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*Title:* PLUTONIUM SPECIATION, SOLUBILIZATION AND  
MIGRATION IN SOILS

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# **Plutonium Speciation, Solubilization, and Migration in Soils**

## **Mid-Year Progress Report**

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### **Goals of Project:**

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, and release mechanisms 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 Test 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.

#### **Technical Description of Work:**

To determine Pu concentrations and speciation at a contaminated DOE site we will first use Thermal Ionization Mass Spectrometry (TIMS) to measure the isotopic  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio and identify the plutonium as originating from global fallout or site activities. For those water and soil samples having the highest concentrations we will use x-ray absorbance spectroscopy to determine the oxidation state and local coordination geometry (speciation) of the Pu. For particular samples we will perform physical separations and radionuclide counting to determine the characteristics of fractions containing portions of the Pu to determine overall concentrations; for example, size fractionation to determine the grain/soil size having the highest Pu concentration—macroscopic localization. We will use scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) to determine the morphology, microscopic localization, and correlations of Pu and other elements in soil samples.

To study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu species we will use established techniques (radiochemical and chemical separations, electrochemistry, optical absorbance spectroscopy, precipitation of microcrystalline and crystalline products) to prepare and isolate particular single species. Because hydroxide and carbonate are such strong ligands for actinides and are present in significant quantities in the environment, we will naturally focus on these types of complexes. We will attempt to obtain detailed metrical parameters for these species using single crystal and powder x-ray diffraction for solids and x-ray absorbance for solids and solution species. Within the budget allocation we will perform solution thermodynamic studies to determine the formation constants (stability) of individual species.

To determine the mechanism(s) of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling we will sorb known species of Pu onto well characterized Mn mineral phases and spectroscopically analyze the product. We also

plan to combine oxidized and reduced forms of Mn with specific Pu species and characterize the product(s), from both simple combination and after applying a potential to perturb the redox equilibrium of the mixture.

We will use standard geochemical codes and critically reviewed databases to model the environmental behavior of plutonium. This work will require first an evaluation of the literature to acquire the most reliable constants for Pu species. Thermodynamic data we measure in other aspects of the project will be included in the model as they become available.

### **Accomplishments to Date:**

This report summarizes research completed in the first half of a three-year project. As outlined in our proposal we are focusing on 1) characterizing the plutonium at an actinide contaminated site, RFETS, including determining the origin, dispersion, and speciation of the plutonium, 2) studying environmentally important plutonium complexes, primarily hydroxides and carbonates, and 3) examining the interactions of plutonium species with manganese minerals. In the first year we focused on site based studies. This year we continue to characterize samples from the RFETS, study the formation and structural and spectroscopic features of environmentally relevant Pu species, and begin modelling the environmental behavior of plutonium.

Our first step in investigating Pu origin, distribution, and redox cycling was to review detailed TIMS measurements and resultant  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios measured for soil samples collected in the RFETS area and samples collected at locations in Colorado that are believed to be representative of global fallout. 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 to providing constraints for remediation and treatment activities.

Samples from the RFETS which are most concentrated in Pu provide an opportunity to determine the species of Pu present. We have recently size fractionated soil samples from the 903 Pad area and analyzed each fraction using radionuclide decay counting, SEM, EDS, XAFS, and fission track measurements. SEM secondary electron images showed that the Pu in the soil fractions was delocalized down to at least the 100Å scale. EDS analysis showed the samples were predominantly aluminosilicates and that Pu was not correlated with any other elements. Particle track images were consistent with the SEM data; radiographs showed dispersed, omnidirectional tracks.

X-ray absorbance experiments were difficult because the 'standard' L3 spectra were not informative due to the presence of elements which absorb in the same energy range. Data were therefore obtained using the L2 absorption edge. One of the fractions was sufficiently concentrated in plutonium that it yielded an informative spectrum. The near edge region of the spectrum has an absorbance maximum indicative of Pu(IV). In fact, just after this measurement we measured the L2 absorbance of pure solid PuO<sub>2</sub> and found the two spectra had the same features (edge, maximum, no near-edge 'shoulder' indicative of Pu(V) or Pu(VI)) at the same energies. Analysis of the EXAFS data indicates there are approximately eight nearest neighbor atoms at a distance of 2.33 Å from the Pu, consistent with PuO<sub>2</sub>.

Not only is this the first definitive spectroscopic data on Pu in an environmental sample, but the data show the Pu in the most concentrated samples from the RFETS is in a highly stable and immobile form, the dioxide. The data also show that Pu is most concentrated in the 0.01-0.02 inch fractions, is dispersed on macroscopic and microscopic scales, and is not highly associated with any other particular element. These results should be very useful to RFETS personnel tasked with addressing concerns regarding plutonium migration from the site and powerful information for those tasked with remediating the site.

We attempted to determine the oxidation state and speciation of plutonium in several other samples, but in all other cases the concentration of Pu relative to other absorbing species was too low to obtain reliable, meaningful data. For example, a sample from a core from pond B-1 had 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 this soil sample. We may attempt to measure the X-ray absorption of samples in this concentration range after a pre-concentration step.

Toward understanding the redox chemistry of Pu under environmental conditions we will be investigating interactions of Pu species with redox active Mn minerals. To substantiate this area of research we investigated what is known about the redox conditions in surface waters at the RFETS. Chemical analyses for pond waters at RFETS are maintained in a database which we have accessed to obtain extensive data for pond C-2, a main drainage pond. The database contains 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, we compared total suspended solids (TSS) and plutonium. 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 C2 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 of the system varies from -0.278 V and +0.750 V. Simple geochemical models and these Eh values 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.

One compliment to the characterization of samples from a Pu contaminated site are laboratory studies of species we know to be predominant in near-neutral pH aqueous solution under environmentally relevant conditions. Plutonium(IV) is the predominant

oxidation state under most conditions and is well known to hydrolyze readily. Depending on the conditions used (Pu concentration, pH, base used, etc.) the resultant products are very low soluble solid plutonium hydroxide, rather intractable polymers, or suspended colloids. Due to its small size, on the order of 20 to 100Å, the colloidal hydroxide is of most concern with respect to environmental migration of plutonium. We have undertaken the study of this material and have performed the first study to determine the coordination geometry about plutonium in this species using EXAFS. The transform modulus of the EXAFS of the colloid was best fit using a model including 6 types of near-neighbor atoms, ~11 oxygen and nitrogen atoms at 2.20-3.31Å and ~8 plutonium atoms Pu at 3.82 Å. For comparison the EXAFS spectrum of plutonium oxide (fcc, fluorite structure) which has been fit by 8 O at 2.33 Å and 12 Pu at 3.84 Å. These data provide metrical parameters against which those from Pu in soils samples from RFETS were compared to conclude that the Pu was present as PuO<sub>2</sub> and not as a colloid. These results have increased importance due to the implication of Pu in a colloidal form as being responsible for the long range migration of Pu at the Nevada Test Site as reported in *Nature* earlier this year.

Another species we have studied is An(CO<sub>3</sub>)<sub>5</sub> which is formed in concentrated carbonate solutions and isolated in the solid form from solutions ranging in carbonate concentrations from approximately 0.1 M to saturated (given the pH is sufficiently high). Conclusive evidence for this species previously existed only for Th(IV), for which there is an X-ray crystal structure for Na<sub>6</sub>Th(CO<sub>3</sub>)<sub>5</sub>·6H<sub>2</sub>O, and solubility experiments which imply the same species in solution. We have determined the solid-state structure of Np(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> and Pu(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> using single crystal X-ray diffraction to characterize these species and consider how structures and bond distances change across the actinide series. When comparing average M--O bond distances relative to ionic radii for each An(IV), Th, Np, and Pu we found the bond length decreases (bond strength increases) although ionic radii increase across the series. For the Np(IV) species versus the Pu(IV) species the bond distance decreases by 0.002 to 0.016Å (depending on the structure) while the metal ionic radius increases by 0.08Å.

Table 2. Actinide--oxygen (carbonate) bond distances with single crystal x-ray structures of M<sub>6</sub>An(CO<sub>3</sub>)<sub>5</sub>

	[Th(CO <sub>3</sub> ) <sub>5</sub> ] <sup>6-</sup>	[Np(CO <sub>3</sub> ) <sub>5</sub> ] <sup>6-</sup>	[Pu(CO <sub>3</sub> ) <sub>5</sub> ] <sup>6-</sup>	[Pu(CO <sub>3</sub> ) <sub>5</sub> ] <sup>6-</sup>
Ave. M--O	2.493(11)	2.431(9)	2.415(7)	2.429(5)
Radius M(IV)	0.87	0.86	0.94	0.94
Reference	Voliotis, P.S.; Rimsky, A <i>Acta Cryst.</i> <b>1975</b> ,	This work.	Clark, D.L., et al. <i>Inorg. Chem.</i> <b>1998</b> , <i>37</i> , 2893.	This work.

**Projections:**

In our proposal we outlined four initial experimental areas: 1) Separate the plutonium in soils at RFETS into Rocky Flats and global fallout sources using isotopic ratios. 2) Begin sampling from collector trays in the French Drain leading from the 903 pad and water and sediments from Pond C-2 on a seasonal basis. 3) Fully characterize the plutonium in soil samples from the sites at RFETS most highly concentrated in plutonium not due to global fallout. 4) Prepare and characterize laboratory samples of the environmentally relevant forms of Pu(IV). We accomplished all of these tasks and are following the experimental plan as outlined for FY99, characterizing soils from the RFETS, examining plutonium species and equilibria, and initiating the study of Pu interactions with Mn minerals.

We will continue RFETS related experiments and geochemical modeling. 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. 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. 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.

**Funding:**

The level of spending for FY98 and FY99 (thus far) matched the allocation. We have searched for a postdoctoral researcher to work on this project, but have not yet identified a suitable candidate. Due to this unexpected change in technical staffing, we may not spend the full allocation and request a small carryover to FY00 when we will have increased staffing costs. The research outlined in the proposal could be performed given the funding requested. Because the project was funded at one third that level, a new scope was outlined and the revised project will be accomplished within budget.

**Issues/Problems:**

The level of funding has been a serious impediment to the project. The scope of the project was revised at the outset such that the key aspects of the site-characterization will be completed; plutonium chemical systems will be characterized, with crucial solution

thermodynamics deemphasized; interactions of plutonium species with manganese minerals will be studied less completely than outlined in the original proposal.

**Corrective Actions:**

To meet the budget shortfall relative to the proposed research we have maintained the nature of the research--site characterization, plutonium and plutonium-mineral chemical studies, geochemical modelling, and connections between these areas, but have reduced the scope, number of samples and systems studied, and thermodynamic measurements.

**Additional Information:**

An important element of this project is interactions between researchers at LANL and personnel performing site assessment and remediation at the RFETS. We maintain contact with the site and pay for travel to this site using funds allocated for this project, including a visit by Wolfgang Runde in October 1998 and a visit by Mary Neu in March of 1999. The latter visit included technical presentations to the Actinide Migration and Remediation Group at RFETS and to the Citizens Advisory Board. These presentations were very well received, particularly because the speciation information we have obtained on soil samples from the site suggests the bulk of the plutonium present is in a highly insoluble, immobile form, PuO<sub>2</sub>. These results will have a significant impact on site remediation, closure and monitoring and should yield substantial savings to the D.O.E.

Our characterization of the plutonium in soil from the RFETS is the first direct speciation of plutonium in an environmental sample. We are preparing a manuscript for Nature, reflecting the importance of this result and comparing it to the recent article therein regarding colloid facilitated transport of plutonium at the Nevada Test Site. Spring 1999 ACS Meeting in Anaheim, Fall ACS meeting in New Orleans, Actinide Migration Conference in Lake Tahoe.

We presented research results at two meetings at the RFETS, the first was a meeting of technical contractors and reviewers who are directing actinide migration and remediation at the site, the second was a meeting of the local Citizens Advisory Board and local officials from the EPA and other agencies. We reported that the predominant oxidation state in a sample taken from the 903 Pad area at RFETS was +IV and the EXAFS spectrum was most consistent with PuO<sub>2</sub>. This news was very

To better understand environmentally relevant actinide species and actinide-mineral systems which affect the stability and mobility of these radioactive contaminants in soils and groundwaters we are 1) studying the plutonium chemistry at a well-characterized actinide contaminated site and 2) studying particular plutonium and plutonium-mineral systems.

Our site based studies began with using Thermal Ionization Mass Spectrometry (TIMS) analysis to obtain plutonium concentrations, distributions, and  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in soils at Rocky Flats Environmental Technology Site (RFETS) to better understand Pu pathways from contamination sources and assess public risk.