

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 radioactive waste (HLW) glass. Current sludge washing processes (e.g. caustic leaching, 3 M NaOH) are not effective in removing Cr. This inefficient removal would result in production of an unacceptably large volume of HLW glass and thus a tremendous increase in the cost of waste disposal. This proposed research seeks to develop fundamental data for chromium (Cr) reactions that are not currently available but are essential for developing effective methodologies for removing Cr from high-level waste (HLW). Our objectives are to study 1) the dissolution of several solid phases (e.g., CrOOH, Cr₂O₃(c), Cr(OH)₃, and Fe and 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., H₂O₂, persulfate, 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 is being obtained. A model describing such behavior is being developed based on these fundamental data, tested with actual HLW tank sludge washing, and incorporated into the Environmental Simulations Program (ESP) model for use by Hanford, Savannah River, and other U. S. Department of Energy (DOE) site personnel for predicting the efficacy of enhanced pretreatment strategies for the removal of Cr from HLW.

RESEARCH PROGRESS AND IMPLICATIONS

Prior to the research performed under our current EMSP project, fundamental information was unavailable on the solubility, speciation, or redox reactivity of Cr(III) in tank-like environments. Consequently, the behavior of Cr, including dissolution and redox, in the proposed sludge washing processes (caustic leaching or oxidative leaching) was not understood, nor could it be predicted.

Our research thus far has consisted of three major components: 1) characterization of Cr species in acidic to highly alkaline solutions, 2) determination and modeling of the solubility of Cr(OH)_{3(am)} in acidic (pH 2.8) to highly alkaline conditions (10.5 m NaOH) and mixed electrolytes containing nitrate, hydroxide and phosphate, and 3) study of the oxidation of Cr(III) by H₂O₂ and persulfate in alkaline solutions. These studies have been conducted in an integrated manner focused on understanding the effect of speciation on chemical behavior (solubility and redox). To enhance the application of our results to “real-world” problems, we compared and tested our results with those from actual tank sludge washing supported by the Tanks Focus Area (TFA). Accomplishments under this EMSP have been communicated in detail in the forms of journal articles, national conference presentations, and regular technical progress reports. The following are only brief summaries and highlights.

Speciation of Cr(III) in Acidic to Strongly Alkaline Solutions

Chromatographic Separation of Cr(III) Oligomers. Several methods have been developed to isolate macro amounts of Cr(III) oligomers using chromatographic techniques. This allowed us to investigate the chemical speciation, the structures of the separated oligomers, and the oxidation of isolated oligomers. The effect of solution pH on the oligomerization was evaluated. A capillary electrophoresis approach was also developed to separate minor quantities of the oligomers and to verify the resolution and separation by chromatography [Friese et al. 2002].

Characterization of Cr(III) species. The separated Cr(III) species were characterized by a variety of methods, including UV-VIS, X-ray absorption spectroscopy (EXAFS), and capillary electrophoresis (CE). Some of our selected results are presented below.

The UV-Vis absorption spectra of solutions containing the separated Cr(III) species (separated by ion exchange) are shown in Figure 1. The energy shift (toward a longer wavelength) and the intensity enhancement of the absorption bands, from the monomer through dimer, trimer, and tetramer, to the aged/unseparated solution are interpreted in the context of the structures of the Cr(III) species and the ligand field theory [Rao et al. 2002].

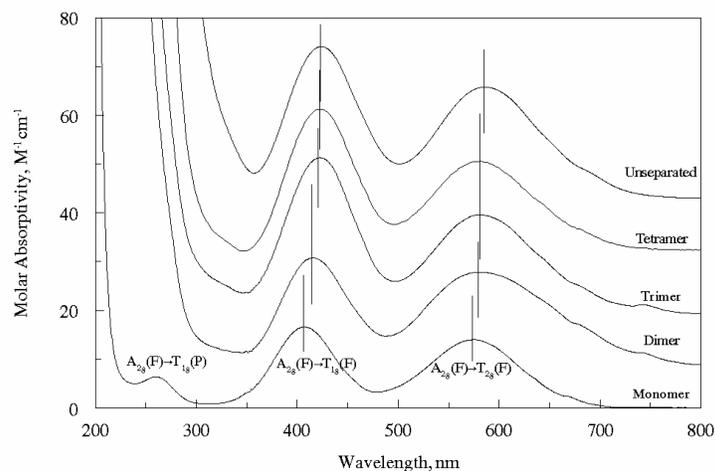


Figure 1. UV/Vis absorption spectra of Cr(III) monomer, dimer, trimer, tetramer and unseparated Cr(III) solutions. The spectra are shifted along y-axis for better viewing.

The UV-VIS absorption bands of the Cr(III) oligomers are quite broad. Consequently, absorption maxima of the separated fractions alone do not guarantee that a single Cr(III) species has been isolated. Yet isolation of a single species is important for resolving EXAFS spectra and for our oxidation studies. Therefore, we have used CE as an additional “quality assurance check” and have verified the purity of our isolated fractions of Cr(III) oligomers. Chromatograms of Cr solutions indicate that the charge density of the oligomers increases with the degree of polymerization [Friese et al. 2002].

Figure 2 shows the Fourier transforms of the EXAFS spectra of a few Cr(III) solution samples. Figure 2a shows the results for the separate d monomer in the solution and on the ion exchange resin. The best fit indicates that there are six oxygens around the Cr at 1.97 Å, but no Cr at 3 Å, confirming the monomeric nature of this Cr(III) species. On the other hand, Figure 2b indicates that the separated Cr(III) dimer, both in solution and on the resin, have one Cr at 2.97 Å, confirming the dimeric nature of this species. Figure 2c shows the effect of alkalinity on the oligomerization of Cr(III) in acidic to highly alkaline solutions. All the spectra show an oxygen shell (6 oxygen atoms) at around 1.99 Å. In all but the spectra for the solution with pH 2, there is the feature (~ 2.99 Å) that results from the Cr-Cr scattering. The intensity of the Cr-Cr scattering increases as the alkalinity is increased. This demonstrates that the oligomerization of Cr(III) is facilitated by higher alkalinity. Such an effect has a significant impact on the solubility of Cr(III) in alkaline solutions, which is described in subsequent discussions on solubility.

Based on the characterization under this EMSP project and the information in the literature [Spiccia et al. 1987, Finholt et al. 1981], the proposed structures of the dimer, trimer, and tetramer of Cr(III) are shown in Figure 3.

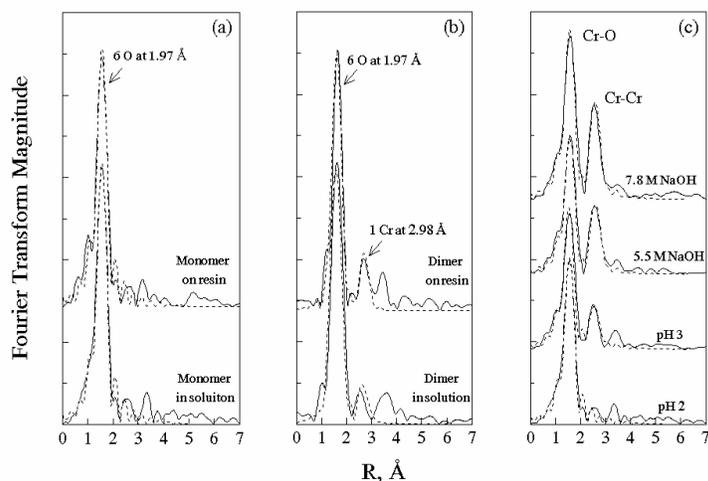


Figure 2. The Fourier transforms of the EXAFS spectra of Cr(III) solutions. Monomer in solution and on resin (a), dimer in solution and on resin (b), and Cr(III) solutions of different alkalinity (c). Solid line: experimental; dashed line: fit.

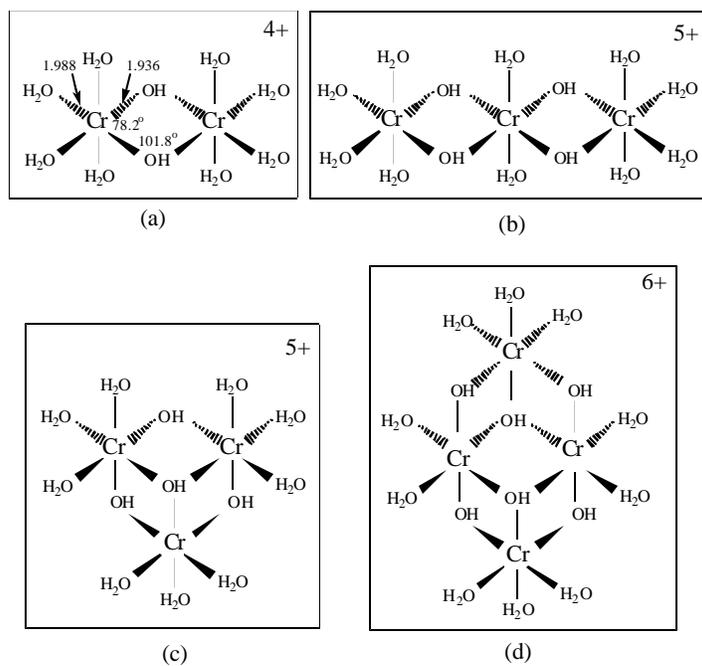


Figure 3. Structures of Cr(III) dimer (a), trimer (b, c) and tetramer (d). The bond lengths (in Å) and angles for the dimer are from Spiccia et al. [1987]. The Cr-Cr distance in the dimer is 3.006 Å.

Chromium (III) hydroxide solids aged in solutions of different alkalinity, at different temperatures, and for different lengths of time were characterized by EXAFS and IR. Figure 4 shows that, in a manner similar to the aqueous species, the nature of the Cr(III) hydroxide solids also depends on the alkalinity, temperature, and aging time. These results are supported by the results from IR spectroscopy [Zhang et al. 2004].

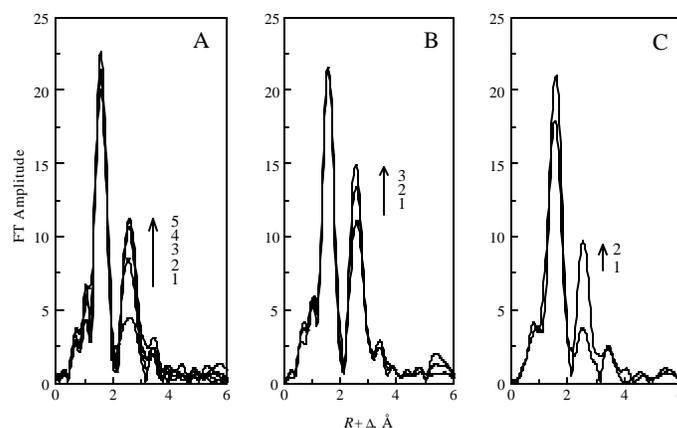


Figure 4. Fourier transform amplitude of Cr(III) hydroxide solids prepared under different conditions. (A) Cr(OH)₃(s) aged at 25 °C for more than 130 days in solutions of different [NaOH]. From 1 to 5: pH 9, 1.5 M, 3 M, 5.5 M and 6 M NaOH. (B) Cr(OH)₃(s) aged in 5.5 M NaOH at different temperatures. From 1 to 3: 25, 50 and 70 °C. (C) Cr(OH)₃(s) precipitated from 5 M NaOH at 25 °C. 1 – freshly precipitated; 2 – aged for 131 days.

Impact of Speciation, Ionic Strength, and Mixed Electrolytes on Cr(OH)₃(am) Solubility and the Development of Thermodynamic Model

The solubility of Cr(OH)₃(am) was measured in NaOH (0.003 to 10.5 m) and mixed/concentrated NaOH/NaNO₃ and NaOH/Na-phosphate solutions at 22 ± 2°C [Rai et al. 2002, 2004]. A combination of techniques (XANES, Raman spectroscopy, absorptive stripping voltammetry, thermodynamic analyses of solubility data) was used to identify aqueous species and to confirm that the soluble Cr was present as Cr(III). Total chemical analyses, XRD, XAS, Raman spectroscopy, and thermodynamic analyses of solubility data were used to identify the solid phases at equilibrium.

Cr(III)-Na⁺-H⁺-OH⁻-H₂O system. The aqueous Cr concentrations in equilibrium with Cr(OH)₃(am) increase dramatically with an increase in NaOH concentrations (Figure 4). Based on the findings in our speciation studies and the thermodynamic analyses of the data, we could model this observed solubility behavior in relatively concentrated NaOH solutions by invoking two dominant Cr(III) species, Cr(OH)₄⁻ and Cr₂O₂(OH)₄²⁻, and by including Pitzer ion-interaction parameters for Na⁺-Cr(OH)₄⁻ and Na⁺-Cr₂O₂(OH)₄²⁻. As shown in Figure 4, the model prediction satisfactorily describes the observed solubility. In order to verify and develop a more comprehensive model applicable from acidic to highly alkaline conditions, solubility studies were also conducted as a function of pH (2.8 – 14). In addition to the species listed above for NaOH >0.001 m, CrOH²⁺ and Cr(OH)₃(aq) were required to provide a reliable prediction of the observed solubility behavior (Fig. 5).

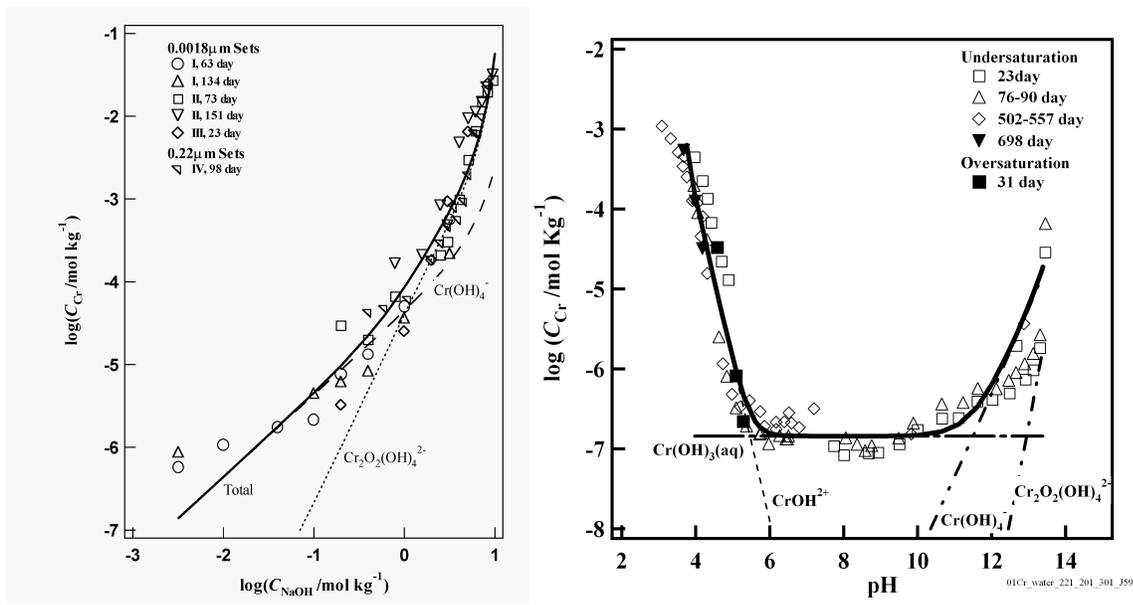


Figure 5. Aqueous chromium concentrations from $\text{Cr}(\text{OH})_3(\text{am})$ suspensions in NaOH (Left) and as a function of pH (Right). Lines represent predicted concentrations using the thermodynamic data reported in Rai et al. [2002 and 2004].

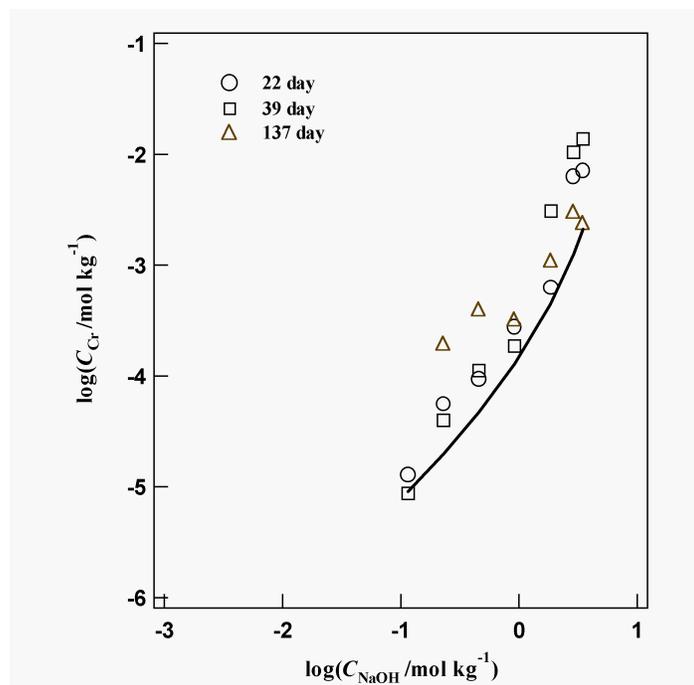


Figure 6. Aqueous chromium concentrations from $\text{Cr}(\text{OH})_3(\text{am})$ suspensions in 4.6 m NaNO_3 containing different concentrations of NaOH. Lines represent predicted concentrations using the thermodynamic data reported in Rai et al. [2002 and 2004].

Cr(III)-Na⁺-H⁺-OH⁻-NO₃⁻-H₂O system. The Cr(III)-hydroxide model was further tested using the experimental Cr(OH)₃(am) solubility in mixed NaOH and NaNO₃ solutions with NaOH varying up to 3.5 m and NaNO₃ varying up to 7.5 m (Rai et al. 2002). The Cr concentrations predicted by the model were in reasonably close agreement with the observed concentrations in mixed NaOH-NaNO₃ solutions (Figure 6). The thermodynamic parameters for the dissolution of Cr(OH)₃(am) in these systems, along with the ion interaction parameters, are provided in detail in Rai et al. [2002]

Cr(III)-Na⁺-OH⁻-H₂PO₄⁻-HPO₄²⁻-PO₄³⁻-H₂O system. Solubility studies of Cr(OH)₃(am) as a function of pH (2.8 -14) at fixed 0.05 m phosphate and as a function of phosphate (varying up to 1.04 m) at fixed pH values of 6, 10, or 13 were conducted to determine the nature of Cr(III)-phosphate species and their impact on the solubility of Cr(OH)₃(am) [Rai et al. 2004]. Phosphate significantly increased the solubility of Cr(III) in a very large range of pH values, and the increases were dramatic in the near neutral region (Figure 7). The study showed that phosphate does not form Cr(III)-phosphate solids in the alkaline region, even in the presence of as high concentrations as 0.6 m Na₃PO₄, and that Cr(OH)₃(am) is the stable phase. Contrary to the data recently reported in the literature [Ziemniak et al. 1998], only a limited number of aqueous species [Cr(OH)₃H₂PO₄⁻, Cr(OH)₃(H₂PO₄)₂²⁻, and Cr(OH)₃HPO₄²⁻] with up to about four orders of magnitude lower values for the formation constants of these species are required to explain Cr(III)-phosphate reactions in a wide range of pH and phosphate concentrations.

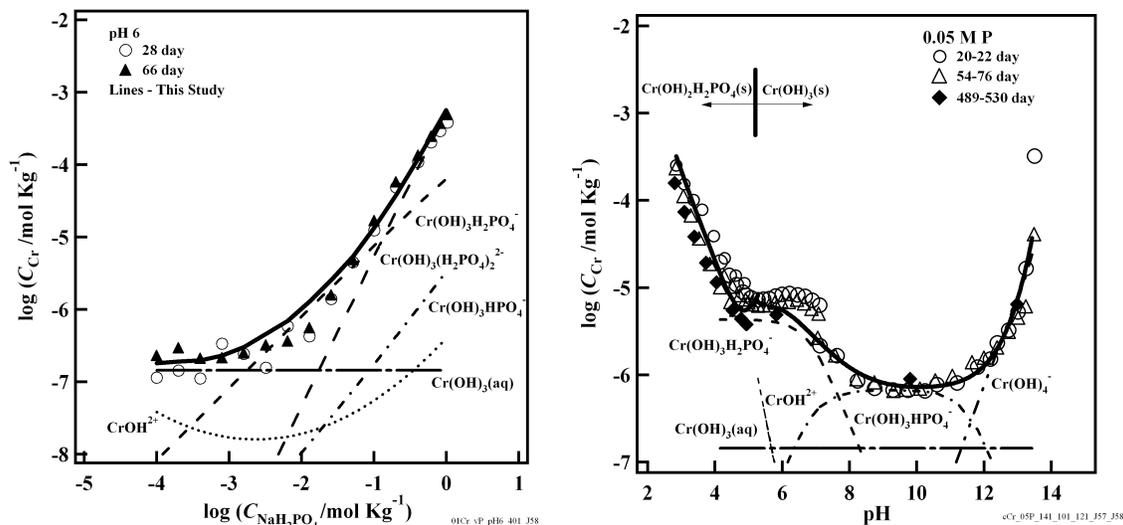


Figure 7. Aqueous chromium concentrations as a function of pH from Cr(OH)₃(am) or Cr(OH)₂H₂PO₄(am) suspensions in 0.05 m phosphate (Left) and from Cr(OH)₃(am) suspensions as function of phosphate concentrations at fixed pH value of 6 (Right). Lines represent predicted concentrations using the thermodynamic data reported in Rai et al. [2002 and 2004].

Thermodynamic model for the system Cr(III)-Na⁺-OH⁻-NO₃⁻-H₂PO₄⁻-HPO₄²⁻-PO₄³⁻-H₂O. A thermodynamic model based on the data discussed above was developed for tank-like chemical environments containing concentrated hydroxide, nitrate, and phosphate (Table 2; Rai et al. 2002, 2004). This model provides reliable predictions for acidic (pH 2.8) to highly alkaline conditions (10.5 m NaOH), and mixed electrolytes containing nitrate and hydroxide (with NaOH varying up to 3.5 m and NaNO₃ varying up to 7.5 m) and phosphate and hydroxide (with NaOH varying up to 0.3 m and phosphate varying up to 1.04 m).

Table 2. Pitzer ion-interaction parameters and other thermodynamic data for Cr(OH)₃(am) solubility in concentrated hydroxide, nitrate, and phosphate systems.

| Species | <u>Binary Parameters</u> | | | | Reference |
|---|--------------------------|------------------|------------------|----------------|---------------------------|
| | b ⁽⁰⁾ | b ⁽¹⁾ | b ⁽²⁾ | C ^E | |
| Na ⁺ -OH ⁻ | 0.0864 | 0.253 | 0.00 | 0.0044 | Pitzer 1991 |
| Na ⁺ -Cr(OH) ₄ ⁻ | 0.045 | 0.31 | 0.00 | -0.003 | Rai et al. 2002 |
| Na ⁺ -Cr ₂ O ₂ (OH) ₄ ²⁻ | 0.41 | 0.7 | 0.00 | -0.03768 | Rai et al. 2002 |
| Na ⁺ -PO ₄ ³⁻ | 0.1781 | 3.851 | 0.00 | -0.0515 | Pitzer 1991 |
| Na ⁺ -HPO ₄ ²⁻ | -0.0583 | 1.4655 | 0.00 | 0.02938 | Pitzer 1991 |
| Na ⁺ -H ₂ PO ₄ ⁻ | -0.0533 | 0.0396 | 0.00 | 0.00795 | Pitzer 1991 |
| Na ⁺ -Cr(OH) ₃ HPO ₄ ²⁻ | -0.0583 | 1.4655 | 0.00 | 0.02938 | Rai et al. 2004 |
| Na ⁺ -Cr(OH) ₃ H ₂ PO ₄ ⁻ | -0.0533 | 0.0396 | 0.00 | 0.00795 | Rai et al. 2004 |
| Na ⁺ -Cr(OH) ₃ (H ₂ PO ₄) ₂ ²⁻ | -0.0583 | 1.4655 | 0.00 | 0.02938 | Rai et al. 2004 |
| <u>Common-Ion Ternary Parameters</u> | | | | | |
| | Value | | | | |
| OH ⁻ -Cr(OH) ₄ ⁻ | 0.014 | | | | Rai et al. 2002 |
| OH ⁻ -Cr(OH) ₄ ⁻ -Na ⁺ | -0.0048 | | | | Rai et al. 2002 |
| H ⁺ -H ₃ PO ₄ (aq) | 0.29 | | | | Pitzer and Silvester 1976 |
| H ₃ PO ₄ (aq)-H ₃ PO ₄ (aq) | 0.053 | | | | Pitzer and Silvester 1976 |
| H ₂ PO ₄ ⁻ -H ₃ PO ₄ (aq) | -0.4 | | | | Pitzer and Silvester 1976 |
| H ⁺ -Na ⁺ | 0.036 | | | | Pitzer 1991 |
| <u>Equilibrium Constants</u> | | | | | |
| Reaction | | | | | log K⁰ |
| Cr(OH) ₃ (am) \rightleftharpoons Cr(OH) ₃ | | | | | -6.84 |
| Cr(OH) ₃ (am) + OH ⁻ \rightleftharpoons Cr(OH) ₄ ⁻ | | | | | -4.36 " 0.24 |
| 2Cr(OH) ₃ (am) + 2OH ⁻ \rightleftharpoons Cr ₂ O ₂ (OH) ₄ ²⁻ + 2H ₂ O | | | | | -5.24 " 0.24 |
| Cr(OH) ₃ (am) + 2H ⁺ \rightleftharpoons CrOH ²⁺ + 2H ₂ O | | | | | 4.09 " 0.38 |
| Cr(OH) ₂ H ₂ PO ₄ (am) + H ⁺ \rightleftharpoons CrOH ²⁺ + H ₂ PO ₄ ⁻ + H ₂ O | | | | | -2.52 " 0.21 |
| Cr(OH) ₃ (am) + HPO ₄ ²⁻ \rightleftharpoons Cr(OH) ₃ HPO ₄ ²⁻ | | | | | -4.87 " 0.3 |
| Cr(OH) ₃ (am) + H ₂ PO ₄ ⁻ \rightleftharpoons Cr(OH) ₃ H ₂ PO ₄ ⁻ | | | | | -4.06 " 0.3 |
| Cr(OH) ₃ (am) + 2H ₂ PO ₄ ⁻ \rightleftharpoons Cr(OH) ₃ (H ₂ PO ₄) ₂ ²⁻ | | | | | -3.36 " 0.3 |

Impact of Speciation on Redox: Oxidation of Cr(III) by Peroxide and Persulfate

Two oxidants were studied, peroxide (H_2O_2) and the persulfate anion (S_2O_8^-). Peroxide is of interest because of its favorable reduction potential relative to Cr(III) oxidation to chromate, and because its use does not add unwanted components to the already complex waste stream. Persulfate is of interest because of work completed by Russian scientists on its oxidation of Cr(III) in alkaline systems. Krot et al. [1999] indicated that persulfate may be preferred over peroxide and other common oxidants because of its reactivity towards Cr(III) and because it could be applied such that little increase in waste volume occurred. However, for both hydrogen peroxide and persulfate, no mechanistic data were available prior to our work under this EMSP.

Oxidation of Aqueous Cr(III) Oligomers by H_2O_2 and Persulfate in Alkaline Solutions. The oxidation of Cr(III) was followed by monitoring the increase of Cr(VI) absorbance at 372 nm. The oxidation was found to be the first order with respect to the concentrations of Cr(III) and H_2O_2 . As to the dependency on the OH concentration, there seem to be two reaction pathways: the major one is inversely dependent on [OH], and the other independent of [OH] (insignificant). A general rate equation is written as

$$R = -d[\text{Cr}_n(\text{III})]/dt = n d[\text{Cr}(\text{VI})]/dt = k[\text{Cr}_n(\text{III})][\text{H}_2\text{O}_2](1/[\text{OH}] + k') \quad (1)$$

$$= k_{\text{OH}}[\text{Cr}_n(\text{III})][\text{H}_2\text{O}_2] \quad (2)$$

$$= k_{\text{obs}}[\text{Cr}_n(\text{III})] \quad (3)$$

where $n = 1, 2$ and 3 for monomer, dimer, and trimer, respectively. Examples of the plots of k_{obs} vs. $[\text{H}_2\text{O}_2]$ are shown in Figure 8 for the monomer, dimer, and trimer, respectively. It can be seen that, at the same concentrations of H_2O_2 and NaOH, the oxidation rate decreases in the order monomer > dimer > trimer > higher ligomers.

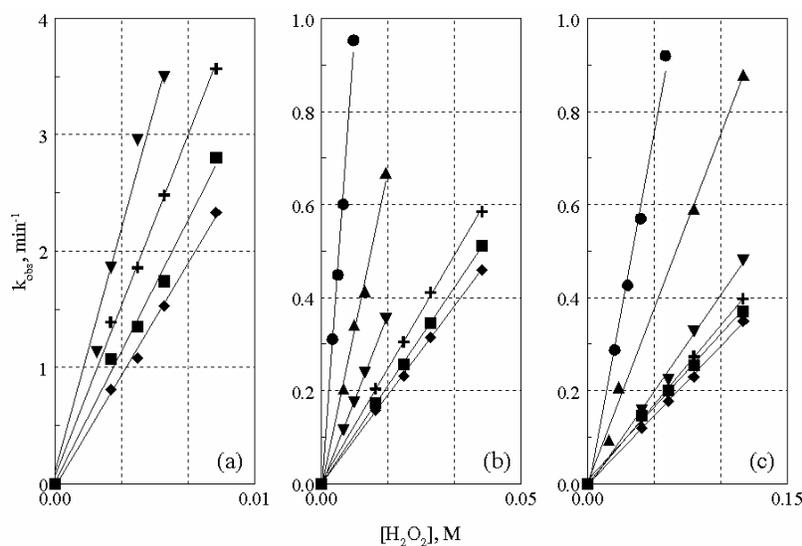


Figure 8. The pseudo first-order rate constant, k_{obs} , as a function of $[\text{H}_2\text{O}_2]$ at constant $[\text{OH}]$. (a) monomer, (b) dimer, (c) trimer. Symbols: $[\text{OH}] = 0.100 \text{ M}$ (?), 0.252 M (?), 0.504 M (?), 0.756 M (+), 1.00 M (|), 1.18 M (?).

Values of the rate constant k [equation 1], calculated from these plots, are provided in Rao et al. [2002]. These values show that the oxidation rate decreases in the order monomer > dimer > trimer > higher oligomers. If $[\text{H}_2\text{O}_2] = 0.01 \text{ M}$ and $[\text{NaOH}] = 1.0 \text{ M}$, the time required for 50% oxidation ($t_{1/2}$, in minutes) would be in the order monomer (0.2) < dimer (6) > trimer (22) > unseparated/aged Cr(III) (410). In a brief summary, our data [Rao et al. 2002] indicate that, 1) H_2O_2 can oxidize Cr(III) to Cr(VI) in alkaline solutions, 2) the oxidation probably occurs through a rate-determining step involving the breaking of the bridging bonds in the oligomers and the concomitant release of one hydroxyl group from the Cr(III) moiety upon the attack by H_2O_2 , and 3) it is likely that more energy is required to break the bridging bonds in higher oligomers. Consequently, the redox reactivity of the Cr(III) species with H_2O_2 decreases as oligomerization proceeds.

Oxidation of Cr(III) by persulfate follows a different kinetics mechanism [Friese et al. 2004]. This is most easily demonstrated by comparing Figure 9 with the results of Cr(III) oxidation by peroxide [Figure 8]. When $[\text{NaOH}] < 1\text{M}$, the reaction rate is best described by multiple first-order processes. When $[\text{NaOH}] > 1\text{M}$, Cr(III) oxidation by persulfate is best described by a single first-order process; note that the linear dependence on oxidant concentration observed with peroxide is only observed with persulfate at very high concentrations of NaOH (e.g., ~ 5M NaOH).

Detailed investigations over wide ranges of conditions (e.g., $[\text{NaOH}]$, $[\text{persulfate}]$, and temperature) have revealed the following important conclusions: 1) There is a very rapid oxidation step probably involving the sulfate radical ($\text{SO}_4^{\cdot-}$) [Koltoff 1951]. The conditions that favor oxidation by the persulfate radical include $[\text{NaOH}] < 1 \text{ M}$, and temperatures elevated to at least 30°C . 2) A second process in the oxidation of Cr(III) by persulfate follows Michaelis-Menton-type kinetics, suggesting the formation of an intermediate species.

For the oxidation of aqueous Cr(III) oligomers with both peroxide and persulfate, there are two implications that are of great significance to the design of oxidative sludge washing to remove Cr: 1) Any processes that can break down the oligomers will facilitate the oxidation, and thus the dissolution of Cr; and 2) Although oxidation occurs in alkaline solutions, high concentrations of NaOH will slow the oxidation.

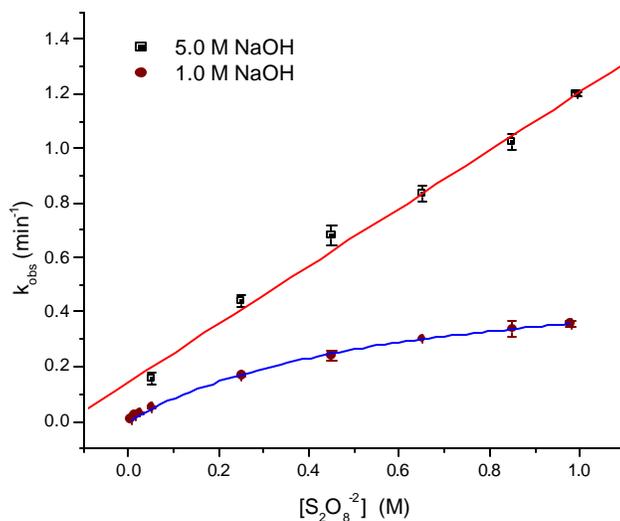


Figure 9. Observed rate constants for the oxidation of Cr(III) by persulfate in NaOH. $[\text{Cr(III)}] = 1 \times 10^{-4} \text{ M}$, $T = 22^\circ \text{C}$. Note that, unlike oxidation by peroxide, the observed reaction rates are only linear with respect to persulfate concentration when $[\text{NaOH}]$ is quite large.

Oxidation of Cr(III) Hydroxide Solids by H₂O₂ in Alkaline Solutions. As Figure 10 shows, freshly precipitated Cr(III) hydroxide was oxidized most rapidly, indicated by the rapid increase of the absorbance of Cr(VI) at 372 nm. Aging the solids decreased the rate of oxidation. The solids that were aged in solutions of higher concentrations of NaOH reacted with hydrogen peroxide more slowly. Based on the information obtained by EXAFS and IR, these results indicate that the solids with a higher degree of oligomerization are oxidized more slowly by hydrogen peroxide in alkaline solutions.

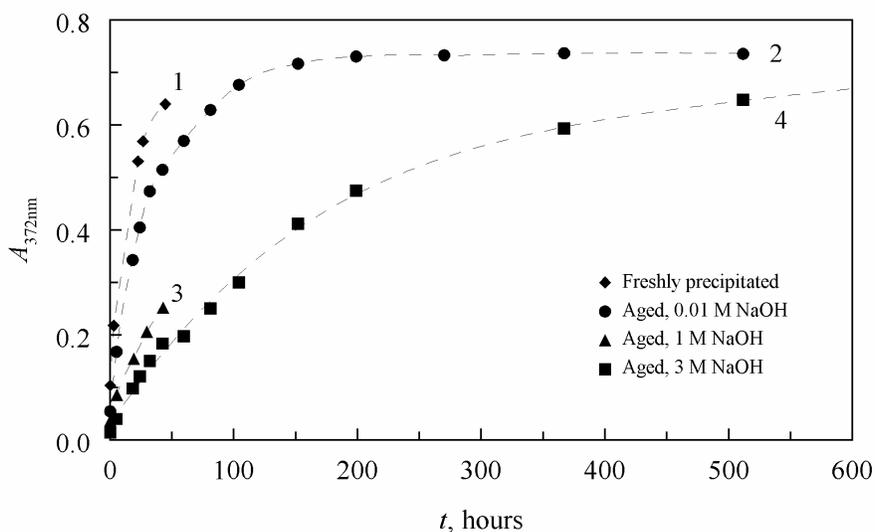


Figure 10. Oxidation of Cr(III) hydroxide solids by H₂O₂ in 1 M NaOH at (22 ± 2) °C.

The trend observed for the oxidation of Cr(III) hydroxide solids parallels that previously observed for the Cr(III) solution species, i.e., the rate constants of the oxidation decrease as the degree of oligomerization becomes higher [Rao et al. 2002]. Full explanations for the observed order are not possible at present because the difficulty in defining concentrations in the heterogeneous systems does not allow us to derive reaction orders and the rate law for the studied reaction. Besides, further experiments are needed to obtain detailed structural information on the Cr(III) species in the solids and the point of attack by hydrogen peroxide.

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

Ideally, the fundamental data developed under this EMSP project need 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 as wide a range of hydroxide concentrations or as rigidly controlled experimental conditions as 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 supported by the TFA [Rapko et al. 1995; Lumetta et al. 1996a, 1997], in most cases three sequential 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. The sludges used in the TFA study represent four major chemical processing operations (REDOX,

TBP, BiPO₄, and PUREX). The washes parallel those being proposed for actually washing the sludges. Of these washes, the caustic washes (3 M NaOH) are expected to dissolve most Cr(III) (e.g. see Fig. 5), and the second caustic wash especially very nearly represents the electrolytes for which we have a valid thermodynamic model. Therefore, we decided to compare the observed Cr concentrations in the caustic washes with those predicted using the thermodynamic model presented in Table 2. It should be mentioned that even the second caustic leachates (the third wash) from different sludges, in addition to containing 3 M NaOH, still contain differing concentrations of aluminum, nitrate, nitrite, and phosphate (e.g. phosphate concentrations vary from very low to as high as 0.03 M in tank T104). As expected, the concentrations of ligands in retrieval washes and the first caustic wash are much higher than those in the second caustic wash (e.g., phosphate levels in dilute NaOH wash from tank T104 is 0.13 M). The comparison of the observed Cr concentrations in the caustic washes to the predicted Cr concentrations from our thermodynamic model is shown in Figure 11. The predicted Cr concentrations, assuming an equilibrium with Cr(OH)₃(am), were fairly close to that observed for the first caustic wash (about one order of magnitude lower for a few sludges), and in excellent agreement with that observed for the second caustic wash. However, the predicted concentrations were up to about three orders of magnitude lower than those observed in the dilute NaOH washes. At present, the exact reason for the significant disagreement for the dilute NaOH wash is not known, but we surmise it may result from the presence of Cr(VI), other electrolytes (e.g., carbonate and sulfate) that were not included in the research investigations under the current EMSP project, and probably the leaching protocols. Nonetheless, the excellent agreement for the second caustic wash (and, to a lesser extent, the first caustic wash) is very encouraging and shows the practical importance of the data developed in this EMSP project for determining the effects of concentrations of different ligands and NaOH for optimizing/predicting the solubilization of Cr(III) from different tanks. The thermodynamic parameters developed under the current program have been included in the TFA's Environmental Simulations Program for use by the site personnel.

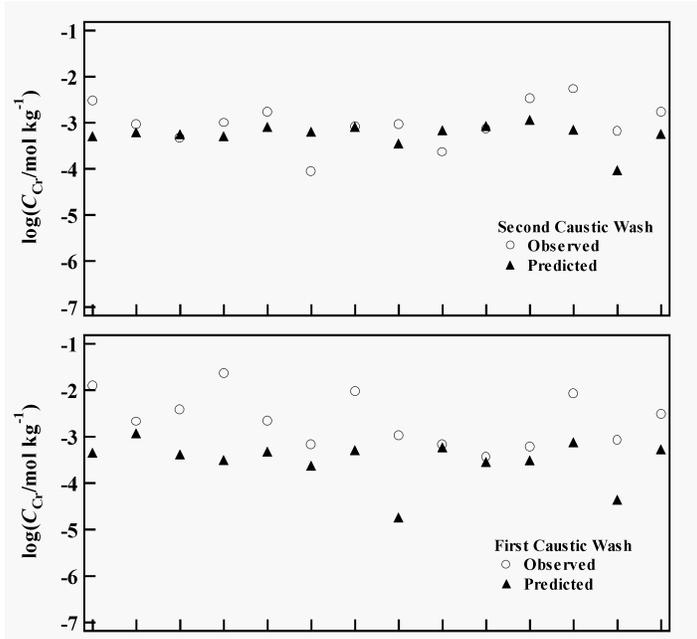


Figure 11. Predicted and observed chromium concentrations in sludge leachates (points on x-axis from left to right represent Hanford tanks S101, S104, S107, S111, BY104, BY108, BY110, T104, C107, BX107, B111, T111, C103, and AN104). Electrolytes in leachates vary from a mixture containing sodium, aluminum, hydroxide, nitrate, nitrite, phosphate, carbonate, and sulfate in various proportions to primarily NaOH [see Rai et al. 2002 for details].

LITERATURE CITED

- Finholt, J. E., M. E. Thompson, R. E. Connick. 1981. Hydrolytic Polymerization of Chromium(III). 2. A trimeric species. *Inorg. Chem.* **20**:4151-4155.
- Friese, J. I., B. Ritherdon, S. B. Clark, L. Rao, and Z. Zhang. 2004. Oxidation of Cr(III) oligomers by persulfate under alkaline conditions. (Manuscript in preparation)
- 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.
- Koltoff, I. M. and I. K. Miller. 1951. The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium. *J. Am. Chem. Soc.* **73**:3055-3059.
- Krot, N. N., F. P. Shilov, A. M. Fedoseev, N. A. Budantseva, M. V. Nikonov, MA. B. Yusov, A. Y.
- Lumetta, G. J., B. M. Rapko, M. J. Wagner, J. Liu, and Y. L. Chen. 1996a. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1996 Studies*. PNNL-11278, Rev.1. Pacific Northwest National Laboratory, Richland, Washinton, USA.
- Lumetta, G. J., I. E. Burgeson, M. J. Wagner, J. Liu, and Y. L. Chen. 1997. *Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1997 Studies*. PNNL-11636. Pacific Northwest National Laboratory, Richland, Washington, USA.
- Pitzer, K. S. 1991. *Activity Coefficients in Electrolyte Solutions*. 2nd Ed., CRC Press, Inc., Boca Raton.
- Pitzer, K. S. and L. F. Silvester. 1976. Thermodynamics of Electrolytes. VI. Weak Electrolytes Including H_3PO_4 . *J. Solution. Chem.* **5**:269.
- Rai, D., N. J. Hess, L. Rao, Z. Zhang, A. R. Felmy, D. A. Moore, S. B. Clark, and G. J. Lumetta. 2002. Thermodynamic Model for the Solubility of $\text{Cr}(\text{OH})_3(\text{am})$ in Concentrated NaOH and NaOH-NaNO_3 Solutions. *Journal of Solution Chemistry* **31**:343-367.
- Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao, S. B. Clark. 2004. Chromium(III) Hydroxide Solubility in the Aqueous $\text{Na}^+ \text{-OH}^- \text{-H}_2\text{PO}_4^- \text{-HPO}_4^{2-} \text{-PO}_4^{3-} \text{-H}_2\text{O}$ System: A Thermodynamic Model. *Journal of Solution Chemistry* (in press).
- Rai, D., B. M. Sass, and D. A. Moore. 1987. Cr(III) Hydrolysis Constants and Solubility of Cr(III) Hydroxide. *Inorg. Chem.* **26**:345-349.
- Rao, L., Z. Zhang, J. I Friese,, B. Ritherdon, S. B. Clark, N. J. Hess, and D. 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.* **2**:267-274.
- Rapko, B. M., G. J. Lumetta, and M. J. Wagner. 1995. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies*. PNNL-10712. Pacific Northwest National Laboratory, Richland, Washington, USA.
- Spiccia, L., H. Stoeckli-Evans, W. Marty, and R. Giovanoli. 1987. A New "Active" Chromium (III) Hydroxide. *Inorg. Chem.* **26**:474.

PLANNED ACTIVITIES

While the studies conducted under our current EMSP project have provided extensive validated fundamental data for aqueous species as well as results of practical importance on the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ and its redox reactivity, they have also pointed out that the extent of Cr leaching in caustic wash, which is being proposed as one of the treatments, and in oxidative dissolution is highly dependent on the nature of the Cr(III) solid phases and aqueous species. Out of a large number of Cr(III)-solid phases [e.g., $\text{Cr}(\text{OH})_3(\text{am})$, $\text{CrO}(\text{OH})$, $(\text{Fe,Cr})(\text{OH})_3(\text{am})$, $\text{Fe}(\text{Cr,Fe})_2\text{O}_4$, FeCr_2O_4 , $\text{Al/Cr}(\text{OH})_3(\text{am})$] that have been identified in tank sludges, $\text{Cr}(\text{OH})_3(\text{am})$ is the most soluble, and other solid phases are expected to have solubilities of many orders of magnitude lower. While caustic wash dissolves a reasonable amount of $\text{Cr}(\text{OH})_3(\text{am})$, it will not be effective with solid phases that have solubilities orders of magnitude lower. Fundamental information about the formation, stability, and oxidative dissolution of these other solid phases is not available and is required to develop effective pretreatment processes to remove Cr from sludges. Developing these fundamental data is the objective of the ongoing research.

INFORMATION ACCESS (scientific communications prepared as part of this project)

Journal Articles

Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao, S. B. Clark. 2004. Chromium(III) Hydroxide Solubility in the Aqueous $\text{Na}^+ - \text{OH}^- - \text{H}_2\text{PO}_4^- - \text{HPO}_4^{2-} - \text{PO}_4^{3-} - \text{H}_2\text{O}$ System: A Thermodynamic Model. *Journal of Solution Chemistry* (in press).

Zhang, Z., L. Rao, Dhanpat Rai, S. B. Clark. 2004. Characterization of Chromium(III) Hydroxide Solids and Their Oxidation by Hydrogen Peroxide. *Materials Research Society Symposium Proceedings* (in press).

J. I. Friese, B. Ritherdon, S. B. Clark, L. Rao, and Z. Zhang. 2004. Oxidation of Cr(III) oligomers by persulfate under alkaline conditions. (Manuscript in preparation)

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.

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 $\text{Cr}(\text{OH})_3(\text{am})$ in Concentrated NaOH and NaOH-NaNO_3 Solutions. *Journal of Solution Chemistry* 31: 343-367.

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. 2003. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. FWP 42380. U. S. Department of Energy, Richland Operations Office.

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, D., 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, D., L. Rao, S. B. Clark, and N. J. Hess. March 2000. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. Project Summary submitted to EMSP.

Rai, D., 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

Presentations

Rai, D., L Rao, and SB Clark, N. J. Hess. 2003. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes” as a part of a symposium on nuclear waste management. 226th American Chemical Society national meeting, September 7-11, 2003, New York City.

Rai, D., L Rao, and SB Clark, N. J. Hess. 2001. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes (11/08/2001) at National DOE/EMSP Workshop, Richland WA.

Rao, L., D. Rai, S. B. Clark, Z. Zhang, N. J. Hess, B. Ritherdon, and J. Friese. 2000. Dissolution of $\text{Cr}(\text{OH})_3(\text{am})/\text{Cr}_2\text{O}_3(\text{c})$ and Oxidation of Cr(III) in Alkaline Solutions. A presentation at the 219th ACS National Meeting, San Francisco, California, March 2000.

Friese, J., B. Ritherdon, O. Gerasimov, S. Lyman, J. Hurst, Z. Zhang, L. Rao, D. Rai, and S. B. Clark. 2000. Oxidation of Trivalent Cr Using Oxidants Relevant to High-Level Radioactive Waste. A presentation at the 219th ACS National Meeting, San Francisco, California, March 2000.

Rai, D., L. Rao, S. B. Clark, N. J. Hess, and A. R. Felmy. 2000. Solubility of Cr(III) Compounds and Their Redox Transformation Reactions: Application to Pretreatment of High-Level Waste Sludges. An oral presentation at the EMSP workshop, Atlanta, Georgia, April 2000.

Rai, D., L. Rao, S. B. Clark, N. J. Hess, and A. R. Felmy. 2000. Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes. Poster presentation at the EMSP workshop, Atlanta, Georgia, April 2000.

Friese, J., B. Ritherdon, S. B. Clark, L. Rao, and Z. Zhang. 2000. Removing Chromium from High-Level Radioactive Waste Streams: Speciation and Reactivity of Cr(III) Oligomers Under Highly Alkaline Conditions. A presentation at the 221th ACS National Meeting, San Diego, California, April 2001.

Rao, L., D. Rai, S. B. Clark, A. R. Felmy, N. J. Hess, Z. Zhang, and B. Ritherdon. 1999. Speciation, Dissolution, and Redox Reactions of Cr(III) in Alkaline Solutions. A presentation at the 218th ACS National Meeting, New Orleans, Louisiana, August 1999.