

**Project Identification Number:** 54893

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

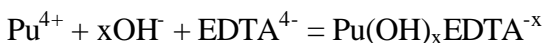
**Publication Date:** March 1, 2000

**Principal Investigators:** Gregory R. Choppin, Florida State University, Tallahassee, Florida 32306-4390, (850) 644-3875 (phone), (850) 644-8281 (fax), choppin@chemmail.chem.fsu.edu, and Dhanpat Rai, Pacific Northwest National Laboratory, P. O. Box 999, MISN P7-50, Richland, Washington 99352, (509) 373-5988 (phone), (509) 372-1632 (fax), dhan.rai@pnl.gov

**Research Objective:** Plutonium contamination is a major problem at many DOE sites. This project seeks to provide fundamental data and models for predicting plutonium speciation and environmental behavior that will allow evaluation of the many processes proposed for remediation of plutonium-containing DOE wastes. Basic to this prediction are 1) the complete fundamental data on aqueous complexation, solubility reactions, and geochemical conditions under which different plutonium oxidation states transform from one to another, and 2) a model containing this fundamental data that can predict site-specific reactions. We propose to summarize existing data and develop additional fundamental data to measure the oxidation state (or states) in a variety of solid/solution systems in the presence and absence of chemicals likely to be present in DOE wastes and which can promote redox transformations and complexation reactions. Specifically, we will 1) develop methodology to determine complexation constants of Pu(IV) with strongly complexing ligands, 2) determine stability constants of Pu(IV) with strong complexants such as EDTA, 3) determine the geochemical conditions under which different reductants (e.g., Fe(0), Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>) can reduce Pu(VI) to Pu(III)/Pu(IV) and oxidants (e.g., MnO<sub>2</sub> and radiolytic products) that can oxidize Pu(IV) to Pu(V)/Pu(VI), and 4) summarize fundamental Pu data for use in a model for predicting Pu behavior under different geologic conditions.

**Research Progress and Implications:** This report summarizes the research through last year of a 3-year project. To obtain reliable values of Pu(IV)-EDTA complexes applicable to a wide range in environmental conditions, we conducted studies on the solubility of PuO<sub>2</sub>(am), the solubility product of which is reasonably well known, at 1) 0.001 or 0.0001 M total EDTA concentrations and pH values ranging from 1 to 13.5 and 2) pH values of approximately 9 and EDTA concentrations ranging from 0.00001 and 0.093 M (Rai et al. 2000a). The aqueous Pu oxidation states of the complexed species were determined by x-ray absorption near edge spectroscopy and solvent extraction and were used to quantify the Pu(IV)-EDTA species. The comparison of our experimental solubility with the predictions based on literature data [Cauchetier and Guichard 1973] showed that the predicted concentrations depended on the pH but were orders of magnitude lower (e.g., at pH 8, the difference is approximately six orders of magnitude), indicating that the existing models were not adequate to represent complexation behavior of Pu(IV) with EDTA at pH values >4. The data were interpreted using the Pitzer ion-

interaction model that is applicable to dilute as well as concentrated electrolytes. Our model was developed based on the solubility of  $\text{PuO}_2(\text{am})$  at 0.0001 M EDTA concentrations and as a function of pH. This model was validated against the data in 0.001 M as a function of pH and the data at pH value of 9 and as a function of EDTA concentrations. The  $\log K^0$  values for the formation of  $\text{Pu}(\text{OH})_x\text{EDTA}^{x-}$  according to the generalized reaction



were determined to be 36.39, 44.74, and 49.64 for  $x = 1, 2,$  and  $3,$  respectively. These different complexed species, as expected, are dominant in different pH regions.

Obtaining reliable thermodynamic data for Pu(V) is difficult because of its redox and/or disproportionation reactions in most aqueous systems. Thus, very limited data are available for this oxidation state. Therefore, it is of interest to determine whether thermodynamic data for Np(V), expected to be a good analog for Pu(V), can be used to predict Pu(V) behavior. The known stability of Pu(V) in  $\text{PuO}_2(\text{am})$  suspensions in slightly acidic to near neutral conditions was used to study the solubility of  $\text{PuO}_2(\text{am})$  in 0.4 and 4.0 M NaCl or  $\text{NaClO}_4$  solutions ranging in  $\text{pC}_{\text{H}^+}$  values from 4 to 9 as a function of time (Rai et al. 2000b). The close agreement between the observed solubility and the predicted solubility using Pitzer ion-interaction parameters of Np(V) with  $\text{Cl}^-$  or  $\text{ClO}_4^-$  indicates that Pu(V), as expected, behaves in an analogous fashion to Np(V) and confirms the value of using Np(V) data to model Pu(V) behavior.

Although Pu(V)/Pu(VI) may be the dominant oxidation state in some specific conditions (e.g., ocean waters, laboratory experiments in aerobic water), there are many reductants in many geologic environments that would reduce the plutonyl species to the tri- or tetravalent states. Therefore, the reduction of  $\text{PuO}_2^+$  was measured (Morgenstern and Choppin 1999) and showed inverse dependence on the  $\text{H}^+$  concentration with a half-life for reduction  $10^{-10}$  M Pu(V) in  $10^{-3}$  M  $\text{H}_2\text{O}_2$  of about 8 days. ( $\text{H}_2\text{O}_2$  is a product of radiolysis of water.) To determine the kinetics of oxidation of Pu(IV) to  $\text{PuO}_2(\text{V})$  and/or  $\text{PuO}_2(\text{VI})$ , studies on the effects of  $\text{MnO}_2$  and NaOCl were also conducted. The data showed Pu(IV) is readily oxidized to  $\text{PuO}_2(\text{V})$  or  $\text{PuO}_2(\text{VI})$  by these oxidants. Rate expressions are being developed to allow predictions of the redox kinetics as a function of pH and redox reagents.