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Project Title: Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes

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Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes

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Research Objective

Pacific Northwest and Lawrence Berkeley National Laboratories, in collaboration with Washington State University, are developing fundamental data on the precipitation/dissolution reactions of Cr(III) compounds and the kinetics of oxidation of Cr(III) to Cr(VI) at room and elevated temperatures and under conditions relevant to high-level waste (HLW) processing. This integrated approach, which involves measuring solubility and oxidation rate constants and spectroscopic characterization of aqueous and solid species as a function of ionic strength, alkalinity, redox conditions, and temperature, will provide thermodynamic and kinetic data. These data are necessary to predict changes in chromium solubility and speciation in response to changes in pretreatment strategies or to develop cost-effective tank waste processing technologies that result from reducing the total amount of chromium in processed waste.

Problem Statement

Chromium, one of the problematic elements in tank sludges, is presently considered to be the most important constituent in defining the total volume of HLW glass to be produced from the Hanford tank wastes. This is because 1) it greatly complicates the vitrification process by forming separate phases in the molten glass, and 2) more importantly, current sludge washing processes are not effective in removing chromium. Inadequate removal of chromium from sludges could result in production of an unacceptably large volume of HLW glass.

The removal of chromium from tank sludges is complicated by factors including the complex chemistry of chromium, lack of fundamental data applicable to the HLW chemical systems (e.g., high heterogeneity, high ionic strength, high alkalinity, and the presence of inorganic and organic ligands), and the need to avoid processes that may adversely enhance the solubility of plutonium and other actinides. Significant gaps exist in the fundamental understanding of chromium chemistry in tank-like environments. Without such data/understanding, these strategies cannot be appropriately evaluated or optimized. The primary objective of the research being carried out under this project is to develop such information for HLW tank processing.

Research Progress

There are two ways of removing chromium from the wastes: solubilization of Cr (III) compounds, and the oxidation of Cr(III) to Cr(VI). Progress was made on both of these aspects. Specifically, studies were conducted 1) to develop appropriate analytical techniques for the analyses of oxidation states and concentrations of Cr in alkaline solutions, 2) measuring the solubilities of Cr(OH)₃(am) and Cr₂O₃(c) in alkaline solutions, and 3) preliminary studies of the oxidation of Cr(III) to Cr(VI) by H₂O₂ in alkaline solutions.

Development of Analytical Techniques

A combination of inductively coupled plasma (ICP) or ICP-MS (mass spectrometry) and absorption spectrophotometry was found to be applicable to the analysis of chromium concentration and oxidation states. The absorption of Cr(VI) at 372 nm is appropriate for determining Cr(VI) in alkaline solutions with NaOH ranging from 0.01 to 8 M (lower detection limit ~1 x 10⁻⁵ M). This absorption band is also
useful for the determination of [Cr]_{total} after the sample is treated with oxidants under alkaline conditions. ICP or ICP-MS analysis of [Cr]_{total} was performed to double-check the results from absorption spectrophotometry.

X-ray absorption spectroscopy was evaluated for its use in determining oxidation states and the nature of the solid compounds. For the solubility results to be meaningful, it is important to be able to separate the solids from solutions. Solubility studies are needed and were conducted in NaOH solutions ranging in concentrations as high as 10 M. Although membrane filters with pore sizes as low as 0.0018 µm (e.g., Amicon Centriflo membrane cones) are available and have been extensively tested for their use in effectively separating chromium solids from solutions of relatively low alkalinity (Rai et al. 1987; Sass and Rai 1987), it is not known whether these filters can be used for separating solids from high alkalinity suspensions. Therefore, some limited studies were conducted to evaluate appropriate filters for use in the solubility studies involving high concentrations of NaOH.

**Solubility of Cr(OH)$_3$(am) in Concentrated NaOH Solutions**

The Cr(OH)$_3$(am) was prepared according to the method described by Rai et al. (1987) and was suspended in NaOH ranging in concentration from 0.01 to 10 M. Three different sets of experiments were conducted. It is expected that, in these relatively concentrated NaOH solutions, the Cr(OH)$_3$(am) solids would precipitate and it should be possible to separate the solids from solutions by centrifugation. However, rather than relying only on centrifugation, we tested two different types of filters (0.2 µm nylon filters that are stable in high NaOH concentrations and syringe filters of 0.0018 µm pore size made of discs cut off from the Amicon Centriflo membrane cones). The observed chromium concentrations in solutions filtered through these two filters were similar (Figure 1), indicating that colloids of sizes >0.0018 µm do not exist in these suspensions, that either of these filters can be used to effectively separate solids from solutions, and that it should be possible to use these results in developing reliable thermodynamic data.

![Figure 1. Comparison of Chromium Concentrations in 0.2 µm and 0.0018 µm Filtrates from Cr(OH)$_3$(am) Suspensions in NaOH](image-url)
The solubility of Cr(OH)$_3$(am) increases dramatically with the increase in NaOH concentrations, especially between 1.0 and 10 M. The observed concentrations at different equilibration periods (16, 27, 45, and 73 days) and from different sets of samples are similar (Figure 2), indicating that the steady-state concentrations are reached rapidly and that the results are reproducible. These results, in conjunction with the data presented by Rai et al. (1987), show that the equilibrium in these systems is reached rapidly.

To develop reliable thermodynamic models based upon these data, it is important to ascertain the oxidation state of chromium in solution and solid phases and identify the aqueous and solid species. Oxidation states were determined by a combination of methods involving chromatographic and XAS techniques. X-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) were used to identify solid phases.

XRD analyses of the solid phases indicated that the solids are amorphous. Oxidation state analyses of most of the aqueous samples by chromatographic technique (Table 1) described by Olsen et al. (1994) and of limited samples by x-ray absorption near-edge structure (XANES) (Figure 3) showed that Cr(III) is the dominant oxidation state in the aqueous and solid phases. XAS experiments were conducted at Stanford Synchrotron Radiation Laboratory (beamline 4-1) to determine the local structure of trivalent chromium hydroxide solids and solutions. The sample descriptions are given in Table 2.

The extended x-ray absorption fine structure (EXAFS) was extracted by fitting a polynomial spline function through the post-edge region and normalizing the difference between this approximation to the solitary atom EXAFS and the actual data with the absorption decrease given by the McMaster tables. Fourier transforms were taken over photoelectron wave vector range from 2.7 to 12.8 Å$^{-1}$ for each sample. Nodes in EXAFS were selected as endpoints to the transform range and a two-sigma-wide Gaussian window was used to dampen the EXAFS oscillations at the transform range endpoints. The phase shift has not been removed from the Fourier transforms; as a result, the peaks in the transform moduli appear 0.2 to 0.5 Å shorter than the actual interatomic distance from the absorber to the shells of neighboring atoms.

![Figure 2. Chromium Concentrations in NaOH Solutions Contacting Cr(OH)$_3$(am)](image-url)
Table 1. Chromium Oxidation State Analyses of 0.0018 μm Filtrates from Cr(OH)$_3$(am) Suspensions in NaOH

<table>
<thead>
<tr>
<th>C$_{\text{NaOH}}$/mol Kg$^{-1}$</th>
<th>% Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>2</td>
</tr>
<tr>
<td>0.40</td>
<td>9</td>
</tr>
<tr>
<td>0.80</td>
<td>18</td>
</tr>
<tr>
<td>1.60</td>
<td>16</td>
</tr>
<tr>
<td>2.53</td>
<td>8</td>
</tr>
<tr>
<td>3.09</td>
<td>10</td>
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<tr>
<td>4.22</td>
<td>2</td>
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<tr>
<td>5.34</td>
<td>2</td>
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<tr>
<td>6.47</td>
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<tr>
<td>7.60</td>
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<td>8.72</td>
<td>&lt;1</td>
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<tr>
<td>9.85</td>
<td>&lt;1</td>
</tr>
<tr>
<td>10.97</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Figure 3. Chromium K-Edge XANES of Solid Phases in Equilibrium with 1.0 m, 2.0, and 3.0 m NaOH

The background-subtracted, normalized XANES spectra for all the chromium samples display a profile that is consistent with the Cr(III) oxidation state, as shown in Figure 3. The XANES profile of Cr(VI) oxidation state is characterized by a sharp pre-edge feature approximately 15 eV lower in energy than the main absorption edge. This pre-edge feature is not observed in any of the XANES profiles for the chromium samples, indicating that little, if any, Cr(VI) is present in these samples.
Table 2. Chromium Hydroxide Samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Form</th>
<th>Description</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>99CROH1-1</td>
<td>Solid</td>
<td>0.2 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH1-2</td>
<td>Solution</td>
<td>0.2 m NaOH</td>
<td>XANES</td>
</tr>
<tr>
<td>99CROH2-1</td>
<td>Solid</td>
<td>1.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH2-2</td>
<td>Solution</td>
<td>1.0 m NaOH</td>
<td>XANES</td>
</tr>
<tr>
<td>99CROH3-1</td>
<td>Solid</td>
<td>2.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH3-2</td>
<td>Solution</td>
<td>2.0 m NaOH</td>
<td>XANES</td>
</tr>
<tr>
<td>99CROH4-1</td>
<td>Solid</td>
<td>3.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH4-2</td>
<td>Solution</td>
<td>3.0 m NaOH</td>
<td>XANES</td>
</tr>
<tr>
<td>99CROH5-1</td>
<td>Solid</td>
<td>5.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH5-2</td>
<td>Solution</td>
<td>5.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH6-1</td>
<td>Solid</td>
<td>8.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
<tr>
<td>99CROH6-2</td>
<td>Solution</td>
<td>8.0 m NaOH</td>
<td>XANES/EXAFS</td>
</tr>
</tbody>
</table>

An attempt was made to collect EXAFS data on all the solid and solution samples; however, the concentration of chromium in some of the less basic solutions was too low for satisfactory EXAFS data. A full analysis of the EXAFS is in progress, but the initial analysis indicates that there is a change in the local structure of the solid phase in equilibrium with the 3.0 m and 5.0 m NaOH solutions. In addition, the chromium concentration is sufficiently high in the 5.0 and 8.0 m NaOH solutions to compare the local structure of the solution with the solid phase in equilibrium with these two samples, and they seem to be identical. The Fourier transforms of the solid phase in equilibrium with 1.0 m and 5.0 m NaOH are compared in Figure 4. There is a significant increase in the transform peak at 3.0 that may reflect a change in the structure of the solid phase.

![Figure 4. Fourier Transform of the Solid Phase in Equilibrium with 1.0 m and 5.0 m NaOH](image-url)
Solubility of Cr₂O₃(c)

Studies on crystalline Cr₂O₃ solubility in concentrated NaOH solutions ranging in concentrations from 0.01 M to 8 M were initiated to check the effect of crystallinity of the initial solids on the solubility and the precipitation/dissolution kinetics of Cr₂O₃(c). The experimental procedures used for this study were identical to those used for Cr(OH)₃(am) with the exception that commercially purchased crystalline Cr₂O₃ was used as the initial solid. The samples have been shaken for 12 days and have not yet been analyzed. However, by observation it is obvious that the Cr concentrations in these solutions are much lower than those using Cr(OH)₃(am) as the starting material, suggesting that the solubility is strongly dependent on the crystallinity of the Cr compound and/or that the dissolution rate is much lower for crystalline Cr₂O₃.

The Effect of Hydrogen Peroxide on the Oxidation of Cr(III) to Cr(VI)

Only preliminary tests have been conducted so far. Several qualitative observations can be made:

- In alkaline solutions, upon addition of excess amounts of H₂O₂, the color of the Cr(III) solution changed completely from greenish blue to yellow in a few minutes, suggesting the aqueous homogeneous redox reaction between Cr(III) and peroxide is fairly rapid.

- In the presence of suspensions of Cr(OH)₃(am) in NaOH solutions, the Cr(OH)₃(am) solid gradually dissolved upon the addition of H₂O₂. When there was sufficient amount of H₂O₂, the color of the solution was found to change from greenish blue to yellow and the Cr(OH)₃(am) solid was eventually dissolved completely. This observation suggests that the oxidative dissolution of Cr(OH)₃(am) in the presence of peroxide is also fast. It takes about 10 minutes to complete the oxidative dissolution for the particular sample tested: about 230 mg Cr(OH)₃(am) solid in 1.5 M NaOH, H₂O₂ in excess with respect to chromium.

- For comparison, oxidative dissolution with a suspension of crystalline Cr₂O₃ in 1 M NaOH was also tested. No change in the color of the solution (very pale due to low concentration of chromium) was observed after addition of a large amount of H₂O₂. There was no identifiable change in the amount of Cr₂O₃ in the suspension, either.

Planned Activities

- Conduct studies to determine the effect of NaNO₃ (one of the important electrolytes present in tank wastes) on the solubility of Cr(OH)₃(am) in systems involving constant NaOH and variable concentrations of NaNO₃, and constant NaNO₃ and variable concentrations of NaOH.

- Develop thermodynamic model for the system Na⁺-Cr³⁺-OH⁻ - NO₃⁻ - H₂O to describe behavior of Cr(III) under conditions relevant to tank wastes.

- Continue the redox studies in homogeneous and heterogeneous systems with hydrogen peroxide, with the objective of obtaining quantitative kinetic data.
• Continue to follow the chromium concentrations in the suspensions of crystalline Cr₂O₃. Because it is difficult to design an “oversaturation” experiment for this solid, efforts will be made to raise the temperature of the Cr(OH)₃(am) suspension (e.g., to 90°C) and monitor any possible changes in the solubility and in the crystallinity of the solid phase.

• Initiate studies to determine the oxidation kinetics of Cr(III) to Cr(VI) in the presence of several oxidants (e.g., O₂, peroxynitrite) and as a function of temperature so that effective oxidative dissolution treatments can be designed for tank sludge washing.

References


Presentations