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

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SUMMARY/PROGRESS REPORT

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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 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, and Ginger Denison is a rising senior who is 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 low 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. In understanding the mechanism of oxidation by hydrogen peroxide it is important to determine whether H_2O_2 or HO_2^- is the actual oxidizing agent in the reaction with chromium hydroxide. We have not yet carried out experiments to answer this question. 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. There is very little information in the literature on the vibrational spectroscopy of HO_2^- . Extensive *ab initio* calculations have been carried out to support this assignment. These calculations show that the O-O stretch and HOO bending modes are mixed, especially in the deuterated species. We see no shift in the 850 cm^{-1} band on deuteration. The strong mixing with the bending mode may be responsible for the coincidence of these two frequencies. Similar mixing of these normal modes has been reported for the neutral hydroperoxide radical, HO_2 . The calculations also suggest that hydrogen bonding of hydroperoxide with water reduces the electron density on the anion with a resulting increase in the frequency of the O-O stretch.

Planned Activities

During the summer of 1999 two students will 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. We also will study the rate of consumption of hydroxide ion using a pH meter to follow $[\text{OH}^-]$. The third reactant, hydrogen peroxide can be followed by its characteristic O-O stretching vibration in the Raman spectrum. Monitoring each of the reactants separately under pseudo first order conditions

will provide a complete understanding of the factors that affect the rate of dissolution of chromium (III) species by hydrogen peroxide in basic solutions.

Cr(III) species in Hanford tank wastes have not been quantitatively characterized, but it is certain that some of the chromium is in the form of the oxide. For this reason we will examine reactions with Cr_2O_3 , which is insoluble and unreactive with hydrogen peroxide at ambient temperature. We will look for reaction at higher temperatures and in the presence of catalysts. Also we plan to carry out experiments using sonication to promote reaction.

Information Access

Three students have given talks at the Southeast Regional ACS meeting and the National Conference of Undergraduate Research. Two posters will be presented at the ACS meeting in New Orleans on August 22, 1999. Poster material is being submitted with this report. Senior papers by Dana Olsen and David Pond are available from the PI. A manuscript on HO_2^- is in preparation.