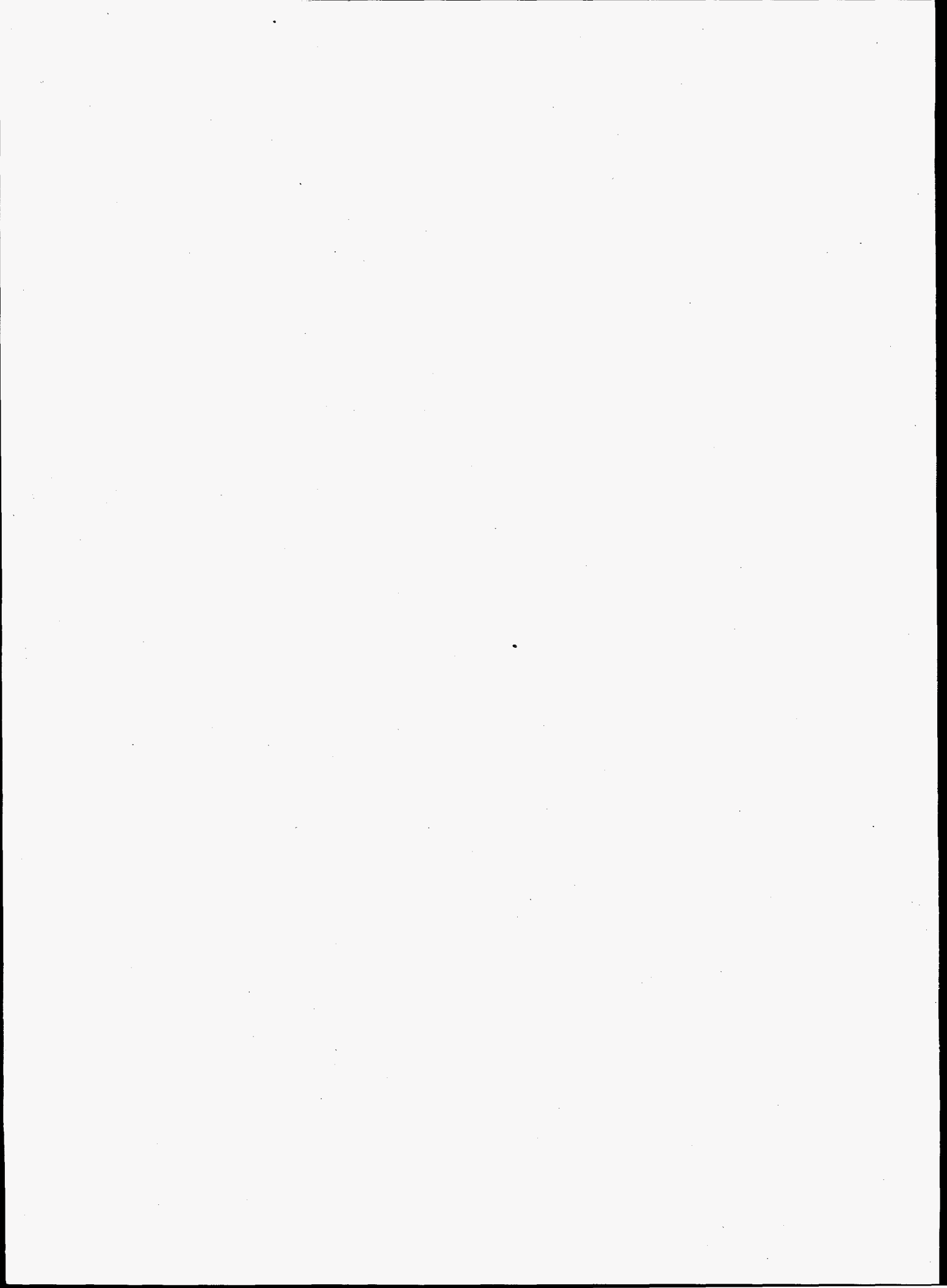
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ABSTRACT

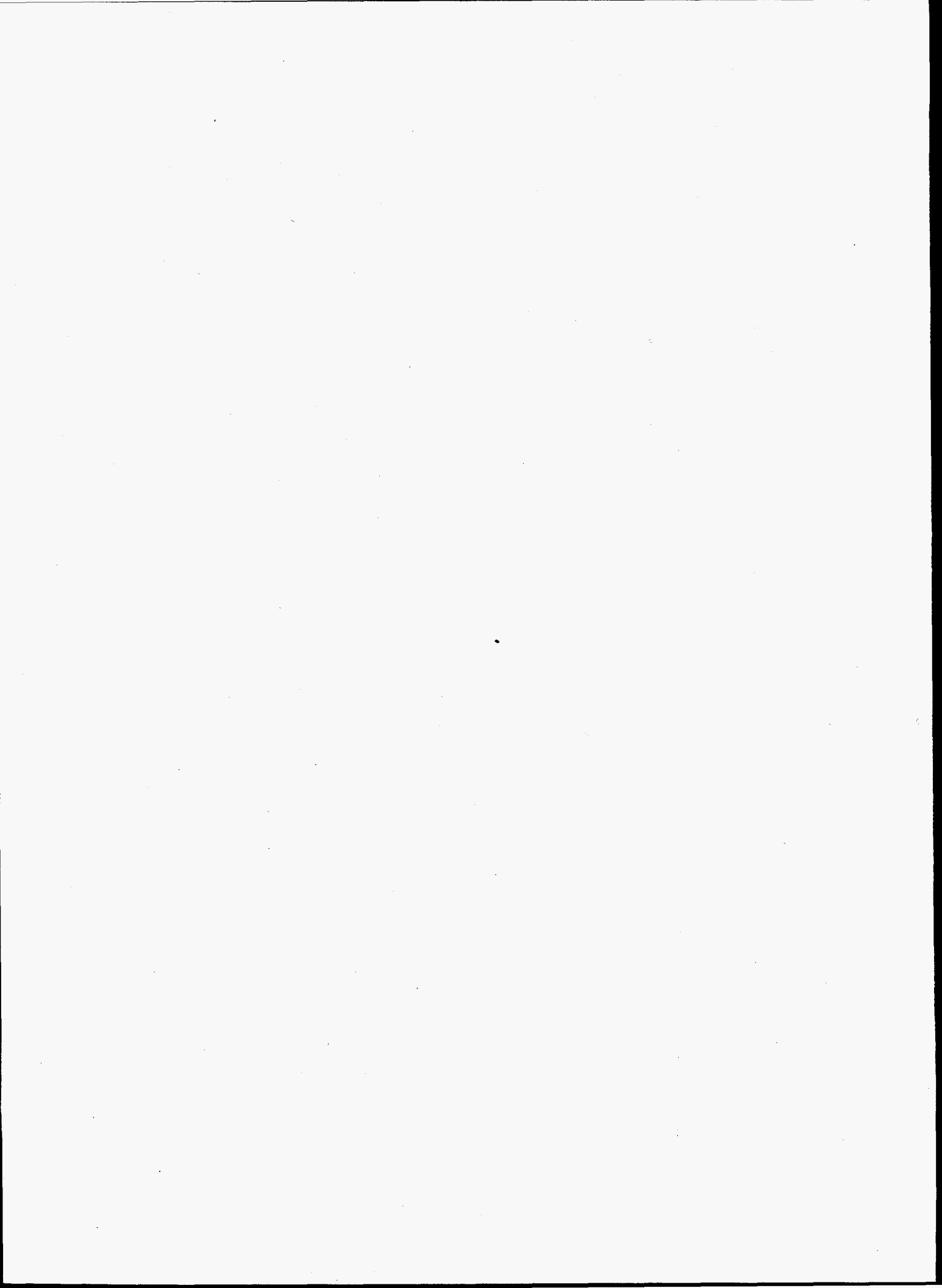
Laboratory experimentation has indicated that the SREX process is effective for partitioning ^{90}Sr from acidic radioactive waste solutions located at the Idaho Chemical Processing Plant. Previous countercurrent flowsheet testing of the SREX process with simulated waste resulted in 99.98% removal of Sr. With this previous test, however, Pb was extracted by the SREX solvent and was not back-extracted in the dilute nitric acid strip section. The Pb concentration increased in the recycled solvent and in the aqueous phase of the strip section, resulting in the formation of a Pb precipitate. Subsequently, studies were initiated to identify alternative stripping agents which will selectively strip Sr and Pb from the SREX solvent. Based on the results of these studies, a countercurrent flowsheet was developed and tested in the 5.5-cm Centrifugal Contactor Mockup using simulated waste. The flowsheet tested consisted of an extraction section (0.15 M 4',4'(5)-di-(tert-butyl)dicyclohexo)-18-crown-6 and 1.2 M TBP in Isopar-L[®]), a 0.05 M nitric acid strip section for the removal of Sr from the SREX solvent, a 0.1 M ammonium citrate strip section for the removal of Pb from the SREX solvent, and a 2.0 M nitric acid equilibration section. The behavior of Sr, Pb, Al, Ca, Hg, Na, Zr, and H⁺ was evaluated. The described flowsheet successfully extracted and selectively stripped Sr and Pb from the SBW simulant. Removal efficiencies of 97.9% and 99.91% were obtained for Sr and Pb, respectively. Essentially all of the extracted Sr (99.998%) and 1.9% of extracted Pb exited with the 0.05 M nitric acid strip product; whereas, 0.002% of the extracted Sr and 97.9% of the extracted Pb exited with the 0.1 M ammonium citrate strip product. Also, 95% of the Hg and 63% of the Zr were extracted by the SREX solvent.



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Development and Testing of a SREX Flowsheet for the Partitioning of Strontium and Lead from Simulated ICPP Sodium-Bearing Waste

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering Laboratory (INEL), formerly reprocessed spent nuclear fuel to recover fissionable uranium. The radioactive raffinates from the solvent extraction uranium recovery processes were converted to granular solids (calcine) in a high temperature fluidized bed. During the course of reprocessing, a secondary waste stream, liquid sodium-bearing waste (SBW), was also generated primarily from equipment decontamination between campaigns and solvent wash activities. This SBW cannot be directly calcined due to the high sodium content and has historically been blended with reprocessing raffinates or non-radioactive aluminum nitrate prior to calcination. Fuel reprocessing activities are no longer being performed at the ICPP, thereby eliminating the option of waste blending to deplete the SBW inventory. Currently, approximately 1.5 million gallons of liquid SBW are temporarily stored at the ICPP in large underground stainless-steel tanks.

The United States Environmental Protection Agency and the Idaho Department of Health and Welfare filed a Notice of Noncompliance in 1992 contending some of the underground waste storage tanks do not meet secondary containment requirements as set forth in Title 40, Part 265.13 of the Code of Federal Regulations. As part of a 1995 agreement between the State of Idaho, the Department of Energy, and the Department of Navy, the SBW must be removed from the tanks by 2012.

Several technologies are currently being evaluated for the treatment and final disposition of SBW inventories. These technologies include blending with nonradioactive chemicals, effectively diluting the sodium, followed by calcination of the liquid; and radionuclide partitioning followed by immobilization of the resulting high-activity and low-activity waste streams. A peer review for the INEL separations group identified the most promising radionuclide separation technologies for evaluation.¹ The Transuranic Extraction process, developed by Horwitz and Schulz², was identified as a primary candidate for separation of the actinides from ICPP SBW. The Strontium Extraction (SREX) process, developed by Horwitz³, was identified as a primary candidate for separation of ⁹⁰Sr from ICPP SBW.

A major emphasis at the ICPP has been directed toward evaluating ⁹⁰Sr separation from SBW using the SREX process. The active extractant used in the SREX process solvent is 4',4'(5')-di-(tert-butyl)dicyclohexo)-18-crown-6 (DtBuCH18C6). Tributylphosphate (TBP) is added to the solvent as a phase modifier to prevent third phase formation and a paraffinic hydrocarbon is used as a diluent. The process has been effectively demonstrated to remove Sr from acidic SBW simulants and actual SBW solution to below the 0.04 Ci/m³ NRC Class A low-level waste requirements.^{4,5} Previous testing of the SREX process with simulated SBW in 5.5-cm centrifugal contactors resulted in 99.98% removal of Sr.⁵ However, Pb was extracted into the SREX solvent and the strip section was ineffective in back-extracting the Pb. Lead built up in the SREX solvent and in the aqueous phase of the strip section, resulting in the formation of a precipitate in the strip section. Alternative stripping agents were subsequently investigated for stripping Pb from the SREX solvent. This report summarizes the results of laboratory experiments to identify alternative stripping agents as well as further SREX flowsheet testing for the extraction and selective stripping of Sr and Pb from simulated SBW using centrifugal contactors.

PURPOSE AND SCOPE

The purpose of this study was to develop and demonstrate a SREX flowsheet which will effectively extract and strip ^{90}Sr and Pb from ICPP SBW under continuous, countercurrent conditions using simulated SBW. Once the applicability of this process to SBW has been established, a comparison of the flowsheet to other technologies currently under development (e.g., cobalt dicarbollide solvent extraction) will be possible.

Laboratory batch contacts were performed using the SREX solvent and simulated SBW in order to evaluate an alternative stripping agent which will back-extract Pb from the SREX solvent without the formation of a precipitate. Ammonium citrate and nitric acid solutions were evaluated as potential stripping agents. Distribution coefficients for Pb and Sr were evaluated for each of the stripping agents. The formation of precipitates was also evaluated. As a result of these experiments, a potential SREX flowsheet was developed for the treatment of ICPP SBW. This flowsheet includes provisions for selectively stripping ^{90}Sr and Pb from the SREX solvent.

Sixteen stages of 5.5-cm diameter centrifugal contactors were procured from Oak Ridge National Laboratory and setup as part of the Centrifugal Contactor Mockup. The modified SREX flowsheet was tested using this mockup. The location of the mockup precludes the use of radioactive solutions. Therefore, all flowsheet testing was performed using non-radioactive SBW simulant. The behavior of Sr and the non-radioactive components was evaluated for the potential flowsheet. Specifically, the ability to effectively strip Pb from the SREX solvent was evaluated. Potential problems such as solids precipitation, which were not apparent with batch contacting experiments, but could arise because of the solvent loading effects due to the countercurrent solution flow in the centrifugal contactors, were also evaluated. Previous flowsheet testing has already demonstrated the ability of the SREX flowsheet to reduce the ^{90}Sr activity to below the NRC Class A LLW limit of 0.04 Ci/m^3 with one cycle of SREX (>99.9% ^{90}Sr removal).⁵ The countercurrent SREX flowsheets developed with non-radioactive SBW simulant will be used for future countercurrent flowsheet development and testing with actual SBW.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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EQUIPMENT DESCRIPTION

All testing was performed in the Centrifugal Contactor Mockup located in building CPP-637. The Centrifugal Contactor Mockup, as shown in Figure 1, consists of sixteen stages of 5.5-cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, flowmeters, filters, AC and DC motor drives, and a sample system.

Four stages of centrifugal contactors (assembled as a single unit or four-pack) were procured from Oak Ridge National Laboratory (ORNL) in 1986. Twelve additional stages were procured from ORNL in 1993. A description of the centrifugal contactors is provided in Table 1. All sixteen stages of contactors are basically identical with the exception of the type of motor.

Solution is fed to the contactors using Masterflex® pumps. Surge lines, consisting of an 18-inch section of 1-inch stainless steel tubing, were placed on the outlet of the pumps to dampen the surging flow. Rotameters were calibrated and used to monitor solution flowrates. Flowrates are adjusted by changing the pump speed using a ten-turn potentiometer.

Aqueous and organic feed solutions are filtered with two in-line sintered metal filters in series (20 micron and 5 micron). The filters are installed in glass tubing so that the buildup of any solids can be observed. In addition, pressure gauges were installed to monitor the pressure drop across the filters resulting from solids accumulation on the filters.

Clear flexible Teflon tubing is used for inlet and outlet connections to the centrifugal contactors. This allows solution flow to be observed and solution characteristics to be noted, i.e., color changes of the organic solution between contactor banks.

Table 1. Centrifugal contactor description.

	Original Four-Pack	Additional Twelve Stages
Size	5.5-cm rotor diameter	5.5-cm rotor diameter
Motor	DC	1/3 HP AC
Controller	Individual DC motor controllers for each motor. 0-5,000 RPM control.	AC variable speed motor drive. 0-3,500 RPM control.
Material of Construction	304L stainless steel	304L stainless steel
Sample Ports	Aqueous and organic exiting each stage. Bottom access only.	Aqueous and organic exiting each stage. Top and bottom access.
Aqueous Feed Stages	Stage 4 only	Stages 2, 3, and 4 of each four-pack

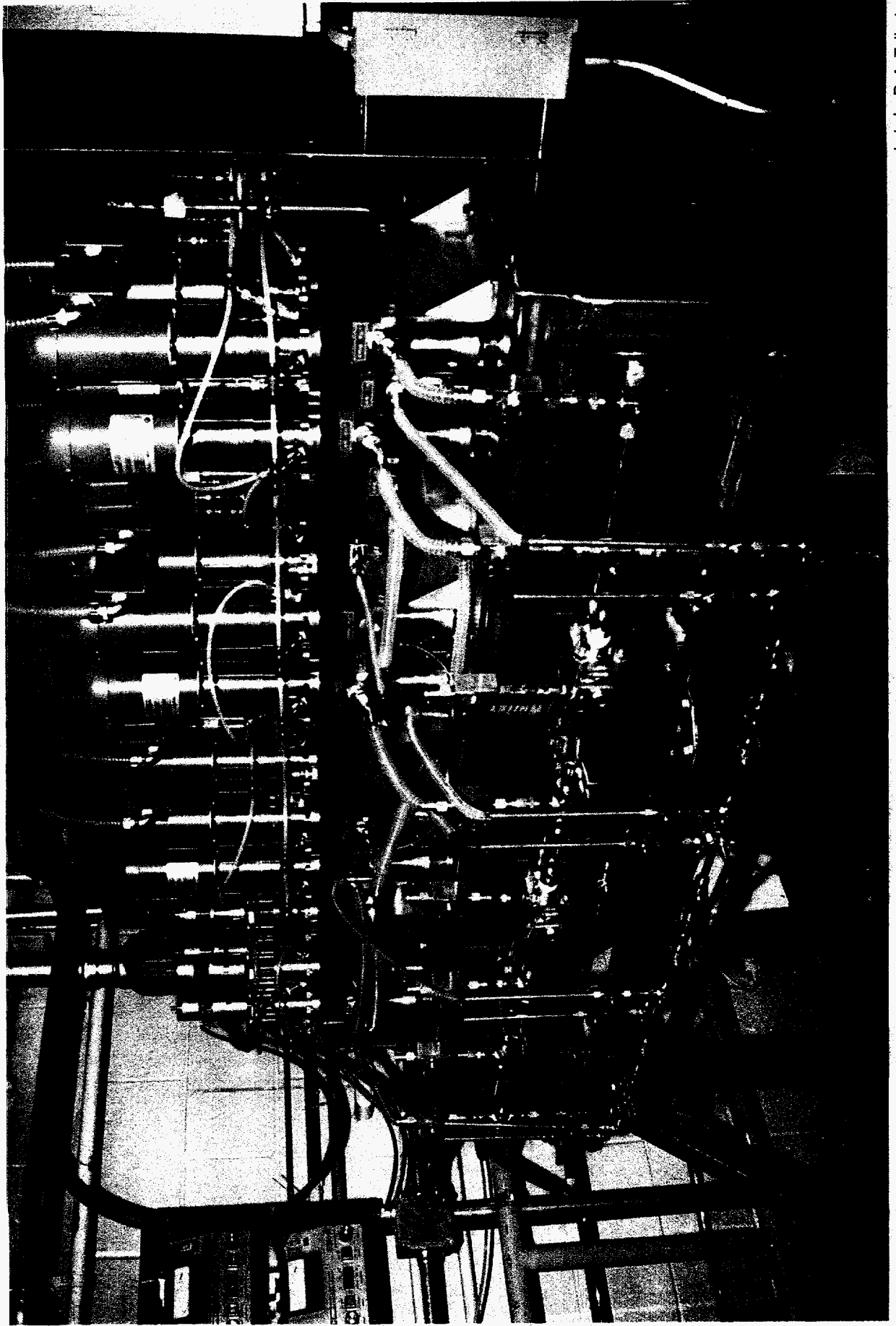


photo by P. A. Tullock

Figure 1. 5.5-cm Centrifugal Contactor Mockup.

The aqueous raffinate, strip product, wash effluent, and solvent recycle streams were sampled by routing the solution draining to a receiving vessel into a sample bottle during the actual flowsheet test. Individual stage samples were taken by draining the contactor stages after shutdown.

An air purge system is connected to the contactor bearing housings. Purge air is required in order to protect the motor body, shaft, and bearings from corrosive process fumes. Air to the bearing housings passes through four rotameters, one for each contactor four-pack. The air flowrate through the rotameters can be adjusted from 0 to 5 scfh. Air from each rotameter is split to feed each of the four bearing housings. Orifices were placed in the lines to each bearing housing to keep the air flowrate into each housing approximately equivalent. The offgas from the bearing purge system combines with the offgas from the feed and product tanks and vents out of the building.

METHODOLOGY/EXPERIMENTAL PROCEDURE

SBW Simulant

For the purposes of this study, the behavior of non-radioactive components in simulated SBW was evaluated. Using the analytical results obtained from characterization of SBW waste solution, a non-radioactive simulant was prepared to represent the average chemical composition of the major non-radioactive matrix components in the SBW tanks. Stable Sr was added to simulate radioactive Sr. The stable Sr was added to the SBW simulant in higher concentrations than the actual waste contains in order to increase the accuracy of the analytical results for Sr. The chemical composition of the SBW simulant is shown in Table 2.

Prior to testing with SBW simulant in the Centrifugal Contactor Mockup, the feed solution was filtered with a 10 micron sintered metal filter to prevent plugging of the filters on the aqueous feed line during operation. Filtering the SBW simulant was required due to the formation of a sodium nitrate precipitate during the makeup of the simulant. This precipitate, which is a gel-like substance, settles to the bottom of the 55 gallon drum in which the SBW simulant is made. Solution is typically pumped out near the top of the liquid to prevent the plugging of the filter and minimize the chance that any solids will remain in the filtered SBW simulant feed. For the testing in the Centrifugal Contactor Mockup, the solution level in the drum was low, resulting in considerable plugging of the filter while pumping. It is expected that some of the precipitate passed through the filter and/or additional precipitate formed in the SBW simulant after being filtered. The specific components evaluated in this study include those species potentially extracted by the SREX solvent: acid, strontium, lead, sodium, aluminum, calcium, zirconium, and mercury.

Table 2. Composition of simulated sodium-bearing waste (SBW).

Component	<i>M</i>	Component	<i>M</i>
Acid (H ⁺)	1.26	K	1.38E-01
Al	5.56E-01	Mn	1.42E-02
B	1.40E-02	Mo	1.49E-03
Cd	2.05E-06	Na	1.32
Ca	9.83E-02	NO ₃	4.46
Ce	3.63E-04	Ni	1.63E-03
Cl	3.52E-02	Pb	9.27E-04
Cs	7.52E-05	PO ₄	<9.18E-03
Cr	5.63E-03	Sr	6.80E-03
F	9.66E-02	SO ₄	3.86E-02
Fe	2.40E-02	Zr	8.76E-03
Hg	1.93E-03		

SREX Solvent

The SREX solvent composition used in all SREX flowsheet studies reported herein was 0.15 *M* 4',4'(5')-di-(tert-butyl)dicyclohexo-18-crown-6 and 1.2 *M* TBP in Isopar L[®] and was prepared by the ICPP Quality Control Laboratory. The extractant was obtained from Eichrom Industries, Darien, IL. The performance of this extractant is extremely sensitive to the purity of the product. The extractant used in these tests was reported to yield a D_{sr} value of 3.8 according to Eichrom quality assurance procedures. The SREX process was originally developed using 1-octanol as the diluent. This selection was made because the flash point and flammability of this diluent were determined to present minimal risk in a process operation. However, octanol is known to form degradation products when placed in contact with nitric acid. The degradation products present unknown potential safety problems in the operation of the SREX process. In addition, it has been determined that the residual presence of 1-octanol in the aqueous phase decreases the performance of CMPO in actinide removal in the TRUEX process during sequential waste treatment processes. An alternative diluent, therefore, has been studied to replace 1-octanol. The alternative solvent is composed of an isoparaffinic hydrocarbon diluent (Isopar L[®] from Exxon Corp.) and 1.2 *M* TBP as a phase modifier. This solvent is compatible with the TRUEX solvent currently being studied at the ICPP.

The purity and composition of the SREX solvent were established prior to performing laboratory studies and prior to use in the centrifugal contactors. D_{sr} was determined using the SREX solvent and 3.0 *M* nitric acid solution in order to evaluate solvent purity and composition. This method of determining the strontium distribution coefficient was established as a quality control procedure for testing the initial SREX solvent and the SREX solvent product from each flowsheet test. If the results were within the acceptable range ($D_{sr} > 2.5$), the solvent was considered suitable for extraction studies.

Due to limited availability and the high cost associated with the DtBuCH18C6, only six liters of SREX solvent was prepared for testing in the Centrifugal Contactor Mockup. This limited quantity of solvent made it necessary to recycle the solvent during each flowsheet test in the centrifugal contactors. The SREX solvent was fed to the contactors out of a carboy and the solvent product leaving the strip section drained back into the feed carboy.

Analytical

All sample analyses were performed by the ICPP Analytical Section. Sr, Pb, Na, and K analyses of the aqueous samples were performed using Inductively Coupled Plasma Atomic Absorption Spectroscopy (ICP-AES). Hg analyses were performed using Cold Vapor Atomic Absorption Spectrophotometry.

Experimental results obtained from batch contacts with SBW simulant indicate 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) is effective at quantitatively back-extracting all metals, except mercury, from the SREX solvent.⁵ Consequently, the organic samples from the flowsheet test were contacted with 0.25 *M* HEDPA in 0.05 *M* nitric acid. To insure quantitative metal recovery in a single contact, an O/A ratio of 0.4 was used. The HEDPA was assumed to strip all of the Sr, Pb, Na, Ca, and Zr, but not the Hg, out of the SREX solvent. The aqueous phase from the HEDPA strip was separated from the solvent and submitted for Sr, Pb, Na, Ca, and Zr analysis. The solvent was then contacted with 0.05 *M* ethylene diamine tetraacetic acid (EDTA) at an O/A of 0.4 to strip the Hg out of the solvent. This procedure provided an indirect measure of organic phase compositions and allowed the use of material balances to validate experimental results. For the batch contacts, the organic phase concentration was determined indirectly by chemical balance. However, selected data points in each of these experiments were reproduced subsequently with radiometric methods.

For batch contact experiments with radioactive tracers, the analysis of both the organic and aqueous phases was performed by gamma spectrometry when ^{85}Sr was employed as the tracer. When ^{210}Pb was employed, each phase was analyzed by liquid scintillation. Corrections for the grow-in of the daughter isotopes were performed for each phase in the liquid scintillation measurements. The measured activities in each phase were utilized to determine distribution coefficients for the measured species.

Lead Stripping Studies

Dilute nitric acid and ammonium citrate solutions were evaluated as potential Pb and Sr stripping reagents. The evaluation of the stripping reagents was performed by contacting a volume of the SREX solvent once with an equal volume of 3 M nitric acid which contained 0.005 M each of $\text{Pb}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$. Aliquots of this organic solution were then placed in separate containers for stripping experiments. The stripping procedure was performed by contacting the organic solution three times in succession with equal volumes of the appropriate stripping solution. The aqueous phases from each contact were sampled after centrifugation for analytical measurement.

Each of the experiments in this study was performed at room temperature (27 ± 2 °C) with equal volumes of the appropriate aqueous solution and organic extractant. It should be noted that the experiments described in this paper did not employ a preconditioning of the organic phase prior to extraction. The equilibrium concentration of acid in the aqueous phase, therefore, is likely to differ from the initial conditions due to the extraction of nitric acid and water by the organic phase. The organic and aqueous solutions were placed in glass centrifuge tubes and placed on a vortex-motion mixer for 1 minute unless otherwise stated. Following mixing, the samples were immediately placed in a centrifuge for one minute at 5,000 rpm. After centrifugation, the phases in each sample were separated for analysis with small volume Pasteur pipets.

Radioactive Sr and Pb tracers were employed for direct measurement of metal concentrations in aqueous and organic phases. The tracers which were employed in the batch extraction experiments were dispensed with a small volume motorized pipet (Rainin Instrument Co., Inc.) directly into individual aqueous solutions in test tubes. The tracer solutions were of sufficient activity to allow a small volume of tracer to be added which did not significantly increase the total volume of the aqueous samples.

SREX Flowsheet Testing in the Centrifugal Contactors

Based on the results of the Pb stripping studies and previous SREX flowsheet development studies performed in the 5.5-cm Centrifugal Contactor Mockup, a SREX flowsheet was recommended for further testing in the mockup. This flowsheet consists of four stages of extraction at an O/A of 1.0, four stages of 0.05 M nitric acid strip at an O/A of 0.5, four stages of 0.1 M ammonium citrate strip at an O/A of 1.0, and four stages of 2.0 M nitric acid rinse at an O/A of 2.0. The resulting flowsheet used for the SREX flowsheet testing is shown in Figure 2. Due to the limited number of contactor stages available (16 stages), only four stages of extraction were tested instead of the desired eight. Results of previous flowsheet testing has already demonstrated that 99.97% Sr removal will be obtained with this flowsheet.

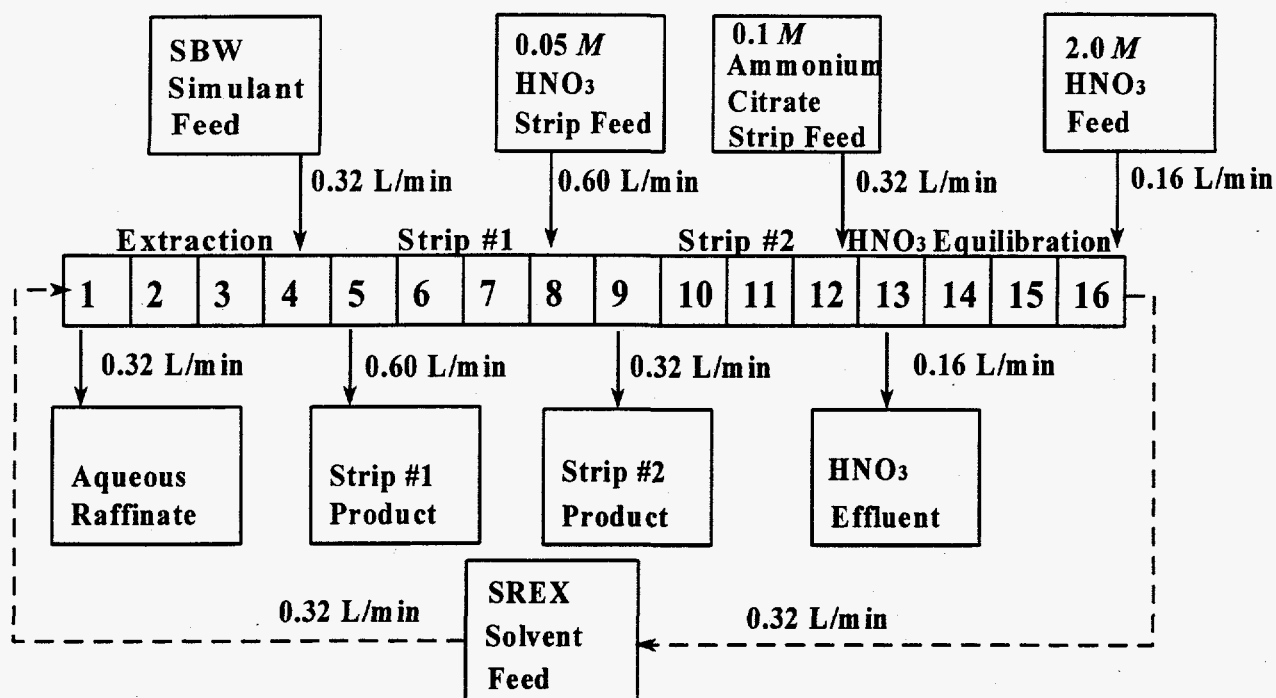


Figure 2. SREX flowsheet test.

The goals of the SREX flowsheet testing were to:

- (1) Demonstrate the overall operability of the 5.5-cm centrifugal contactors with the SREX flowsheet.
- (2) Determine the concentrations and distribution coefficients of Sr, Pb, and H⁺ for each stage at steady-state conditions.
- (3) Evaluate the effectiveness of the SREX flowsheet in stripping Pb from the SREX solvent.
- (4) Determine if any precipitate or third phase formation problems exist with this flowsheet.

SREX flowsheet testing was performed as follows. The centrifugal contactor motors were started at 3,000 rpm. All aqueous solution flows, except for the SBW simulant, were established. 2.0 M nitric acid was used as an initial SBW feed. When aqueous solution was observed exiting each of the sections, solvent flow was initiated. SBW simulant feed was started when solvent was observed exiting the extraction section. Forty-five minutes after the start of the aqueous feeds, the raffinate, strip products, acidification effluent, and solvent effluent streams were sampled. Based on the results of previous SREX flowsheet testing, the flowsheet was expected to have reached steady-state within 30 minutes after the start of SBW feed. Level readings on each of the feed tanks were also noted in order to determine actual solution flowrates based on tank depletion rates. The centrifugal contactors were then shutdown by simultaneously stopping the feed pumps and contactor motors. 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 each of the 16 stages.

The following procedure was used to obtain aqueous and organic samples from each stage; 1) 20 mLs of aqueous were drained out of the contactor stage to flush the drain line, 2) 20 mLs of aqueous sample were drained into a sample bottle for analysis, 3) the remaining aqueous and a portion of the organic were drained from the contactor stage, 4) 15 mLs of organic were drained into a clean sample bottle, and 5) 10 mLs of organic were pipetted off of the top and transferred to a sample bottle for analysis.

RESULTS AND DISCUSSION

Lead Stripping Studies

Nitric Acid Dependence for the Extraction of Strontium and Lead

The extraction of Sr and Pb from nitric acid solutions by the SREX solvent has been studied in batch solvent extraction experiments. The measured distribution coefficients for Sr and Pb are dependent upon the initial concentration of nitric acid in the aqueous phase as shown in Figure 3. The extraction curves show that the extraction of Pb from nitric acid solutions is more efficient than the extraction of Sr. In addition, the slopes of the plotted regression lines are dissimilar. The figure indicates that at low concentrations of nitric acid, the difference between the measured distribution coefficients for Pb and Sr is larger than the measured difference at higher acid concentrations. The extraction plots for Pb and Sr suggest that at higher acid concentrations, highly efficient removal of Pb and Sr is possible.

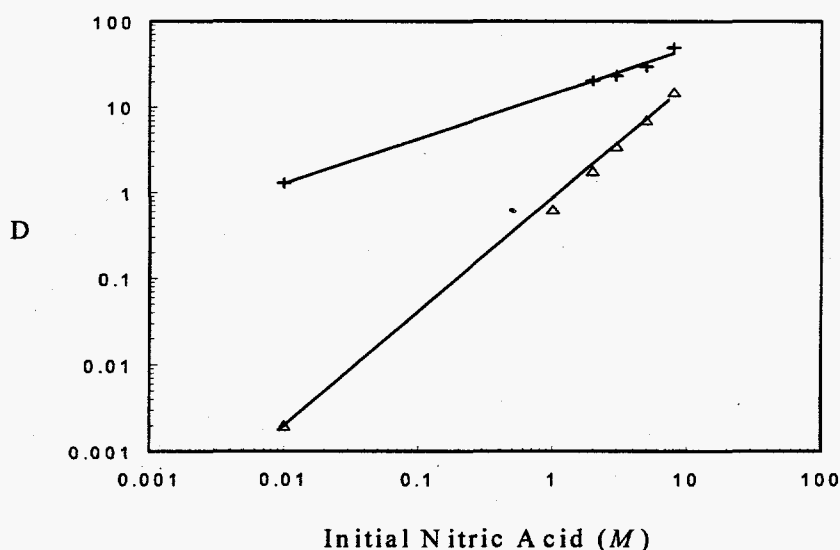


Figure 3. Dependence of distribution coefficients on initial nitric acid concentration for 0.001 M Pb (+) and 0.001 M Sr (Δ). Organic phase: 0.15 M DtBuCH18C6 and 1.2 M n-tributyl phosphate in Isopar L[®].

Stripping Behavior of Strontium and Lead

The stripping behavior of Sr and Pb have been evaluated to determine effective methods for removing the extracted species from the loaded organic phase. This study utilized a simulated SBW and was performed by contacting the SREX solvent three times with equal volumes of the simulated SBW solution. The metal-loaded organic was then divided into three equal fractions for separate stripping procedures. The organic fractions were then contacted sequentially with four equal volumes of 0.01 M nitric acid, 1 M nitric acid, or 0.1 M ammonium citrate. Tables 3 and 4 display the results of the study.

The numbers shown are the amount of the metals in the aqueous phase, expressed as percent of the total quantity of the metal which was initially present in the organic phase after the extraction procedure, for each strip contact.

The case where 0.01 *M* nitric acid was used as the stripping reagent exhibits excellent stripping of Sr but inadequate stripping for Pb. The low results for Pb can be predicted from the acid dependent plot for Pb in Figure 3. This curve shows that when the aqueous phase contains 0.01 *M* nitric acid, the distribution coefficient for Pb remains above 0.5. This suggests that 0.01 *M* nitric acid will not strip Pb from the loaded solvent efficiently. Tables 3 and 4 indicate that 1 *M* nitric acid is not effective for stripping either Sr or Pb from the loaded SREX solvent. This result is also expected based upon the extraction curves discussed previously.

The appearance of a cloudy precipitate in the aqueous phase, when dilute nitric acid was employed as a stripping reagent, was observed frequently during this investigation. This precipitate was determined to be composed primarily of insoluble lead complexes. This observation, and the inadequate stripping behavior discussed above, indicates that another stripping reagent must be identified for the stripping of Pb. Ammonium citrate has been reported to be effective for removing Pb from extraction chromatographic resins based upon the DtBuCH18C6 extractant.⁶ This reagent may be decomposed under high thermal conditions and, therefore, may result in only slight increases in total mass in the resulting final waste form. Therefore, 0.1 *M* ammonium citrate has been investigated as an alternative stripping reagent. Tables 3 and 4 display the data obtained from this study. Highly effective stripping of both Sr and Pb were obtained with this reagent. The Sr fraction was stripped quantitatively in the first two contacts. The Pb fraction was distributed among the four contacts with 86% of the fraction being stripped in the third contact. It should be noted that no precipitate was observed in the aqueous phases during this experiment. The elimination of the insoluble precipitates and the efficient removal of Pb from the organic phase indicates that ammonium citrate may be an effective reagent for use in the SREX process. These distribution coefficients were measured in pure Pb and Sr solutions which contained no additional interferences. Competing extractable ions may alter the selectivity and measured distribution coefficients.

Table 3. Amount of Sr present in aqueous phase as percent of total.

Stripping Reagent	Contact 1	Contact 2	Contact 3	Contact 4	Total
0.01 <i>M</i> nitric acid	59.6	36.7	0.20	0.08	96.6
1 <i>M</i> nitric acid	31.3	30.5	16.6	7.90	86.3
0.1 <i>M</i> ammonium citrate	55.5	47.4	0.29	0.05	103

Table 4. Amount of Pb present in aqueous phase as percent of total.

Stripping Reagent	Contact 1	Contact 2	Contact 3	Contact 4	Total
0.01 <i>M</i> nitric acid	0.88	3.78	30.3	40.4	75.4
1 <i>M</i> nitric acid	1.15	0.89	0.67	1.06	3.77
0.1 <i>M</i> ammonium citrate	1.18	7.71	86.2	2.18	97.3

Batch Contact Solvent Extraction Flowsheets

The data from the extraction and stripping studies have been used to propose an experimental batch contact flowsheet for demonstration of the simultaneous extraction of Sr and Pb from SBW. The organic phase, consisting of 0.15 *M* DtBuCH18C6 in 1.2 *M* TBP in Isopar L, was contacted four times in succession with simulated SBW. The organic phase was separated from the aqueous phase in each contact and transferred to the next contact.

Four contacts of 0.05 *M* nitric acid were employed following the extraction contacts as a method to remove nitric acid from the organic phase. A 0.05 *M* nitric acid solution was selected in order to allow efficient acid scrubbing and strontium stripping, while avoiding the Pb precipitate which occurs with 0.01 *M* nitric acid. Finally, four contacts of 0.1 *M* ammonium citrate were employed to accomplish the metal stripping procedure. The results of the experimental flowsheet are presented in Table 5.

The measured distribution coefficients for Sr and Pb in the extraction contacts of the flowsheet reflected the expected range of values for Sr. The Pb distribution coefficients were found to be sufficiently high to remove the Pb in quantitative amounts in all four extraction contacts. The subsequent contacts with 0.05 *M* nitric acid efficiently stripped Sr from the loaded organic. These contacts did not, however, strip Pb from the organic phase. The Pb fraction remained primarily in the organic phase until the final strip contacts with 0.1 *M* ammonium citrate. The largest portion of the Pb fraction was stripped from the organic phase on the first contact with ammonium citrate. This is due to the fact that most of the nitric acid which resided in the organic phase following the extraction contacts, was removed by the 0.05 *M* nitric acid contacts. Based on these results, the countercurrent flowsheet shown in Figure 2 was developed and tested in the 5.5-cm Centrifugal Contactor Mockup.

Table 5. Distribution coefficients for batch contact flowsheet.

Contact	Aqueous Phase	Sr	Pb
1	SBW simulant	4.2	587
2	SBW simulant	3.9	113
3	SBW simulant	3.8	89
4	SBW simulant	4.0	75
5	0.05 <i>M</i> nitric acid	0.6	74
6	0.05 <i>M</i> nitric acid	0.12	40
7	0.05 <i>M</i> nitric acid	<0.01	23
8	0.05 <i>M</i> nitric acid	<0.01	3.4
9	0.1 <i>M</i> ammonium citrate	<0.01	0.32
10	0.1 <i>M</i> ammonium citrate	<0.01	<0.1
11	0.1 <i>M</i> ammonium citrate	<0.01	<0.1
12	0.1 <i>M</i> ammonium citrate	<0.01	<0.1

SREX Flowsheet Testing

Contactactor Operation

Actual solution flowrates were calculated from feed tank depletion rates and are compared to the desired flowrates in Table 6. Due to the use of a small amount of aqueous feed in the 55 gallon feed vessel, a tank depletion flowrate was not determined for the aqueous feed. The SREX solvent was recycled during testing so a tank depletion rate could not be determined. However, the organic feed rotameter was calibrated with the SREX solvent prior to testing and a flowrate of 0.32 L/min was obtained for the rotameter setting at which the SREX flowsheet testing was performed.

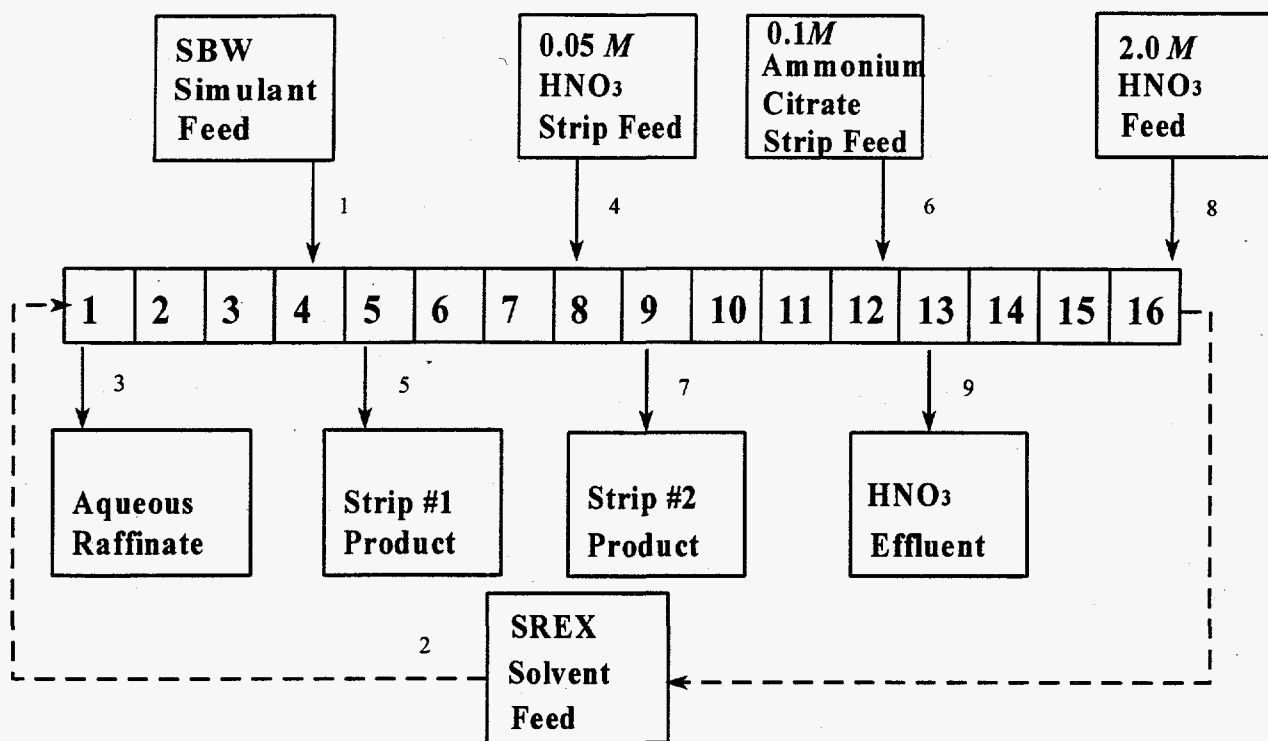
The 5.0 and 20.0 micron filters on the feed lines accumulated solids, causing partial plugging during operation. Also, a gel-like precipitate, consistent with the precipitate present in the SBW feed makeup vessel, was observed in stages 3 and 4 of the extraction section after shutdown. The precipitate was analyzed as primarily Na, Ca, Al, Sr, and P. Na, Ca, and Al is also the major composition of the precipitate in the feed makeup vessel. Therefore, it is believed that obtaining the SBW feed from the bottom of the makeup vessel resulted in the carryover and/or formation of this precipitate in the feed for the flowsheet test. This precipitate is not representative of actual SBW solution and, therefore, is not expected to be present if actual SBW were being used. Flooding was not observed during testing.

Table 6. Flowrates and O/A ratios for SREX flowsheet testing.

Section	Phase	Flowrate (L/min)		O/A Ratio		Total Flow (L/min)
		Desired	Actual	Desired	Actual	
All	Org.	0.32	nd	---	---	---
Extraction	Aq.	0.32	nd	1.0	nd	0.64
Strip #1	Aq.	0.60	0.66	0.53	0.48	0.98
Strip #2	Aq.	0.32	0.31	1.0	1.0	0.63
Nitric Acid Equilibration	Aq.	0.16	0.15	2.0	2.1	0.47

Concentrations at Shutdown

The concentrations of Sr, Al, Ca, H⁺, Hg, Na, Pb, and Zr in each stream immediately prior to shutdown are given in Figure 4. Material balances for Sr, Al, Ca, H⁺, Hg, Na, Pb, and Zr are given in Table 7. The values in Table 7 were normalized to obtain an overall material balance of 100%. Distribution coefficients were calculated for Sr and Pb for each of the 16 stages. The resulting distribution coefficients are given in Table 8. A discussion of the behavior of each component follows.



Component	SBW Feed 1	SREX Solvent Feed 2	LAW Raff. 3	Strip #1 Feed 4	Strip #1 Product 5	Strip #2 Feed 6	Strip #2 Product 7	HNO ₃ Feed 8	HNO ₃ Effluent 9
H ⁺ (M)	1.35	---	1.00	0.05	0.55	---	---	2.0	0.79
NH ₄ (M)	---	---	---	---	---	0.1	0.1	---	---
Sr (M)	6.80E-03	7.42E-07	1.27E-04	---	2.85E-03	---	1.48E-07	---	<4.57E-08
Pb (M)	9.27E-04	<3.84E-06	<7.67E-07	---	8.00E-06	---	8.58E-04	---	<7.67E-07
Al (M)	0.56	---	0.57	---	0.023	---	1.99E-05	---	3.00E-05
Ca (M)	9.83E-02	---	4.81E-02	---	2.39E-03	---	3.60E-05	---	3.79E-05
Hg (M)	1.93E-03	---	3.01E-05	---	4.54E-05	---	4.86E-04	---	7.93E-06
Na (M)	1.32	---	0.95	---	5.48E-02	---	1.69E-04	---	1.10E-04
Zr (M)	8.77E-03	---	1.41E-03	---	4.50E-03	---	7.47E-05	---	3.86E-06
Flowrate (L/min)	0.32	0.32	0.32	0.60	0.60	0.32	0.32	0.16	0.16

Figure 4. SREX flowsheet test steady state concentrations.

Table 7. Percentage of component in each of the effluent streams for SREX flowsheet testing.

Stream	Sr	Pb	Al	Ca	Hg	Na	Zr
Aqueous Raffinate	1.9% (2.1%) ^a	0.083% (0.090%)	101.9% (92.4%)	49.0% (90.6%)	1.6% (5.0%)	71.7% (89.3%)	16.1% 37.4%
Strip #1 Product	86.3% (97.9%)	1.8% (1.9%)	8.4% (7.6%)	5.0% (9.3%)	4.8% (15.7%)	8.5% (10.6%)	26.7% (62.1%)
Strip #2 Product	0.002% (0.002%)	89.6% (97.9%)	0.003% (0.003%)	0.04% (0.07%)	24.3% (78.7%)	0.012% (0.015%)	0.21% (0.48%)
Nitric Acid Effluent	<3E-4% (<4E-4%)	<0.04% (<0.04%)	0.002% (0.002%)	0.02% (0.03%)	0.2% (0.6%)	0.004% (0.005%)	0.02% (0.05%)
Solvent Effluent	0.01%	0.4%	nd ^c	nd	nd	nd	nd
Mass Balance ^b	88.2%	91.5%	110.3%	54.0%	30.9%	80.3%	43.0%

a. Normalized percentage.

b. The mass balance is the amount of a component accounted for based on the sample analysis results.

c. Not determined.

Table 8. Sr and Pb distribution coefficients for SREX flowsheet testing.

Section	Stage	D _{Sr}	D _{Pb}
Extraction	1	2.5	>14
	2	2.4	>8.3
	3	3.1	>260
	4	2.0	45
Strip #1	5	0.80	156
	6	0.33	3.3
	7	0.093	4.8
	8	1.8	4.2
Strip #2	9	3.9	0.075
	10	0.15	<0.55
	11	0.22	nd ^a
	12	1.8	nd
Nitric Acid Equilibration	13	>15	nd
	14	>14	nd
	15	17	nd
	16	15	nd

a. Not determined.

Strontium. The Sr concentration was reduced from $6.80\text{E-}03\text{ M}$ in the feed to $1.27\text{E-}04\text{ M}$ in the raffinate. This corresponds to 97.9% Sr removal with only four extraction stages. Distribution coefficients in the extraction section ranged from 2.0 to 3.1, which is consistent with results from previous testing.⁵ Re-equilibration of the stage 2 aqueous and organic phases resulted in the Sr distribution increasing from 2.4 to 3.2 (33% increase). Low stage efficiency was also observed in previous SREX flowsheet testing at the INEL and at ANL. The 0.05 M nitric acid strip section was very effective in back-extracting the Sr from the SREX solvent. 99.97% of the Sr was stripped from the SREX solvent with the four strip stages.

Lead. Distribution coefficients for Pb in the extraction section ranged from >8 to > 261 . As a result, 99.9% of the Pb was extracted into the SREX solvent. The 0.05 M nitric acid strip section (Sr strip) back-extracted 1.9% of the Pb from the solvent. Distribution coefficients in this section ranged from 3.3 to 156. The four stages of ammonium citrate strip effectively removed all but 0.4% of the Pb from the SREX solvent.

Aluminum, calcium, mercury, sodium, and zirconium. As expected, Hg and Zr were extracted by the SREX solvent (95% of the Hg and 63% of the Zr). In addition, 7.6% of the Al, 9.4% of the Ca and 10.6% of the Na were extracted. These species were effectively stripped from the SREX solvent in the two strip sections. It should be noted that the overall material balances were very poor for each of these species. It is expected that the poor material balances are a result of the precipitates (Na, Ca, Al) present in the feed solution and in the extraction section.

Acid. Distribution coefficients for H^+ ranged from 0.66 to 0.75 in the extraction section, 0.13 to 0.41 in the nitric acid strip section, 0.023 to 0.037 in the ammonium citrate strip section, and 0.26 to 0.31 in the nitric acid equilibration section. These distribution coefficients are in good agreement with H^+ data from previous SREX testing.⁵ The 0.05 M nitric acid strip back-extracted 99.3% of the H^+ from the SREX solvent. As a result, the H^+ concentration in the ammonium citrate strip section remained low enough to effectively strip the Pb from the SREX solvent.

Potassium. Samples from this test were not analyzed for potassium. The SREX solvent will typically extract potassium. Previous testing in the 5.5-cm Centrifugal Contactor mockup resulted in 53% of the potassium extracted with eight extraction stages ($D_K = 0.6$). The extracted potassium was effectively stripped from the SREX solvent with dilute HNO_3 .

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Lead and strontium were extracted and selectively stripped from the SBW simulant. Removal efficiencies of 97.9% and 99.91% were obtained for Sr and Pb, respectively (four extraction stages). It should be noted that a Sr removal efficiency of 99.98% was previously demonstrated with eight extraction stages.⁵ 99.998% of the extracted Sr and 1.9% of extracted Pb exited with the 0.05 M nitric acid strip product. 0.002% of the extracted Sr and 97.9% of the extracted Pb exited with the 0.1 M ammonium citrate strip product.

Mercury and zirconium were extracted (95% of the Hg and 63% of the Zr) by the SREX solvent and successfully stripped in the ammonium citrate and nitric acid strip sections, respectively.

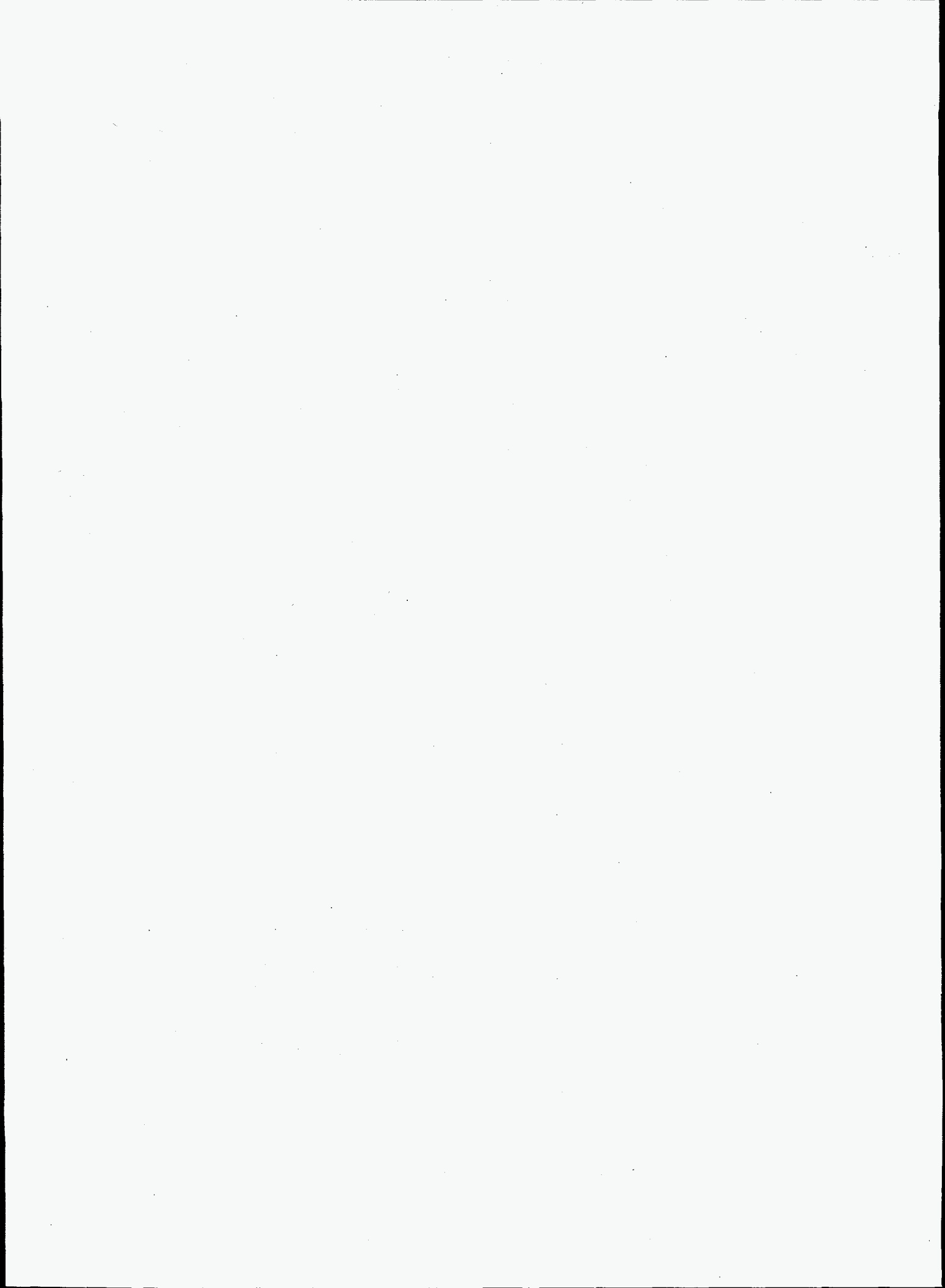
Flooding and/or third phase formation were not observed during testing. A gel-like precipitate, consistent with the precipitate present in the SBW feed makeup vessel, was observed in stages 3 and 4 of the extraction section after shutdown. The precipitate was analyzed as primarily Na, Ca, Al, Sr, and P. Na, Ca, and Al is also the major composition of the precipitate in the feed makeup vessel. Therefore, it is believed that obtaining the SBW feed from the bottom of the makeup vessel resulted in the carryover and/or formation of this precipitate in the feed for the flowsheet test. This precipitate is not representative of actual SBW solution and, therefore, is not expected to be present if actual SBW were being treated.

Recommendations

This flowsheet should be used as a basis for performing SREX flowsheet testing with actual tank waste in the 2.0-cm centrifugal contactors located in the Remote Analytical Laboratory hot cell.

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APPENDIX A
EXPERIMENTAL DATA

Table A-1. Stage samples after shutdown

Stage	H ⁺	H ⁺	Sr	Sr	Pb	Pb
	Aq.(M)	Org.(M)	Aq.(M)	Org.(M)	Aq.(M)	Org.(M)
1	1.003	0.755	1.31E-04	3.23E-04	< 7.67E-07	1.11E-05
2	1.177	0.778	4.36E-04	1.06E-03	< 7.67E-07	6.37E-06
3	1.247	0.846	1.21E-03	3.70E-03	< 7.67E-07	2.00E-04
4	1.293	0.844	3.12E-03	6.14E-03	1.39E-05	6.28E-04
5	0.549	0.223	2.92E-03	2.34E-03	7.53E-06	1.17E-03
6	0.166	0.043	1.09E-03	3.61E-04	4.61E-04	1.53E-03
7	0.048	0.0066	1.90E-05	1.77E-06	3.00E-04	1.44E-03
8	0.046	0.006	3.77E-07	6.85E-07	2.23E-04	9.30E-04
9	0.128	0.003	2.05E-07	7.99E-07	8.94E-04	6.66E-05
10	0.139	0.004	5.26E-06	7.99E-07	6.92E-06	< 3.84E-06
11	0.136	0.005	5.51E-06	1.20E-06	< 7.67E-07	< 3.84E-06
12	0.139	0.005	4.11E-07	7.42E-07	< 7.67E-07	< 3.84E-06
13	0.788	0.208	< 4.57E-08	6.85E-07	< 7.67E-07	< 3.84E-06
14	1.22	0.343	< 4.57E-08	6.28E-07	< 7.67E-07	< 3.84E-06
15	1.528	0.474	4.57E-08	7.99E-07	< 7.67E-07	< 3.84E-06
16	1.731	0.496	4.57E-08	6.85E-07	< 7.67E-07	< 3.84E-06

I-V

Table A-2. Steady State Samples

	H ⁺	H ⁺	Sr	Sr	Pb	Pb	Al	Ca	Hg	Na	Zr
	Aq.(M)	Org.(M)	Aq.(M)	Org.(M)	Aq.(M)	Org.(M)	Aq(ppm)	Aq(ppm)	Aq(ppm)	Aq(ppm)	Aq(ppm)
Raffinate	1.022	nd	1.27E-04	nd	< 7.67E-07	nd	15280	1929.2	6.03	21800	128.44
Strip #1 prod.	0.479	nd	2.85E-03	nd	8.00E-06	nd	612.8	95.76	9.1	1260	103.5
Strip #2 prod	0.139	nd	1.48E-07	nd	8.58E-04	nd	0.537	1.444	97.4	3.88	1.717
HNO ₃ effluent	0.786	nd	< 4.57E-08	nd	< 7.67E-07	nd	0.81	1.521	1.59	2.53	0.352
Solvent effluent	nd	nd	nd	7.42E-07	nd	< 3.84E-06	nd	nd	nd	nd	nd
Feed	1.346	nd	6.80E-03	nd	9.27E-04	nd	15000	3940.8	388	30400	799.4