

## SUMMARY/PROGRESS REPORT

Project ID Number: 54828

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

Principal Investigator: Charles A. Arrington, Jr.  
Chemistry Department  
Furman University  
Greenville, SC 29613  
(864)294-3369 [tony.arrington@furman.edu](mailto:tony.arrington@furman.edu)

Undergraduate Students: Six undergraduate students from Furman have worked on this project at Los Alamos National Laboratory during the summers of 1996, 1998, and 1999.

### **Report:**

#### Research Objective

We are 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 third year of the grant was carried out at Los Alamos National Lab. During the summer of 1999 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Laboratory. Ginger Denison, a senior, and Shane Golden, a junior, continued the research during the current academic year at Furman. Both students will return for summer research at Los Alamos in the summer of 2000. Ginger is going to graduate school at Indiana University.

Ginger carried out an extensive set of experiments using UV-visible spectroscopy to low the production of chromate ion,  $\text{CrO}_4^{2-}$ , the product of oxidation of  $\text{Cr}(\text{OH})_4^-$  by  $\text{H}_2\text{O}_2$  in basic solutions. The reactions were carried out under pseudo first order conditions with  $\text{OH}^-$  and  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  and  $\text{OH}^-$  by including two reactions. One reaction involves the conjugate base,  $\text{HOO}^-$  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  $\text{HOO}^-$  by reaction of  $\text{H}_2\text{O}_2$  with  $\text{OH}^-$ .

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  $\text{OH}^-$  a new Raman band appears at  $850\text{ cm}^{-1}$ . We identify this band as the O-O stretch of the hydroperoxide anion. Because hydrogen peroxide is a stronger acid than water,  $\text{HO}_2^-$  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  $\text{HO}_2^-$ . We have examined the Raman spectrum of aqueous solutions of  $\text{HO}_2^-$  formed by reaction of  $\text{OH}^-$  with  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{O}_2$  with  $\text{H}_2\text{O}$  and with  $\text{D}_2\text{O}$ . 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  $\text{HOO}^-$  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.

### Planned Activities

During the summer of Ginger Denison will continue work with the PI at LANL. We will continue to investigate the kinetics of oxidation of Cr(III) in basic solution using hydrogen peroxide as the oxidizing agent. We plan to determine the multi-exponential rate constants for samples with different aging histories covering periods up to several weeks of aging. Mathcad will be used to model the dependence of effective rate constants on the concentrations of hydroxide and hydrogen peroxide. Data collected over the past year cover a wide range of concentration conditions. These data will be used to test the general model of a complex reaction involving at least two different reactions with different oxidizing agents.

### Information Access

Four 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. Senior papers by students who have worked on this project are available from the PI.