

FINAL REPORT

Project ID Number: 54828

Project Title: Processing High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water

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Undergraduate Students: Seven undergraduate students from Furman worked on this project at Los Alamos National Laboratory during the summers of 1997, 1998, 1999, and 2000.

Report:

Research Objective

We have been engaged in a collaborative research effort with Los Alamos staff scientists Steven Buelow and Jeanne Robinson, staff members in group CST-6. The work proposed by these LANL staff scientists is directed towards the destruction of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Our own work has been focused on a careful kinetic study of oxidation reactions of hydrogen peroxide with chromium hydroxide. This reaction occurs readily at ambient temperatures.

Research Progress and Implications

Most of the work during the four years of the grant was carried out at Los Alamos National Lab. During each of the summers from 1997 to 2000 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Laboratory. We give below reports for each of the four years.

Summary

The original goal of studying the kinetics of redox reactions in supercritical water was changed with our recognition that the high temperatures and pressures of this medium make it unlikely that large scale remediation efforts will actually use supercritical water. Our experimental efforts were directed towards the characterization of the relatively rapid reaction of chromium(III) hydroxide with hydrogen peroxide in strongly basic solutions. The kinetics of this reaction have proven to be complex and a complete kinetic model represent a considerable challenge. We have developed a general model that involves several reactions that are pseudo first order in chromium and that have complex dependence on both hydroxide ion and hydrogen peroxide concentrations. Both hydrogen peroxide and its conjugate base, HO_2^- , are involved as oxidizing agents. In this regard we have examined the Raman spectrum of HO_2^- and will publish the assignment of its vibrational spectrum in water.

1997

All of the work during this first year was carried out at Los Alamos National Lab. During the summer program at LANL all equipment and supplies were provided through Dr. Buelow's program at LANL. We have now set up a Raman spectroscopy lab at Furman. Using departmental funds we purchased an optical bench, a laser, and a CCD detector, and a grant from the Dreyfus Foundation assisted in the purchase of a Raman spectrometer. We are now able to carry out experiments using the Raman system at Furman. Our plan is to continue the summer collaboration at LANL and carry out experiments at Furman during the academic year.

During the summer of 1997 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Lab. Dana Olsen is a senior chemistry major, and Robb Lanning a junior chemistry major. The research was conducted in collaboration with Steven J. Buelow, a staff scientist in Group CST-6. Our EMSP grant was written as a collaborative program of research with Dr. Buelow, continuing an association of six years.

The first two weeks of the summer program were spent setting up the Raman spectrometer system with a high temperature-high pressure cell. Initial experiments examined the reaction of nitrate anion with organic species such as ethanol and acetate anion. These early experiments gave erratic results because of high levels of scattered light from the Raman cell caused by particle formation at high temperatures.

Beginning with the third week we began working more directly with Dr. Buelow and a post doctoral fellow and graduate student who were working on his EMSP project. This goal of this project is to find ways of removing Cr(III) compounds from Hanford tank wastes before the solids are formed into glass ingots for permanent storage. High chromium content results in imperfect, cracked glass ingots.

Our efforts began with an examination of spectroscopic methods for characterization of solids formed when Cr(III) solutions are made basic. The chemistry of chromium in basic solutions is amazingly complex with hydroxides and oxides present in varying degrees of oligomerization. It is important to learn how the history of the sample affects the distribution of products, especially the temperature of the solution and its pH. A number of experiments were carried out on seven samples prepared in the laboratory. These samples were prepared by Dr. Ding, the post doctoral fellow, following literature procedures to make $\text{Cr}(\text{OH})_3$, $\text{CrO}(\text{OH})$, and Cr_2O_3 . Other samples were prepared then calcined at various temperatures up to 700°C . We determined that infrared spectra of the samples in KBr pellets provided the most reliable diagnostic information in a short time. Both Raman spectra and X-ray photoelectron spectra provided some structural information but were not as useful as IR spectra. The IR spectra indicated the presence and relative amounts of $\text{Cr}(\text{OH})_3$, Cr_2O_3 , and CrO_4^{2-} . We also observed a band attributed to carbonate, which forms when carbon dioxide is absorbed from the atmosphere by the basic solution.

Along with these spectroscopic characterization studies we began experiments on the dissolution and oxidation of chromium (III) compounds. All of the samples prepared by Dr. Ding were treated by several different methods. Visible spectra of samples treated with DI water and filtered showed the presence of chromate in the water for samples calcined at 200°C or higher. None of the Cr(III) compounds dissolved. The same samples were stirred with aqueous solutions of oxalic acid. No additional solubility was noted with oxalic acid.

All of the samples showed rapid reaction with basic hydrogen peroxide solutions with formation of yellow supernatant solutions. Quantitative results were obtained for the fraction of each sample dissolved in this treatment. Infrared spectra of the remaining solid showed that everything except Cr_2O_3 was dissolved in this reaction.

A number of experiments were conducted to determine if Cr(III) compounds could be oxidized by NO_3^- in high temperature water. These reactions were carried out in the high temperature Raman cell. In none of the experiments did we observe a decrease in the intensity of the nitrate band at 1050 cm^{-1} , nor did we see the chromate band at 850 cm^{-1} grow in. The dark green color of the solutions reduced the intensity of scattered Raman light, and formation of solids above 300°C blocked the laser beam at the lower diamond window.

Dana Olsen followed the change in pH as $\text{Cr}(\text{NO}_3)_3$ was added to NaOH solutions of in an attempt to learn something about the stoichiometry of chromium hydroxide formation. She found that in the early stages more than 4 hydroxides reacted with chromium. The final stoichiometry was convincingly close to the 1:3 ratio expected for $\text{Cr}(\text{OH})_3$.

Robb Lanning studied the kinetics of the reaction of Cr(III) with basic hydrogen peroxide by following the change in pH as the reaction proceeds. The data he generated at different concentrations of reactants convince us that the reaction is complex and not easily interpreted in terms of a simple order rate equation.

In the course of Robb's experiments we noted that the addition of NaOH to H_2O_2 resulted in the reduction of the O-O stretch band and appearance of a new band, which we tentatively assign to the HO_2^- anion. We have been unable to find a literature reference to the Raman spectrum of this species. We will carry out the experiment with D_2O_2 to confirm this assignment.

1998

Most of the work during the second year of the grant was carried out at Los Alamos National Lab. During the summer of 1998 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Laboratory. David Pond graduated from Furman in May, 1999, and Ginger Denison continued working at LANL again in the summer of 1999. We are now able to carry out experiments using the new Raman system recently installed at Furman. Two students, David Pond and Robb Lanning, who worked on the project in 1997, continued their research for one semester at Furman during the 1998-99 academic year.

We began work with a new high pressure diamond-window cell machined from Inconel. The diamond windows are seated using gold gaskets. We were never able to get a seal to hold above 374 °C. The Inconel may be too hard to provide a seal at higher temperatures or the coefficient of thermal expansion may be too large. As a result of the shortcomings of this cell we devoted our attention to two sets of experiments that could be carried out at ambient temperatures: kinetics of the reaction of chromium hydroxide with hydrogen peroxide in basic solution, and spectroscopy of the hydroperoxide anion, HO_2^- .

Ginger Denison carried out an extensive set of experiments using UV-visible spectroscopy to follow the production of chromate ion, CrO_4^{2-} , the product of oxidation of $\text{Cr}(\text{OH})_4^-$ by H_2O_2 in basic solutions. The reactions were carried out under pseudo first order conditions with OH^- and H_2O_2 present in excess. The rate of reaction was found to depend on the aging of the chromium hydroxide solutions, getting slower the longer the solution ages before reaction. We attribute this behavior to oligomerization of the chromium hydroxide solution. The decay of chromium hydroxide concentration with time cannot be fit to a single exponential function. We get good fits of the data to two or three exponential functions. Such behavior is consistent with different degrees of polymerization leading to forms of the hydroxide that react at different rates—slower rates at higher degrees of polymerization. The rate of reaction was found to decrease with increasing concentration of hydroxide ion under our experimental conditions. The rate initially increased with increasing hydrogen peroxide concentration, but at the higher concentrations of H_2O_2 the rate of reaction decreases. The reaction was carried out over a temperature range from 15 to 25 °C. The Arrhenius plot of these data gives an activation energy of 53 kJ/mol. The rapid reaction of chromium hydroxide at room temperature makes this reaction promising as a means of treating Hanford tank wastes which are high in chromium concentration.

The second set of experiments has grown out of our observation of the O-O stretching vibration in the Raman spectrum in the solutions prepared for the kinetic studies. In the presence of OH^- a new Raman band appears at 850 cm^{-1} . We identify this band as the O-O stretch of the hydroperoxide anion. Because hydrogen peroxide is a stronger acid than water, HO_2^- is the dominant form of hydrogen peroxide in basic solution. We want to determine which species is the actual oxidizing reagent in the reaction with chromium hydroxide, but have not yet designed experiments to answer this question. There is very little information in the literature on the vibrational spectroscopy of HO_2^- . We have examined the Raman spectrum of aqueous solutions of HO_2^- formed by reaction of OH^- with H_2O_2 and Na_2O_2 with H_2O and with D_2O . Evaporation of these solutions provides crystalline solids, for which we have obtained infrared and Raman spectra. Extensive *ab initio* calculations have been carried out to confirm this assignment.

1999

Ginger Denison and Shane Golden carried out an extensive set of experiments using UV-visible spectroscopy to follow the production of chromate ion, CrO_4^{2-} , the product of oxidation of $\text{Cr}(\text{OH})_4^-$ by H_2O_2 in basic solutions. The reactions were carried out under pseudo first order conditions with OH^- and H_2O_2 present in excess. The rate of reaction was found to depend on the aging of the chromium hydroxide solutions, getting slower the longer the solution ages before reaction. We attribute this behavior to oligomerization of the chromium hydroxide solution. The decay of chromium hydroxide concentration with time cannot be fit to a single exponential function. We get good fits of the data to two or three exponential functions. Such behavior is consistent with different degrees of polymerization leading to forms of the hydroxide that react at different

rates— slower rates at higher degrees of polymerization. The rate of reaction was found to decrease with increasing concentration of hydroxide ion under our experimental conditions. The rate initially increased with increasing hydrogen peroxide concentration, but at the higher concentrations of H_2O_2 the rate of reaction decreases. The reaction was carried out over a temperature range from 15 to 25 °C. The Arrhenius plot of these data gives an activation energy of 63 kJ/mol. The rapid reaction of chromium hydroxide at room temperature makes this reaction promising as a means of treating Hanford tank wastes which are high in chromium concentration.

We have been able to fit the dependence of the effective rate constants for Cr(III) decay on concentration of H_2O_2 and OH^- by including two reactions. One reaction involves the conjugate base, HOO^- as the oxidizing agent, and the other involves neutral hydrogen peroxide as the oxidizing agent. The order of reaction is complex and depends critically on the acid base equilibrium for formation of HOO^- by reaction of H_2O_2 with OH^- .

The second set of experiments has grown out of our observation of the O-O stretching vibration in the Raman spectrum in the solutions prepared for the kinetic studies. In the presence of OH^- a new Raman band appears at 850 cm^{-1} . We identify this band as the O-O stretch of the hydroperoxide anion. Because hydrogen peroxide as a stronger acid than water, HO_2^- is the dominant form of hydrogen peroxide in basic solution. We want to determine which species is the actual oxidizing reagent in the reaction with chromium hydroxide, but have not yet designed experiments to answer this question. There is very little information in the literature on the vibrational spectroscopy of HO_2^- . We have examined the Raman spectrum of aqueous solutions of HO_2^- formed by reaction of OH^- with H_2O_2 and Na_2O_2 with H_2O and with D_2O . Evaporation of these solutions provides crystalline solids, for which we have obtained infrared and Raman spectra.

Extensive *ab initio* calculations have been carried out to confirm this assignment. Agreement between the calculated and experimental vibrational frequencies is obtained only when two waters of hydration attached to HOO^- are included in the calculation. For a series of species with O-O bonds a good correlation exists between the calculated charge on oxygen atoms and the observed vibrational wavenumber.

2000

Ginger Denison continued work with the PI at LANL. She continued to investigate the kinetics of oxidation of Cr(III) in basic solution using hydrogen peroxide as the oxidizing agent. She determined the multi-exponential rate constants for samples with different aging histories covering periods up to several weeks of aging. Work is continuing on the kinetics of samples of chromium hydroxide that have been aged for more than one year. These reactions are slower than those of recently prepared samples, but we have found that at temperatures above 35 °C the reaction does proceed to convert Cr(III) to Cr(VI). At higher temperatures a greater fraction of the chromium hydroxide reacts. Mathcad was used to model the dependence of effective rate constants on the concentrations of hydroxide and hydrogen peroxide. Data collected during the grant period cover a wide range of concentration conditions. These data are being used to test the general model of a complex reaction involving at least two different reactions with different oxidizing agents.

Kristen Little worked at Los Alamos with David Morris on the speciation of europium as a surrogate for uranium in clays using emission spectroscopy. David has had an EMSF grant, and Kristin's project was related to his interest in remediation of soils contaminated with uranium.

Information Access

Five students have given talks at the Southeast Regional ACS meeting and the National Conference of Undergraduate Research. Two posters were presented at the ACS meeting in New Orleans on August 22, 1999. Ginger Denison presented a talk on her work at the annual meeting of the Beckman Scholars in Newport Beach, CA in August, 2000. Kristin Little will present her work at the NCUR meeting in Lexington, KY in March, 2001. Senior papers by students who have worked on this project are available from the PI. A manuscript on the vibrational spectrum of HO_2^- is nearly complete and will be submitted to JACS.