

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 sludgewashing 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 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 (H₂O₂, 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 work for FY05 (10/1/2004 – 9/30/2005).

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

The rates of Cr(III) oxidation by two oxidants, peroxide (H₂O₂) and the persulfate (S₂O₈²⁻), 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 the oxidation, and thus the dissolution of Cr; and 2) Although oxidation occurs in alkaline solutions, high concentrations of NaOH will slow the oxidation.

In this reporting period a new oxidant, hypochlorite, was selected for the study of Cr(III) oxidation in alkaline solutions. Hypochlorite is a common ingredient in household cleaning agents and is known to be strongly oxidizing. Its potential use in oxidizing Cr(III) in alkaline solutions and facilitating the removal of Cr from tank wastes makes such study highly relevant to the pretreatment of nuclear wastes.

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).

Figure 1 shows the pseudo first-order rate constants of the oxidation of Cr(III) by hypochlorite as functions of the concentrations of NaClO and NaOH. The rate of Cr(III) oxidation by hypochlorite increased as the concentrations of Cr(III) and hypochlorite were increased, with a first-order dependency on both [Cr(III)] and [NaClO]. However, the rate of oxidation decreased as the concentration of hydroxide was increased. The reaction order with respect to [OH] is either -0.5 or -1, depending on the models selected to fit the data.

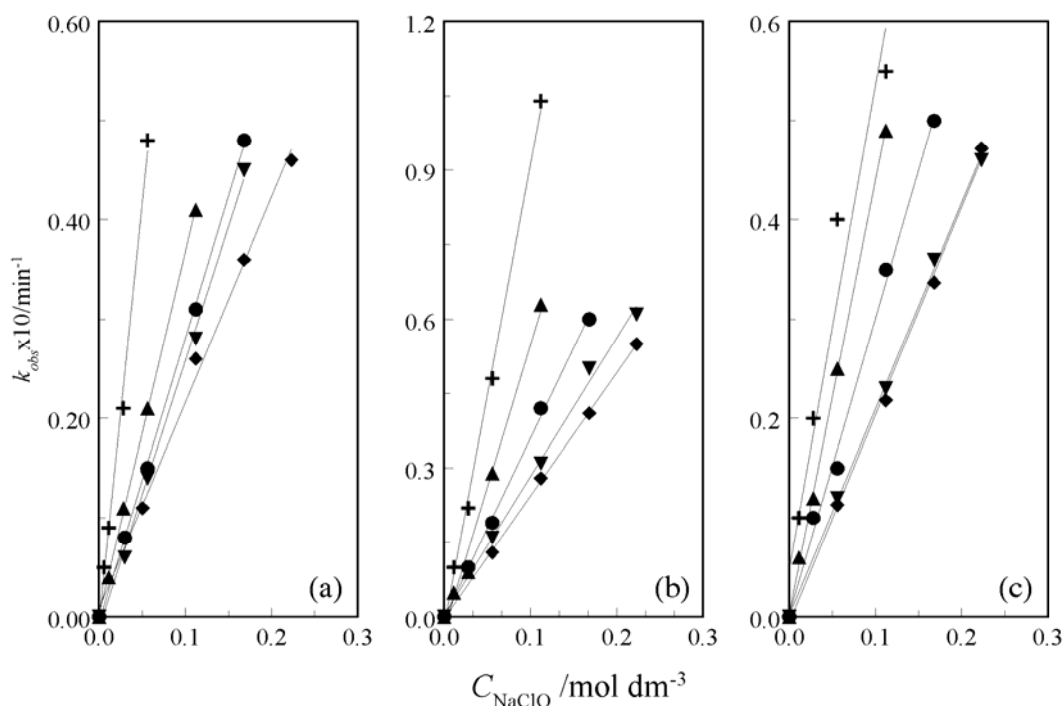


Figure 1 The pseudo first-order rate constant, k_{obs} , as a function of C_{NaClO} at different C_{NaOH} . Symbols: C_{NaOH} (mol dm⁻³) = 0.104 (+), 0.250 (▲), 0.500 (●), 0.750 (▼), 1.00 (◆). $C_{Cr} = 1.4 \times 10^{-4}$ mol dm⁻³. (a) monomer (b) dimer; (c) trimer.

A probable rate equation, similar to that for the oxidation by hydrogen peroxide (Rao et al. 2002), can be suggested for the oxidation of Cr(III) to Cr(VI) by hypochlorite:

$$d[\text{Cr(III)}]/dt = -k_{\text{obs}}[\text{Cr(III)}] = -k[\text{Cr(III)}][\text{NaClO}](1/[\text{OH}^-] + k') \quad (1)$$

The parameters of the rate equation determined in this work are summarized in Table 1, in comparison with the data for hydrogen peroxide (Rao et al. 2002). The results show the following similarities between the two oxidants: 1) both hypochlorite and peroxide can oxidize Cr(III) to Cr(VI) in alkaline solutions; and 2) for both oxidants, the rate of oxidation decreases as the concentration of sodium hydroxide is increased. The results also show the following differences between the two oxidants: 1) in general, the oxidation of Cr(III) by hypochlorite is slower than that by peroxide at the same alkalinity and concentrations of oxidants (see the values of τ in Table 1); 2) the reaction pathway independent of $[\text{OH}^-]$ is more important in the oxidation by hypochlorite than that by peroxide, suggested by the larger k' for hypochlorite; and 3) the rate of oxidation by hypochlorite seems less affected by the degree of oligomerization of Cr(III) than that by peroxide.

Table 1. Comparison of reaction rates for the oxidation of Cr(III) by hypochlorite and peroxide. The error limits in brackets for k and k' represent 3σ .

Cr(III) Species	Hypochlorite			Peroxide ^a		
	k , min ⁻¹	k' , mol ⁻¹ dm ³	τ^b , min	k , min ⁻¹	k' , mol ⁻¹ dm ³	τ^* , min
Monomer	0.071 (5)	1.9 (1)	480	327 (6)	0.07 (9)	0.3
Dimer	0.076 (3)	2.6 (1)	370	11.3 (3)	0.0 (1)	9
Trimer	0.039 (9)	5.2 (2)	410	1.33 (4)	1.34 (4)	32
Unseparated and aged in 8 M NaOH	0.0048 (26)	2.6 (10)	5800	0.032 (2)	0.53 (1)	2040

^a [Rao et al. 2002]

^b Reaction lifetime $\tau = 1/k_{\text{obs}}$. τ is calculated for [oxidant] = 0.01 M and $[\text{OH}^-] = 1$ M.

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). Presented in this report are the results of Cr(III) interactions with carbonate.

Studies on the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ were conducted as a 1) function of pH and time, and at fixed partial pressures of $\text{CO}_2(\text{gas})$ of 0.003 or 0.03 atmospheres (or 0.3 or 3 % $\text{CO}_2(\text{gas})$), 2) function of K_2CO_3 concentrations and time and at a fixed hydroxide concentration of 0.01 M, and 3) function of KHCO_3 concentrations and time (Figures 2 and 3). The observed concentrations at different equilibration periods are similar to each other in all of these sets, indicating that the steady state concentrations are reached in less than about 20 days. These data are consistent with the earlier studies (Rai et al. 2004) where equilibrium with $\text{Cr}(\text{OH})_3(\text{am})$ is reached in similar time frames. The $\text{Cr}(\text{OH})_3(\text{am})$ solubility is observed to increase dramatically at pH values between about 8 and 9 for the sets with fixed partial pressures of $\text{CO}_2(\text{gas})$ (Figures 2), at $>0.03 \text{ M KHCO}_3$ (Figure 3), and at $>0.32 \text{ M K}_2\text{CO}_3$ (figure 3). The comparison of the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ in the absence and in the presence of different concentrations of $\text{CO}_2(\text{gas})$ (Figure 4) shows that 1) the observed Cr concentrations in the acidic regions of both systems are similar, and 2) the dramatic increases in the Cr concentrations in the presence of carbonate must result from complexation of Cr(III) with carbonate. These data in conjunction with solid phase characterizations will be used to develop a comprehensive thermodynamic model for predicting the leachability of Cr(III) solids and aqueous speciation of Cr(III) in radioactive tank-waste/solutions under different sludge-washing scenarios.

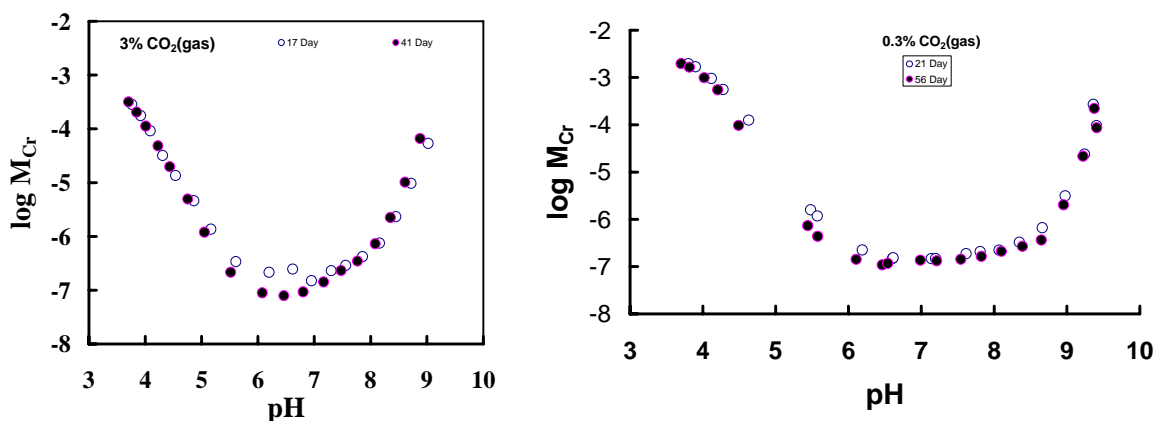


Figure 2. $\text{Cr}(\text{OH})_3(\text{am})$ solubility as function of pH and time in the presence of 3% $\text{CO}_2(\text{gas})$ (left) and 0.3% $\text{CO}_2(\text{gas})$ (right).

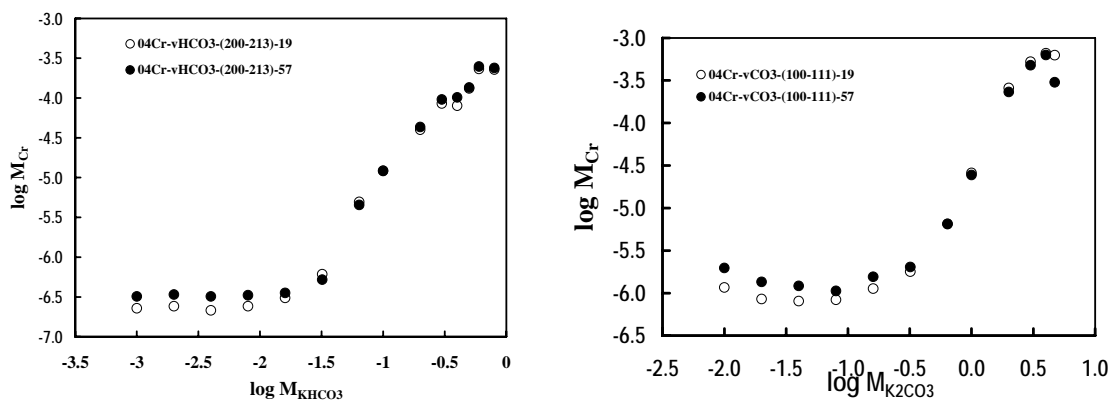


Figure 3. $\text{Cr}(\text{OH})_3(\text{am})$ solubility as function of time (open circles 19 days and closed circles 57 days) and KHCO_3 (left) and K_2CO_3 (right).

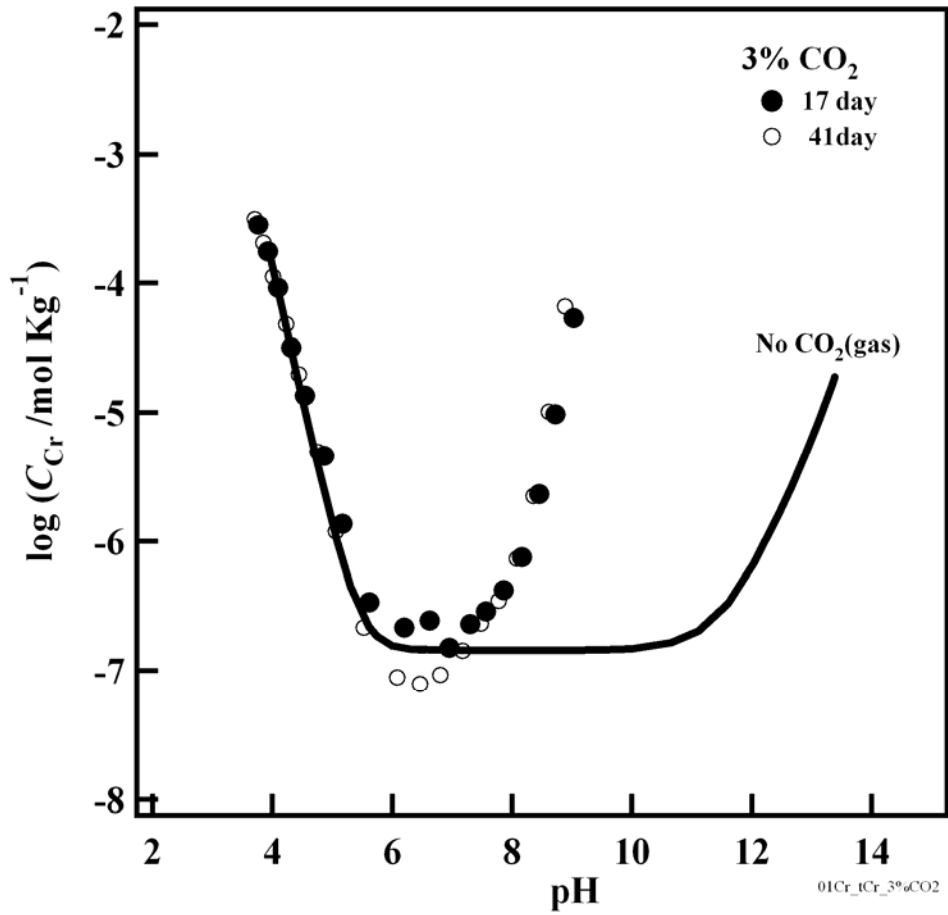


Figure 4: Comparison of $\text{Cr}(\text{OH})_3(\text{am})$ solubility in presence and absence of 3% $\text{CO}_2(\text{gas})$. Solid line shows solubility in the absence of $\text{CO}_2(\text{gas})$.

LITERATURE CITED

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Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao, S. B. Clark. 2004. Chromium(III) Hydroxide Solubility in the Aqueous Na⁺-OH⁻-H₂PO₄⁻-HPO₄²⁻-PO₄³⁻-H₂O System: A Thermodynamic Model. *Journal of Solution Chemistry* 33: 1213-1242.

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.

Zhang, Z., L. Rao, Dhanpat Rai, S. B. Clark. 2004. Characterization of Chromium(III) Hydroxide Solids and Their Oxidation by Hydrogen Peroxide. In *Scientific Basis for Nuclear Waste Management XXVIII*, edited by John M. Hanchar, Simcha Stroes-Gascoyne, and Lauren Browning (Mater.Res. Soc. Symp. Proc. 824, Warrendale, PA , 2004), CC6.5.

PLANNED ACTIVITIES

The kinetic studies of the oxidation of Cr(III) by hypochlorite will continue, with the emphasize on oxidation of Cr(OH)₃ solids in alkaline solutions and revealing the reaction mechanisms. Studies on the solubility of Cr(OH)₃(am) in the carbonate system will be continued and the emphasis of these studies will shift from the aqueous phase to the characterization of the solid phase in the presence of carbonate. The resulting data from the Cr(III)-carbonate system will be used to prepare a journal article on this topic. Studies on the solubility of Cr(III) solid solutions (e.g., (Fe,Cr)(OH)₃(am)) will be initiated.

INFORMATION ACCESS

Journal Articles

Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao, S. B. Clark. 2004. Chromium(III) Hydroxide Solubility in the Aqueous Na⁺-OH⁻-H₂PO₄⁻-HPO₄²⁻-PO₄³⁻-H₂O System: A Thermodynamic Model. *J. Sol. Chem.* 33, 1213-1242 (2004).

Zhang, Z., L. Rao, Dhanpat Rai, S. B. Clark. 2004. Characterization of Chromium(III) Hydroxide Solids and Their Oxidation by Hydrogen Peroxide. In *Scientific Basis for Nuclear Waste Management XXVIII*, edited by John M. Hanchar, Simcha Stroes-Gascoyne, and Lauren Browning (Mater.Res. Soc. Symp. Proc. 824, Warrendale, PA , 2004), CC6.5.

Jiang, H., L. Rao, Z. Zhang, D. Rai. Characterization and Oxidation of Chromium(III) by hypochlorite in Alkaline Solutions. A manuscript in preparation.

Rai, Dhanpat, D. A. Moore, N. J. Hess, L. Rao. Chromium(III) Hydroxide Solubility in the Aqueous K^+ - H^+ - OH^- - H_2CO_3 - HCO_3^- - CO_3^{2-} - H_2O System: A Thermodynamic Model. A manuscript in preparation.

Presentations

L. Rao. Characterization and Oxidation of Chromium(III) by hypochlorite in Alkaline Solutions. Submitted for presentation at the Global 2005 international conference on Nuclear Energy System for Future Generation and Global Sustainability, Tsukuba, Japan, October 2005.