DEMONSTRATION OF THE SREX PROCESS FOR THE REMOVAL OF \(^{90}\text{Sr}\) FROM ACTUAL HIGHLY RADIOACTIVE SOLUTIONS IN CENTRIFUGAL CONTACTORS

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ABSTRACT

The SREX process is being evaluated at the Idaho Chemical Processing Plant (ICPP) for the separation of \(^{90}\text{Sr}\) from acidic radioactive wastes stored at the ICPP. These efforts have culminated in a recent demonstration of the SREX process with actual tank waste. This demonstration was performed using 24 stages of 2-cm diameter centrifugal contactors installed in a shielded hot cell at the ICPP Remote Analytical Laboratory. An overall removal efficiency of 99.995% was obtained for \(^{90}\text{Sr}\). As a result, the activity of \(^{90}\text{Sr}\) was reduced from 201 Ci/m\(^3\) in the feed solution to 0.0089 Ci/m\(^3\) in the aqueous raffinate, which is below the U. S. NRC Class A LLW limit of 0.04 Ci/m\(^3\) for \(^{90}\text{Sr}\). Lead was extracted by the SREX solvent and successfully partitioned from the \(^{90}\text{Sr}\) using an ammonium citrate strip solution. Additionally, 94% of the total alpha activity, 1.9% of the \(^{241}\text{Am}\), 99.94% of the \(^{239}\text{Pu}\), 99.97% of the \(^{239}\text{Pu}\), 36.4% of the K, 64% of the Ba, and >83% of the Zr were extracted by the SREX solvent. Cs, B, Cd, Ca, Cr, Fe, Mn, Ni, and Na were essentially inextractable.

I. INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering and Environmental Laboratory (INEEL), 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, acidic liquid sodium-bearing waste (SBW), was also generated primarily from equipment decontamination between campaigns and solvent waste 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 5.7 million liters of liquid SBW are temporarily stored at the ICPP in large underground stainless-steel tanks. As part of a 1995 agreement between the State of Idaho, the U. S. Department of Energy, and the U. S. 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 radionuclide partitioning followed by immobilization of the resulting high-activity and low-activity waste streams. A recent peer review identified the most promising radionuclide separation technologies for evaluation. The Strontium Extraction (SREX) process, developed by Horwitz\(^2\), was identified as a primary candidate for separation of \(^{90}\text{Sr}\) from ICPP SBW.

A major emphasis at the ICPP has been directed toward evaluating \(^{90}\text{Sr}\) separation from SBW using the SREX process. The extractant used in the SREX process solvent is \(4',4'-(5')\)-di-\((\text{tert-butyl)dicyclohexo\)\)-18-crown-6 (DtBuCH\(_{18}\)C6). Tributyl phosphate (TBP) is added to the solvent as a phase modifier to prevent third phase formation and a paraffinic hydrocarbon is used as a diluent. Previously, all testing at the INEEL has been performed using batch contacts with actual and simulated SBW\(^5\), and using small-scale centrifugal contactors (2-cm and 5.5-cm rotor diameter) with SBW simulants.\(^6\) This report summarizes the results of SREX flowsheet testing for the separation of \(^{90}\text{Sr}\) from actual SBW solution (tank WM-183) using 2-cm diameter centrifugal contactors in a shielded cell facility.

II. PURPOSE AND SCOPE

The purpose of this study was to demonstrate the effectiveness of the SREX process for the treatment of ICPP SBW under continuous, countercurrent conditions using actual ICPP tank waste. Once the effectiveness of this process has been established for SBW, a comparison of the flowsheet to other technologies currently under development will be possible.

Installation of the 2-cm centrifugal contactors in the ICPP Remote Analytical Laboratory (RAL) shielded hot cell allowed the use of actual SBW in testing of the SREX process. This allowed the removal efficiencies of \(^{90}\text{Sr}\) to be determined and the effectiveness of the process in reducing the activity of \(^{90}\text{Sr}\) to below U. S. NRC Class A LLW requirements to be evaluated. In addition, the behavior of the actinides, Pb, Na, K, Al, Ba, B, Cd, Ca, Cr, Fe, Mn, Hg, Ni, and Zr in the process was evaluated.

III. EXPERIMENTAL PROCEDURE

A. WM-183 waste.

Sodium-bearing waste, obtained from tank WM-183, was
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used as feed solution for this testing. Currently, approximately 5.7 million liters of SBW are stored in six tanks. The composition in each tank varies; however, the composition of the solution in tank WM-183 is representative of the solution in all the tanks. The chemical composition of the WM-183 waste is shown in Table I.

<table>
<thead>
<tr>
<th>Component</th>
<th>Conc.</th>
<th>Component</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid (M)</td>
<td>1.72</td>
<td>SO₄ (M)</td>
<td>0.066</td>
</tr>
<tr>
<td>Al (M)</td>
<td>0.62</td>
<td>Zr (M)</td>
<td>&lt;6.6E-03</td>
</tr>
<tr>
<td>B (M)</td>
<td>0.013</td>
<td>Alpha (nCi/g)</td>
<td>506</td>
</tr>
<tr>
<td>Ca (M)</td>
<td>0.042</td>
<td>²⁴¹Am (nCi/g)</td>
<td>33.9</td>
</tr>
<tr>
<td>Cl (M)</td>
<td>0.011</td>
<td>²³⁸Pu (nCi/g)</td>
<td>327</td>
</tr>
<tr>
<td>Cr (M)</td>
<td>0.016</td>
<td>²³⁹Pu (nCi/g)</td>
<td>126</td>
</tr>
<tr>
<td>Fe (M)</td>
<td>0.051</td>
<td>U (mg/L)</td>
<td>114</td>
</tr>
<tr>
<td>Hg (M)</td>
<td>0.0023</td>
<td>²³⁷Np (nCi/g)</td>
<td>&lt;6.5</td>
</tr>
<tr>
<td>K (M)</td>
<td>0.096</td>
<td>⁹⁰Tc (Ci/m³)</td>
<td>0.036</td>
</tr>
<tr>
<td>Na (M)</td>
<td>0.77</td>
<td>¹³⁷Cs (Ci/m³)</td>
<td>218</td>
</tr>
<tr>
<td>NO₃ (M)</td>
<td>5.24</td>
<td>⁹⁰Sr (Ci/m³)</td>
<td>201</td>
</tr>
<tr>
<td>Pb (M)</td>
<td>0.0015</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. SREX solvent.

The SREX solvent composition used in all SREX flowsheet studies reported herein was 0.15 M 4',4''-(tert-butylcyclclohexa)-18-crown-6 and 1.5 M TBP in Isopar L® and was prepared by the ICPP Quality Control Laboratory. The extractant was obtained from Eichrom Industries, Darien, IL. The SREX process was originally developed at Argonne National Laboratory 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 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 1.5 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 use in the centrifugal contactors. The alternative solvent is composed of an isoparaffinic hydrocarbon diluent (Isopar L® from Exxon Corp.) and 1.5 M TBP as a phase modifier. This solvent is compatible with the TRUEX solvent currently being studied at the ICPP.

Prior to performing the flowsheet testing, the SREX solvent was pre-equilibrated with HNO₃ by contacting the solvent with 3 M HNO₃ twice at an organic to aqueous volume ratio (O/A) of 1. With this pre-equilibration, the HNO₃ concentration of the SREX solvent feed was approximately 1.0 M. Pre-equilibration of the solvent prevents the extraction of HNO₃ from the acidic waste, which would result in lower ⁹⁰Sr distribution coefficients in the extraction section.

C. SREX Flowsheet Demonstration

Based on the results of previous SREX flowsheet development studies performed with simulated waste solution in a 5.5-cm centrifugal contactor pilot plant and the results of batch laboratory extraction experiments, a SREX flowsheet was recommended for testing in the 2-cm centrifugal contactors. This flowsheet consists of ten stages of extraction at an O/A of 1.0, two stages of 2 M HNO₃ scrub at an O/A of 4.0, four stages of 0.05 M HNO₃ 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 3.0 M HNO₃ rinse at an O/A of 2.0. The resulting flowsheet used for the SREX flowsheet testing with SBW simulant is shown in Figure 1.

The goals of the SREX flowsheet demonstration were to:

1. Demonstrate the overall operability of the 2-cm centrifugal contactors with the SREX flowsheet using actual tank waste.
2. Determine the removal efficiencies and distribution coefficients of ⁹⁰Sr, the actinides, and the non-radioactive components for the SREX flowsheet.
3. Evaluate the ability of the SREX flowsheet to decontaminate the tank waste to below the NRC Class A LLW requirement of 0.04 Ci/m³ for ⁹⁰Sr.
4. Evaluate the effectiveness of the SREX flowsheet in selectively stripping Pb and ⁹⁰Sr from the SREX solvent.
5. 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 WM-183 waste, were established. A solution of 1.7 M HNO₃, 0.6 M Al₂(NO₃)₃, and 0.6 M NaNO₃ was used as an initial waste feed solution. When aqueous solution was observed exiting each of the sections, solvent flow was initiated. Actual WM-183 feed was started when solvent was observed exiting the extraction section. Level readings on each of the feed tanks were noted in order to determine actual solution flowrates.
based on tank depletion rates. Approximately 150 minutes after the start of WM-183 feed, samples were taken of the aqueous raffinate, strip #1 product, strip #2 product, acidification effluent, and solvent effluent streams. 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 any of the 24 stages.

After shutdown, individual stage samples were taken as follows. The solution from each stage was drained into individual 60 mL sample bottles. The phases were re-equilibrated by shaking the bottles remotely for several minutes each. Re-equilibration of the phases serves to evaluate distribution coefficients of the individual species under conditions of chemical equilibrium (100% stage efficiency). The re-equilibrated solution from each stage was then poured into a clean separatory funnel, allowed to stand for five to ten minutes, and the aqueous and organic phases were separated.

IV. RESULTS AND DISCUSSION

A. Contactor Operation

Precipitate or third phase formation was not observed during testing or after shutdown. Flooding (the carryover of aqueous solution with organic or organic solution with aqueous) was not observed during testing.

B. Concentrations at Shutdown

The removal efficiencies obtained for $^{90}$Sr, $^{239,240}$Pu, $^{241}$Am, $^{137}$Cs, total alpha, Ba, B, Cd, Ca, Cr, Fe, Pb, Mn, Hg, Ni, Na, K, and Zr are given in Table II. Distribution coefficients were calculated for $^{90}$Sr, total alpha, Pb, Na, and K for several of the 24 stages. The resulting distribution coefficients are given in Table III. A discussion of the behavior of each component follows.

<table>
<thead>
<tr>
<th>Component</th>
<th>Removal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}$Sr</td>
<td>99.995%</td>
</tr>
<tr>
<td>Alpha</td>
<td>94%</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>1.9%</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>0.4%</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>99.94%</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>99.97%</td>
</tr>
<tr>
<td>Ba</td>
<td>64%</td>
</tr>
<tr>
<td>B</td>
<td>&lt;26%</td>
</tr>
<tr>
<td>Ca</td>
<td>2.3%</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.9%</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0%</td>
</tr>
<tr>
<td>Pb</td>
<td>&gt;97%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3%</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;6.7%</td>
</tr>
<tr>
<td>Na</td>
<td>0.5%</td>
</tr>
<tr>
<td>K</td>
<td>36.4%</td>
</tr>
<tr>
<td>Zr</td>
<td>&gt;82%</td>
</tr>
</tbody>
</table>

1) Strontium-90. The $^{90}$Sr activity was reduced from $7.38E+06$ dpm/ml in the feed to $320$ dpm/ml in the raffinate at steady state conditions. This corresponds to a removal efficiency of 99.995%. The resulting activity of $^{90}$Sr in the raffinate is $0.0089$ Ci/m³ which is below the NRC Class A LLW limit of $0.04$ Ci/m³.

Distribution coefficients in the extraction section ranged from 4.8 to 6.5, which is higher than results from previous testing ($D_S = 2$ to 3).4 The higher distribution coefficients for this testing are attributed to the higher nitrate concentration of the WM-183 simulant than the average SBW simulant used previously ($5.2$ M vs. $4.5$ M) and also to the higher purity solvent used for this testing.

The 0.05 M nitric acid strip section was very effective in back-extracting the $^{90}$Sr from the SREX solvent, resulting in 99.999% of the $^{90}$Sr being stripped from the SREX solvent.
with the four strip stages. As a result, 0.007% of the $^{90}$Sr in the feed exited with the strip #2 product (Pb strip).

Experimental distribution coefficients obtained for $^{90}$Sr were used in conjunction with the Generic TRUEX Model (GTM) in order to determine the operating efficiency of the contactors during testing. The best fit of the GTM data to the experimental data was obtained at an operating efficiency of 91% in the extraction section. The predicted aqueous phase $^{90}$Sr activities are compared to the experimental activities in Figure 2. Note that the $^{90}$Sr activity in the aqueous phase begins to deviate from the GTM predicted activities on stage 5 and does not continue to decrease on stages 1 through 3. This is believed to be due to the residual activity in the contactors from previous testing. Without the contamination in the contactors, the GTM predicts the $^{90}$Sr activity in the raffinate would have been approximately two orders of magnitude lower than were obtained with this testing (3 dpdml). The same contamination from residual activity is also apparent from the aqueous samples on stages 17 through 24. Activities of these samples also levels off, while the GTM predicts much lower activities.

2) Lead. Greater than 97% of the Pb was extracted by the SREX solvent. Pb concentrations were below analytical detection limits so the actual removal efficiency can not be calculated. However, the extraction distribution coefficients for Pb ranged from >1.5 to >22, indicating that the actual Pb removal efficiency was >99%. The extracted Pb was successfully stripped in the ammonium citrate strip section. Less than 6% of the Pb exited with $^{90}$Sr in the dilute nitric acid strip section. The actual amount of Pb exiting with the $^{90}$Sr in the strip #1 product could not be calculated due to analytical detection limits.

3) Actinides. The SREX solvent consists of 0.15 M 4',4'(5')-di-(tert-butyldicyclohexo)-18-crown-6 and 1.5 M tributyl phosphate in an Isopar-L diluent. The 1.5 M tributyl phosphate in an Isopar-L diluent is very similar to the PUREX solvent and, therefore, is expected to extract uranium and plutonium, but not americium, from the SBW. Removal efficiencies of 99.94% and 99.97% were obtained for $^{238}$Pu and $^{239}$Pu, respectively. However, only 2% of the $^{241}$Am was extracted from the SBW. As a result, the total alpha activity was reduced from 506 nCi/g in the SBW feed to 23 nCi/g in the raffinate, which corresponds to the activity of $^{241}$Am in the SBW feed (35 nCi/g). Therefore, the alpha activity can only be reduced with the SREX process to approximately 25 nCi/g, which is below the NRC Class B and C limit of 100 nCi/g for non-TRU waste but above the NRC Class A limit of 10 nCi/g.

The 0.05 M HNO$_3$ strip section was ineffective in back-extracting the actinides from the SREX solvent. However, the 0.1 M ammonium citrate strip section was very effective in back-extracting the actinides. Distribution coefficients for the actinides in the ammonium citrate strip section ranged from 0.02 to 0.03.

4) Other non-radioactive components. As expected K, Ba, and Zr were extracted by the SREX solvent. Pb concentrations were below analytical detection limits so the actual removal efficiency can not be calculated. However, the extraction distribution coefficients for Pb ranged from >1.5 to >22, indicating that the actual Pb removal efficiency was >99%. The extracted Pb was successfully stripped in the ammonium citrate strip section. Less than 6% of the Pb exited with $^{90}$Sr in the dilute nitric acid strip section. The actual amount of Pb exiting with the $^{90}$Sr in the strip #1 product could not be calculated due to analytical detection limits.
V. CONCLUSIONS

Lead and strontium were extracted and selectively stripped from the actual waste from tank WM-183. Removal efficiencies of 99.995% and >97% were obtained for \(^{90}\)Sr and Pb, respectively. With this removal efficiency for \(^{90}\)Sr, the activity of \(^{90}\)Sr was reduced to 0.0089 Ci/m\(^3\) which is below the NRC Class A LLW limit of 0.04 Ci/m\(^3\) for \(^{90}\)Sr. Experiments indicate that even further \(^{90}\)Sr decontamination would have been obtained if the centrifugal contactors used for testing did not contain residual contamination from previous actinide flowsheet development work.

The SREX flowsheet separated 94% of the total alpha activity from the WM-183 waste. This high removal efficiency is due to the nearly complete extraction of Pu (99.94%) by the TBP in the SREX solvent. However, only 1.9% of the \(^{241}\)Am was extracted. Since \(^{241}\)Am accounts for approximately 6% of the total alpha activity in the WM-183 waste, the alpha activity can only be reduced with the SREX process to approximately 25 nCi/g, which is below the U. S. NRC Class B and C limit of 100 nCi/g for non-TRU waste but above the U. S. NRC Class A limit of 10 nCi/g.

With the SREX flowsheet tested, 36.4% of the K, 64% of the Ba, and >82% of the Zr were extracted by the SREX solvent. The K, Ba, and Zr were effectively stripped in the ammonium citrate strip section. Only very small fractions of the Al, B, Ca, Cr, Fe, Mn, and Ni were extracted from the SBW.

Flooding, precipitate, and/or third phase formation were not observed during testing.

The operational efficiency of the centrifugal contactors was determined to be approximately 91% for the extraction section.

VI. ACKNOWLEDGMENT

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VII. REFERENCES


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