Cesium Removal from Surrogate Pyroprocessing Salt by Electrodeposition

Chemical and Fuel Cycle Technologies Division
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Cesium Removal from Surrogate Pyroprocessing Salt by Electrodeposition

prepared by
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Chemical and Fuel Cycle Technologies Division, Argonne National Laboratory

June 30, 2024
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ACKNOWLEDGEMENTS

This report was produced under the auspices of U.S. Department of Energy, Office of Nuclear Energy Nuclear Fuel Cycle and Supply Chain, Material Recovery and Waste Form Development Campaign. Issuance of this report meets milestone M3FT-24AN0301020111.
1. INTRODUCTION

Active metals in used nuclear fuel dissolve into the salt during pyroprocessing and are not removed by electrorefining or drawdown operations. The buildup of $^{137}$Cs over time increases the heat load and ionizing radiation level of the salt such that it must be replaced frequently, resulting in a significant amount of salt waste. An effective means of managing cesium in the molten salt electrolyte would increase the efficiency of pyroprocessing and decrease the volume of salt waste requiring disposal. A previous report summarized issues that must be addressed when developing a removal strategy and assessed the suitability of existing methods and remaining technological gaps to their application (Rose and Thomas 2023). Cesium is extremely stable in molten salt as a chloride—even more stable than the LiCl-KCl eutectic base salt used for pyroprocessing fuel—which makes removing cesium a challenge. However, sufficiently strong atomic interactions occur between active metal species and liquid metals that make the electrodeposition of active metal fission products into liquid metal electrodes energetically favorable. The feasibility of recovering cesium from LiCl-KCl pyroprocessing salt through electrodeposition into liquid metals is being assessed by identifying potentially effective liquid metals and performing tests to determine the effectiveness of electrodepositing cesium from a LiCl/KCl salt into these liquid metals.

Previous studies investigating the electrodeposition of Sr$^{2+}$, and Ba$^{2+}$ into zinc, cadmium, bismuth, lead, tin and antimony have shown that alkali and alkaline earth metals can be electrodeposited at liquid metal cathodes (Kim et al., 2018). The removal of Ba$^{2+}$ and Sr$^{2+}$ was measured to be more efficient than the removal of monovalent cations due to the greater thermochemical driving force for alloying those elements with the liquid metal (Jang et al. 2022). Because the equilibrium potentials are dependent on the interactions of the active metal in the liquid metal, it is likely that the other alkali metals Li$^+$, and K$^+$, will deposit from LiCl/KCl salt with the Cs$^+$. Therefore, application of this method to recover active metals from pyroprocessing salt will benefit from the use of a liquid metal and set of operating conditions that sufficiently increase the reduction potential of cesium to remove cesium from the waste salt with an acceptable amount of co-deposited lithium and potassium.
2. SELECTION OF LIQUID METALS AND TEST PARAMETERS

Tests with two liquid metals were used to assess the feasibility of removing cesium and other active metals from molten LiCl-KCl salt by electrodeposition. Like cesium chloride, alkaline earths chloride compounds are more stable than the LiCl-KCl eutectic base salt, as illustrated in Figure 1. Figure 1 shows the deposition potentials of pure alkali metals and alkaline earth metals and for those metals dissolved in bismuth at 5 or 10 mol %. Dissolution into bismuth changes the deposition potentials of strontium and barium more than it changes those of lithium and potassium, such that the deposition potentials of strontium and barium are more positive than those of lithium and potassium. This means strontium and barium can be deposited without co-depositing lithium and potassium. The deposition potential of cesium is expected to be more negative.

Barium and strontium have been deposited from ternary salts LiCl-KCl-BaCl₂ and LiCl-KCl-SrCl₂ into several liquid metals. Tables 1 and 2 show results from Nigl et al. (2020) for the percentage of current through a deposition cell associated with recovery of barium and strontium, respectively, as well as the co-deposition of lithium and potassium in each set of tests. Although not directly predictive of the deposition behavior of cesium, the deposition behavior of barium and strontium into liquid metals is informative regarding the affinity of the different liquid metals for deposition of alkali metals. Cesium is a monovalent cation while barium and strontium are divalent cations, and the electrodeposition of cesium from LiCl-KCl into the liquid metals must be demonstrated. The data from Nigl et al., 2020 were used to inform the selection of liquid metals that were used to assess the feasibility for application to other active metals.
Table 1. Percent of charge consumed by electrolysis products during deposition from LiCl-KCl-BaCl₂ electrolyte, from (Nigl et al., 2020)

<table>
<thead>
<tr>
<th>Metal or Alloy (mol %)</th>
<th>Deposition of Ba</th>
<th>Deposition of Li</th>
<th>Deposition of K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>74</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>Pb</td>
<td>53</td>
<td>39</td>
<td>8</td>
</tr>
<tr>
<td>Sn</td>
<td>45</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>Sb</td>
<td>63</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>50 Bi - 50 Sb</td>
<td>85</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>60 Bi – 40 Sb</td>
<td>85</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>70 Bi – 30 Sb</td>
<td>80</td>
<td>17</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2: Percent of charge consumed by electrolysis products during deposition from LiCl-KCl-SrCl₂ electrolyte, from (Nigl et al., 2020)

<table>
<thead>
<tr>
<th>Metal or Alloy (mol %)</th>
<th>Deposition of Sr</th>
<th>Deposition of Li</th>
<th>Deposition of K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>52</td>
<td>43</td>
<td>5</td>
</tr>
<tr>
<td>Pb</td>
<td>39</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>43</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>Sb</td>
<td>51</td>
<td>46</td>
<td>3</td>
</tr>
<tr>
<td>50 Bi - 50 Sb</td>
<td>45</td>
<td>49</td>
<td>6</td>
</tr>
<tr>
<td>60 Bi – 40 Sb</td>
<td>34</td>
<td>52</td>
<td>14</td>
</tr>
<tr>
<td>70 Bi – 30 Sb</td>
<td>22</td>
<td>59</td>
<td>19</td>
</tr>
</tbody>
</table>
As indicated in Table 1, the fraction of the current corresponding to the deposition of barium in Bi-Sb alloys was highest, at 80-85% of the current, while that for the co-deposition of lithium was only 13-17%. As indicated in Table 2, the fraction of the deposition current corresponding to deposition of strontium in pure bismuth was highest at 52% of the current. The use of bismuth also minimized co-deposition of lithium: only 43% of the charge consumed was for depositing lithium. Deposition of lithium in the other liquid metals ranged from 46% to 60% of the charge consumed.

Bismuth was the most efficient cathode material of those tested for deposition of Sr. The Bi-Sb alloys were most effective for Ba deposition, and the test with 50-50 mol % alloy had the highest amount of charge for Sr deposition with the least amount of charge for co-deposition of Li and K.

The two materials selected for assessing cesium deposition at 500 °C were pure bismuth and a 50-50 mol % alloy of Bi-Sb. Figure 2 shows the Bi-Sb phase diagram from Okamoto, 2012, locating the 50-50 mol % alloy, which is expected to be liquid at the test temperature of 500 °C. Alloys with higher antimony concentrations have melting points higher than 500 °C. Note that the bismuth and antimony are predicted to separate when cooled to below 150 °C.

Figure 2. Phase diagram for Bi-Sb alloy.
3. DEMONSTRATIONS OF Cs DEPOSITION INTO LIQUID METALS

3.1 Methods

Mixtures of LiCl (ACS Reagent, 99.9 %), KCl (ACS Reagent, 99.9 %), and CsCl (anhydrous, 99.9%) were used for each test and each reagent was baked out overnight at 300 °C to remove adsorbed water before use. Appropriate amounts of each salt were added to an alumina crucible to generate approximately 100 g of the LiCl-KCl eutectic with 10 wt % CsCl. Working electrodes consisted of either bismuth or equimolar amounts of bismuth and antimony contained in boron nitride crucibles. All tests were conducted at 500 °C. The liquid metals were melted in the boron nitride crucibles prior to the deposition tests. A 65 mol % lithium in bismuth alloy was used as the reference electrode, which was contained in a boron nitride crucible with a 1-mm hole in the side to provide salt contact. The open circuit potential of the reference electrode is known to be 0.716 V vs. Li+/Li0 (Gasior and Moser, 2001). Tungsten rods served as the electrical leads for the working and reference electrodes. A graphite rod attached to an 18-8 stainless steel rod served as the counter electrode for all tests.

A schematic of the electrochemical cell is shown in Figure 3. During lithium depletion tests, a lithium depletion electrode was placed around the working electrode containing the liquid metal, as depicted in Figure 3. This electrode also had a 1-mm diameter stainless steel electrical lead contacting the liquid metal. Working electrodes with and without the surrounding lithium depletion electrode are depicted in Figure 3, but only one working electrode was used in a test.

![Figure 3. Schematic of the electrochemical cell used to deposit cesium into liquid metals.](image)
Deposition parameter values were chosen based on the thermochemical properties of the liquid metals used to alloy with the constituent alkali metals. In Figure 4, the deposition potentials for pure lithium, potassium and cesium are compared to the equilibrium potentials for depositing those species into liquid bismuth at 5 mol % (open squares) and 10 mol % (filled squares) of each alkali metal. Note that electromotive force measurements of Rb⁺ in bismuth (Petric, 1988) are used to represent Cs⁺ in bismuth in Figure 4 due to a lack of availability of measurements for Cs⁺ in bismuth. Electrodeposition of Cs into liquid bismuth and the liquid Bi-Sb alloy was conducted during at a constant voltage of 0.65 V vs. Li⁺/Li⁰ in initial tests (indicated as Deposition Potential A) and at 0.1 V vs. Li⁺/Li⁰ in subsequent tests (indicated as Deposition Potential B).

![Figure 4](image)

**Figure 4.** Equilibrium potentials for active metals and for 5 and 10 mol % active metals in bismuth at 500 °C

The liquid metal electrodes were allowed to cool in the salt after deposition in the initial tests. Two methods were used to improve separation of cesium from the molten salt in subsequent tests. The first method was to use a lithium depletion electrode surrounding the liquid metal electrode. Lithium will alloy with this electrode material without generating pure lithium metal, thereby depleting lithium from salt near the liquid metal electrode to decrease the amount of lithium co-deposited into the liquid metal. Deposition tests were conducted with bismuth and Bi-Sb liquid metal electrodes surrounded by a lithium depletion electrode.

The second method was to immediately remove the liquid metal electrode from the salt at the conclusion of deposition. Deposited cesium metal will chemically reduce the base salt constituent lithium and potassium metal if left in contact with the melt for extended periods of time. Tests were conducted in which cesium was deposited into bismuth and 50:50 mol % Bi:Sb alloy with immediate removal of the electrode from the salt after deposition.
Characterization of the liquid metal electrodes after deposition testing was done by using scanning electron microscopy with associated energy-dispersive X-ray spectroscopy (SEM/EDS). The entire electrode was embedded in epoxy, sectioned vertically perpendicular to the salt metal interface and dry-polished to 1200 grit in an inert atmosphere glovebox prior to characterization. Figure 5 shows a schematic of a cross sectioned electrode in the boron nitride crucible as prepared for SEM analysis with a red box indicating a typical analysis region. Surface analyses were performed on materials generated in initial demonstration tests rather than bulk analysis of the salt or alloy because of the greater sensitivity of SEM/EDS and the capacity to measure local concentrations at the metal/salt interface.

3.2 Deposition Tests with Bi and Bi-Sb Alloy

Initial tests were performed to assess the feasibility of electrodepositing cesium into liquid bismuth or 50:50 Bi-Sb alloy cathodes. An electrode with 2.236 g bismuth was submerged into 100 g of eutectic LiCl-KCl containing 10 wt % CsCl. A constant voltage of 0.65 V vs. Li⁺/Li⁰ (Deposition Potential A in Figure 4) was applied to the cathode and 258 coulombs of charge were passed, equivalent to deposition of twice the initial cesium content in the salt. The cathode was left in the salt to cool after deposition. In a separate test, a 50:50 mol % Bi-Sb alloy a mixture of 1.357 g of bismuth and 0.783 g of antimony was submerged into a fresh mixture of 100 g of eutectic LiCl-KCl containing 10 wt. % CsCl and was subjected to a constant voltage of 0.65 V vs. Li⁺/Li⁰. A total of 247 coulombs of charge was passed, equivalent to 115 C/g electrode. The cathode was left in
the salt to cool after deposition. Figure 6 shows the currents measured at the imposed voltage during each deposition test over time. Currents were ~1.52 A in the test with the bismuth electrode and ~1.64 A in the test with the Bi-Sb alloy electrode. The stability of the currents over time indicates secondary phase nucleation did not occur at either electrode-electrolyte interface during deposition. The greater cathodic (more negative) current achieved in the test with the Bi-Sb electrode indicates the affinity for alkali metals to alloy is higher with antimony than with bismuth due to the more electronegative nature of antimony. The large currents achieved by both electrodes suggests significant total amounts of metal were deposited during the course of each test. Based upon the thermodynamic differences shown in Figure 4, significant co-deposition of lithium and potassium is expected to have occurred.

![Figure 6. Cell currents during initial electrodeposition tests at 0.65 V vs. Li+/Li0.](image)

3.3 **Deposition Tests with Lithium Depletion Electrode**

In the lithium depletion electrode electrodeposition test, a 50:50 mol % Bi-Sb alloy consisting of a mixture of 1.247 g bismuth and 0.726 g antimony was submerged into 100 g of eutectic LiCl-KCl containing 10 wt % CsCl. A constant voltage of 0.1 V vs. Li+/Li0 was applied to the lithium depletion electrode to deposit lithium and to the alloy electrode to deposit cesium. A total of 113 coulombs of charge was passed to the lithium depletion electrode first and then 225 coulombs of charge were passed to the Bi-Sb alloy (115 C/g). The cathode and depletion electrodes were both promptly removed from the salt after the test.
Figure 7 shows the currents measured during deposition to the lithium depletion electrode (top) and then during deposition to the Bi-Sb alloy (bottom). The cathodic current during the deposition into the lithium depletion electrode was initially smooth and as high as ~0.65 A, but quickly decreased to near -0.1 A with very noisy behavior in which the current oscillated between near 0 A and -0.15 A. This is attributed to saturation of the lithium depletion electrode and the slow diffusion of deposited lithium into the depletion electrode. During deposition to the Bi-Sb alloy, the current became steady at ~0.15 A and was lower than that measured for the depletion electrode due to the successful depletion of electroactive ions near the liquid metal electrode. After ~ 650 s, the current decreased to ~0.05 A indicating a phase transition occurred in the Bi-Sb, likely the nucleation of an additional phase. The current remained steady, indicating that the nucleated phase does not block the surface of the electrode and is likely not a floating solid.

Figure 7. Cell current during electrodeposition to the lithium depletion electrode (top) and to the Bi-Sb electrode (bottom).

The deposition of alkali metals into Bi-Sb in the test without the depletion electrode occurred with much greater current (approximately -1.64 A in Figure 6) than in the test with the depletion electrode (approximately -0.15 A in Figure 7). It is likely that the depletion electrode successfully decreased the lithium concentration in the salt local to the Bi-Sb electrode and the amount of lithium that was deposited in the Bi-Sb electrode. Depletion of lithium in the salt will concentrate both CsCl and KCl in the vicinity of the deposition. However, the difference between the equilibrium potentials of potassium and cesium is much smaller than that between lithium and cesium. Because the current was low (~0.15 A), the deposition was likely of some species present in low concentration in the salt. The concentration of cesium was approximately five-times lower.
than the concentration of potassium. Significantly less codeposition of potassium than lithium had been observed during deposition tests with barium and strontium (Nigl et al., 2020).

Deposition into a bismuth electrode surrounded by a depletion electrode was attempted but an electrical short occurred between the lead wires for the bismuth electrode and the depletion electrode that resulted in very low currents to the bismuth electrode. It is likely no deposition to the bismuth electrode occurred in that test, but deposition of lithium to the lithium depletion electrode did occur. This test is being repeated.

### 3.4 Deposition Tests with Bismuth and Bi-Sb Alloy with Rapid Removal

Back reaction (oxidation) of cesium with LiCl into CsCl and lithium metal is expected to have occurred when liquid metal electrodes with active metal deposits were allowed to cool in the salt after polarization was stopped. Therefore, additional tests were run in which the alloy electrode was quickly removed from the salt after deposition to minimize the effect of back reactions. These tests were performed in the salts remaining after the lithium depletion electrode tests with bismuth and the Bi-Sb electrodes had been completed. For deposition into bismuth, an electrode with 1.828 g of bismuth was submerged into the salt bath that had less than the original 100 g of eutectic LiCl-KCl containing 10 wt % CsCl. Constant voltage was applied to the cathode equivalent to 0.1 V vs. Li⁺/Li⁰. A total of 211 coulombs of charge were passed. The electrode was removed from the salt immediately after deposition to minimize the extent of back reaction.

For deposition into a 50:50 mol% Bi-Sb alloy, a mixture of 1.249 g of bismuth and 0.727 g antimony was submerged into the salt bath that had less than the original 100 g of eutectic LiCl-KCl containing 10 wt % CsCl after the failed test with the lithium depletion electrode. Constant voltage was applied to the cathode equivalent to 0.1 V vs. Li⁺/Li⁰ and 200 coulombs of charge were passed. The electrode was removed from the salt prior to cooling.

As seen in Figure 8, the deposition into bismuth generated a higher cathodic (more negative) current than deposition into the Bi-Sb alloy, at ~0.8 A. Because of the high current attained, the targeted amount of charge passed occurred within a much shorter test duration, and the test was stopped. The different durations are attributed to differences in salt compositions: salt in the test with the Bi-Sb alloy had been depleted of lithium, potassium and cesium by deposition on both the lithium depletion electrode and the liquid Bi-Sb alloy, whereas the salt in the test with bismuth was only depleted of lithium due to the electrical short. This indicates the current measured in the test with the Bi-Sb alloy was due primarily to deposition of cesium. That current is significantly lower than was measured in initial tests without lithium depletion (see Figure 6).
Figure 8. Cell current during electrodeposition at 0.1 V vs. Li$^+/\text{Li}^0$. 

$50-50\text{mol}\% \text{Bi-Sb}$
4. ANALYSIS OF ELECTRODEPOSITS

Alloy electrodes from each test were embedded in epoxy, then cross sectioned perpendicular to the salt-alloy interface and dry-polished in an argon atmosphere glovebox. The sectioned and polished electrodes were transported from the glovebox to the SEM inside a container under argon atmosphere. It is expected that these samples contained deposited lithium metal and were highly reactive to moisture in the air. The samples were briefly exposed to air during transfer from the container to the SEM chamber, which was quickly evacuated. Methods to mitigate air exposure are being evaluated. SEM/EDS analysis was performed on the samples to examine the distribution of active metals near the surface of the metal electrode in contact with the salt. Secondary electron imaging (SEI) was used to evaluate texture and back-scattered electron imaging (BSE) was used to highlight compositional differences: heavier elements generate higher contrast than lighter elements. Although EDS does not detect lithium, the contrast of phases in SEM-BSE images is sensitive to its presence. Compositional EDS analyses were performed as spot analyses, small area analyses, and to generate X-ray maps of the rastered image. Analyses of the solidified electrode surfaces are more sensitive to alkali metal deposition than analysis of the depleted salt.

4.1 Analyses of Electrodeposits from Deposition Tests with Bi and Bi-Sb alloy

Bismuth Electrode

Figure 9 shows an SEM-BSE photomicrograph of the cross-sectioned surface of the bismuth electrode used in the initial test and had remained in the salt after electrodeposition and solidification (discussed in Section 3.2). Although it is expected that a significant fraction of the deposited alkali metals had redissolved in salt during back reactions, this provides a baseline for

Figure 9. SEM-BSE photomicrograph of the bismuth electrode that was cooled in contact with the salt after electrodeposition.
materials generated in subsequent tests. The image includes regions of the bismuth electrode across the lower third of the image (light grey), salt on the right side of the image (dark grey), and regions of bismuth surrounded by a darker material (possibly salt) in the upper left of the image. It is possible that the darker contrast of the phases in the top two-thirds of the image are due to lithium being deposited in (alloyed with) the bismuth. Liquid bismuth that was suspended in the salt during the test would not have been polarized and deposition would not have occurred into that material. In either case, the image indicates a single static interface between molten bismuth and molten salt was not maintained as the electrode was cooled.

Figure 10 shows the same SEM-BSE photomicrograph from Figure 9 locating where EDS spot analyses were performed. These analyses show that there are regions near the surface of the bismuth electrode that contain detectable amounts of cesium and potassium.

Results of EDS analyses are given in Table 3. Locations 1, 2, and 3 are below the interface of the salt and bismuth electrode and cesium and potassium are not detected. Spot analyses at 5, 6, and 7 show a high concentrations of bismuth and spot 4 has a significant concentration of potassium. In the photomicrograph, materials at spots 4, 5, 6 and 7 all appear to have a different morphology than the electrode material at spots 1, 2, and 3. It is unclear if this morphology is of a salt-filled porous bismuth structure or indicates lithium deposited in the bismuth. Locations 8 and 9 have detectable amounts of cesium and potassium, but the concentrations are lower than expected based on the measured deposition currents. Cesium is expected to deposit at the surface of the electrode contacting the salt, and the current passed during the deposition test was sufficient to deposit twice the amount of cesium present in the salt. It is suspected that deposited cesium and potassium reacted with LiCl in the salt to reform CsCl and KCl and lithium metal while the
Table 3. Normalized concentration of elements (at. %) determined by EDS analysis at locations indicated in Figure 10

<table>
<thead>
<tr>
<th>Location</th>
<th>Potassium</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.1</td>
<td>99.9</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.0</td>
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</tr>
<tr>
<td>4</td>
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<td>83.0</td>
</tr>
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<td>100.0</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>0.1</td>
<td>97.9</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>0.5</td>
<td>99.5</td>
</tr>
</tbody>
</table>

electrode was immersed in the salt but not polarized. Those salt phases are more thermodynamically stable than the metallic deposits when the electrode is not polarized. This may explain the morphology at spots 4, 5, 6, and 7, as well as the lower-than-expected cesium content.

*Bi-Sb Electrode*

Figure 11 shows a BSE photomicrograph of the Bi-Sb electrode that was cooled in the salt after electrodeposition (discussed in Section 3.2). The photomicrograph contains several dark grey regions in the center of the image that were found to be rich in potassium and have detectable amounts of cesium. There is a light grey region at the bottom and left side of the image adjacent to the dark grey regions that is rich in bismuth. There is a medium grey region between the potassium-rich dark grey regions and along the right side of the image rich in antimony. These light and medium grey regions have an irregular morphology which may be an artifact of the
coarseness of the sample surface. It is unclear if the segregation of these phases occurred upon cooling the electrode or if the potassium rich region formed during deposition. The Bi-Sb phase diagram (see Figure 2) indicates de-alloying will at low temperatures, which could explain how the observed cesium and potassium-rich inclusion phases formed.

Figure 12 shows EDS X-ray maps for bismuth, potassium and antimony in regions in the SEM-SEI image in Figure 11. This mapping confirms that the dark gray regions in the center of the image are rich in potassium and do not contain significant bismuth or antimony. Notably the top portion of those dark grey regions does not contain potassium, bismuth or antimony; it is likely deposited lithium, which is not detectable using EDS. The EDS maps in Figure 12 also confirm that bismuth and antimony separated when the electrode was cooled to room temperature.

Figure 12. EDS X-ray maps of the region imaged in Figure 11, indicating the presence of Bi, Sb, and K.

Figure 13 shows the BSE image from Figure 11 with locations of EDS spot analyses performed to measure the compositions of the potassium-rich dark grey regions (locations 3, 4, 5 and 6) in the center of the image or in the surrounding bismuth-rich regions (locations 1, 8, and 10) and the antimony-rich regions (locations 2, 7 and 9). The measured elemental concentrations of potassium, antimony, cesium, and bismuth in each of these areas are shown in Table 4. Note the
reported results of EDS spot analyses are affected by the surface roughness of the analyzed regions, but indicate constituents that are present. Results are presented to the nearest 0.1 at % to facilitate comparisons, but are only qualitative.

![BSE-SEM photomicrograph of the Bi-Sb electrode which was allowed to cool in the salt after electrodeposition, with marked locations for EDS analysis.](image)

**Figure 13.** BSE-SEM photomicrograph of the Bi-Sb electrode which was allowed to cool in the salt after electrodeposition, with marked locations for EDS analysis.

**Table 4. Normalized concentrations of elements (at. %) determined by EDS analysis at locations indicated in Figure 13**

<table>
<thead>
<tr>
<th>Location</th>
<th>Potassium</th>
<th>Antimony</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>44.7</td>
<td>0.0</td>
<td>55.0</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>96.7</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>87.4</td>
<td>3.6</td>
<td>3.8</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>82.5</td>
<td>5.7</td>
<td>3.5</td>
<td>8.3</td>
</tr>
<tr>
<td>5</td>
<td>91.2</td>
<td>3.8</td>
<td>4.2</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>85.4</td>
<td>4.8</td>
<td>3.5</td>
<td>6.3</td>
</tr>
<tr>
<td>7</td>
<td>0.3</td>
<td>96.6</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>78.8</td>
<td>0.0</td>
<td>20.4</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>64.0</td>
<td>0.0</td>
<td>35.0</td>
</tr>
<tr>
<td>10</td>
<td>1.1</td>
<td>7.0</td>
<td>0.0</td>
<td>91.8</td>
</tr>
</tbody>
</table>

The measured concentrations given in Table 4 indicate trace amounts of cesium are present in the potassium-rich dark grey regions seen in the center of the image shown in Figures 11 and 13, but not in Bi-rich or Sb-rich domains. Segregation of electrodeposited species into distinct regions (K and Cs) could occur during electrodeposition or coalesce upon cooling. The high potassium concentration relative to cesium (compared to the ~5:1 ratio in the salt) could indicate preferential deposition of potassium, or that back reaction of cesium occurred preferentially.
4.2 Analysis of Electrodeposits from Deposition Tests with Lithium Depletion Electrode

Figure 14 is a BSE photomicrograph showing the top edge of the Bi-Sb alloy recovered from the test with the depletion electrode (see Section 3.3). The field of view includes several distinct regions. There are regions of salt at the top and down both sides of the image, and a bright Bi-Sb alloy region in the bottom center. There are distinct grey streaks of an antimony-rich phase throughout the Bi-Sb alloy and a prominent cap of an antimony-rich phase sitting atop the Bi-Sb alloy. The antimony-rich cap has two distinct regions: the medium grey colored phase contains trace amounts of cesium and the darker grey phase does not contain cesium.

![Image of Bi-Sb alloy](image)

Figure 14. BSE-SEM photomicrograph of the Bi-Sb electrode from the lithium depletion electrode test, which was removed from the salt after electrodeposition of cesium to mitigate back reactions.

Figure 15 shows EDS X-ray maps of the region in the micrograph in Figure 14 for bismuth, antimony, cesium, potassium, chlorine and oxygen. The antimony-rich cap is clearly seen in the antimony map and is devoid of potassium, bismuth and chlorine. There are trace amounts of cesium appearing in the top portion of that antimony rich cap. The oxygen detected in the outer layer of the cap in Figure 15 is likely Li$_2$O formed by reaction of deposited lithium metal and moisture from exposure to air during transfer of the specimen from the container into the SEM.

Figure 16 shows the BSE-SEM image of the Bi-Sb alloy electrode from Figure 14, with locations of EDS spot analyses indicated as well as a white box indicating the region where a magnified image was taken (shown in Figure 17).

Figure 15. EDS X-ray maps of Bi, Sb, Cs, K, Cl and O in the region imaged in Figure 14.

Figure 16. BSE-SEM photomicrograph of the Bi-Sb alloy electrode from the lithium depletion test, which was removed from the salt after electrodeposition to mitigate back reactions, with marked locations for EDS analysis.
The measured elemental concentrations of oxygen, chlorine, potassium, antimony, cesium, and bismuth in each of these identified spots are shown in Table 5. Spot 1 is located in the salt and contains cesium and chlorine, indicating the material is salt. Spots 2 and 3 are within the two different regions of the antimony-rich cap. Spot 2 is in the lighter colored region showing measurable cesium concentration and oxygen content (indicative of Li₂O). Spot 3 is the darker grey region in the cap and shows no cesium content in that phase, but a similar oxygen content. The composition of spot 4 is similar to that of spot 3 indicating it is also an antimony-rich phase with possible lithium deposition. Spots 5 and 6 are located deeper into the bulk of the Bi-Sb electrode and contain no detectable cesium and only trace amounts of chlorine, potassium and oxygen.

Table 5. Normalized concentration of elements (at %) in the Bi-Sb alloy electrode after the lithium depletion test, determined by EDS analysis at locations indicated in Figure 16

<table>
<thead>
<tr>
<th>Location</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Potassium</th>
<th>Antimony</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.5</td>
<td>32.6</td>
<td>21.6</td>
<td>0.3</td>
<td>7.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>15.7</td>
<td>2.8</td>
<td>0.6</td>
<td>79.1</td>
<td>1.8</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>17.8</td>
<td>2.4</td>
<td>2.6</td>
<td>77.0</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>17.9</td>
<td>0.9</td>
<td>0.1</td>
<td>80.6</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>1.5</td>
<td>0.0</td>
<td>72.6</td>
<td>0.0</td>
<td>22.8</td>
</tr>
<tr>
<td>6</td>
<td>6.8</td>
<td>4.9</td>
<td>0.0</td>
<td>11.6</td>
<td>0.0</td>
<td>76.7</td>
</tr>
</tbody>
</table>

Figure 17 is a higher magnification photomicrograph from the region in the white box in Figure 16, including the left side of the antimony-rich cap and an adjacent cesium-rich salt phase. The two phases are more clearly distinguished here as two distinct shades of grey: the darker grey in the center of the cap and the lighter grey layer surrounding it. A difference in morphology of the salt can also be seen between the more crystalline regions of salt above and below the cap and the cesium-rich salt region to the left of the cap, which appears to be more amorphous.

Figure 18 shows EDS X-ray maps of the region in the micrograph in Figure 17 for the elements: bismuth, antimony, cesium, potassium, chlorine and oxygen. As in the maps in Figure 14, the cap is largely antimony with cesium and oxygen being found in the lighter grey outer portion of the cap. No potassium or chlorine are found within the cap. The presence of cesium and oxygen (indicative of lithium) in the lighter grey outer region of the cap indicates that deposition of these active metals is preferred into antimony rich phases rather than bismuth rich phases. The preference for deposition into antimony rather than bismuth was noted by Nigl et al. (2020) for strontium and barium.
Figure 17. High magnification image of Antimony-Rich Region in Micrograph in Figure 16 (marked with white box).

Figure 18. EDS X-ray maps of Bi, Sb, Cs, K, Cl and O in the region imaged in Figure 17.
Figure 19. BSE-SEM photomicrograph of the region imaged in Figure 17 with marked locations for EDS analysis.

Figure 19 is the same photomicrograph shown in Figure 17 with marked locations for EDS spot analyses. The concentrations of oxygen, chlorine, potassium, antimony, cesium, and bismuth measured in each of these areas are shown in Table 6. Spots 1 and 2 from the amorphous salt region adjacent to the left side of the antimony rich cap are confirmed to be salt by the high concentrations of chlorine, potassium, and cesium that are detected. Spots 3 and 5 in the lighter grey outer layer of the cap are primarily antimony with measurable cesium and oxygen contents, consistent with the EDS maps in Figure 18. Spot 4 in the darker grey inner region of the antimony-rich cap does not contain cesium or bismuth, but has a significant oxygen content, possibly indicating lithium is present in this area.

Table 6. Normalized concentrations of elements (at %) in the Bi-Sb alloy electrode after the lithium depletion test, determined by EDS analysis at locations indicated in Figure 19

<table>
<thead>
<tr>
<th>Location</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Potassium</th>
<th>Antimony</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.6</td>
<td>35.2</td>
<td>1.4</td>
<td>0.3</td>
<td>15.4</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>19.1</td>
<td>43.6</td>
<td>36.0</td>
<td>0.0</td>
<td>1.4</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>17.0</td>
<td>5.5</td>
<td>0.7</td>
<td>75.9</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>20.3</td>
<td>2.6</td>
<td>0.2</td>
<td>76.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>17.0</td>
<td>5.1</td>
<td>0.2</td>
<td>76.8</td>
<td>0.9</td>
<td>0.0</td>
</tr>
</tbody>
</table>
4.3 Analyses of Electrodeposits from Deposition Tests with Bi and Bi-Sb Alloy with Rapid Removal

*Bismuth Electrode*

A BSE photomicrograph of the cross-sectioned interface of the salt and bismuth electrode that was removed from the salt prior to cooling after electrodeposition (See Section 3.4) is shown in Figure 20. The image contains distinct regions that are indicated in the figure: the top surface of the bismuth electrode in the center of the image, salt phases (dark grey) from entrained electrolyte on the right side of the image, and the electrode (light colored) on the left side of the image. There are also several inclusion phases in the center of the image.

![Figure 20](image)

Figure 20. BSE-SEM photomicrograph of the top edge of the Bi electrode that was removed from the salt after electrodeposition of Cs to mitigate back reactions.

Figure 21 is a magnified view of the center of the micrograph from Figure 20 showing the bismuth salt interface, with regions of interest indicated. There is a dense layer of salt material at the interface with amorphous morphology, while the salt far from the surface (upper right corner) is crystalline. It is unclear if the morphology of salt adjacent to the electrode is a result of lithium depletion or induced by concentration gradients generated during deposition or cooling.

Figure 22 shows EDS X-ray maps of the region shown in Figure 20 that indicate the distributions of Bi, Cs, K, Cl and O. This mapping confirms that the dark gray regions indicated to be cesium inclusions in Figures 20 and 21 also contain a minor amount of potassium. The lack of chlorine in these regions indicates that cesium and potassium are likely present in the metallic form and were electrodeposited into the bismuth.
The salt local to the electrode was depleted in lithium relative to eutectic LiCl-KCl by using the lithium depletion electrode. Although EDS is not sensitive to lithium, it is reasonable to assume that deposited lithium was present in deposition electrode because the deposition potential used in the test was more cathodic than the lithium deposition potential. The oxygen distribution indicated in Figure 22 is coincident with bismuth and likely results from reaction between deposited lithium and moisture introduced during the brief air exposure when the specimen was transferred from the container into the SEM chamber. The deposition tests were performed under inert atmosphere in the absence of oxide compounds. Reaction between lithium metal and the
moisture in the air would proceed rapidly. The widespread oxygen detected across the bismuth electrode and not in the salt (upper right side of image) is indicative of lithium deposition into the bulk of the bismuth electrode. The low concentration of bismuth, and lack of chlorine or potassium in the far bottom left corner of the images in Figure 22 and the high concentration of oxygen in that same location also indicate that metallic lithium is likely present in the interior of the bismuth electrode.

Figure 23 shows overlaid bismuth and cesium EDS maps of the region in Figure 20 to more clearly show that the inclusions in the bismuth electrode are separate phases enriched with cesium.

![Figure 23. SEM-BES Micrograph of the region in Figure 20 and overlaid EDS X-ray maps for Bi and Cs.](image)

Figure 24 shows the same BSE micrograph shown in Figure 20 locating where EDS spot analyses were performed to quantify relative concentrations of cesium, bismuth, potassium and chlorine in different areas of the image. Shown in Table 7, analyses at points 2, 3, and 4 indicate that the cesium inclusions contain significant concentrations of cesium and potassium. The low concentrations of chlorine in these spots suggest these inclusions are deposited metal, and not salt. Additionally, the concentrations of bismuth in these spots are low or not detectable. Spot 1 has significant cesium concentration but also chlorine and oxygen, indicating this spot right at the salt-metal interface may be a mixture of salt and deposited metal (lithium).

Analysis at Location 5 shows high chlorine and potassium contents, which suggests this may be an inclusion of the test electrolyte. EDS analysis of the bismuth matrix close to the cesium-rich deposit, Location 6, indicates there is no detectable cesium content. The high concentration of oxygen in Location 6 may indicate of the presence of lithium alloyed with bismuth.
Figure 24. BSE-SEM photomicrograph of the bismuth electrode that was removed from the salt after electrodeposition to mitigate back reactions, with marked locations for EDS analysis.

Table 7. Normalized concentration of elements (at. %) determined by EDS analysis at locations indicated in Figure 24

<table>
<thead>
<tr>
<th>Location</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Potassium</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.7</td>
<td>10.3</td>
<td>4.0</td>
<td>11.1</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>73.6</td>
<td>1.5</td>
<td>6.9</td>
<td>18.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>75.6</td>
<td>0.9</td>
<td>11.6</td>
<td>11.9</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>78.0</td>
<td>1.3</td>
<td>10.7</td>
<td>9.3</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>48.0</td>
<td>27.6</td>
<td>22.8</td>
<td>1.6</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>80.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>19.3</td>
</tr>
</tbody>
</table>

**Bi-Sb Electrode**

Figure 25 shows a BSE micrograph of the cross-sectioned Bi-Sb electrode in which electrodeposition in LiCl-KCl with 10 wt % CsCl was performed, and the electrode removed from the salt prior to cooling. This image was taken from a region close to the surface of the electrode and shows the Bi-Sb alloy (light gray), boron nitride crucible material (dark gray, lower right corner), and a region indicated as cesium rich (middle gray, lower left corner) confirmed by EDS shown in later figures. As observed before with the bismuth electrode, a distinct region of cesium is observed embedded in the microstructure.
Figure 25. BSE-SEM photomicrograph of the Bi-Sb electrode that was removed from the salt after electrodeposition of cesium to mitigate back reactions.

Elemental X-ray maps of the region shown in Figure 25 are shown in Figure 26. These maps confirm the presence of a cesium rich region in the alloy. As before, the cesium rich region appears to be co-located with potassium, but not with Cl, Bi, or Sb. The absence of chlorine suggests this is a metallic phase and not salt. The maps show the distributions of bismuth and antimony in the matrix. They do not appear to coexist as an alloy, but rather as a separated mixture. Based on the phase diagram in Figure 2, separation upon cooling is expected.

Figure 26. EDS X-ray maps of the region imaged in Figure 25, indicating the presence of Bi, Sb, Cs, K, and Cl.
Figure 27 shows the BSE image from Figure 25 locating where EDS spot analyses were performed. The results are shown in Table 8. Locations 1 and 2 contain significant quantities of cesium, potassium, and oxygen, but very little or no detectable Cl, Bi, and Sb. This is consistent with what is seen in the EDS X-ray maps in Figure 26. The high oxygen content may also indicate that lithium metal is also deposited here with the cesium and potassium metal. As was the case in tests with the Bi electrode, the applied potential is more cathodic than the deposition potential for lithium and it is expected that the electrode contains a significant amount of deposited lithium. As with other specimens, it appears that the active metal is either deposited as a distinct phase or separates from the bismuth and antimony upon cooling. Spot analyses in the bulk of the Bi-Sb material (Locations 3, 4) show that while the relative concentrations of bismuth and antimony differ, there is no detectable cesium in these regions. It is notable that

![Figure 27. BSE-SEM photomicrograph of the Bi-Sb alloy electrode that was removed from the salt after electrodeposition to mitigate back reactions, with marked locations of EDS analysis.](image)

<table>
<thead>
<tr>
<th>Location</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Potassium</th>
<th>Antimony</th>
<th>Cesium</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.5</td>
<td>0.5</td>
<td>9.2</td>
<td>0.0</td>
<td>15.8</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>77.1</td>
<td>0.5</td>
<td>8.5</td>
<td>0.0</td>
<td>14.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>36.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>58.4</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
<td>0.0</td>
<td>0.0</td>
<td>80.2</td>
<td>0.0</td>
<td>14.3</td>
</tr>
<tr>
<td>5</td>
<td>62.4</td>
<td>7.0</td>
<td>7.8</td>
<td>0.0</td>
<td>22.8</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>74.3</td>
<td>1.3</td>
<td>3.5</td>
<td>11.8</td>
<td>9.1</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>68.0</td>
<td>2.5</td>
<td>0.0</td>
<td>29.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
there is very little oxygen content in the high antimony region in spot 4. Spot analyses of the other cesium rich regions present in the Bi-Sb matrix (Locations 5, 6) indicate the presence of cesium and potassium. Location 5 contains significant chlorine indicating the area is at least in some part salt. Location 6 indicates some antimony, but this may be due to signal overlap caused by the interaction volume of the electron beam. The analysis of another phase present in the microstructure (Location 7) shows this is rich in antimony and oxygen. The presence of this distinct phase with low contrast by backscatter, and no detected Bi, K, or Cs, may suggest this is a Li-Sb phase. This cannot be confirmed however due to the insensitivity of the EDS technique to lithium. As noted previously, the high oxygen content in the analyzed locations is likely due to generation of Li₂O during the brief exposure to air during transfer into the SEM chamber.
5. CONCLUSIONS AND RECOMMENDATIONS

The removal of cesium from a LiCl-KCl salt mixture by electrochemical deposition into a liquid metal was demonstrated to occur and process conditions necessary for the effective removal of cesium (and other active metals) from a surrogate pyroprocessing salt by electrodeposition in liquid metals were determined. The back reaction between deposited cesium and LiCl/ KCl is thermodynamically favorable and was suspected to be the cause of the low cesium concentrations detected in initial tests relative to that expected based on the measured deposition currents. Electrodes used in subsequent tests were promptly removed from the salt after deposition rather than cooling in the salt to mitigate the effects of back reaction. Further, the local depletion of lithium near the liquid metal electrode done prior to and during drawdown increased the amount of cesium deposited into the liquid metal electrodes. Applying techniques to attenuate the deposition of lithium and potassium into the liquid metal electrodes and back reaction of active metal deposits will further enhance the effectiveness of drawdown operations to remove cesium.

The distributions of cesium and co-deposited lithium and potassium in the metal cathodes were measured by using SEM/EDS to provide qualitative insights into the deposition behavior. Cesium deposited in bismuth electrodes appears to form locally concentrated inclusions in the bismuth. It is inferred from the oxygen content in electrodes that deposited lithium is distributed fairly uniformly throughout the bulk of the bismuth electrode. The mechanisms that lead to the observed segregation of localized concentrated cesium and the inferred uniform lithium distributions across the liquid bismuth cathodes should be elucidated in further testing. Cesium was observed to deposit preferentially into antimony-rich phases of the Bi-Sb alloy electrode. The preferential deposition of cesium into the antimony suggests deposition into pure antimony at 650 °C may be effective. These tests were conducted at 500 °C to match electrorefining operations, but the method could be applied separately. The new insights gained in these tests indicate that the electrodeposition of cesium into liquid metals as a means of removing cesium from pyroprocessing salt is technically feasible and warrant further investigation.

The goal of collecting cesium in the liquid metal phase is to provide a salt with a composition suitable for reuse in pyroprocessing operations by reducing the heat load and radiotoxicity of the salt caused by the accumulation of active metal fission products, such as cesium. Follow-on tests to quantify the decrease cesium concentrations in waste salt that can be achieved by extensive electrodeposition of cesium into liquid metals are in progress. The decreased cesium content of the salt and separation factor that can be achieved by applying this method will be measured under optimal processing conditions and performing pre- and post-test analyses of the bulk salt and electrode.
REFERENCES


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Lemont, IL 60439

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