

Project Title: Plutonium Speciation, Solubilization and Migration in Soils

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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 contaminated DOE sites; 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 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 fundamental 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 well-characterized contaminated sites, 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. Because we are obtaining plutonium speciation information from real sites and significantly advancing of environmentally important systems, our research will also enable defensible long-term stewardship of DOE sites.

Research Progress and Implications

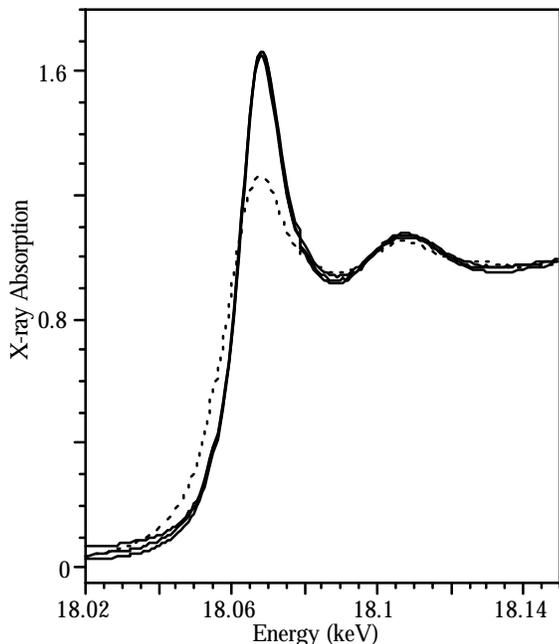
This report summarizes work after two years of a three-year project. In this year we are focusing on 1) the interactions between plutonium compounds and redox-active iron and manganese minerals, 2) the interactions between plutonium compounds and sediments from the Hanford site, 3) the application of our findings to remediation efforts at RFETS and other sites.

Our most significant finding in the first two areas is that while Mn(IV) minerals very effectively oxidize and adsorb Pu and U species, sediments rich in Mn do not necessarily adsorb Pu in the same way. For example, we have found that under all of the conditions we have

studied (varying pH, [Pu], Mn/Pu ratio, ionic strength, time, etc.) Pu(IV) and Pu(V) species are oxidized by and sorbed to synthetic δ -MnO₂. Even in the presence of a 90:10 weight percent excess of goethite, a mineral which has been previously shown to sorb Pu(V) to yield a final surface bound or precipitated Pu(IV) species, Pu(V) was oxidized and sorbed as Pu(VI). The only exception was that the nitrilotriacetic acid complex of Pu(IV) was not oxidized by the mineral, but was instead sorbed as the complex and retained the +IV oxidation state. This

suggests that Pu complexed by strong anthropogenic and biogenic chelators will generally remain in the +IV state.

In contrast to these single and mixed mineral studies, we found that sediments from the Hanford site, even those with significant Mn content, sorb Pu(V) to yield predominantly Pu(IV) species. The figure at left shows the X-ray absorbance (XAS) spectra of a Pu(V) carbonate standard (dashed) and three Hanford sediments to which a Pu(V) solution was added (solid). Although the edge energies and white line position are at higher energy, consistent with Pu(V) or Pu(VI); the white line intensities, near-edge contours and near-neighbor distances, indicate a majority of Pu present as Pu(IV), within a mixture of species. The solution speciation, monitored as a function of time, suggests minor Pu(V) and Pu(VI) species present. Electron micrographs of the sediments do not show any localized Pu, supporting the conclusion that delocalized sorption (and not precipitation) is the predominant Pu-mineral interaction.



Our site-related studies are on-going, but our soils characterization results have already impacted decisions at RFETS. Using XAS, we showed unambiguously that Pu in soils taken from the 903 Pad is in oxidation state (IV), and in the form of PuO₂. It had been presumed but never proven that Pu in RFETS soils existed as PuO₂. Our first spectroscopic confirmation of the speciation is consistent with the observed insolubility of Pu in site waters, and supports a growing evidence that physical (particulate) transport is the dominant mechanism for Pu migration at RFETS. This recognition not only identified the need for the Site to develop a soil erosion model, but significantly helped in gaining public trust that an erosion model was correct for the Site, and that soluble transport models are inappropriate for Pu in RFETS soils. It has been estimated that these results saved millions of dollars by focusing Site-directed efforts in the correct areas, and will aid the DOE in its effort to cleanup and close the RFETS by 2006. We are developing interactions with the NTS and Hanford sites to provide similar assistance with their site characterization and remediation programs.

Planned Activities

During the next 18 months we will continue mineral and sediment sorption studies retaining our focus on redox-active phases and Pu species. We've recently obtained core

samples from the Hanford site with which we intend to investigate Pu speciation and sorption. And we are initiating similar collaborations with personnel who have access to Pu-contaminated soils at the NTS.

Information Access

One Page Adobe Acrobat File attached.