

Environmental Management Science Program

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Plutonium Speciation, Solubilization, and Migration in Soils

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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, transport, and release mechanisms is needed. Key scientific goals include: determine Pu concentrations and speciation at a contaminated DOE site; study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu (III, IV, and V) species; determine the mechanism of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling; and model the environmental behavior of plutonium.

Research Progress and Implications

This report summarizes work after seven months of a three-year project. In the first year of this project we are focusing on the origin, speciation, and mobility of plutonium at the Rocky Flats Environmental Test Site (RFETS).

We have reviewed detailed thermal ionization mass spectrometry (TIMS) measurements and resultant $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios determined for soil samples collected in the RFETS area and samples collected at locations in Colorado that are believed to be representative of global fallout. These studies were performed to investigate potential migration within and releases from the RFETS site due to the fires and other events of the 1950s and 1960s and potential releases from the area 903 pad in the late 1970s. Non-fallout isotopic ratios are localized directly east of the site, with only slight divergence north and south of the site—contradicting previous suspicions of long-range contamination from RFETS in the north/south direction. These data allow us to put actinide processes in context regionally and better interpret extensive information collected on site where soil and watershed contamination is much higher. As detailed characterization of the microscopic and molecular state of Pu constituents develops, this context will be essential for remediation and treatment activities.

We have also received extensive data from the site for radiochemical activities in surface water. These data are the basis for evaluating the validity of particulate transport models used by the site, and coupled behavior of ^{241}Am and $^{239/240}\text{Pu}$. Over most of the actinide concentration range, Am and Pu activities are roughly correlated, consistent with a particulate transport model. However, at the lowest activities the relative activity of Am spreads toward higher values. Three possible mechanisms have been identified: mixing with contaminant source material enriched in Am, variation in the relative mobilities of Am and Pu, and contribution of natural Th to the low level counting results. Further evaluation is critical to coupling the detailed chemical and physical model sought by this project to remediation and treatment actions at Rocky Flats and other sites contaminated with low levels of actinides.

Chemical analyses from the database for 1992 through 1994 for pond C-2, a main drainage pond at RFETS, include constituents important for understanding the geochemistry of natural waters, including bicarbonate, chloride, sodium, sulfate, sulfide, and some metals. Radiochemical analyses were conducted almost monthly between 1992 and 1995. Seasonal variation in the plutonium

concentrations in Pond C-2 is observed for 1992, 1993 and 1994. To evaluate whether these seasonal patterns are related to colloidal plutonium, total suspended solids (TSS) and plutonium are compared. The 1994 TSS data exhibit a pattern that correlates with plutonium. This relationship suggests that colloidal plutonium may, in part, cause the observed seasonal fluctuations. Sulfur and manganese exhibit trends in C-2 Pond water that correlate with the plutonium pattern, suggesting that geochemical processes, in addition to colloid formation, are contributing to the observed variation in soluble plutonium. The most prominent changes observed in pond C-2 are temperature, from 27.4 to 4.5°C, and dissolved oxygen content, from 0.5 to 7.8 mg/L. Given the water analysis, including redox sensitive species, the Eh (redox potential) of the system varies from -0.278 V and +0.750 V. (The potential dictates the oxidation state(s) of plutonium which are stable, and thus controls the solubility of plutonium.) These variations and simple geochemical models were used to attempt to determine the processes occurring within Pond C-2. The observed trends in sulfate and plutonium are duplicated; however, the models do not yet duplicate the magnitude of change observed for plutonium and sulfate or the pattern observed for manganese.

We have received and are analyzing a number of soil and water samples from the RFETS. We attempted to determine the oxidation state of the plutonium in a sample from a core from pond B-1 using X-ray absorption near-edge spectroscopy (XANES). Unfortunately, the sample has a relatively high concentration of Zr or another element which has an absorption edge very close in energy to the Pu edge. (Zirconium has an absorption edge at 17999.35 eV; plutonium species have absorption edges of 18056, 18058, 18060 and 18061 eV for Pu III-VI, respectively). We did not observe an absorption edge corresponding to the Pu in the soil sample. We may attempt to remeasure the X-ray absorption after a pre-concentration step and using another absorption edge for plutonium which does not have the same interference problem. For comparison, we recently measured the XANES spectrum of 3.2 mg/g or 372 nCi ²³⁹Pu sorbed onto smectite. The spectrum for this sample shows two edge features, one at 18000 eV and the other at ~18060 eV, suggesting the presence of zirconium and Pu(IV) or Pu(V). The observation of the Pu edge for this mineral sample is encouraging since we have received soil samples which have comparable Pu concentrations.

Planned Activities

This year we will continue RFETS related experiments and geochemical modeling. We will determine the overall Pu content and isotopic ratios for sediments and waters from RFETS. We will characterize the Pu in soil samples by determining morphology, degree of mineralization, and bulk distribution between types of phases using a combination of techniques. Sequential filtration studies may indicate the size distribution of host particle and allow us to determine if Pu is migrating via resuspended particles or via redox transformation to different chemical species. We will attempt to determine the overall Pu oxidation state. We will continue to model the chemistry of ponds at RFETS and attempt to explain the seasonal variations in soluble Pu. To obtain more precise data for the geochemical modelling we will work with the site to measure the redox potential in the ponds.

In the following years we will continue to characterize the Pu in RFETS soils and perform laboratory studies on Pu carbonate and hydroxo species, both as pure systems and interacting with Mn ions and oxides. We anticipate that our soils characterization studies from the first year will confirm our choice of the Pu(III, IV, and V) single carbonate and Pu(III and IV) hydroxide systems and will allow us to refine our targets for fundamental studies. Obtaining characteristic spectra and determining the stability and properties of the species will not only provide spectroscopic and thermodynamic data to compare with environmental samples, but also allow us to unravel the equilibrium constants of important actinide systems. Investigating the Mn/Pu redox cycle and Pu sorption mechanisms and geochemical of Pu will further improve our understanding of the complex environmental behavior of Pu.