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Project Title: Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes (First Year of Funding: FY 1998)

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Research Objective: Chromium, one of the problematic elements in tank sludges, is presently considered to be the most important constituent in defining the total volume of HLW glass to be produced from the Hanford tank wastes. This is because 1) it greatly complicates the vitrification process by forming separate phases in the molten glass and, 2) more importantly, current sludge washing processes are not effective in removing Cr. Inadequate removal of chromium from sludges could result in production of an unacceptably large volume of HLW glass.

The removal of Cr from tank sludges is complicated by factors including the complex chemistry of Cr, lack of fundamental data applicable to the HLW chemical systems (high heterogeneity, high ionic strength, high alkalinity and the presence of inorganic and organic ligands, etc.), and the need to avoid processes that may adversely enhance the solubility of Pu and other actinides. Significant gaps exist in the fundamental understanding of Cr chemistry in tank-like environments. Without such data/understanding, these strategies cannot be appropriately evaluated or optimized. The primary objective of the research being carried out under this project is to develop such data/understanding for HLW tank processing. Pacific Northwest and Lawrence Berkley National Laboratories in collaboration with Washington State University are developing fundamental data on the precipitation/dissolution reactions of Cr(III) compounds and the kinetics of oxidation of Cr(III) to Cr(VI) at room and elevated temperatures and under conditions relevant to high-level waste processing. This integrated approach involving measurement of solubility and oxidation rate constants and spectroscopic characterization of aqueous and solid species as a function of ionic strength, alkalinity, redox conditions and temperature will provide thermodynamic and kinetic data. These data are necessary to predict changes in Cr solubility and speciation in response to changes in pretreatment strategies or to develop cost effective tank waste processing technologies that result from reducing the total amount of Cr in processed waste.
**Research Progress and Implications:** This report summarizes research after 1.5 years of a 3-year project. There are two ways of removing chromium from the wastes, solubilization of Cr (III) compounds and the oxidation of Cr(III) to Cr(VI). Progress was made on both of these aspects. Specifically, studies were conducted to 1) to measure the solubility of Cr(OH)$_3$(am) in NaOH and in mixed solutions containing NaOH and NaNO$_3$, and 2) determine oxidation of Cr(III) to Cr(VI) by H$_2$O$_2$ in alkaline solutions.

The Cr(OH)$_3$(am) was prepared according to the method described by Rai et al. (1987) and was suspended in NaOH ranging in concentration from 0.01 to 10 M. The observed Cr concentrations in solutions filtered through 0.2µm and 0.0018µm were similar, indicating that colloids of sizes > 0.0018 µm do not exist in these suspensions and that either of these filters can be used to effectively separate solids from solutions. X-ray diffraction analyses of the solid phases indicated that the solids were amorphous. Oxidation state analyses of most of the aqueous samples by chromatographic technique and of limited samples by XAS showed that Cr(III) is the dominant oxidation state in the aqueous and solid phases. The solubility of Cr(OH)$_3$(am) were observed to increase dramatically with the increase in NaOH concentrations, especially between 1.0 and 10 M where the observed Cr concentrations increased from $10^{-4.5}$ to 0.1 M. A gradual decrease in Cr concentrations were observed at longer equilibration periods, reflecting more likely a change in chemical potential of the solid phase.

Thermodynamic interpretations of these data will be done using Pitzer formulism to develop models applicable to tank wastes containing concentrated electrolytes.

Chromium (III) in alkaline solutions was found to exist in species with various degrees of oligomerization. A cation exchange technique was successfully used to separate monomeric, dimeric, and trimeric Cr(III) species from the “bulk” Cr(III) solution. The separated species have been characterized by UV/Vis absorption spectroscopy. Kinetic experiments indicate that the three Cr(III) species with lower degrees of oligomerization (monomer, dimer, trimer) are easily oxidized by hydrogen peroxide in alkaline solutions as compared with the “bulk” Cr(III). The oxidation of the monomer, dimer, and trimer followed a first-order reaction order with respect to the concentration of Cr and hydrogen peroxide, but a reversed first order with respect to the concentration of NaOH.

**Planned Activities:** Studies on the 1) solubility of Cr(OH)$_3$(am) in different electrolytes will be continued and will be used to develop a thermodynamic model to predict Cr(III) behavior in tank solutions, 2) kinetics of oxidation of Cr(III) to Cr(VI) in the presence of different oxidants and at room and elevated temperatures will be continued to provide fundamental data for effective oxidants, relevant to tank solutions, to oxidize Cr(III) to Cr(VI).