

Environmental Management Science Program Report Progress Report  
Plutonium Speciation, Solubilization, and Migration in Soils, Project 59996  
DOE Report Number (LAUR# 00-1277), March 8, 2000

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**Research Objective:**

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. To properly control Pu migration in soils within Federal sites and onto public lands, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation and environmental transport is needed. The key scientific goals of this project are: to determine Pu concentrations and speciation at a contaminated DOE site; to study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu species; to determine the mechanism(s) of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling; and to model the environmental behavior of plutonium. Our long-term goal is to use characterization, thermodynamic, mineral interaction, and mobility data to develop better models of radionuclide transport and risk assessment, and to enable the development of science-based decontamination strategies.

This research will fill important gaps between basic actinide science and the problems impeding site clean-up, plutonium disposition, and accurate risk assessment. Information gained will allow for the development of technologies and clean-up approaches targeting particular plutonium contaminants and improved assessment of risks associated with actinide migration, site remediation, and decontamination. By combining very specific study of plutonium at the Rocky Flats Environmental Technology Site (RFETS), a well-characterized contaminated site, with laboratory studies on the most important plutonium and mineral component systems, we will provide essential knowledge of contaminant characteristics and distinguish critical geochemical processes and mechanisms.

### **Research Progress and Implications:**

This report summarizes work performed in the first 5 months of the 3<sup>rd</sup> year of a 3-year project. In the first two years we focused on 1) characterizing Pu in contaminated samples from the RFETS, 2) fundamental stability and migration studies of Pu(IV) colloids, 3) fundamental studies of An(IV) carbonates, and 4) thermodynamic database development and geochemical modeling (summarized in progress report 6/15/99). This fiscal year our focus is on 1) Pu-Mn phase interactions, 2) fundamental studies of  $\text{Pu}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$  species, 3) colloid migration and 4) site-specific geochemical modeling.

From site remediation and site closure perspectives, our most important results are the first direct speciation and distribution analyses of Pu in samples from a contaminated site. Using a combination of techniques, we found that Pu in soil samples from the 903 pad area at RFETS is dispersed on micro- and macroscopic scales (and not locally concentrated or associated preferentially with any other element) and is Pu(IV) with spectroscopic features most consistent with  $\text{PuO}_2$ . These research results are very powerful for explaining very limited observed mobility of Pu, predicting future behavior, and evaluating/revising remediation, closure, and monitoring plans.

We compiled and evaluated available Pu thermodynamic data and removed inconsistencies to obtain an updated, defensible database for modeling. Accurate thermodynamic data are key to reliably model the geochemistry of plutonium. Despite numerous reviews of thermodynamic data for Pu species, few databases contain the most recent data provided in the literature. We are now poised to use this database and site conditions to predict Pu speciation and resultant mobility.

We have prepared and extensively characterized manganese phases and performed a number of Pu sorption and coprecipitation experiments. Sorption kinetics, oxidation state changes, speciation as a function of loading, and total binding were all studied for a number of Pu species.

### **Planned Activities:**

Confirming our thermodynamic calculations (and predictions in the literature), we identified plutonium to be in the +IV state in the RFETS soil samples investigated. Potential release and dissolution scenarios include the formation of the  $\text{Pu}(\text{OH})_4(\text{aq})$  solution species. The carbonate content of ground- or surface waters will affect the speciation and dictate the formation of mixed Pu(IV) hydroxocarbonato species,  $\text{Pu}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$ . These species have much higher stabilities and increase the solubility of  $\text{PuO}_2$  by orders of magnitude compared to  $\text{Pu}(\text{OH})_4(\text{aq})$ . We will synthesize the ternary species, obtain characteristic optical spectra, and determine their stability. We have prepared and characterized the limiting carbonate in this series,  $\text{Pu}(\text{CO}_3)_5^{6-}$ , as well as the U(IV) and Np(IV) analogs, and are now in a position to identify the other Pu(IV) solution species. The stability constants obtained will be used to evaluate species potential formation and importance given conditions at specific contaminated sites.

We will use our Pu thermodynamic database to calculate the speciation of Pu(IV) under RFETS conditions and to define stability ranges for Pu(IV) species that may control the release of Pu from its characterized source  $\text{PuO}_2$ . Detailed Pu-Mn interactions and colloid migration studies will also be continued.

### **Optional Proprietary Information:**

As outlined in our original proposal in this third year of our project we are studying the interactions of plutonium with redox active metal oxides and oxyhydroxides. Because of correlations between dissolved plutonium and manganese in settling pond waters at the RFETS, we are focusing on manganese phases formed by manganese in both extremes of its redox cycle.

We have prepared  $\text{MnO}_2$  using the accepted method of  $\text{KMnO}_4$  reduction and have characterized this material. We determined the surface area (SA) of the solid to be  $214 \text{ m}^2/\text{g}$  using the ethylene glycol method and  $41.1 \text{ m}^2/\text{g}$  using the BET method. The much higher SA determined using the ethylene glycol method was expected, given the ability of the organic molecule to diffuse into pore and interstitial spaces, and likely more closely reflects the SA accessible to metal ions. Atomic adsorption measurements were made on dissolved fractions of a freeze-dried sample to determine Mn and K content. The sample has approximately 10 wt% K, but the results also suggest that there may be a half a mole of hydrated water for every mole of  $\text{MnO}_2$  meaning the K to Mn ratio is higher than 10%. The X-ray diffraction pattern indicates the  $\text{MnO}_2$  sample is primarily amorphous with some crystallinity and contains four broad peaks at d-spacings of 7.24, 3.65, 2.43, 1.41  $\text{\AA}$ , consistent with patterns reported in the literature. The optical diffuse reflectance spectra of the material shows a broad absorbance band centered at 500 nm, consistent with Mn(IV).

The morphology of the  $\text{MnO}_2$  sample was studied using both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM does not have the resolution necessary to observe the fine structure of the  $\text{MnO}_2$  particles. TEM analysis suggests individual aggregate size ranges from 10-100 nm with individual particles about 2 nm. TEM micrographs of the  $\text{MnO}_2$  are similar to literature reports. Under the electron beam the amorphous  $\text{MnO}_2$  sample crystallizes due to local heating (temperatures reach  $\sim 100\text{-}150^\circ\text{C}$ ). The  $\text{MnO}_2$  is most likely transforming into the alpha form of  $\text{MnO}_2$ , cryptomelane.

Three Pu(V) sorption experiments have been completed; two at low coverage, 27 and 35% site occupancy, and one at full 100% loading. Two Pu(IV) colloidal sorption experiments have been completed, one at 20% loading and one at full 100% loading. An absorption experiment using chelated Pu(IV), Pu(IV) NTA, at the equivalent of 100% loading, has also been completed. Sorption rates and amounts were determined by separating the solution and solid phases and using LSC to determine the Pu distribution. Samples of the resultant Pu-sorbed manganese oxide solids were analyzed using diffuse reflectance, electron microscopy, and X-ray absorption. Surprisingly, preliminary XANES spectra analyses suggest that Pu(V) is not reduced upon sorption, and with long equilibrium times may even be oxidized. Even more surprising, there is some evidence that some of the colloidal Pu(IV) hydroxide is oxidized in the sorption process. Only the complexed Pu(IV) appears to be 100% +IV upon absorption to  $\text{MnO}_2$ . Preliminary SEM images are also very interesting in that they show localized Pu in the initially colloidal Pu(IV) hydroxide sorption samples and delocalized Pu in the initially Pu(V) and Pu(IV) NTA samples.