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Project Title: **Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate**

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**Enhanced Sludge Processing of HLW:
Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Oxidants**

Mid-Year Progress Report

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Goals of Project:

The objective of this project is to develop the scientific basis for hydrothermal separation of chromium from High Level Waste (HLW) sludges. Our work is aimed at attaining a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions that will ultimately lead to an efficient chromium leaching process.

Technical Description of Work:

We will determine the rates of oxidation and the products for the reactions of chromium(III) oxides and hydroxides, mixed Fe:Cr species, and other selected minerals in simple hydrothermal solutions containing NaOH, O₂, and NaNO₃. We will also examine the effects of additional components (EDTA, aluminate, carbonate, nitrite, phosphate, chloride, nickel, iron) on reaction chemistry. Studies will be conducted at temperatures and pressures ranging from 150 to 450 °C and 10 to 40 MPa. The phase behavior and diffusion constants of selected species and mixtures will be determined. A reaction model will be formulated from experimental results and compared to experimental data for validation. The speciation of TRU will be examined in waste simulants at hydrothermal conditions optimal for chromium dissolution.

Accomplishments to Date:

This report summarizes our research over the first 2.5 years of a 3 year project. We have examined the dissolution of chromium(III) oxides/hydroxides using different oxidants as a function of temperature, oxidant, alkalinity, and added organics and metals. Work on this project began in September 1996.

During the first year, the research focused on four areas:

- (1) Review and evaluation of scientific literature on the chemistry and reactions of chromium in aqueous solutions.
- (2) The design and construction of batch, stirred batch, and packed bed reactors.
- (3) The initial measurement of reaction rates for chromium oxide in simple mixtures of water, nitrates, and hydroxides.
- (4) The measurement of the diffusion coefficients and electrical conductances of aqueous inorganic nitrate solutions.

During the second year, research focused on two areas:

- (5) The detailed determination of the kinetics of dissolution of chromium hydroxide by oxygen.
- (6) The initial determination of the dissolution of chromium hydroxide by nitrate.

During the third year, the research has focused on four areas:

- (7) Development of a global kinetic model for the dissolution of chromium hydroxide by oxygen in alkaline solution.
- (8) Development of a reaction model for the dissolution of chromium hydroxide by oxygen.
- (9) Determining the effects of added organics, and metals on reaction kinetics.
- (10) Examining the reactions of TRU under hydrothermal conditions.

Following, we present a summary of the accomplishments, the results in each area, and a discussion of the possible applications to HLW sludges.

(1) Evaluation of Literature: A literature review and analysis has been completed on the preparation and aqueous chemistry of chromium oxide. Thermodynamically, the forms of chromium oxide depend on the temperature and its environment. The dissolution of chromium oxide with different reagents was reported. Segal and Williams (1986) studied the oxidative dissolution of chromium (III) oxide (calcined at 1000 °C under argon) by large excess of potassium permanganate at temperature range 43-140 °C. They found that the dissolution rate depends on the temperature, concentration of oxidant, and pH. The calcined temperature affecting dissolution rate has been reported (Rodenas et al., 1993; Reartes et al., 1995; Mills and Sawunyama, 1993; Blesa et al., 1994), mostly in acid conditions. However, there is no report concerning the possible forms of chromium oxide other than Cr(III) in the dissolution study.

Cr(III) and Cr(VI) are both found in Hanford tank sludge (Blanchard et al., 1995). Cr(III) in tank sludge is proposed as chromium in Cr:FeOOH and with disordered oxygen. The form of the chromium in the tank wastes is not well known and so at this time it is not possible to prepare tank wastes simulants which we are confident will mimic tank sludge.

Blanchard, D. L.; Conradson, S. D.; Hess, N. J.; Melethil, P. K.; Report, TWRSPP-95-048, 1995.
Segal, M. G.; Williams, W. J. J. Chem. Soc., Faraday Trans. 1, 82, 3245 (1986).
Rodenas et al. Can. J. Chem. 71, 771 (1993).
Reartes et al. Langmuir 11, 2277 (1995).
Mills, A.; Sawunyama, P. J. Chem. Soc., Faraday Trans., 89(18), 3389 (1993).
Blesa et al. Chemical Dissolution of Metal Oxides. CRC Press, 1994.

(2) Design and construction of reactors: Three new types of experimental reactors for study of the dissolution of chromium oxide were built for this project. These include: small, Teflon-lined, batch reactors; stirred batch reactor systems; and a packed-bed flow reactor system.

The small batch reactors are Teflon coated swagelock bulkhead unions. The reactors are heated for reaction times varying from hours to days using a fluidized sand bath.

The stirred batch reactor is a 300 ml, high pressure SS#316 vessel. The reactor is Teflon lined and nickel coated to minimize the leaching of chromium from the stainless steel. The thermocouple and magnetic stir bar are Teflon coated, while Teflon tubing and filters are used in the sampling system. Temperature and pressure indicators monitor reactor conditions. Oxidation reactions are initiated by rapidly pumping the oxidant into the reactor after it has reached operating temperature. Samples are removed periodically (minutes to hours) to determine reaction kinetics.

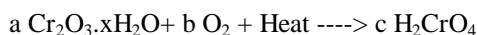
The packed-bed flow reactor is a high pressure SS# 316 tube. A concentric nickel liner runs the length of the pressure vessel and is sealed to the pressure vessel at both ends. High pressure distilled water flows between the pressure vessel and nickel liner walls to balance the pressure in the liner. Chromium oxide samples are loaded into the central section of the liner. The soluble reagents are pressurized, heated, and pumped through the solid packed bed. Filters at the exit of the bed keep the solid material stationary. The reactor effluent is cooled, depressurized, collected and analyzed. The reaction time for the soluble material is determined by mass flow rate, bed free-volume, and the density of the reaction mixture at reaction temperature and pressure. The reaction time for the solid material is determined by the total flow duration. At the end of the experiment the bed material is removed and analyzed. The bed material may contain both unreacted starting material and insoluble products that could not be transported out of the reactor.

In collaboration with two other separate Los Alamos projects examining the hydrothermal oxidation of combustible wastes, batch and flow reactor systems were built and installed in the Los Alamos plutonium

facility. These reactors are being used by this project in the third year to study the chemistry of TRU at selected hydrothermal conditions.

(3) *Initial Kinetics experiments:* Initial kinetics experiments were performed using the small Teflon lined batch reactors heated in a sand bath. Hydrated chromium oxide was prepared by adding sodium hydroxide solution to a chromium nitrate solution at room temperature. The resulting gel was washed and then dried at 120 °C for 24 hours. Separate samples were calcined at 120, 200, 300, 450, 700 °C for 5 hours in air.

Dissolution/reaction experiments for the samples calcined at the various temperatures were performed at 25, 100 and 200 °C. The samples were reacted separately with deionized water, NaNO₃ / NaOH, and nitric acid solutions. The use of nitric acid or NaNO₃/NaOH did not significantly increase the amount of Cr dissolved. The samples calcined at 120 °C show little dissolution of Cr. The greatest dissolution occurs for the samples calcined in the 200 to 300 °C range. These results suggest that at higher calcine temperatures (>120 °C) some of the Cr(III) is converted to Cr(VI) via the reaction:



The Cr(VI) produced during calcining easily dissolves, leaving the insoluble Cr₂O₃ behind. Calcining in an inert atmosphere of argon or nitrogen should reduce the amount of Cr(VI) in the samples.

(4) *Diffusion Experiments:* The molecular diffusion of inorganic nitrate species in sub and supercritical water were measured at temperatures between 200 and 500 °C and pressures between 25 and 100 MPa. In the concentrated salt solutions the critical slowing down of the diffusion was significant as far as 30 MPa from the phase transition pressures. Ordinary binary mass diffusion was about 15 times faster at the higher temperatures than at 25 °C. Experimental results agree well with predictions from the Stokes-Einstein equation, where the diffusing species is represented as a hydrated contact pair. A manuscript summarizing the results of this work has been prepared and submitted to *International Journal of Thermophysics*. A paper discussing the work was presented at the Thirteenth Symposium on Thermalphysical Properties.

The electrical conductances of aqueous solutions of inorganic nitrates at 25 to 505 °C and 100 to 490 bar were measured. The alkali nitrates show behavior similar to the alkali chloride series: the electrical conductance decreases with decreasing cation radius. This seemingly paradoxical result is due to the stronger electric field and hence the greater tendency for ion pairing and larger solvation spheres associated with the smaller cations. Nearly complete ion association is observed at low-density supercritical conditions. A manuscript summarizing the results of this work has been published in the *Journal of Supercritical Fluids*.

(5) *Detailed Kinetics Measurements:* Chromium hydroxide, Cr(OH)₃ • 3H₂O, was selected as the first chromium compound for this study. Based on available literature, chromium hydroxide should be the main chromium compound in the HLW sludge. Dissolution experiments on chromium hydroxide were conducted in two types of reactors: a stirred batch system and a continuous flow reactor. Liners of nickel or Teflon were used to prevent corrosion or leaching of chromium from the reactors. Chromium hydroxide was prepared according to literature reports.

The two oxidants investigated were O₂ and nitrate. Dissolution/reaction experiments for chromium hydroxide in a batch reactor by O₂ were performed at reaction temperatures ranging from 75 to 200 °C. The dissolution of chromium hydroxide using oxygen follows:

(a)

When nitrate was used as an oxidant, the experiments were performed in both continuous flow and batch reactors at temperatures ranging from 250 to 410 °C and pressures ranging from 2 to 26 MPa. The reaction is

(b)

All experiments were performed in alkaline solutions from 0.01 to 4 M NaOH. A caustic environment was chosen because the Hanford waste is alkaline and neutralization is not practiced. Anions (CrO_4^{-2} , NO_3^- , NO_2^-) were measured by ion chromatography.

Dissolution of chromium hydroxide under alkaline conditions with oxygen was studied at temperatures ranging from 70 to 200 °C. Hydroxide concentrations were varied from 0.01 to 4 M (pH 12 to 14.5) and oxygen concentrations in solution were varied from 0.4 to 4.4 mM to determine the effect of oxygen concentration and the caustic environment on the dissolution rates.

An increase in hydroxide concentration increased the dissolution rate with all other conditions being similar. The dependence was found to be almost linear; with a doubling of hydroxide concentration the dissolution rate nearly doubled. The oxygen concentration was determined based on the overall system pressure, the partial pressure of oxygen and the headspace volume. Henry's Law constants were used to determine the concentration of dissolved oxygen in solution. An increase in oxygen concentration increased the dissolution rate but at a much lesser rate than the effect of hydroxide concentration. A four-fold increase in oxygen concentration was required to double the chromium dissolution rate. Temperature had the most significant effect on chromium dissolution with oxygen. Increasing the temperature 100 °C (from 100 to 200 °C) increased the rate nearly 150 times. The effects of chromium hydroxide surface morphology have not yet been determined.

(6) *Dissolution by Reaction with Nitrate:* Nitrate was used as an oxidant for dissolution of chromium at higher temperatures to 400 °C. At reaction temperatures below 250 °C, no dissolution of chromium was observed. At a nitrate concentration of 0.125 M, hydroxide concentration of 1.0 M and temperatures ranging from 250 to 400 °C, the rate of oxidation to CrO_4^{-2} per gram of $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ is:

(7) *Global Kinetic Rate Expression:* From experiments performed on the reaction of chromium hydroxide with oxygen under alkaline conditions during the second and third years, a global rate expression for Reaction (a) was determined. The global rate can be expressed as follows:

where r is the rate per unit weight of chromium, W_0 is the initial mass of chromium, k is the rate coefficient, and $[\text{OH}^-]$ and $[\text{O}_2]$ are the concentration of hydroxide and oxygen in solution, respectively. The dimensions of k depend on the values of a and b , and are frequently found to be non-integral. The initial rate of dissolution in each experiment was used in the fit and it was assumed that the reactions exhibit Arrhenius behavior. The result of the regression, with 95% confidence, is the rate expression:

(8) *Mechanism for Dissolution of Chromium Hydroxide by Oxygen:* The chemistry of chromium(III) at different pH levels has been well studied by others. The hydrolysis behavior of Cr^{3+} is characterized by the slow kinetics of its polymerization reactions. The formation of Cr(III) hydroxides is an extension of the polymerization reactions. The empirical formula, $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, is consistent with large polymers formed by $[-\text{Cr}(\text{OH})_3(\text{H}_2\text{O})-]_n$ chains. The solubility of chromium (III) hydroxides depends on their degree of polymerization and the solution environment (pH, ionic strength, and temperature). Solubilized Cr^{3+} is formed ($\text{Cr}(\text{OH})_4^-$) when adding chromium salt into alkaline solution (pH > 12.6). Chromium (III) hydrolysis constants and solubility of chromium hydroxide have been studied (Rai et al. 1987).

Our results show that hydrolysis of chromium (III) on solid surfaces is essential for oxidative dissolution of chromium hydroxide by oxygen, and the degree of polymerization of chromium hydroxide prepared is high enough to resist the formation of dissolved chromium species (e.g. $\text{Cr}(\text{OH})_4^-$). Thus the reaction mechanism can be illustrated as follows:

The adsorption of oxygen on the surface of chromium is less important because the concentration of hydroxide in solution is normally three orders of magnitude higher than the concentration of oxygen. This simplified rate of dissolution derived from Langmuir-Hinshelwood model can be expressed as

The initial rate of dissolution for a reaction temperature of 125 °C was used to determined by linear regression of the equation:

Rai, D.; Sass, B. M.; Moore, D. A. *Inorganic Chemistry* **1987**, *26*, 345-349.

(9) *Determining the effects of added organics, and metals on reaction kinetics:* Experiments examining the effects of added organic material and metal ions are in progress. Thus far, neither the addition of organic material or other metals seems to significantly alter the reaction rates.

(10) *Examining the reactions of TRU under hydrothermal conditions:* Several experiments examining the behavior of TRU under hydrothermal conditions have been completed. These experiments are in collaboration with another DOE project. At high temperatures, plutonium and americium react with oxygen to form insoluble solids that are easy to remove by filtration. More experiments are planned.

In conclusion, oxidative dissolution of chromium hydroxide can be accomplished at high temperatures with nitrate and at relatively low temperatures with molecular oxygen. We have determined the reaction rates for both systems. We have also determined diffusion constants and speciation of nitrates at relevant hydrothermal conditions. Our results suggest that at reaction temperatures (>125 °C) slightly higher than the current baseline sludge washing conditions, chromium can be rapidly and efficiently dissolved from HLW sludge using oxygen or air. Our results also show that increasing the hydroxide concentration will increase the rate of reaction and decrease the required operating pressures to near ambient.

Projections:

During the remainder of FY99 we will complete our scope of work by completing areas (7), (9) and (10). We will finish analyzing the data for these areas, and prepare and submit two manuscripts. We have already written a manuscript describing our work in areas (3), (5), (7), and (8) and will submit it to the journal, *Environmental Science and Technology*.

Additional Information:

Collaborative work on this project is being performed with Professors Earnst Gloyna and Keith Johnston of The University of Texas at Austin, Professor Tony Arrington of Furman University, and Rosemary Effiong of Xavier University in Louisiana. A graduate student from Professors Gloyna's group spent two years at Los Alamos measuring chromium dissolution kinetics. Professor Arrington and several undergraduate students from Furman have spent three summers at Los Alamos performing kinetics and spectroscopic experiments. Rosemary Effiong and two undergraduate students have spent two summers at Los Alamos performing kinetics experiments. In addition graduate and undergraduate students from The University of Toledo, Toledo, Ohio and the University of New Mexico have spent summers at Los Alamos working on the project.

Three manuscripts have been prepared based on work performed for this project:

Electrical conductances of aqueous solutions of inorganic nitrates at 25-505 °C and 100-490 bar, Marcel G. E. Goemans, Timothy J. Funk, Michael A. Sedillo, Steven J. Buelow and Graydon K. Anderson, Published in the *Journal of Supercritical Fluids* **11**(1997) pp 61-72.

Molecular Diffusion of inorganic nitrate species and ketones in subcritical and supercritical water,† M.G.E. Goemans, T.J. Butenhoff, E. F. Gloyna, G. K. Anderson, and S. J. Buelow, Submitted to the *International Journal of Thermophysics*.

Oxidative dissolution of chromium trihydroxide by oxygen under hydrothermal conditions,† Zhong Y. Ding, Tykler Mosher, Bernie Foy, Jeanne Robinson, and Steven Buelow, To be submitted to *Environmental Science & Technology*.