Environmental Management Science Program

Project ID Number 54765

Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate

Steven J. Buelow, Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, New Mexico 87545
Phone: 505-667-1178
E-mail: buelow@lanl.gov

Jeanne M. Robinson
Los Alamos National Laboratory
MS J567
Los Alamos, New Mexico 87545
Phone: 505-665-4834
E-mail: jeanne.robinson@lanl.gov

June 1, 1998

54765

Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate

Steven J. Buelow, Los Alamos National Laboratory

Jeanne M. Robinson, Los Alamos National Laboratory

Research Objective

The objective of this project is to develop the scientific basis for hydrothermal separation of chromium from High Level Waste (HLW) sludges. Our worked is aimed at attaining a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions that will ultimately lead to an efficient chromium leaching process.

Research Progress and Implications

This report summarizes our research over the first 1.5 years of a 3 year project. We have examined the dissolution of chromium hydroxide using different oxidants as a function of temperature and alkalinity. The results and possible applications to HLW sludges are discussed below.

Chromium hydroxide, $Cr(OH)^3\ ^3H_2O$ was selected as the first chromium compound for this study. Based on available literature, chromium hydroxide should be the majority chromium compound in the HLW sludges. Dissolution experiments on chromium hydroxide were conducted in two types of reactors: a stirred batch system and a continuous flow reactor. Liners of nickel or teflon were used to prevent corrosion or leaching of chromium from the reactors. Chromium hydroxide, i.e. $Cr(OH)^3\ ^3H_2O$, was prepared according to literature reports.

The two oxidants investigated were O_2 and nitrate. Dissolution/reaction experiments for chromium hydroxide in a batch reactor by O_2 were performed at reaction temperatures ranging from 75 to 200° C. The dissolution of chromium hydroxide using oxygen follows:

(1) When nitrate was used as an oxidant, the experiments were performed in both continuous flow and batch reactors at temperatures ranging from 250 to 410° C and pressures ranging from 300 to 4000 psi.

The reaction is:

(2) All experiments were performed in alkaline solutions from 0.01 to 4 M NaOH. A caustic environment was chosen because the Hanford waste is alkaline and neutralization is not practiced. Anions ($CrO_{4^-}^{2}$, NO_{3^-}, NO_{2^-}) were measured by ion chromatography. Dissolution of chromium hydroxide under alkaline conditions with oxygen was studied at temperatures ranging from 70 to 200° C. Hydroxide concentrations were varied from 0.01 to 4 M (pH 12 to 14.5) and oxygen concentrations in solution were varied from 0.4 to 4.4 mM to determine the effect of oxygen concentration and the caustic environment on the dissolution rates. The rate of oxidation to $CrO_{4^-}^{2}$ per 0.15 grams of $Cr(OH)^3\ ^3H_2O$ is:

(3) An increase in hydroxide concentration increased the dissolution rate with all other conditions being similar. The dependence was found to be almost linear, with a doubling of hydroxide concentration the dissolution rate nearly doubled. The oxygen concentration was determined based on the overall system pressure, partial pressure of oxygen and headspace volume. Henry's Law constants were used to determine the concentration of dissolved oxygen concentration in solution. An increase in oxygen concentration increased the dissolution

rate but at a much lesser rate than the effect of hydroxide concentration. A four-fold increase in oxygen concentration was required to double the chromium dissolution rate. Temperature had the most significant effect on chromium dissolution with oxygen. Increasing the temperature 100° C (from 100 to 200° C) increased the rate nearly 150 times. The effects of chromium hydroxide surface morphology have not yet been determined.

Nitrate was used as an oxidant for dissolution of chromium at higher temperatures to 400° C. At reaction temperatures below 250° C, no dissolution of chromium was observed. At a nitrate concentration of 0.125 M, hydroxide concentration of 1.0 M and temperatures ranging from 250 to 400° C, the rate of oxidation to CrO_{4}^{-2} per 0.15 grams of $Cr(OH)^3$ ^3H_2O is:

(4) The diffusion and speciation of nitrate species at these conditions was also examined. The study of the effect of nitrate and hydroxide concentrations on chromium dissolution is in progress.

In conclusion, oxidative dissolution of chromium hydroxide can be accomplished at high temperatures with nitrate and at relatively low temperatures with molecular oxygen. We have determined the reaction rates for both systems. We have also determined diffusion constants and speciation of nitrates at releavent hydrothermal conditions. Our results suggest that at reaction temperatures (>125° C) slightly higher than the current baseline sludge washing conditions, chromium can rapidly and efficiently dissolved from HLW sludge using oxygen or air. Our results also show that increasing the hydroxide concetration will increase the rate of reaction and decrease the required operating pressures to near ambient.

Planned Activities

The activities related to this project will continue in two directions: high temperature dissolution using nitrate and lower temperature dissolution using oxygen. The effects of process parameters (temperature, pressure, and concentration) will be continuously evaluated. Different forms of chromium(III) oxides possibly present in HLW waste and the effect of organic and inorganic compounds will be examined.