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BEHAVIOR OF ACTINIDE IONS DURING SLUDGE WASHING
OF ALKALINE RADIOACTIVE WASTES

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ABSTRACT

It is difficult to accurately predict actinide behavior during the alkaline leaching of Hanford’s radioactive sludges due to the diverse chemical and radiolytic conditions existing in these wastes. The results of Pu dissolution during experimental washing of sludge simulants from the BiPO₄, Redox, and PUREX processes shows that ≤ 2.1% Pu is dissolved during contact with alkaline media, but up to 65.5% Pu may be dissolved in acidic media. The dissolution of Cr, Fe, Nd, and Mn has also been observed, and the results of solid state, radioanalytical, and spectroscopic investigations are detailed.

INTRODUCTION

Various processes were used at Hanford for the large-scale purification of Pu for defense uses. When production of ²³⁹Pu commenced at Hanford in 1944, Pu(IV) was coprecipitated with BiPO₄ while U(VI) remained in solution as a SO₄²⁻ complex. After solid-liquid separation, the Pu(IV) in the BiPO₄ precipitate was oxidized to soluble Pu(VI) by BiO₃³⁻, MnO₄⁻, or Cr₂O₇²⁻ prior to further purifications that included LaF₃ coprecipitation [1]. This solid-liquid-based separation was replaced eight years later by the Redox process in which Pu(VI) and U(VI) were partitioned into methyl isobutyl ketone from concentrated aqueous Al(NO₃)₃. Separation of Pu(VI) from U(VI) was accomplished by addition of Fe(II), causing reduction to Pu(III) that reports to the aqueous phase [2]. After only a few years in operation, the Redox process was replaced by PUREX solvent extraction in which U(VI) and Pu(IV) are extracted from 3-4 M HNO₃ into 30% (v/v) tri-n-butyl phosphate in an aliphatic hydrocarbon diluent. Recovery of Pu again involves reduction to the trivalent state, principally by U(IV) or Fe(II) [2].

An understanding of the processing history and chemistry unique to each Pu purification process is now important because wastes from these activities must be remediated. Acidic production waste effluents were adjusted to above pH 9 with NaOH prior to tank storage. The results of such a drastic pH change are the formation of hydrolytic polymers and large quantities of NaNO₃ that have now stratified into sludge, supernatant, and saltcake layers. Vitrification is the preferred radioactive waste immobilization strategy, but the borosilicate glass formulations are sensitive to the presence of the P, Al, and Cr that reside in the sludge materials. Hanford’s alkaline radioactive waste remediation strategy proposes a high temperature leach of the residual sludge materials with 3 M NaOH [3] to remove the P, Al, and Cr. Based on the available experimental data, it has been assumed that actinide ions will remain in the sludge during leaching procedures. Unfortunately, this assumption does not account for the diverse redox and solution chemistry of the actinides that is readily perturbed by hydrolysis, complexation, solubility, disproportionation, or redox reactions involving matrix ions [4]. Because sludge washing operations will encounter a heterogeneous mixture of solids whose thermodynamic and kinetic behavior with respect to actinide and matrix ion dissolution is only poorly understood, the
present work investigates how the mobilization of Pu is influenced by the concurrent dissolution of Cr, Mn, and Fe from BiPO₄ (Cycle 3), Redox, and PUREX sludge simulants.

EXPERIMENTAL

Details of the synthesis, sludge washing, and spectroscopic analyses appear elsewhere [5]. Modifications to the published [6] synthesis of the BiPO₄ (Cycle 3) sludge simulant were made: 100% La was substituted with 33.3% each of La, Nd, and Eu. Al, Ti, and Fe are present in actual sludge samples and were added to the simulant referred to as BiPO₄ (Modified). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on BiPO₄, BiPO₄ (Modified), and PUREX simulant sludges that had been dried at 120 °C. All SEM examinations were performed on a JEOL 6400 instrument. EDS data collection employed a Noran detector with data reduction by the Vantage software package. Consecutive sludge washing experiments generally involved sorption of $^{238}$Pu(III/IV) or $^{238}$Pu(VI) from a pH = 9.5(5) solution onto the desired sludge simulant followed by contact with a 0.10 M Na₂CO₃ + 0.50 M NaOH + 1.0 M NaNO₃ tank waste supernatant simulant. The remaining sludge washing operations involved consecutive contact of each $^{238}$Pu-containing sludge simulant with 0.01 M NaOH + 0.01 M NaNO₂, 3.0 M NaOH, H₂O, 0.05 M glycolic acid + 0.10 M NaOH, 0.10 M HNO₃, 2.0 M HNO₃, and 0.50 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). All Pu percentages are relative to the activity of Pu initially added to the sludge simulant slurry.

RESULTS

One thousand-fold magnification (Figure 1) of the BiPO₄ (Modified) simulant reveals the apparent formation of μm-sized crystallites with well defined edges, whereas the PUREX surfaces appear less ordered. A variety of P-based (e.g., BiPO₄, FePO₄, AlPO₄, La₄(P₂O₇)₃, etc.) and Cr-based (e.g., Cr(O)OH, Bi₁₃CrO₆₀, Fe(Cr/Fe)₂O₄, etc.) crystalline phases have been identified in Hanford sludge samples [3, 7].

Despite the sampling limitations of EDS, the principal components in the BiPO₄ and PUREX sludge simulants are readily identified (Figure 1). The compositions of the actual BiPO₄, Redox, and PUREX sludge materials and the simulants prepared here are reported in Table I. In general the analyses compare favorably, except that all three simulants analyzed by EDS contain > 3-4 times the Mn found in the actual wastes.

Figure 2 shows negligible dissolution of Pu by the tank waste supernatant simulant or by 0.01 M NaOH + 0.01 M NaNO₂ (the sluice liquid in Hanford sludge pretreatment). Dissolution of Pu(III/IV) (1.4%) and Pu(VI) (2.1%) from the PUREX simulant by 3.0 M NaOH is low but potentially significant. Plutonium is not effectively removed from the sludge simulants by H₂O or 0.05 M glycolic acid + 0.10 M NaOH. Contact of the Redox sludge simulant with 0.10 M HNO₃ showed release of 19.5% Pu(III/IV) and 31.6% Pu(VI) in unfiltered samples [5], underscoring the importance of transport by suspended solids. Sludge washing with 2.0 M HNO₃ effected the greatest dissolution of Pu(III/IV) and Pu(VI) from all four sludge simulants. The BiPO₄ (Modified) simulant releases the most Pu activity: Pu(III/IV) = 65.5% and Pu(VI) = 19.7%. The remaining three simulants all release ≤ 9.9% Pu. Sludge washing of BiPO₄ and BiPO₄ (Modified) simulants by the strong chelating agent HEDPA (derivatives of which have been proposed as final radioactive waste forms [8]) causes dissolution of ≈ 3.4 times more Pu(VI) than Pu(III/IV).

Chromium removal from the solids targeted for vitrification is a primary objective of sludge pretreatment at Hanford [3]. Contact of the BiPO₄, BiPO₄ (Modified), and Redox simulants
Figure 1: SEM and EDS analyses of BiPO₄ (Modified) and PUREX sludge simulants dried at 120 °C.

Figure 2: % Pu dissolved in wash solutions after contact with the BiPO₄, BiPO₄ (Modified), Redox, and PUREX sludge simulants at 23(2) °C. Solution concentrations are reported in the Experimental section.
TABLE I
Analyses of Bulk Constituents in Radioactive Waste Sludges and Simulant Sludge Materials

<table>
<thead>
<tr>
<th>Component</th>
<th>BiPO₄ Waste Analysis %</th>
<th>BiPO₄ Simulant Analysis %</th>
<th>BiPO₄ (Modified) Simulant Analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al + Fe</td>
<td>1.4</td>
<td>0.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Bi</td>
<td>23.6</td>
<td>5.5</td>
<td>22.2</td>
</tr>
<tr>
<td>Cr</td>
<td>5.3</td>
<td>7.6</td>
<td>6.7</td>
</tr>
<tr>
<td>La</td>
<td>10.5</td>
<td>16.9 (La + Nd + Eu)</td>
<td>7.5 (La + Nd + Eu)</td>
</tr>
<tr>
<td>Mn</td>
<td>7.2</td>
<td>33.1</td>
<td>24.3</td>
</tr>
<tr>
<td>Na</td>
<td>11.8</td>
<td>1.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Ti</td>
<td>1.7</td>
<td>0.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Anions</td>
<td>12.0</td>
<td>13.8 (P)</td>
<td>8.9 (P)</td>
</tr>
<tr>
<td>Volatiles</td>
<td>14.3</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>O₂</td>
<td>12.2</td>
<td>21.5</td>
<td>20.6</td>
</tr>
</tbody>
</table>

**Redox**

<table>
<thead>
<tr>
<th>Component</th>
<th>Waste Analysis %</th>
<th>Component</th>
<th>Waste Analysis %</th>
<th>Simulant Analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>25.4</td>
<td>Al</td>
<td>7.4</td>
<td>NM</td>
</tr>
<tr>
<td>Ca</td>
<td>1.5</td>
<td>Ca</td>
<td>1.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Cr</td>
<td>3.8</td>
<td>Fe</td>
<td>23.6</td>
<td>29.9</td>
</tr>
<tr>
<td>Fe</td>
<td>5.1</td>
<td>K</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>1.1</td>
<td>Mn</td>
<td>2.2</td>
<td>11.6</td>
</tr>
<tr>
<td>Na</td>
<td>15.8</td>
<td>Na</td>
<td>12.2</td>
<td>28.2</td>
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<tr>
<td>Si + Ti</td>
<td>6.2</td>
<td>Si + Ti + Zr</td>
<td>4.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Anions</td>
<td>0.5</td>
<td>Anions</td>
<td>1.7</td>
<td>NM</td>
</tr>
<tr>
<td>Volatiles</td>
<td>21.0</td>
<td>Volatiles</td>
<td>25.3</td>
<td>NM</td>
</tr>
<tr>
<td>O₂</td>
<td>19.6</td>
<td>O₂</td>
<td>21.1</td>
<td>28.8</td>
</tr>
</tbody>
</table>

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*a*Modifications to the BiPO₄ sludge syntheses are described in the Experimental section.
bValues are in % (w/w) for sludges dried to 120 °C. "Volatiles" represents organics and water lost by firing to 750 °C. O₂ calculated by difference [9]. cElemental analyses by EDS. dNM = not measured. eSEM and EDS on the Redox simulant could not be performed due to restrictions on the analysis of radioactive (U) samples in the instrument.

with 3.0 M NaOH afford visible absorption spectra that closely match the 2 x 10⁻⁴ M Na₂CrO₄ standard spectrum (Figure 3). The comparatively low absorbance for the BiPO₄ simulant may be an artifact of Cr removal by the preceding wash [5]. The BiPO₄ (Modified) and Redox wash solutions may be calculated (ɛ from [10]) to yield CrO₄²⁻ concentrations of 1.3 x 10⁻⁴ and 9.5 x 10⁻⁵ M, respectively, in 3.0 M NaOH. These values are in agreement with the decreasing Cr contents of the sludge simulants (Table I).

Absorptances for the 2.0 M HNO₃ Redox and PUREX wash solutions are negligible because Fe is almost quantitatively removed from these simulants by the preceding 0.10 M HNO₃ wash. However, dissolution of Fe(III) from the BiPO₄ and BiPO₄ (Modified) simulants yield spectra that resemble the 0.4 M Fe(NO₃)₃ standard spectrum, including similar λ_max peak shapes, and shoulders between 400-450 nm. An examination of the = 700-900 nm wavelength region (inset) in the 2.0 M HNO₃ wash solutions after contact with the BiPO₄ simulants shows very weak
Figure 3: Absorption spectra of 3.0 M NaOH, 2.0 M HNO₃, and 0.50 M HEDPA wash solutions after contact with the respective sludge simulants.

bands that are characteristic for Nd(III). The Nd(III) concentration, and by inference that of La and Eu, is \(3.5 \times 10^{-3}\) M [11].

Contact of the BiPO₄, BiPO₄ (Modified), and PUREX sludge simulants with 0.50 M HEDPA generates wash solutions purple in color. The visible spectra of these solutions show almost featureless broad bands centered around 513 nm. There is no absorption in this region in the wash solution from the Redox sludge, as it contains the least Mn (Table I). Contact of pristine MnO₂ with 0.50 M HEDPA affords a spectrum (inset) similar to those from the BiPO₄, BiPO₄ (Modified), and PUREX sludge simulants. Examination of standard spectral data [12] for aqueous Mn(III) shows \(\lambda_{\text{max}}\) values of \(\approx 500-550\) nm with an intense high energy band below 400 nm. Based on these and other observations [5], it can be surmised that a Mn(III)/HEDPA complex is responsible for the broad bands observed in the 0.50 M HEDPA wash solutions from the BiPO₄, BiPO₄ (Modified), and PUREX sludge simulants.
CONCLUSIONS

The radioanalytical and spectroscopic data indicate that ≤ 2.1% Pu is liberated during CrO$_4^{2-}$ dissolution by the Hanford 3.0 M NaOH leach solution. However, related results have established that transport of actinides from the sludges by suspended solids will likely be observed during large-scale sludge pretreatment operations [5]. Experimental sludge washing by 2.0 M HNO$_3$ causes dissolution of Pu(III/IV), Pu(VI), Fe(III), and Nd(III) from the two BiPO$_4$ simulators. Stabilization of Mn(III) by complexation with HEDPA is accompanied by dissolution of up to 4.1% Pu(III/IV) and 14.3% Pu(VI) from the BiPO$_4$ and BiPO$_4$ (Modified) sludge simulators. Future research will focus X-ray diffraction studies of sludge simulants in which Pu is present during the precipitation/hydrolysis reactions and on correlating Pu mobilization with transition metal dissolution.

ACKNOWLEDGMENTS

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REFERENCES

BiPO₄ (Modified) Sludge Simulant

PUREX Sludge Simulant
Baseline Sludge Washing → Experimental Sludge Washing

Wash Solution

% Pu in Solution

- BiPO₄
- BiPO₄ (Modified)
- REDOX
- PUREX

Supernatant, Hydroxide + Nitrite, 3.0 M Hydroxide, Water, 0.05 M Glyeolic, 0.10 M Nitric, 2.0 M Nitric, 0.50 M HEDPA
3.0 M NaOH Wash

- BiPO₄
- BiPO₄ (Modified)
- Redox
- PUREX

2.0 M HNO₃ Wash

0.4 M Fe(NO₃)₃ in 2.0 M HNO₃

Nd(III) Bands

0.50 M HEDPA Wash

- MnO₂/HEDPA
- Mn(VII)/H₂O