Continuation Progress Report

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

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Recipient Organization: Furman University, Greenville, SC 29613

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All of the work done so far 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. I am now setting up a Raman spectroscopy lab at Furman. Using departmental funds we have purchased an optical bench, a laser, and a CCD detector and are ready to order a monochromator. Over the next few months I expect to use the equipment and supplies budget of the DOE grant to get the supplies needed to carry out experiments at Furman. Our plan is to continue the summer collaboration at LANL and carry out experiments at Furman during the academic year.

Report:

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 Ran-ran cell caused by particle formation.

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 $Cr(OH)_3$, CrO(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 $Cr(OH)_3$, 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 $Cr(NO_3)_3$ 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 $Cr(OH)_3$.

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 H202 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 D202 to confirm this assignment. If this assignment proves to be legitimate, we will submit a note to the ***Journal of Physical Chemistry.***