Environmental Management Science Program

Project ID Number 54893

Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes

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June 1, 1998

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Research Objective

The goal of our research is to develop data to allow successful modeling of the effects of redox chemicals present in Hanford waste tanks on the oxidation state and chemical speciation of plutonium in the wastes.

Research Progress and Implications

As of May 1998, scoping experiments on PuO_2^{2+} in a solution of 1.0 M NaCl and pH 8 in the dark showed no reduction of PuO_2^{2+} concentration over a week nor was reduction observed when this experiment was repeated with 10^{-5} M H_2O_2 . Reduction was observed over hours/days as the H_2O_2 concentration was raised above 10^{-3} M. The rate of reduction in the dark was measured at $\text{pH} = 8$, 1.0 M (NaCl) for $[\text{H}_2\text{O}_2] = 10^{-2}$ to 4×10^{-2} and $[\text{PuO}_2^{2+}] = 1.2 \times 10^{-10}$ to 3.5×10^{-10} M and first order kinetics observed. From the rate constants, we calculate for $[\text{H}_2\text{O}_2] = 10^{-2}$ M and $[\text{PuO}_2^{2+}] = 10^{-6}$ M, a half life of reduction in the dark of 0.06 min and for $[\text{H}_2\text{O}_2] = 10^{-6}$ M, $[\text{PuO}_2^{2+}] = 10^{-6}$ M, of 10 hr. These data indicate that radiolytic production of H_2O_2 in the wet tank wastes would serve to reduce PuO_2^{2+} (and PuO_2^{2+}) to Pu(IV), thereby reducing the concentration of dissolved Pu due to the strong hydrolytic tendency of the Pu(IV).

The oxidation of Pu(IV) by NaOCl is also being investigated. As of May, 1998, the methodology to measure the oxidation state speciation at tracer Pu(IV) concentrations has been developed and scoping experiments conducted. At $\text{pH} = 4.7$, $I = 1.0$ M (NaCl), $[\text{Pu(IV)}] = 10^{-10}$ M and $[\text{NaOCl}] = 10^{-5}$ to 10^{-3} M, no oxidation (i.e., PuO_2^{2+}) has been observed. Experiments are now underway at $\text{pH} = 8$.

To understand the role of complexation by the strong organic ligand in the tank wastes in the redox speciation of Pu, we are measuring the stability constant of Pu(IV) with EDTA. Attempts to use arsenazo (III) as a chromophoric competing ligand were unsuccessful and as of May, 1998, we are studying competition experiments of Pu(IV) and Fe(III) with EDTA by absorption spectrophotometry. A value of $\log K = 24.0 \pm 0.1$ has been obtained for $I = 1.0$ m (NaCl).

Planned Activities

In FY 98, experiments on PuO_2^{2+} reduction by H_2O_2 will be conducted at varying pH values to determine the influence of the H^+ and OH^- concentration. These studies will be continued in FY 99 at 0.4 m and 4.0 m (NaCl) ionic strengths. This should allow calculation of the rates of reduction of Pu(V) under conditions relevant for the tank wastes and for environmental systems. The NaOCl studies in FY 98 will measure pH , NaOCl and Pu(IV) concentration dependencies to develop a useful rate equation. Again, the experiments will cover 0.4, 1.0 and 4.0 m (NaCl) media in FY 99. The measurements of the stability constants of Pu(IV)EDTA will be performed at $I = 0.3$ m and $I = 3$ m (NaCl) during the remainder of FY 98. We plan to measure the FeEDTA- constant under these conditions in FY 99. The research in that year will focus on similar measurements for the formation of Pu(IV)DTPA-. These values will allow modeling of the role of EDTA and DTPA in Pu speciation in the tank wastes.

In the remainder of FY 98 and FY 99, experiments will also be conducted to determine the effects of Fe(II) and ferridoxin (common to electron transport system in anaerobic bacteria) on the oxidation states of Pu. Specifically, effects of pH, concentrations of FeCl_2 , FeClO_4 , and ferridoxin will be evaluated on the solubility of $\text{PuO}_2(\text{am})$. Total concentrations and oxidation states of aqueous Pu and Fe, along with changes in solid phases as a function of time, will be monitored. The oxidation states will be monitored using a combination of solvent extraction, and spectrophotometric and x-ray absorption spectroscopies. The results will provide information on the expected dominant Pu species in environments containing Fe(II) and microbially produced reducing agents.