

**SPECIATION, DISSOLUTION, AND REDOX REACTIONS OF CHROMIUM
RELEVANT TO
PRETREATMENT AND SEPARATION OF HIGH-LEVEL TANK WASTES
EMSP Project 81896**

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RESEARCH OBJECTIVES

Chromium, one of the problematic elements in tank sludges, is considered the most important constituent in defining the total volume of high-level waste (HLW) glass. This proposed research seeks to develop fundamental data for Cr reactions that are not currently available but are essential for developing pretreatment processes for removing Cr from HLW sludges. Our objectives are to study 1) the dissolution of several solid phases (e.g., CrOOH, Cr₂O₃(c), and (Fe,Cr) binary hydroxides, identified to be important from sludge leaching studies) in highly alkaline solutions and in the presence of other electrolytes (e.g., carbonate, phosphate, sulfate, nitrite), and 2) the effect of the nature of Cr solid phases and aqueous species on their redox reactivity with a variety of potential oxidants (e.g., O₂ and ferrate). This information will provide critical support for developing enhanced pretreatment strategies for removing Cr from HLW and will achieve a major cost reduction in HLW disposal.

Thermodynamic and kinetic data concerning the behavior of Cr in multi-component, highly non-ideal electrolyte systems will be obtained. A model describing such behavior will be developed based on these fundamental data, tested with actual HLW tank sludge washing, and incorporated into the ESP model for use by Hanford, Savannah River, and other DOE site personnel for predicting the efficacy of enhanced pretreatment strategies for the removal of Cr from HLW.

RESEARCH PROGRESS AND IMPLICATIONS

The primary focus of the research program is to characterize the chemical species of Cr(III) in high level nuclear waste systems and to investigate the reactivity (both solubility and redox reactions) of Cr(III) species under these conditions. In the previous years, we have successfully separated and characterized the Cr(III) oligomers in solutions of wide pH range, and the effects of oligomerization on the redox transformations [from Cr(III) to Cr(VI)] and on the solubility of Cr(OH)₃(s) have been investigated (Friese et al. 2002, Rai et al. 2002, Rao et al. 2002). The results have been presented in publications in peer reviewed journals and at national meetings.

Further fundamental data in several different areas are required to design effective technologies for retaining the actinides in, and removing Cr from, the high-level radioactive waste sludges. These areas include 1) determining the effects of changes in the solution conditions (e.g., pH, temperature, aging time) on the changes in solid $\text{Cr}(\text{OH})_3(\text{s})$ phase, which in turn affects its solubility and redox reactivity, parameters of great importance in sludge washing to remove chromium either by alkaline or oxidative washing; 2) determining the complexation constants of Cr(III) with ligands, other than hydroxide, present in many tanks in significant concentrations (e.g., phosphate and sulfate) and their impact on Cr(III) speciation and removal; and 3) determining the reactivity and solubility of Cr(III) solid solutions/co-precipitates with Fe(III) and Al(III). The progress made in these different areas is briefly summarized below.

Characterization of $\text{Cr}(\text{OH})_3(\text{s})$ in equilibrium with solutions of different $[\text{NaOH}]$, at different temperatures, and various aging times

Effect of alkalinity on $\text{Cr}(\text{OH})_3(\text{s})$. Figure 1A shows the Fourier transform magnitude of the EXAFS spectra for $\text{Cr}(\text{OH})_3(\text{s})$ in equilibrium with solutions of different $[\text{NaOH}]$. The peak at $\sim 1.99 \text{ \AA}$ is for Cr-O scattering, and the peak at $\sim 2.99 \text{ \AA}$ is for Cr-Cr scattering. The Cr-Cr peak provides information on the degree of oligomerization. As shown in Figure 1, when the alkalinity of the solution is increased, the degree of oligomerization increases.

Effect of temperature on $\text{Cr}(\text{OH})_3(\text{s})$. Figure 1B shows the Fourier transform magnitude of the EXAFS spectra for $\text{Cr}(\text{OH})_3(\text{s})$ equilibrated with aqueous solutions of 5.5 M NaOH at different temperatures. Again, the peak at $\sim 1.99 \text{ \AA}$ is for Cr-O scattering, and the peak at $\sim 2.99 \text{ \AA}$ is for Cr-Cr scattering, and provides information on the degree of oligomerization. The figure shows that when the temperatures increase from 25 to 70 °C, the degree of oligomerization in the solid phase increases.

Effect of aging time on $\text{Cr}(\text{OH})_3(\text{s})$. Figure 1C shows the Fourier transform magnitude of the EXAFS spectra for $\text{Cr}(\text{OH})_3(\text{s})$ equilibrated with aqueous solutions for different aging time intervals ranging from 1 day to 131 days. The data indicate that the Cr-Cr scattering increases with the aging time within ~ 3 months (94 days), but there is no significant increase after that time.

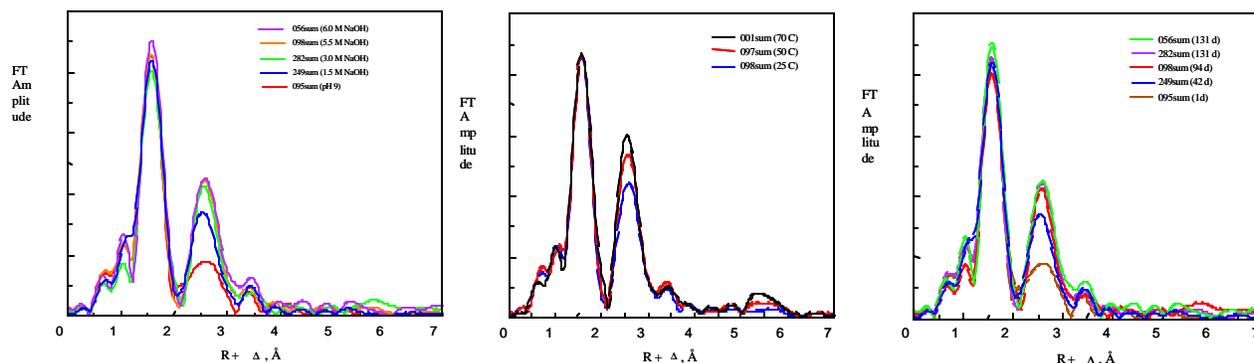


Figure 1. EXAFS analyses of $\text{Cr}(\text{OH})_3(\text{s})$ samples. A (left) – In equilibrium with solutions of NaOH. B (middle) – In equilibrium with 5.5 M NaOH at different temperatures. C (right) – In equilibrium with NaOH solutions aged for different times.

Investigation of the reactivity of Cr(OH)₃(s) obtained under different conditions – relationship between the nature of the solids and reactivity

Oxidation of Cr(OH)₃(s) with different degree of oligomerization. Experiments are being conducted on the redox reactivity of Cr(III) solids obtained at different alkalinity, temperature, and aging times. Cr(III) solids are oxidized by hydrogen peroxide. Preliminary results indicate that the oxidation rates are lower for solids obtained at higher alkalinity, at higher temperature, and after longer aging time. These experiments are expected to be completed in the coming months. A correlation between the equilibrium conditions and the redox reactivity will be summarized and discussed in terms of the change in the nature of the solids and the redox reaction mechanism.

Solubility of Cr(OH)₃(s) with different degree of oligomerization. Earlier solubility experiments at two temperatures show that the solubility of Cr(III) solids is lower at a higher temperature. We may design further experiments at a few different temperatures to confirm the correlation.

Phosphate complexes of Cr(III) and their Impact on solubilization of Cr(OH)₃(am)

A poor agreement was observed for the Cr concentrations in solutions from the reaction of unwashed radioactive-waste-sludges with NaOH as compared with those predicted in equilibrium with Cr(OH)₃(am) at the experimental NaOH concentrations (Rai et al. 2002). In particular, the observed experimental Cr concentrations were higher than those predicted. We surmised from these data that one of the reasons for disagreement may have been the effect of other ligands, such as phosphate and sulfate, that are present in significant concentrations in many tanks. Because of the unavailability of the reliable thermodynamic data for Cr(III) reactions with these ligands, we initiated studies with the Cr(III)-phosphate system. In these experiments, precipitated Cr(OH)₃(am) was equilibrated for different periods with 1) 0.05 M phosphate solution at different pH values (Figure 2A) and 2) a range in phosphate concentrations at fixed pH values of 6, 10, and 13 (Figures 2B, data for only pH 6 are presented). Because of general inability to accurately quantify pH values of concentrated electrolytes such as solutions $> \sim 0.05$ M phosphate used in this study, Pitzer's thermodynamic model (Sternner et al. 1997) was used to calculate HCl or NaOH concentrations required to prepare pH 6 solutions from NaH₂PO₄ stock, pH 10 from Na₂HPO₄, and pH 13 from Na₃PO₄.

The equilibrated solids were analyzed using EXAFS. The EXAFS analyses showed that the equilibrated solids in all cases were similar and were consistent with the presence of Cr(OH)₃(am). The similarity of observed Cr concentrations at different equilibration periods indicated that steady-state concentrations are reached in < 29 days in these systems. These observations, in conjunction with previous studies, assured that the equilibrium is reached in the time frames selected for equilibrations.

The solubility of Cr(OH)₃(am) as a function of pH and in the absence of and presence of 0.05 M phosphate indicates that the solubility in the presence of phosphate is higher at all pH values and is higher by about two orders of magnitude in relatively acidic conditions (Fig. 2A). When the solubility of Cr(OH)₃(am) was determined as a function of phosphate concentrations, the observed solubilities at any given pH were higher than those observed in the absence of phosphate (Figs. 2B). However, dramatic increases were observed at high phosphate concentrations and especially at the lower pH values (e.g., see Fig. 2B). The observed solubilities were about four orders of magnitude higher in the presence of one molar phosphate at pH 6. These data indicate that Cr(III) forms relatively strong complexes with

phosphate and that the nature of the complexes vary with the changes in pH. Thermodynamic interpretations of these data are in progress.

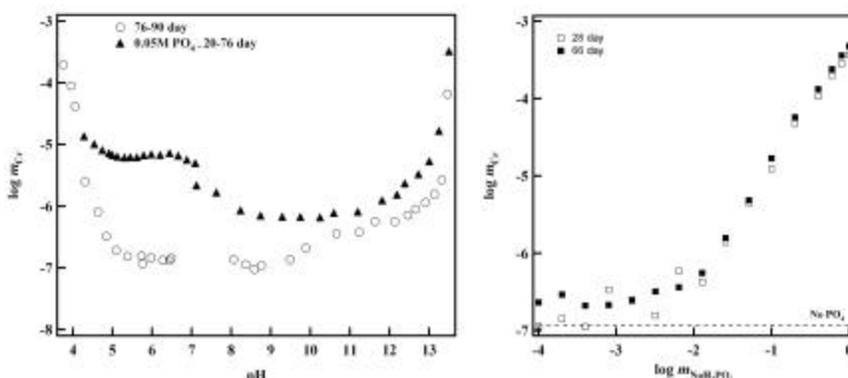


Figure 2. Solubility of Cr(OH)₃(am). A (left) – In the presence and absence of 0.05 M phosphate. B (right) – As a function of NaH₂PO₄ at pH value of about 6.

End-User Connection: Tests Against Data on Washed Solids from High-Level Tanks

Ideally, the fundamental data developed under this EMSP project needs to be tested with well-designed protocols of actual sludge washing. However, extensive studies with actual sludges are extremely expensive and beyond the scope of this EMSP funding. As a result, we decided to use the data that is available in technical reports from PNNL [Rapko et al. 1995; Lumetta et al. 1996a, 1997] on the washing of Hanford tank sludges. Although these data do not cover a sufficiently wide ranges of hydroxide concentrations or rigidly controlled experimental conditions we desire, they do provide a limited data set to test the applicability of fundamental data developed under the current EMSP.

In the study of the pretreatment of Hanford tank sludges [Rapko et al. 1995; Lumetta et al. 1996, 1997], three washings were performed on sludges from 14 different Hanford tanks: 1) retrieval and dilute NaOH washes, 2) first caustic leach, and 3) second caustic leach. These sludges are representative of the four major chemical processing operations (REDOX, TBP, BiPO₄, and PUREX). Comparisons were made of the observed Cr concentrations in the three washes to the predicted Cr concentrations from our thermodynamic model (Rai et al. 2002). The predicted Cr concentrations were about three orders of magnitude lower than the observed for the first wash, fairly close to the observed for the second wash (about one order of magnitude lower for a few sludges), and in excellent agreement with the observed for the third wash. At present, the exact reason for the significant disagreement for the first wash is not known, but we surmise it may result from the presence of Cr(VI), other electrolytes (e.g., carbonate) that were not included in the research investigations under the current EMSP project, and probably the leaching protocols. Nonetheless, The excellent agreement for the third wash (and, to less extent, the second) is very encouraging. If the effect of other electrolytes is significant, the extended studies proposed in this renewal will generate an improved thermodynamic model to account for the effects of these electrolytes. If the disagreement is mainly due to the leaching protocols, we will recommend modifications of the leaching protocol to the TFA investigators so that the future leaching tests provide more meaningful and informative results. The interim thermodynamic parameters developed under the

current program are being included into the TFA's Environmental Simulations Program for use by the site personnel.

PLANNED ACTIVITIES

The main output from this project will be the fundamental data to develop/improve technologies to effectively remove Cr from high-level radioactive waste sludges. Some of the specific future technical goals/accomplishments are listed below.

- Complete studies on the effect of alkalinity, time, and temperature on the speciation and solubility of Cr hydroxide.
- Complete studies on the kinetics of Cr(III)/Cr(VI) transformation reactions in the presence of different oxidants and as a function of solid-phase characteristics and temperature.
- Complete studies on the phosphato complexes of Cr(III).
- Initiate studies on the sulfato complexes of Cr(III).
- Initiate studies on the solubility of solid solutions/coprecipitates of Cr(III) with Fe(III)/Al(III).
- Prepare manuscripts for open literature publications.

INFORMATION ACCESS

Publications resulting from this project are listed below.

Journal Articles

Rai, Dhanpat, N. J. Hess, L. Rao, Z. Zhang, A. R. Felmy, D. A. Moore, S. B. Clark, G. J. Lumetta. 2002. Thermodynamic Model for the Solubility of Cr(OH)₃(am) in Concentrated NaOH and NaOH-NaNO₃ Solutions. *Journal of Solution Chemistry* 31: 343-367.

Friese, J. I., B. Ritherdon, S. B. Clark, Z. Zhang, L. Rao, and Dhanpat Rai. 2002. Chromatographic Separation and Characterization of Hydrolyzed Cr(III) Species. *Analytical Chemistry* 74: 2977 - 2984.

Rao, L., Z. Zhang, J. I Friese,, B. Ritherdon, S. B. Clark, N. J. Hess, and Dhanpat Rai. 2002. Oligomerization of chromium(III) and its impact on the oxidation of chromium(III) by hydrogen peroxide in alkaline solutions. *J.Chem.Soc., Dalton Trans.* 2002(2): 267 – 274.

Technical Reports

Rai, Dhanpat, L. Rao, and S. B. Clark. 2002. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. In: Science to Support

DOE Site Cleanup: The Pacific Northwest National Laboratory Environmental Management Science Program Awards. PNNL-13928, Pacific Northwest National Laboratory, Richland, WA, PP. 1.39 – 1.51.

Rai, Dhanpat, L. Rao, S. B. Clark, N. J. Hess, and G. J. Lumetta. 2000. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. In: *Science to Support DOE Site Cleanup: The Pacific Northwest National Laboratory Science Program Awards*. PNNL-13262, Pacific Northwest National Laboratory, Richland, WA, PP. 1.15 – 1.17.

Rai, Dhanpat, L. Rao, S. B. Clark, N. J. Hess, and G. J. Lumetta. 1999. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. In: *Science to Support DOE Site Cleanup: The Pacific Northwest National Laboratory Science Program Awards*. PNNL-12208, Pacific Northwest National Laboratory, Richland, WA, PP. 1.61 – 1.86.

CITED LITERATURE

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Lumetta, G. J., B. M. Rapko, M. J. Wagner, J. Liu, and Y. L. Chen, *Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1996 Studies*. PNNL-11278, Rev 1 (Pacific Northwest National Laboratory, Richland, Washington, 1996).

Lumetta, G. J., I. E. Burgeson, M. J. Wagner, J. Liu, and Y. L. Chen, *Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1997 Studies*. PNNL-11636 (Pacific Northwest National Laboratory, Richland, Washington, 1997).

Rai, Dhanpat, N. J. Hess, L. Rao, Z. Zhang, A. R. Felmy, D. A. Moore, S. B. Clark, G. J. Lumetta. *Journal of Solution Chemistry* 31: 343-367 (2002).

Rao, L., Z. Zhang, J. I. Friese, B. Ritherdon, S. B. Clark, N. J. Hess, and Dhanpat Rai. *J.Chem.Soc., Dalton Trans.* 2002(2): 267 – 274 (2002).

Rapko, B. M., G. J. Lumetta, and M. J. Wagner, *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies*. PNL-10712 (Pacific Northwest National Laboratory, Richland, Washington, 1995).

S. M. Sterner, A. R. Felmy, J. R. Rustad, and K. S. Pitzer, *Thermodynamic Analysis of Aqueous Solutions Using INSIGHT*. PNWD-SA-4436 (Pacific Northwest National Laboratory, Richland, Washington, 1997).