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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 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. Such inefficient removal would result in the 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 form high-level waste (HLW). Our objectives are to study 1) the dissolution of several solid phases (e.g., CrOOH, Cr_2O_3(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 (H_2O_2, persulfate, hypochlorite, etc.). 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.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the research conducted through September 2006 and represents a two years effort of a three year project

Kinetic Studies of the Oxidation of Cr(III) by Hypochlorite

The rates of oxidation of Cr(III) by two oxidants, peroxide (H_2O_2) and the persulfate ($S_2O_8^-$), have been reported in previous reports and journal articles (Rao et al. 2002, Zhang et al. 2004). It was found that the degree of oligomerization of Cr(III) significantly affects the rate of oxidation. The results indicate that: 1) any processes that can break down the oligomers will facilitate oxidation, and thus the dissolution of Cr; and 2) although oxidation does occur in alkaline solutions, high concentrations of NaOH will slow the oxidation.

In this reporting period, hypochlorite was selected for the study of Cr(III) oxidation in alkaline solutions, and the extensive data and results obtained on this system have been published in the open literature (Jiang et al. 2006) and are briefly discussed below. The dissolved species of Cr(III) hydroxide of different degrees of oligomerization were separated by an ion chromatography technique developed previously and characterized by UV/Vis absorption spectroscopy. Kinetic experiments were conducted to determine the rate of Cr(III) oxidation, separated and unseparated, in alkaline solutions by hypochlorite. The rate of oxidation by hypochlorite is compared with that by hydrogen peroxide. The kinetic data, in conjunction with the information from characterization, help to reveal the effect of oligomerization on the rate of oxidation of Cr(III). Results indicate that hypochlorite can oxidize Cr(III) to Cr(VI) in alkaline solutions, but the rate of oxidation by hypochlorite is slower than that by hydrogen peroxide at the same alkalinity and concentrations of oxidants. The rate of Cr(III) oxidation by both oxidants decreases as the concentration of sodium hydroxide is increased, but the oxidation by hypochlorite seems less affected by the degree of Cr(III) oligomerization than that by peroxide. Compared with oxidation by hydrogen peroxide, where the major reaction pathway has an inverse order with respect to concentration of NaOH, oxidation by hypochlorite has a significant reaction pathway independent of [OH_].

Solubility of Cr(III) Solids and Complexation Reactions of Cr(III) with Inorganic Ligands

The solubility of $Cr(OH)_3$(am) in dilute to concentrated hydroxide, nitrate, and phosphate solutions and the complexation/ion-interaction reactions of Cr(III) with these ligands, along with the thermodynamic interpretations of Cr leaching behavior of the actual high-level radioactive waste tank sludges in caustic solutions, have been presented in previous reports and journal articles (Rai et al. 2002 and 2004).

In addition to hydroxide and phosphate, aqueous-phase carbonate can be present in the tanks in significant concentrations, and it can form strong complexes with Cr(III). Despite the fact that high concentrations of carbonate can be present in tanks and can form significant complexes with Cr(III), no thermodynamic data for this system are available to predict the effect of carbonate on the aqueous behavior of Cr(III) in tanks. Therefore, extensive studies on the solubility of amorphous Cr(III) hydroxide solid in a wide range of pH (3-13), at two different fixed partial pressures of CO_2(gas) (0.003 or 0.03 atm.), and as functions of K_2CO_3 concentrations (0.01 to 5.8 m) in the presence of 0.01 M KOH and $KHCO_3$ concentrations (0.001 to 0.826 m) at room temperature (22 ± 2°C) were carried out to obtain reliable thermodynamic data for important Cr(III)-carbonate reactions. A combination of techniques (XRD, XANES, EXAFS, UV-Vis-NIR spectroscopy, and thermodynamic analyses of solubility data) was used to characterize solid and aqueous species. Pitzer's ion-interaction approach was used to interpret the solubility data. Only two aqueous species [$Cr(OH)(CO_3)_2^{2-}$) and $Cr(OH)_4CO_3^{3-}$] are required to explain Cr(III)-carbonate reactions in a wide range of pH, CO_2(gas) partial pressures, and bicarbonate and carbonate concentrations. Calculations based on density functional theory support the existence of these species. The log K^0 values of reactions involving these species [$Cr(OH)_3(am) + 2CO_2(gas) = Cr(OH)(CO_3)_2^{2-} + 2H^+$; $Cr(OH)_3(am) + OH^- + CO_3^{2-} = Cr(OH)_4(CO_3)^{3-}$] were found to be –(19.07 ± 0.41), -(4.19

± 0.19), respectively. No other data on any Cr(III)-carbonato complexes are available for comparisons. A manuscript on Cr(III) carbonato complexes is being drafted (Rai et al. 2006) and will be submitted in the first quarter of FY2007 for publication in Journal of Solution Chemistry.

PLANNED ACTIVITIES

A third year funding will not be available for this project. A small amount of carry-over funds that are available will be used to finish drafting and submitting a manuscript on Cr(III)-carbonato complexes for open literature publication.

INFORMATION ACCESS

Journal Articles

Rai, Dhanpat,D. A. Moore, N. J. Hess, L. Rao, S. M. Heald. 2006. Chromium(III) Hydroxide Solubility in the Aquesou K^+-H^+-OH^--CO_2- HCO_3^-- CO_3^{2-}-H_2O System: A Thermodynamic Model. *Journal of Solution Chemistry* (To be submitted in first quarter of FY 2007).

Jiang, H., L. Rao, Z. Zhang, and Dhanpat Rai. 2006. Characterization and oxidation of chromium(III) by sodium hypochlorite in alkaline solutions. *Inorganica Chimica Acta* **359**: 3237-3242.

Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao, S. B. Clark. 2004. Chromium(III) Hydroxide Solubility in the Aqueous Na^+-OH^--$H_2PO_4^-$-HPO_4^{2-} -PO_4^{3-} -H_2O System: A Thermodynamic Model. *Journal of Solution Chemistry* 33: 1213-1242.

Rao, L., A. Yu. Garnov, Dhanpat Rai, Y. Xia, R. C. Moore. 2004. Protonation and Complexation of Isosaccharinic Acid With U(VI) and Fe(III) in Acidic Solution: Potentiometric and Calorimetric Studies. *Radiochimica Acta* 92: 575-581

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* 824: CC6.5.1 – CC6.5.6.

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-$NaNO_3$ 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.