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**SUBJECT: REPORTS FOR RESEARCH CONDUCTED UNDER THE TECHNICAL
TASK PLAN AL17SP23**

Dear Mr. Gilbertson & Mr. Hirsch:

Los Alamos National Laboratory is pleased to submit the last remaining report of the Final Reports for research conducted under the Technical Task Plan AL17SP23.

TITLE:	PI:
PLUTONIUM SPECIATION, SOLUBILIZATION, AND MILGRATION IN SOILS	MARY P. NEU

In accordance with the guidance memo, this report was also submitted electronically to EMSP web page. Should you have any questions please feel free to contact our office call me at 505 667-5338.

Regards,



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Title: PLUTONIUM SPECIATION, SOLUBILIZATION, AND
MILGRATION IN SOILS

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Submitted to: DOE

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FINAL REPORT

U.S. Department of Energy

Environmental Management Science Program

Plutonium Speciation, Solubilization, and Migration in Soils

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Executive Summary

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. There is scientific uncertainty about the levels of risk to human and environmental health posed by this accumulation and whether Pu is migrating from Federal reserves onto public lands. To properly control Pu migration in soils, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation, transport, and release mechanisms is needed. Some of the specific questions we attempted to answer are: Based upon fundamental data, what are the most common forms of plutonium formed under environmental conditions? What are the major gaps in fundamental data that limit our ability to make accurate predictions about Pu environmental chemistry and radionuclide migration? What are the characteristics of these forms, and would they tend to make plutonium mobile or immobile under site-specific conditions? If one directly detects and studies plutonium in samples from contaminated sites, what are the forms identified? Is plutonium in these forms at risk of being released to DOE and civilian property?

To address these issues we took the following three-faceted approach: 1) Measure the plutonium concentration and identify the form of plutonium present in real environmental samples. 2) Perform laboratory experiments to study environmentally important forms of plutonium that have not been adequately characterized previously, including hydroxide, carbonate, and halide compounds and plutonium sorbed to key minerals. 3) Model plutonium

geochemistry and predict its environmental form given fundamental data and site characteristics. Our major findings are summarized below and within the following full report.

Plutonium in Real Samples from Rocky Flats. We characterized plutonium in soil and water samples from the Rocky Flats Environmental Test Site (RFETS). In this substudy our most important finding was that plutonium in a soil sample from a past release site (903 pad area) is in the +IV oxidation state and appears to be present as plutonium dioxide, a generally very low soluble and immobile form, the same stable form of plutonium that is used for long-term storage. We also found that the plutonium is dispersed on micro- and macroscopic scales (and not locally concentrated or associated preferentially with any other element). To determine how mobile the plutonium contamination at RFETS is, we used Thermal Ionization Mass Spectrometry (TIMS) an ultra sensitive method of measuring actinides, capable of detecting $\sim 10^6$ atoms of plutonium to determine Pu concentrations and the isotopic $^{240}\text{Pu}/^{239}\text{Pu}$ ratio. This method allows us to identify the source(s) of the plutonium. Plutonium originating from the RFETS would have a ratio close to 0.06; where as that originating from global fallout isotopic would have higher ratios, up to 0.183. We reviewed detailed TIMS measurements on 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. We determined that non-fallout

isotopic ratios are localized directly east of the site, with only slight divergence north and south of the site. This contradicts previous suspicions of long-range contamination from RFETS in the north/south direction. These research results are very powerful for explaining the observed very limited solubility and mobility of Pu, predicting future behavior, and evaluating remediation, closure, and monitoring plans.

Characteristics of Different Forms of Plutonium. We studied the formation, optical and structural characteristics, and stability of several forms of plutonium, including Pu(IV) hydroxides, Pu(IV) carbonates, Pu(VI) chlorides, and plutonium interacting with a synthetic manganese mineral. Fundamental studies of colloidal Pu(IV) hydroxides revealed that colloid formation is not necessarily prevented by the presence of chelating ligands or high ionic strength. Structural studies using X-ray absorbance (XANES and EXAFS) techniques showed the Pu coordination sphere in these species are quite complicated, as expected. The near-neighbor distances show the colloids have structural features similar to plutonium dioxide, consistent with microscopy and diffraction studies reported in the literature. The EXAFS data and analysis also suggest terminal hydroxo groups, coordinated nitrates and waters in the Pu coordination sphere in addition to terminal oxide, bridging hydroxide, and bridged plutonium.

Single crystals of Np(IV) and Pu(IV) pentacarbonates suitable for X-ray structural analysis were obtained. The overall structures are comparable to the previously reported structure of the analogous Th(IV) species. Isolating the same species for a series of light actinides has given us a rare opportunity to reveal trends across this segment of the periodic table and make some

conclusions about the structure and bonding similarities and differences between tetravalent actinides.

We investigated the transport behavior of ionic Pu and colloidal forms of Pu in aqueous media. Ionic forms of Pu used were Pu(III, IV, VI) and colloidal forms included real, colloidal Pu(IV) hydroxide and pseudo colloids, formed between latex or clay particles and Pu. Several different solid phases, including sand, alumina, charcoal, kaolin, and bentonite, were selected and employed in both batch and flow experiments. The greatest retentions of the ionic forms of Pu were observed for the clay-like materials. The behavior of the colloids was complex; colloid stability was not as predicted. Removal of the colloid's counter ion can destabilize the colloid leading to removal of the Pu via sorption to available substrates. This was observed, for example when colloidal Pu(IV) hydroxide was combined with kaolin or bentonite—a gel formed at the surface of the clay.

We have prepared and extensively characterized manganese phases and performed a number of Pu sorption and co-precipitation experiments. Sorption kinetics, oxidation state changes, speciation as a function of loading, and total binding were all studied for MnO₂ combined with colloidal Pu(IV) hydroxide, chelated Pu(IV) (the NTA complex) and the PuO₂⁺ ion. As expected, all of the Pu species associated rapidly with the MnO₂. XANES spectra of the Pu-MnO₂ solids isolated from the sorption experiments revealed some surprising results with respect to oxidation state changes upon sorption. It is generally hypothesized that Pu(V) is

reduced to Pu(IV) upon sorption to metal oxides via the formation of strong surface complexes. XANES spectra of PuO₂⁺—MnO₂ sorption samples clearly show the Pu(V) is not reduced, and in fact is oxidized to Pu(VI) during the sorption process. Also quite surprising, XANES spectra of colloidal Pu(IV) hydroxide—MnO₂ sorption samples suggest a mixture of Pu(IV), Pu(V), and Pu(VI). Only the Pu(IV)-NTA complex appeared to be stable with respect to oxidation or reduction during the sorption process. SEM data for all of these samples are consistent with our initial interpretation of the XAS data. Micrographs of colloidal Pu(IV) hydroxide—MnO₂ sorption samples showed localized Pu(IV), consistent with an expected surface precipitate. Micrographs of the Pu(V) and Pu(IV)NTA sorption samples did not show any evidence of localized Pu(IV), consistent with broadly distributed Pu surface complexation.

Geochemical Modeling. We compiled and evaluated available Pu thermodynamic data and removed inconsistencies to obtain an updated, defensible database for geochemical modeling. Despite numerous reviews of thermodynamic data for Pu species, few existing databases contain the most recent data provided in the literature. Accurate thermodynamic data are key to reliably model the environmental behavior of plutonium. We also collected and reviewed a large amount of analytical data from the RFETS to estimate bounding conditions (Eh, pH) at the site. We are now poised to use our database and site conditions to predict Pu speciation and resultant mobility.

Project Highlights.

- Plutonium in soil samples from RFETS was determined to be in the tetravalent state and in a highly immobile form.
- Plutonium outside the RFETS boundary was found to generally be typical of global fallout. There does appear to be some migration in the East/West direction, but little migration in the North/South direction.
- Colloidal plutonium(IV) hydroxide can form even in the presence of strong organic chelators or high ionic strength. The behavior of colloidal forms of plutonium and plutonium sorbed onto colloids of other material are not understood or readily predicted, but advances have been made.
- The synthetic mineral delta-MnO₂ can oxidize plutonium in the pentavalent and tetravalent states to the hexavalent state. This is in contrast to most minerals, which generally reduce pentavalent plutonium and strongly sorb the plutonium in a tetravalent form. (Forms of hexavalent and pentavalent plutonium are more soluble and mobile than related forms of tetravalent plutonium.)
- The soluble chloride complexes of plutonium(VI) have been characterized with respect to their thermodynamic formation constants.
- A technically sound, defensible database of plutonium compounds has been produced and can now be used for geochemical modeling and transport predictions.
- The research described was performed by collaborating researchers at Los Alamos, Oak Ridge, and Argonne National Laboratory. We also had extensive communication with personnel at the

Rocky Flats and Hanford sites. One graduate student and three postdoctoral researchers were trained in plutonium chemistry and were full contributors to the program.

Research Objectives:

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium (Pu) in soils for 50 years. To properly control Pu migration within Federal areas and onto public lands, to better evaluate the public risk, and to design effective remediation strategies, a fundamental understanding of Pu speciation and environmental transport is needed. Our goal is to use characterization, mobility, thermodynamic, and mineral-interaction data to develop better models of radionuclide transport and risk assessment which will enable the development of science-based decontamination strategies. In addition, if direct characterization of Pu in samples from a contaminated site reveal that the Pu is predominantly in an exceedingly low soluble, low mobility form, then acceptable, reasonable limits for site remediation and closure can be set in a directly defensible manner.

Our overarching research approach has the following three interrelated facets: characterization of Pu in samples from a contaminated site; fundamental study of environmentally-relevant Pu species; and thermodynamic geochemical modeling of Pu speciation and mobility. This approach differs from those of most other projects funded at a similar level because of its very broad scope and the range of specific methods and techniques used in the research. While one can argue that our approach is overly ambitious, it is absolutely mandated by the state of actinide environmental science. Unlike most other contaminant metals, the knowledge on Pu within each of these subfields is woefully inadequate to support site remediation and stewardship. There are also clear transition paths for each type of information, i.e. site characterization results can be used by owners and stake holders to better understand their contamination problems and remediation issues; fundamental data on Pu species can fill important gaps in existing geochemical databases; thermodynamic modeling using improved data and better defined site conditions can be used to predict long-term contaminant behavior and can suggest particular Pu species for further study. Within this context, the specific tasks described in our original proposal are the following:

- Site Characterization. The total plutonium content in soils surrounding the Rocky Flats Environmental Technology Site (RFETS) had been thoroughly characterized previously; however, less work has been done to separate plutonium in these soils into its sources (site activities at Rocky Flats or global fallout) and no work has successfully determined the speciation of the plutonium. Personnel at the site supported this effort by providing information, samples, and mechanisms to disseminate our results. Task 1) Characterize the plutonium in soils and groundwaters from the RFETS site, determining both the speciation, including concentration, isotopic ratio (239/240), oxidation state and specific chemical form, and the distribution, from a microscopic level (particle size, association with other elements) to a macroscopic level (depth in soil, location). To our knowledge, characterization with this level of detail has never been done for an environmental plutonium sample. Task 2) Communicate these results to the site to assist in site management, remediation, and stewardship.

- Fundamental Studies of Environmentally-Relevant Pu Species. Complimenting characterization of Pu contaminated samples from RFETS are laboratory studies of species we know to be predominant in near-neutral pH aqueous solution. To study the formation, stability, and structural and spectroscopic features of these Pu species we are using multiple 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 naturally focused on these types of complexes. In addition to Pu solution complexes and solids, Pu species sorbed onto mineral phases are known to be very important. For example, Pu concentrations in settling ponds at RFETS have shown seasonal variation that correlates well with Mn concentrations. To determine the mechanism(s) of interaction between Pu and Mn minerals and the potential release of Pu via redox cycling, we are performing experiments where Pu species are sorbed onto well-characterized Mn mineral phases. These studies will provide a background for understanding the interactions of Pu with redox active transition metal oxides and for predicting how Pu-mineral interactions affect actinide geochemistry at the RFETS and other contaminated DOE sites. Task 1) Determine the formation, stability, structural characteristics, and spectroscopic features of environmentally relevant plutonium (III, IV, and V) species, using a multimethod approach. 2) Determine the mechanism(s) of interaction between plutonium species and manganese oxide minerals and their effects on plutonium speciation and solubility for both the reduced and oxidized state of the mineral. 3) Determine the impact of seasonal mineral redox cycling on plutonium solubility.
- Thermodynamic Geochemical Modeling of Pu. Accurate thermodynamic data are key to reliable modeling of the plutonium behavior in natural systems. Despite numerous reviews on plutonium chemistry and thermodynamics, recent data on Pu compounds have not been included in databases, and older data, which are incorrect remain. Task 1) Critically review all available stability constants for Pu species and generate a defensible database for thermodynamic modeling. Task 2) Using these refined data, generate stability field diagrams for Pu species as a function of Eh and pH.

The bulk of the research proposed was completed at Los Alamos National Laboratory (LANL). Colloid studies were performed both at LANL and at Oak Ridge by Dr. R. G. Haire and colleagues. The D.O.E. Office of Science, Basic Energy Sciences (BES) supported this work indirectly because X-ray absorbance studies were conducted at both the Stanford Synchrotron Radiation Laboratory (SSRL) and the Advanced Photon Source, and these institutions are supported by BES. Personnel at RFETS and Kaiser Hill organizations were very helpful in obtaining samples from RFETS for detailed analyses and they covered the initial sampling costs.

Methods and Results:

I. Site Characterization Studies. We set out to characterize plutonium in waters, soils, and sediments from the RFETS. Our most important finding is that the Pu concentrations in nearly all the samples we obtained from the site were far below the detection limit for the techniques that can be used to determine speciation. We were able to, for the first time, determine the exact form of Pu in an environmental sample--plutonium in samples from the area 903 pad at RFETS has spectroscopic signatures most consistent with plutonium dioxide, PuO₂. This solid has exceedingly low solubility, consistent with the low concentrations of Pu in samples external to the site and with the finding that the source of this Pu is global fallout from past nuclear weapons testing.

We used Thermal Ionization Mass Spectrometry (TIMS) an ultra-sensitive analytical method, capable of detecting $\sim 10^6$ atoms of plutonium in environmental samples, to determine Pu concentrations and the isotopic $^{240}\text{Pu}/^{239}\text{Pu}$ ratio which allowed us to identify the sources of the plutonium. Plutonium originating from the site would have a ratio close to 0.06; whereas that originating from global fallout would have higher isotopic ratios, up to 0.183.

We reviewed detailed TIMS measurements on 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. We determined that non-fallout isotopic ratios are localized directly east of the site, with only slight divergence north and south of the site. This contradicts previous suspicions of long-range contamination from RFETS in the north/south direction (Figure 1). 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.

We analyzed a large number of samples from the RFETS, including many sediment and water samples from the drainage and settling ponds. Consistent with the TIMS study, we found very low Pu concentrations, far below concentrations necessary to obtain any detailed speciation information. An additional problem was the presence of interfering elements. For example, 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). (X-ray absorbance measurements were performed at the Stanford Synchrotron Radiation Laboratory on samples that were multiply contained and shipped to the site using approved Laboratory and Department of Transportation procedures.) Unfortunately, the sample has a relatively high concentration of Zr or another element that 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 could not observe an absorption edge corresponding to the Pu in the soil sample. We then measured the XANES spectrum of 3.2 $\mu\text{g/g}$ or 372 nCi ^{239}Pu sorbed onto smectite. The spectrum for this sample showed 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 encouraged us to continue analyses on soil samples we received that had comparable Pu concentrations:

The samples on which we were able to obtain the most detailed Pu characterization were soil samples from the 903 Pad area, a past waste storage area within the RFETS site, which had been remediated (upper layer of soil had been removed). These samples, collected in March of 1998, had among the highest Pu concentrations obtained at the site in recent years. They provided an opportunity to determine the speciation and other chemical and physical details of contaminant Pu. We size fractionated two soil samples, a sample A from borehole BH94098, depth 0.0 to 0.5 ft. and a sample B from borehole BH91598f, depth 0.8 to 1.5 ft. The samples were fractionated using mesh into the following sizes: > 0.0234 inch, 0.0234-0.0164 inch, 0.0116-0.0164 inch, and >0.0116 inch. Because Am and Pu concentrations are generally highly correlated in samples at the RFETS site, each fraction was analyzed for ²⁴¹Am using gross gamma counting. (The counter used for the gamma analyses has an efficiency of approximately 18% for a solution at 2 mL height in the same sample holders and geometry used for these samples.) The results of the gross counting are summarized in Table 1. Representative samples were isolated and packaged for X-ray absorbance measurements at the Stanford Synchrotron Radiation Laboratory. Representative samples were also isolated and mounted on conducting stubs for autoradiography, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. (Note that fractions A1 and B1 were quite large, mostly pebbles, and were not suitable for analyses.)

Table 1. Fractionations of soils from the RFETS and Gross Gamma Counting Results.

	Size	Net CPS/g gross gamma ²⁴¹ -Am
A1	> .0234 inch	
A2	0.0234-0.0164 inch	8.995
A3	0.0116-0.0164 inch	22.97
A4	>0.0116 inch	8.832
B1	> .0234 inch	
B2	0.0234-0.0164 inch	30.2
B3	0.0116-0.0164 inch	41.71
B4	>0.0116 inch	78.19

Throughout the years, X-ray absorbance experiments were previously difficult because the 'standard' L_{III} spectra were not informative due to the presence of elements which absorb in the same energy range. Data were therefore obtained on the soil fractions using the L_{II} absorption edge. Two of the fractions, B2 and B3, were sufficiently concentrated in plutonium to yield

spectra that showed absorbance edges (Figure 2). The near-edge regions of the spectra have an absorbance maxima and edge features indicative of Pu(IV). In fact, directly after measuring the soil samples, we measured the L_{II} absorbance of pure solid PuO₂ and found the spectra had the same features at the same energies (edge, maximum, no near-edge 'shoulder' indicative of Pu(V) or Pu(VI)). (See first derivative spectra of fractions B3 and PuO₂ in Figure 3.) Clearly, the bulk of the Pu in these soil fractions is in the +IV state.

Fraction B3 contained enough Pu to yield features in the spectrum beyond the edge, into the EXAFS region (Figure 4). Although the signal to noise in this spectrum of an environmental sample is far from ideal, analysis of the EXAFS data indicates nearest neighbor atoms at a distance of 2.33 Å from the Pu in the soil sample, consistent with PuO₂. By ratioing the intensities of the signals from the nearest neighbor atoms and the noise in spectra of the soil fraction and PuO₂, one can estimate that there are approximately eight nearest neighbor atoms, again consistent with PuO₂. Another way to approach interpretation of the data is to note that features one would expect for other likely Pu(IV) species and observe they are not present in the spectrum. Three likely species are Pu(IV) hydroxide, colloidal Pu(IV), and Pu(IV) carbonate. From extensive previous studies on these species in both the solution and solid states we know they have nearest neighbor atoms at distances of 2.18-2.21 Å, 2.18-2.21 Å, and 2.45 Å, respectively. Even though the concentrations are very low, yielding data that are not very high quality, distances of 0.1 Å are easily resolved and we would clearly have a different spectrum if these species were present at a significant ratio of the total Pu.

We studied the elemental composition and localization of Pu in these same soil fractions (A2-A4 and B2-B4) using radiography, electron microscopy (SEM), and energy dispersive spectral analysis (EDS). We anticipated that the microscopic and elemental analysis of micron and submicron sized plutonium-containing particles from RFETS would allow for the identification and characterization of soil constituents which serve as actinide sinks. EDS analysis showed the samples were predominantly aluminosilicates (consistent with the geology of the RFETS region) and that Pu was not correlated with any other elements (Figure 5b1-b3). Al, Si, K, and O dominated the spectra; other elements were absent or present in only micrometer scale spots at trace levels. SEM secondary electron images and elemental maps (obtained by scanning the field for X-rays corresponding to Pu M and L lines) show that the Pu in the soil fractions was delocalized down to at least the 100Å scale (Figure 5a-c). Radiography particle track images are consistent with the SEM data. Radiographs were measured for dozens of subsamples of the soil fractions with measurement times of one to five days. Nearly all radiographs showed dispersed, omni-directional tracks (Figure 6a,b,d), indicating delocalized radioactivity. A single radiograph for a subsample of fraction B4 showed some localized radioactivity (Figure 6c). This same sample was analyzed by SEM and EDS and no evidence for Pu localization was observed (Figure 7).

Not only is this the first definitive spectroscopic data on Pu in an environmental sample, but the data show that the Pu in the most concentrated samples from the RFETS is in a highly stable and immobile form, the dioxide PuO₂. 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. Plutonium that had been susceptible to weathering or other chemical mobilizing processes would likely be more localized and/or associated with another redox active element. These results should be very powerful and useful to RFETS personnel tasked with addressing concerns regarding plutonium migration from the site and for those tasked with remediating the site.

II. Fundamental Studies of Environmentally-Relevant Pu Species. A. Hydroxides and Carbonates. Complimenting characterization of Pu contaminated samples from RFETS are laboratory studies of species we know to be predominant in near-neutral pH aqueous solution under environmentally relevant conditions. To study the formation, stability, and structural and spectroscopic features of these Pu species we are using 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 naturally focused on these types of complexes. We are attempting 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.

Plutonium(IV) is the primary 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-solubility 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, prepared colloidal Pu hydroxides in concentrated electrolyte solutions, and have performed the first study to determine the coordination geometry about plutonium in these species using EXAFS.

We synthesized colloidal Pu(IV) hydroxide using the standard preparative method beginning by increasing the pH of a Pu(IV), nitric acid solution to pH = 10, to yield a finely divided green precipitate. The solid was washed several times and then peptized using dilute (0.010 M) nitric acid to yield a transparent, green solution that had the characteristic optical absorbance spectrum (UV/vis) of colloidal Pu(IV) hydroxide. The conventional wisdom is that this material does not form in the presence of organic chelators or at very high ionic strength. Surprisingly, we observed the formation of colloidal species both in the presence of 0.10 M citrate and in saturated NaCl, nitrate solution. In the presence of citrate, the UV/vis spectrum of the Pu(IV) species initially formed at pH = 10 is that of a simple citrate complex. However, after one day the spectrum contained the absorbance bands initially present and new bands characteristic of

colloidal Pu(IV) hydroxide (Figure 8). In a saturated NaCl, nitrate solution the precipitation/resuspension behavior and UV/vis spectra were identical to those observed in nitrate only solution. It is noteworthy that a colloidal species did not form in saturated NaCl when nitrate was absent. The colloidal nature of these materials was confirmed using dynamic light scattering measurements.

Despite their long-standing importance in Pu chemistry, there is still much to learn about colloidal hydroxide species, particularly the formation and impressive stability of these colloids. We investigated the coordination geometry about Pu in several samples, both colloid solutions (transparent suspensions) and solids isolated from the solutions by simple water evaporation. The transform modulus of the EXAFS spectrum of the 'standard' colloid was best fit using a model including 6 types of near-neighbor atoms, ~11 oxygen and nitrogen atoms at 2.20-3.31 Å and ~8 plutonium atoms Pu at 3.82 Å (Figure 9). For comparison, we have measured numerous EXAFS spectra of plutonium oxide (fcc, fluorite structure) which has 8 O at 2.33 Å and 12 Pu at 3.84 Å. The EXAFS spectrum of the colloid formed in citrate solution was similar to the spectrum of the colloid formed in nitrate solution, but some of the light atom distances changed and analysis revealed an additional near-neighbor Pu at 4.45 Å, suggesting bridging citrate.

The EXAFS spectra of colloidal species provided metrical parameters against which those from Pu in soil samples from RFETS were compared to conclude that the Pu was present as the oxide or in a form much like PuO₂ and not as a colloid (or sorbed hydroxide). These results have increased importance due to the implication that a colloidal form may be responsible for the long range migration of Pu at the Nevada Test Site as reported in *Nature* last year.

We also studied An(IV) carbonates, beginning with An(CO₃)₅⁶⁻ (An = Th, U, Np, Pu) species which form in concentrated carbonate solutions and are 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 Na₆Th(CO₃)₅•6H₂O, and solubility experiments which imply the same species in solution. We have determined the solid-state structure of Np(CO₃)₅⁶⁻ and Pu(CO₃)₅⁶⁻, using single crystal X-ray diffraction, in order to characterize these species, considered how structures and bond distances change across the actinide series, and now have a basis for study of other carbonate and mixed hydroxocarbonate species (Figure 10). (Single crystals of the corresponding U(IV) species have eluded us, but we continue to attempt to isolate them and complete the series.) When comparing average M—O bond distances relative to ionic radii for each An(IV) (Th, Np, Pu) we found the bond length decreases by about the same magnitude as the ionic radii decreases across the series (parameters listed in Table 2). For the Np(IV) species versus the Pu(IV) the bond distance decreases by 0.002 to 0.016 Å (depending on the structure) while the metal ionic radius decreases by approximately 0.01 Å. The bond distances and ionic radii for Th(IV) are significantly longer than for the Np and Pu species, each

by about the same distance. These data suggest that An--carbonate bonds are about the same strength across the series and that Np(IV) is a much better homolog for Pu(IV) than is Th(IV).

Table 2. Actinide--oxygen (carbonate) bond distances in the anion from single crystal x-ray structures of $M_6An(CO_3)_5$.*

	$[Th(CO_3)_5]^{6-}$	$[Np(CO_3)_5]^{6-}$	$[Pu(CO_3)_5]^{6-}$ a	$[Pu(CO_3)_5]^{6-}$ b
Ave. M--O	2.493(11)	2.431(9)	2.415(7)	2.429(5)
Radius M(IV)	0.94	0.87	0.86	0.86
Reference	Voliotis, P.S.; Rimsky, A <i>Acta Cryst.</i> 1975 , <i>B31</i> , 2612, 2615.	This work.	Clark, D.L., et al. <i>Inorg. Chem.</i> 1998 , <i>37</i> , 2893.	This work.

*The Pu(IV) carbonate complex structure a is for the anion amidst dozens of water molecules and several equivalents of Na_2CO_3 . The M—O distance may be affected by the extensive hydrogen bond network present. In contrast, the $Pu(CO_3)_5^{6-}$ anion in structure b is isolated and therefore more directly comparable to other published bond distances.

II. *Fundamental Studies of Environmentally-Relevant Pu Species. B. Actinide Colloid Formation, Stability, and Migration.* Studies were conducted to investigate the transport of both ionic and colloidal forms of plutonium in aqueous media in the presence of solid phases. Several different solid phases were selected and employed in both batch and flow-type experiments with plutonium. The solid phases included: sand, alumina, charcoal, kaolin, and bentonite. Ionic forms of plutonium included: Pu(III); Pu(IV); and Pu(VI). Both real and pseudo colloids of plutonium were examined.

An important aspect of these studies was to obtain a well-characterized plutonium colloid and use it to perform the investigations. We prepared a stock Pu(IV) colloid solution by peptizing Pu(IV) hydroxide solids with dilute nitric acid. It was determined that the resulting colloid consisted of non-aggregated, nominal diameter 25 Å particles of Pu (IV) in solution. X-ray diffraction analysis showed the core material to be PuO_2 , consistent with previous findings. Ionic plutonium nitrate and chloride solutions were used. The Pu(III) was prepared by reduction with hydroxylamine; Pu(IV) by treatment with nitrous oxide; and the Pu(VI) by oxidation with peroxydisulfate or chromate.

Analyses of the materials was done using UV/vis spectrophotometry, alpha counting (gross alpha and pulse height), X-ray diffraction and microscopy (scanning, transmission). Flow type experiments, with/without pressure, were conducted using a 1 cm diameter by 9 cm in length quartz columns filled with different solid matrices. In addition, stainless steel Millipore columns with filters were used to hold the solid phases. Flow rates up to 5ml/minute were employed. Batch type experiments were also performed. In this case, a weighed quantity of the material to

be tested was contacted with the aqueous plutonium and equilibrated. Subsequently, the phases were separated by a filtration or centrifugation. The phases were then analyzed to determine the distribution of the plutonium between the two phases.

We found that colloidal materials were not removed by sand or Bioglas (small porous spheres of glass), while charcoal and alumina removed ~ 50% of the colloid from solution. In the latter cases, the colloid could not be removed by washing with large quantities of water or solutions containing the colloid's normal counter ions. This removal is considered due to the initial removal of the colloids counter ions, due to unfavorable or "competing" pH conditions. Both the charcoal and alumina matrix offered basic conditions, which resulted in gelation of the Pu. The gelation could not be reversed by mild measures such as washing with water or replacement of the initial counter ions.

With various clay materials (Kalin, Bentonite, etc.), the plutonium colloid was removed completely from solution. The colloid formed a gel on the surface of the clays, which would not wash off with water or reverse flushing. Upon air drying the gel layer "cracked" and pieces of the gel could be removed. This gel material could not be re-suspended by further treatment with water or a solution that provided fresh counter ions for the gelled colloid particles. The conclusion was that the negatively charged counter ions were replaced with hydroxyl ions, which led to secondary particle aggregation or agglomeration via condensation. The resulting aggregates were not able to produce colloidal particles with the subsequent mild treatments with fresh aqueous solutions. Thus, in this regard both Kaolin and bentonite were very effective in removing the plutonium colloid from solution, and re-suspension of the colloid could not be accomplished by addition of water or dilute acid.

With the solutions of ionic plutonium, the removal of the plutonium by the solid matrices generally occurred via complexation, ion-exchange reactions, precipitation or hydrolysis reactions due to pH conditions that led to insoluble materials. The behavior of Pu(VI) was similar to that of other actinyl (VI) ions and Pu(III) like lanthanide (III) ions with the exception that the Pu(III) was readily oxidized to Pu(IV) when the pH became slightly basic. Polymerization followed by precipitation was often encountered with the Pu(IV) ionic solutions. The plutonium in weakly acidic solutions of Pu(IV) was precipitated when coming in contact with charcoal, alumina, etc.

The behavior of the ionic materials was varied with the greatest retardation/retention being observed for the clay-like materials. An unexpected result was observed for mixtures of actinide ions and sand. The untreated, "analytical grade" sand as received, or following washing with acids and/or organic solvents, showed significant uptake of plutonium and americium. However, after calcination of this sand at 1000 °C in air, there was essentially no retention of the ionic forms under the same experimental methods. The conclusion is that some complexing material, perhaps an organic material such as a humic acid, was present in the sand and was only removed/de-activated by the calcination. This emphasizes one of the complexities that can be

encountered with “environmental” materials –they often contain a variety of components that may effect significantly the behavior of the material being examined.

II. Fundamental Studies of Environmentally-Relevant Pu Species. C. Interactions Between Pu Solution Species and Mn Solid Phases. Pu concentrations in settling ponds at RFETS have shown seasonal variation that correlates astonishingly well with Mn concentrations. To determine the mechanism(s) of interaction between Pu and Mn minerals and the potential release of Pu via redox cycling we are performing experiments where Pu species are sorbed onto well-characterized Mn mineral phases. These studies will provide a background for understanding the interactions of environmentally important plutonium complexes with redox active transition metal oxides and for predicting how plutonium-mineral interactions affect actinide geochemistry at the RFETS and other contaminated DOE sites.

Delta-MnO₂, also referred to as birnessite, was chosen for initial studies because it is believed to be the form of MnO₂ that is precipitated out of groundwater during redox cycling. We have prepared delta-MnO₂ using the accepted method of KMnO₄ reduction. The resulting product was divided into two portions, a freeze-dried sample and a sample stored as a suspension in Milli-Q water. All analysis and experiments have been performed using the freeze-dried sample unless otherwise indicated. This material has been characterized using a number of analytical methods. We determined the surface area (SA) of the solid to be 214 m²/g using the ethylene glycol monoethyl ether method and 41.1 m²/g using the BET method, two very common accepted surface area determination techniques. The much higher SA determined using the ethylene glycol method may be due to 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 absorption 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 of a mole of hydrated water for every mole of MnO₂. The X-ray diffraction pattern indicates the MnO₂ sample is primarily amorphous with some crystallinity and contains four broad peaks at d-spacings of 7.24, 3.65, 2.43, 1.41 Å, consistent with patterns reported in the literature for birnessite. There is no difference in the XRD pattern for the freeze-dried material versus a filtered and air-dried material. 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 MnO₂ 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 MnO₂ particles. TEM analysis suggested that the individual aggregate size ranges from 10-100 nm with individual particles of about 2 nm. The TEM micrographs of the MnO₂ (Figure 11) are similar to those reported for delta-MnO₂ in the literature. Under the electron beam the amorphous MnO₂ sample crystallizes due to local heating (temperatures reach ~100-150°C), most likely transforming into the alpha form of MnO₂, cryptomelane.

Three Pu(V) sorption experiments have been completed; two at low coverage, 27 and 35% loadings, and one at full 100% loading. The amount loading is based on the conservative assumption that one coordinated Pu molecule covers approximately 1 nm² and the actual SA of MnO₂ is the SA determined by the ethylene glycol method. To relate surface adsorption to stoichiometry under these assumptions, 100% loading would imply 0.03 moles of Pu for every one mole of MnO₂. In each case, a Pu(V) stock solution at pH=3.5-4.5 was added to unbuffered MnO₂ suspensions (mg quantities) in Milli-Q water at pH=8.2, 7.4, and 8.1, respectively. For the two lower coverage loadings, the Pu(V) stock solution was added in one increment, whereas for the 100% loading, the Pu(V) stock was added in a titration of six increments with at least one hour of equilibration time between each addition. Adjustments to pH were made using KOH or NH₄OH. Na⁺ ions are also introduced into the system from the preparation of the plutonium stock solutions. During the course of the adsorption of plutonium, the pH of the solution decreased due to the loss of H⁺ from the MnO₂ surface. Although the pH of the solution was not adjusted once the plutonium was added to the MnO₂, the pH was carefully monitored to ensure it remained above the point-zero-charge (PZC) of MnO₂. Final measured pH of the samples was 6.8, 4.7, 7.1, respectively.

Two colloidal Pu(IV) hydroxide sorption experiments have been completed, one at 20% loading and one at full 100% loading. Again, the 100% loading experiment was done as a titration with at least one hour of equilibration time between each of the eight additions. Pu(IV) colloid suspended in Milli-Q water at pH=5 was added to unbuffered MnO₂ solutions at pH= 6.7 and 7.5 respectively. The final pH value was not determined for the lower loading, but the final pH for the 100% loading solution was 4.6. The adsorption of chelated Pu(IV), as Pu(IV) NTA at the equivalent of 100% loading, has also been completed. The unbuffered MnO₂ solution had an initial pH value of 6.7 and a final pH value after adsorption of 5.4.

Sorption rates and amounts were determined by separating the solution and solid phases and using LSC to determine the Pu distribution. The majority of the adsorption occurs within the first few hours. Small fluctuations in concentration are observed with continued monitoring. LSC of the final equilibrium solutions provides information on how much of the added Pu species sorbed or precipitated onto the MnO₂. For the Pu(V) sorption experiments, 0.4%, 0.03%, and 12% of the original Pu(V) added remained in solution for the three loadings, 27%, 35%, and 100% respectively. For the Pu(IV) colloid sorption experiments, 0.03%, and 3.6% of the original Pu(IV) added remained in solution for the 20% and 100% loadings, respectively. Interestingly, 38% of the Pu(IV)NTA complex originally added remained in solution. Confirming our hypothesis that Pu bound by an organic ligand will show less propensity for surface complexation or precipitation. These data also provide information on how well the surface area represents available binding sites. And we find the available binding slightly lower than the SA determined using the ethylene glycol method. The cation exchange capacity of the

MnO₂ must be determined to provide a more accurate estimate of potential Pu binding sites. These experiments are currently in progress.

Samples of the resultant Pu-sorbed manganese oxide solids were analyzed using X-ray absorption and diffuse reflectance spectroscopies and electron microscopy. Surprisingly, preliminary XANES spectra analyses (Figure 12) indicate that Pu(V) is not reduced in the process of sorption. Even more surprising, the data suggest that some of the colloidal Pu(IV) hydroxide is oxidized in the sorption process. Only the complexed Pu(IV), Pu(IV)NTA, appears to be 100% +IV upon absorption to MnO₂. SEM images are also very interesting in that they show localized Pu (Figure 13) in the initially colloidal Pu(IV) hydroxide sorption samples and delocalized Pu (Figure 14) in the initially Pu(V) and Pu(IV) NTA samples. The former is consistent with surface precipitation of colloidal Pu(IV) hydroxide, while the latter is consistent with surface complexation of molecular species. (SEM is capable of detecting plutonium concentrations down to 0.5 wt %, depending on the exact experimental conditions. The penetration depth into the sample at the accelerating voltages used is approximately 0.40 microns.)

III. Thermodynamic Geochemical Modeling of Pu. Accurate thermodynamic data are key to reliable modeling of the plutonium behavior in natural systems. Despite numerous reviews on plutonium chemistry and the thermodynamics recent data on Pu compounds have not been implemented in databases. This work required first an evaluation of the literature to acquire the most reliable constants for Pu species and an evaluation of chemical analyses data from the site to determine representative boundary conditions. We started to compile a thermodynamic database for the control of soluble Pu concentration by solid phase solubility and system redox potential to account for the complex Pu redox chemistry. The updated database focused on compounds with Pu in the +IV, +V, and +VI oxidation states, the most important species for natural systems. In Table 3, the thermodynamic data compiled for future geochemical modeling of the site-specific behavior of Pu are summarized.

For Pu(IV) the tetrahydroxide species, Pu(OH)₄(aq), dominates solution speciation under most natural conditions. While mixed Pu(IV) hydroxocarbonate complexes have been postulated, no reliable spectroscopic confirmation on the stoichiometry of these complexes exist. The stabilities of the most environmentally relevant Pu(V) species, PuO₂OH(aq) and PuO₂CO₃⁻, have been determined spectroscopically and we include these data in the database. Pu(VI) hydroxo and carbonate complexes have been investigated for years and we included the recently reported stability constants in the database. Fluoride complexes may form at low pH where hydroxide and carbonate complexation is minimal, and we also included the available data on Pu(IV) and Pu(VI) fluorides into the database.

Another component necessary for geochemical modeling is bounding conditions at the site of interest. 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. The most prominent changes observed in pond C-2 are variations in temperature from 27.4 to 4.5 °C, and in 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. This range covers the stability region of Pu(IV), (V), and (VI) with the higher oxidized Pu species favored with increasing Eh. With the changes in Eh, temperature, and manganese concentrations seasonal fluctuations in dissolved Pu concentrations were observed. 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. 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.

Table 3. Thermodynamic stability constants and $\Delta_f G^\circ_{298}$ values (species in bold) for environmentally relevant Pu compounds. $\Delta_f G^\circ_{298}$ values of auxiliary species used in the calculations are also provided (33, 34). Superscript zero (⁰) indicates the thermodynamic standard state, defined as the stable state at 1 bar pressure and the temperature under consideration (25°C).

Reaction	log K ⁰ or log β^0	$\Delta_f G^\circ_{298}$ (kJ mol ⁻¹)	Reference
PuO₂²⁺	---	-767.0±6.6	1, 2
PuO₂⁺	---	-857.5±6.7	1-4
Pu⁴⁺	---	-477.8±3.4	1,2,5-7
Pu³⁺	---	-578.6±3.3	8
PuO₂²⁺ + OH⁻ = PuO₂OH⁺	8.1±0.2	-970.5±6.6	9
PuO₂²⁺ + 2 OH⁻ = PuO₂(OH)₂(aq)	14.3±0.2	-1162±6.6	9
PuO₂²⁺ + CO₃²⁻ = PuO₂CO₃(aq)	9.4±0.3	-1348.6±6.8	10-13
PuO₂²⁺ + 2 CO₃²⁻ = PuO₂(CO₃)₂²⁻	14.9±0.6	-1906.9±6.8	10-13
PuO₂²⁺ + 3 CO₃²⁻ = PuO₂(CO₃)₃⁴⁻	17.6±0.4	-2449.1±6.8	10-13
PuO₂²⁺ + F⁻ = PuO₂F⁺	4.6±0.3	-1075.1±6.8	14, 15
PuO₂²⁺ + 2 F⁻ = PuO₂F₂(aq)	7.3±0.5	-1371.6±7.3	15
PuO₂⁺ + H₂O = PuO₂OH(aq) + H⁺	-9.7±0.1	-1039.1±6.7	16
PuO₂⁺ + CO₃²⁻ = PuO₂CO₃⁻	5.1±0.1	-1414.7±6.7	16
PuO₂⁺ + 2 CO₃²⁻ = PuO₂(CO₃)₂³⁻	6.6±1.0	-1951.2±8.8	Estimated from NpO ₂ (CO ₃) ₂ ³⁻
PuO₂⁺ + 3 CO₃²⁻ = PuO₂(CO₃)₃⁵⁻	4.9±0.7	-2469.4±7.8	Estimated from PuO ₂ (CO ₃) ₃ ⁴⁻
Pu⁴⁺ + H₂O = PuOH³⁺ + H⁺	-0.5±0.4	-712.2±4.1	6, 17-20
Pu⁴⁺ + 4 H₂O = Pu(OH)₄ + 4 H⁺	-9±1	-1375±7	Estimated from Np(OH) ₄
Pu⁴⁺ + 5 CO₃²⁻ = Pu(CO₃)₅⁶⁻	-1.4±0.1	-3109.7±3.5	1
Pu⁴⁺ + F⁻ = PuF³⁺	8.8±0.3	-809.9±6.5	21-26
Pu⁴⁺ + 2 F⁻ = PuF₂²⁺	15.7±0.3	-1131.2±6.7	21-26
Pu³⁺ + H₂O = PuOH²⁺ + H⁺	-7.0±0.5	-775.8±4.4	27

$\text{Pu}(\text{OH})_3(\text{s}) = \text{PuO}_2^{2+} + 3 \text{OH}^-$	-26.2±0.8	-1200.1±5.7	28
$\text{PuO}_2 \cdot 2\text{H}_2\text{O} = \text{Pu}^{4+} + 4 \text{OH}^-$ or $\text{Pu}(\text{OH})_4(\text{am}) = \text{Pu}^{4+} + 4 \text{OH}^-$	-57±3	-1432±17	4, 29
$\text{PuO}_2(\text{c}) + 2 \text{H}_2\text{O} = \text{Pu}^{4+} + 4 \text{OH}^-$	-60.2±0.2	-976.2±3.6	29
$\text{PuO}_2(\text{OH})_2(\text{s}) = \text{PuO}_2^{2+} + 2 \text{OH}^-$	-22.7±1.1	-1211.2±9.1	9, 30
$\text{PuO}_2(\text{OH})(\text{am}) = \text{PuO}_2^+ + \text{OH}^-$	-8.9±0.6	-1065.6±7.5	31, 32
$\text{PuO}_2\text{CO}_3(\text{s}) = \text{PuO}_2^{2+} + \text{CO}_3^{2-}$	-14.2±0.3	1376.1±6.8	11
H_2O	---	-237.18±0.080	33, 34
OH^-	---	-157.30±0.090	33, 34
CO_3^{2-}	---	-527.98±0.120	33, 34
HCO_3^-	---	-586.94±0.120	33, 34
F^-	---	-281.75±0.670	33, 34

Relevance, Impact, and Technology Transfer:

We focused on the chemistry, geochemistry and environmental mobility of plutonium because the nature and spread of plutonium contamination is of major concern at many D.O.E. sites. Also, because the aqueous chemistry of plutonium, beyond material processing and separations has only been studied in the last two decades by a small number of research groups, there are tremendous scientific knowledge gaps that need to be filled for site clean-up, risk assessment and stewardship. The three areas that we have studied are of short-, medium-, and long-term interest. For example, the characterization data for Pu in samples from the RFETS was used immediately to inform stakeholders and concerned citizens and to provide more direct scientific underpinnings to the prediction that Pu is very unlikely to be highly mobile at the site via chemical and hydrological processes. (Our data support the current thinking that at the dry, windy, high altitude site, with predominantly surface and shallow subsurface contamination, the main mechanisms of Pu transport are wind and erosion.) In contrast, the new structural and thermodynamic data we have obtained and reported support geochemical modeling, and indirectly, risk assessment. And all facets of our research enable improved, science-based stewardship of contaminated sites.

In terms of how the new scientific knowledge that is generated by this project can improve technologies and cleanup approaches, the most obvious result to draw on is the speciation of Pu in samples from the RFETS. Because we have directly shown the the Pu is in the form of PuO_2 , or very similar, the site can now prove that the source is low-soluble and has exceedingly low potential to become mobile. This knowledge should be used by those responsible for site closure to significantly reduce future costs, schedules, and risks and meet DOE compliance

requirements. Perhaps most importantly, it suggests to the site and to other stakeholders that the risk due to this Pu source may be downgraded, and it may not be necessary to remediate to the very low level initially proposed. In the other areas, we now have arguably the most reliable set of thermodynamic data for environmentally-relevant Pu species. We can use this database to calculate source term and near field concentrations and to identify shortcomings in our current knowledge that must be filled for more accurate fate and transport predictions. We have also characterized important aquo, hydroxo, and carbonate complexes. This fundamental data is important to support geochemical modeling and transport predictions, as well as to support development of remediation technologies specific for these types of species.

In the broadest sense there are three major contributions from this project, and these are: 1) A significant improvement in our understanding of plutonium environmental chemistry, including characterization of environmental samples, new pure Pu species characterized, and a critically-reviewed thermodynamic database. 2) Data delivered directly to RFETS to assist in their characterization, remediation, and closure efforts. 3) Bright new researchers trained in the areas of actinide and environmental chemistry, including three postdoctoral researchers and one graduate student. (All with Ph.D.s from respected departments—Northwestern, Colorado School of Mines, Florida State University, and the University of Tennessee).

Project Productivity: The project clearly accomplished all of the proposed goals. In addition, the project produced more research results than anticipated in both the areas of fundamental research on plutonium species and characterization of plutonium in true environmental samples. The project ran on schedule; however, there were carryovers for some fiscal years because there were not always personnel available. The work plan was revised when the project was initially funded because the original proposal had a much broader and more ambitious scope, with three times the budget allocated. At that time we decided to scale back the amount of research that was performed, but not the nature and three-faceted approach. This turned out to be a critical decision because we were able to make substantial progress in all three areas, and this was not at all certain at the outset of the program. We believe the integration of laboratory experiments, characterization of real samples, and modeling are key to understanding the environmental behavior of actinide contamination in soils and groundwaters and our research has definitely shown that all three aspects must be considered and are best considered by an interactive team.

Personnel Supported: Technical Staff Researchers (LANL): M.P. Neu, W. Runde, S.D. Conradson, D.W. Efurud, D.R. Janecky, C.D. Tait, S.D. Reilly, M.R. Lin; Technical Staff Researcher (ORNL): R.G. Haire; Technical Staff Researcher (ANL): L. Soderholm; Postdoctoral Researchers (LANL): C. VanPelt, D.M. Smith and J.P. Kaszuba; Graduate Student: E. Bliss; Academic Collaborator: Prof. N. Stump, Winston-Salem State University.

Presentations, Publications, Interactions, and Collaborations:

A very important element of this project has been the 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 RFETS using funding for this project, including visits by Wolfgang Runde in October 1998 and 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_2 . It is important to note that all of the stakeholders were most impressed by the direct speciation information we obtained for samples from the site. Scientists have defensibly predicted that the bulk of the Pu present at the site is tetravalent and therefore highly insoluble and immobile. However, spectra *proving* that prediction were much more convincing to concerned citizens, regulatory officials, and site remediation representatives. Our 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. We are also drafting manuscripts for submission to *Inorganic Chemistry* reporting the crystal structures of the tetravalent carbonates and to *Radiochimica Acta* describing the formation, stability, and structural characteristics of colloidal Pu(IV) species. The Pu thermodynamic database and site-specific geochemical modeling results will be submitted to *Applied Geochemistry* for publication. Once completed, the Pu-Mn oxide sorption studies will be submitted to *Environmental Science and Technology*. The research that E. Bliss completed are also published as part of his Ph.D. thesis, obtained from the University of Tennessee, Summer 2000.

Results from this research were presented in one or more presentations at the following conferences: at the EMSP workshop in Chicago, July, 1998; the Geological Society of America Meeting in 1998, the Spring 1999 National American Chemical Society Meeting in Anaheim; the Fall National American Chemical Society Meeting in New Orleans; the Seventh International Radionuclide Migration Conference in September, 1999; the EMSP workshop in Albuquerque, October, 1999, the and will be presented at the EMSP workshop in Atlanta, April, 2000 and the Pu Futures Conference in Santa Fe, July, 2000. Results were also presented in academic seminars by R.G. Haire and E. Bliss including at the University of Tennessee and the oral defense of E. Bliss. Exact titles and authors and meeting details are available upon request, for examples: 1) Kaszuba, John P., Neu, Mary, Runde, Wolfgang, Clark, David L., Efurud, D.W., Janecky, David R., Tait, C. Drew, and Haire, Richard G., 1998, Modeling of actinide geochemistry for reactive transport and waste isolation: Geological Society of America, Abstract GSA v. 30, no. 7, p. A-87. 2) EMSP Scientific Workshop, July 27-30, 1998, Rosemont, IL, Poster presented: Neu, Mary, Runde, Wolfgang, Clark, David L., Efurud, D.W., Janecky, David

R., Kaszuba, John P., Tait, C. Drew, and Haire, Richard G., 1998, Plutonium speciation, solubilization, and migration in soils: Environmental Management Science Program Workshop, Chicago, Illinois, July 27-30: U.S. Department of Energy, Office of Environmental Management, CONF-980736, p. 232-234.

This project included a collaboration between investigators at LANL and ORNL. And our interactions with RFETS, because they have been so detailed and helpful, should be considered a collaboration. Through this project we have fostered new collaborations with Lynne Soderholm at ANL for X-ray absorbance studies of new systems and with John Zachara at PNNL for characterization of samples from the Hanford site. Several other site contacts have been made i.e. with Dean Peterman at INEEL and Major Thompson at SRS, but no formal collaborations have arisen from these interactions thus far.

Transitions:

Our results in the area of environmental sample characterization have and are being used by the RFETS. These results have also been the impetus for similar studies on building materials from RFETS to assess decontamination and disposal strategies and on environmental samples at the Hanford and INEEL sites. Our results on fundamental plutonium species will be used by actinide scientists to further our understanding of plutonium and actinide chemistry. They are also directly applicable in geochemical modeling studies, i.e. the charges and structures of the species are very important in parameterizing their expected interactions with soil components. Our thermodynamic database, along with site characteristics, is being used to improve geochemical modeling and transport predictions

Future Work:

We have requested new support from the EMSP to study additional environmental samples and plutonium complexes. There are still substantial gaps in our understanding of plutonium (solution)-mineral (solid) interactions and those are key to the next improvements in geochemical transport and risk predictions. The project has already led to a great deal of related work, including the characterization of samples from RFETS and other sites for a variety of purpose. The results have also supported other fundamental studies by us and others of both a fundamental and applied nature. For example, research in the DOE NABIR program hinges on our understanding of actinide geochemistry and speciation.

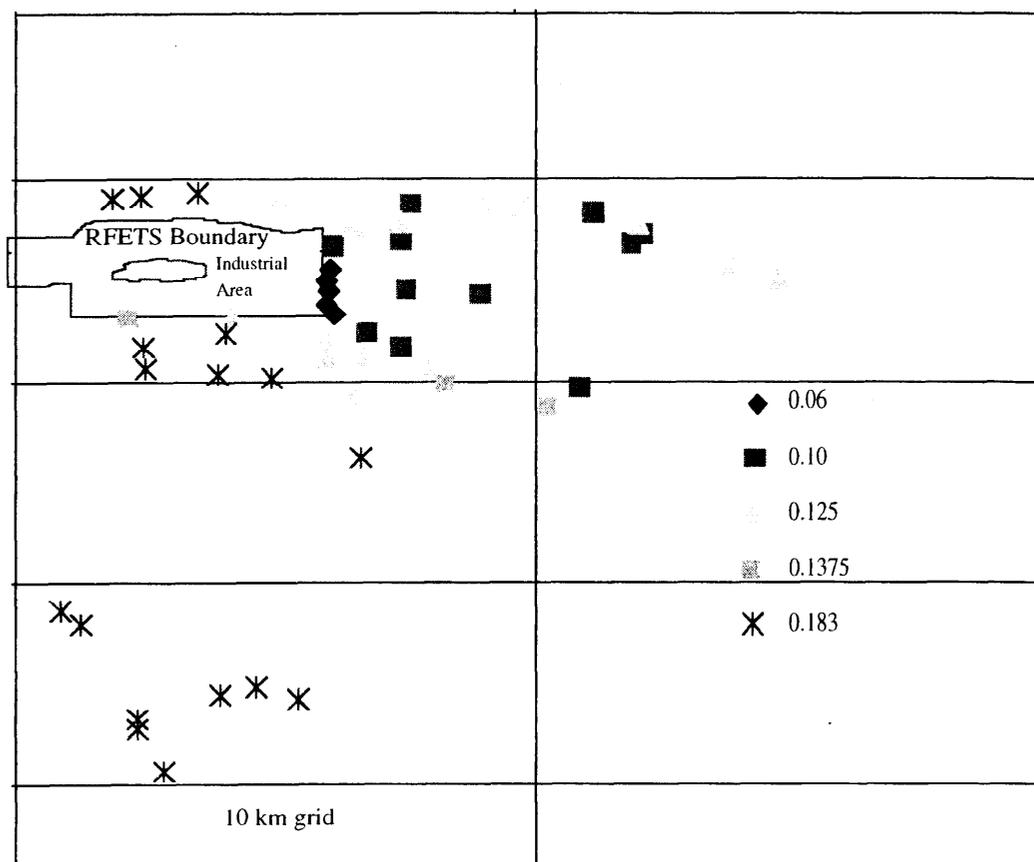
Literature Cited

1. Capdevila, H.; Vitorge, P.; Giffaut, E. *Radiochimica Acta* **1992**, 58-59, 45-52.
2. Capdevila, H.; Vitorge, P. *Radiochimica Acta* **1995**, 68, 51-62.
3. Riglet, C.; Robouch, P.; Vitorge, P. *Radiochimica Acta* **1989**, 46, 85-94.
4. Rai, D. *Radiochim. Acta* **1984**, 35, 97-106.
5. Connick, R. E.; McVey, W. H. *J. Am. Chem. Soc.* **1951**, 73, 1798-1804.

6. Rabideau, S. W.; Lemons, J. F. *J. Am. Chem. Soc.* **1951**, *73*, 2895-2899.
7. Rabideau, S. W.; Cowan, H. D. *J. Am. Chem. Soc.* **1955**, *77*, 6145-6148.
8. Fuger, J. F.; Oetting, F. L. *The chemical thermodynamics of actinide elements and compounds. Part 2: The actinide aqueous ions*; International Atomic Energy Agency: Vienna, 1976, pp 65.
9. Pashalidis, I.; Kim, J. I.; Ashida, T.; Grenthe, I. *Radiochim. Acta* **1995**, *68*, 99-104.
10. Sullivan, J. C.; Woods, M.; Bertrand, P. A.; Choppin, G. R. *Radiochimica Acta* **1982**, *31*, 45-50.
11. Robouch, P.; Vitorge, P. *Inorg. Chim. Acta* **1987**, *140*, 239-42.
12. Ullman, W. J.; Schreiner, F. *Radiochimica Acta* **1988**, *43*, 37-44.
13. Pashalidis, I.; Czerwinski, K. R.; Fanghänel, T.; J.I., K. *Radiochim. Acta* **1997**, *76*, 55-62.
14. Choppin, G. R.; Rao, L. F. *Radiochim. Acta* **1984**, *37*, 143-146.
15. Sawant, R. M.; Chaudhuri, N. K.; Patil, S. K. *Journal of Radioanalytical and Nuclear Chemistry* **1990**, *143*, 295-306.
16. Bennett, D. A.; Hoffman, D.; Nitsche, H.; Russo, R. E.; Torres, R. A.; Baisden, P. A.; Andrews, J. E.; Palmer, C. E. A.; Silva, R. J. *Radiochimica Acta* **1992**, *56*, 15-19.
17. Rabideau, S. W. *J. Am. Chem. Soc.* **1957**, *79*, 3675-3677.
18. Metivier, H.; Guillaumont, R. *J. Inorg. Nucl. Chem., Supp.* **1976**, 179-183.
19. Nitsche, H.; Silva, R. J. *Radiochimica Acta* **1996**, *72*, 65-72.
20. Kraus, K. A.; Nelson, F. *The Hydrolytic behavior of Uranium and the Transuranic Elements. Part II. The +3 and +4 Oxidation States*; Oak Ridge National Laboratory, 1948.
21. Krylov, V. N.; Komarov, E. V. *Sov. Radiochem.* **1969**, *11*, 94-96.
22. Krylov, V. N.; Komarov, E. V.; Pushlenkov, M. S. *Sov. Radiochem.* **1969**, *11*, 97-98.
23. Bagawde, S. V.; Ramakrishna, V. V.; Patil, S. K. *Journal of Inorganic & Nuclear Chemistry* **1976**, *38*, 2085-2089.
24. Bagawde, S. V.; Ramakrishna, V. V.; Patil, S. K. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1339-1345.
25. Chitnis, R. T.; Talnikar, S. G.; bhogale, R. G.; Patil, S. K. *J. Radioanal. Chem.* **1979**, *50*, 53-60.
26. Nash, K. L.; Cleveland, J. M. *Radiochim. Acta* **1984**, *36*, 129-134.
27. Kraus, K. A.; Dam, J. R. In *The Transuranium Elements*; G. T. Seaborg, J. J. Katz and W. M. Manning, Eds.; McGraw-Hill: New York, 1949; pp 466-499, 528-549.
28. Felmy, A. R.; Rai, D.; Schramke, J. A.; Ryan, J. L. *Radiochim. Acta* **1989**, *48*, 29-35.
29. Kim, J. I.; Kanellakopoulos, B. *Radiochim. Acta* **1989**, *48*, 145-150.
30. Kim, J. I.; Bernkopf, M.; Lierse, C.; Koppold, F. In *Geochemical Behavior of Disposed Radioactive Waste. ACS Symposium Series*; Scott-Barney, Navratil and Schulz, Eds. 1984; Vol. 246; pp 115-134.

31. Kraus, K. A.; Nelson, F. *The Hydrolytic of Uranium and the Transuranic Elements*; Oak Ridge National Laboratory, 1948.
32. Zaitseva, V. P.; Alekseeva, D. P.; Gel'man, A. D. *Sov. Radiochem.* **1968**, *10*, 526-529.
33. Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. *Computers & Geosciences* **1992**, *18*, 899-947.
34. Shock, E. L.; Helgeson, H. C. *Geochimica et Cosmochimica Acta* **1988**, *52*, 2009-2036.

Thermal Ionization Mass Spectral (TIMS) Data for Samples Near the RFETS



$^{240}\text{Pu}/^{239}\text{Pu}$ ratios determined using TIMS to identify source of Pu in soil samples collected near the RFETS.

Plutonium originating from the site would have a ratio close to 0.06; whereas that originating from global fallout has higher ratios up to 0.183.

The RFETS area is approximately 30 km².

TIMS and compilation of data
performed by D.W. Efurd and D.R. Janecky.

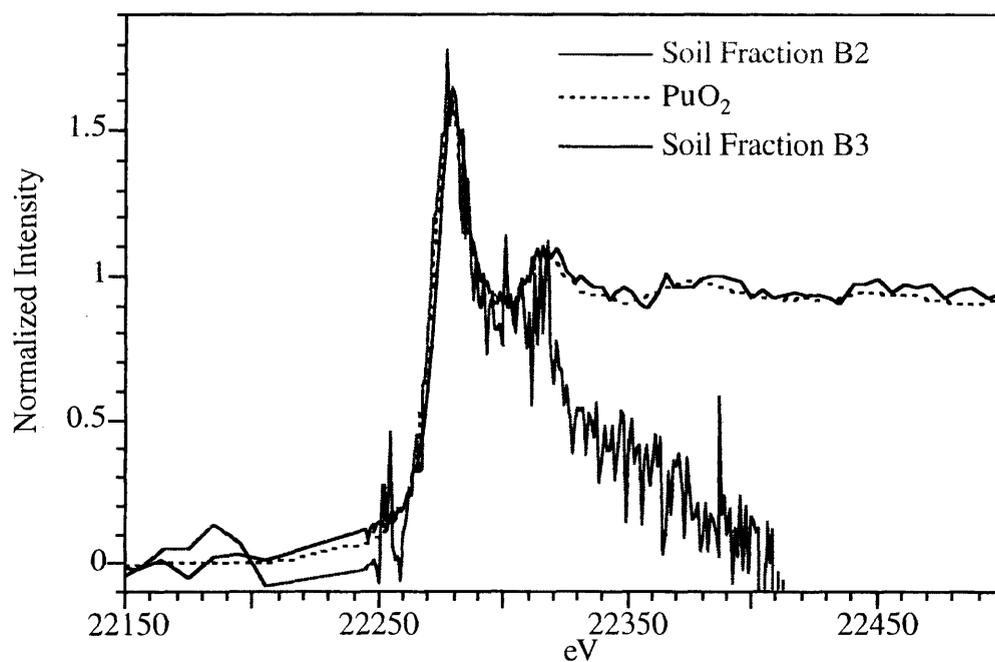


Figure 2. X-ray Absorbance Near-Edge Spectra (XANES) of fractions B2 and B3 of RFETS 903 area pad soil sample and standard solid PuO₂. Spectra shown are averages of multiple scans acquired over the plutonium L2 absorbance edge energy range.

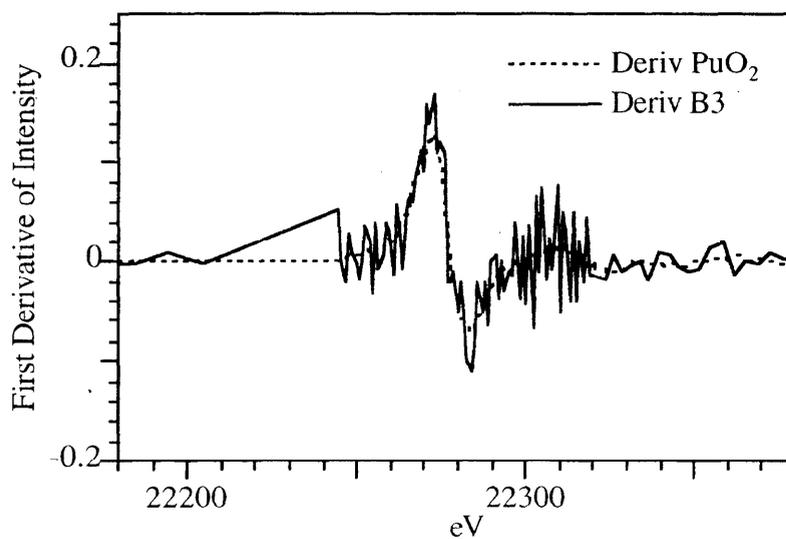


Figure 3. First derivatives of X-ray Absorbance Near-Edge Spectra (XANES) of fraction B3 of RFETS 903 area pad soil sample and standard solid PuO₂.

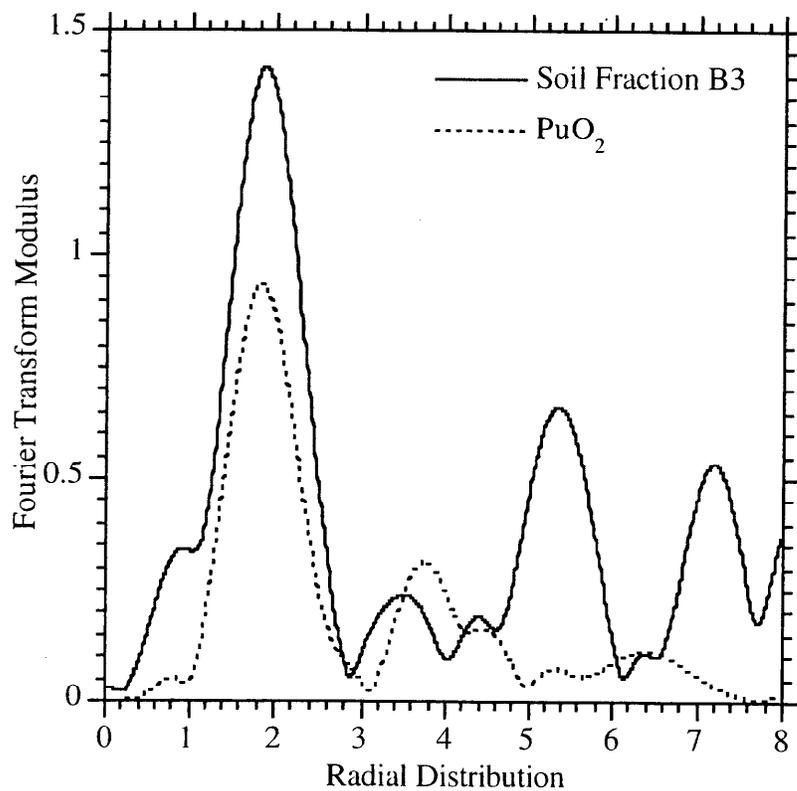


Figure 4. X-ray Absorbance Near-Edge Spectra (XANES) of fractions B2 and B3 of RFETS 903 area pad soil sample and standard solid PuO₂. Spectra shown are averages of multiple scans acquired over the plutonium L2 absorbance edge energy range.

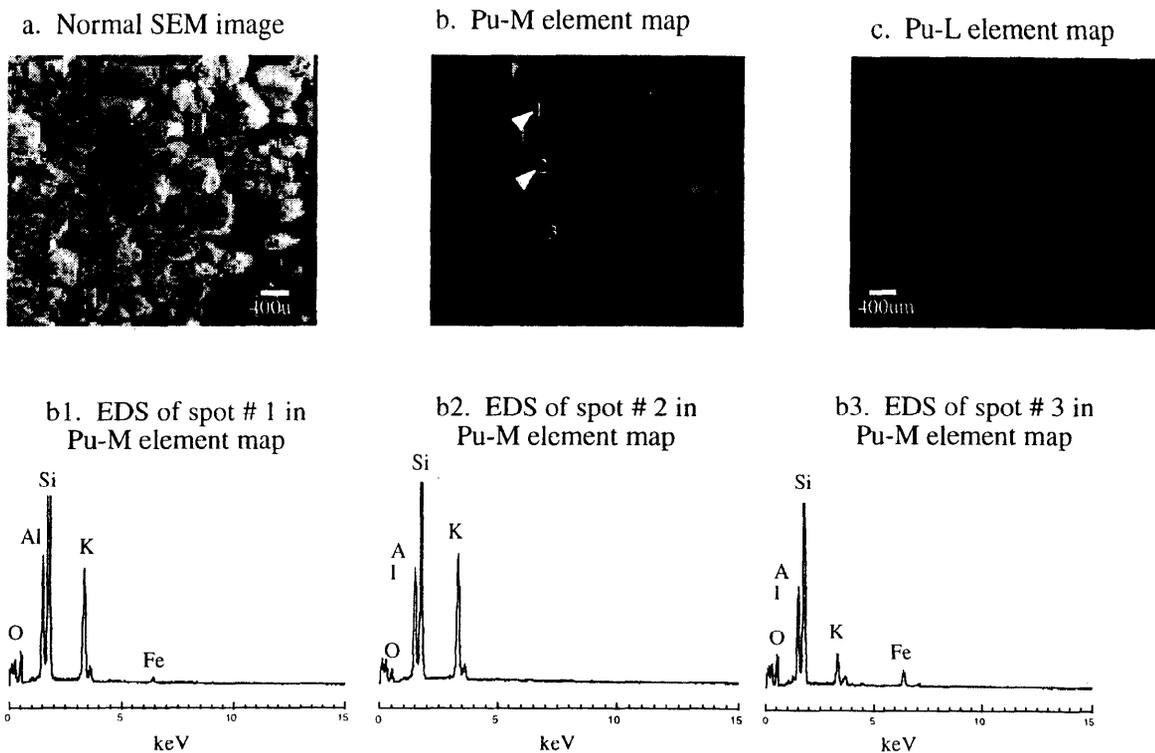


Figure 5. Scanning electron micrographs and energy dispersive spectral analysis (EDS) of soil fraction B3 from the 903 pad area of RFETS.

- a) Normal SEM image showing approximately 400-600 μm size soil particles with irregular morphology.
- b) Elemental map of the same image using the M line of Pu.
 - b1-b3) EDS spectra measured at bright spots in M element map, confirm overall aluminosilicate composition and bright spots in M line map are in fact coincident with K line of K.
- c) Elemental map of the same image using the L line of Pu.

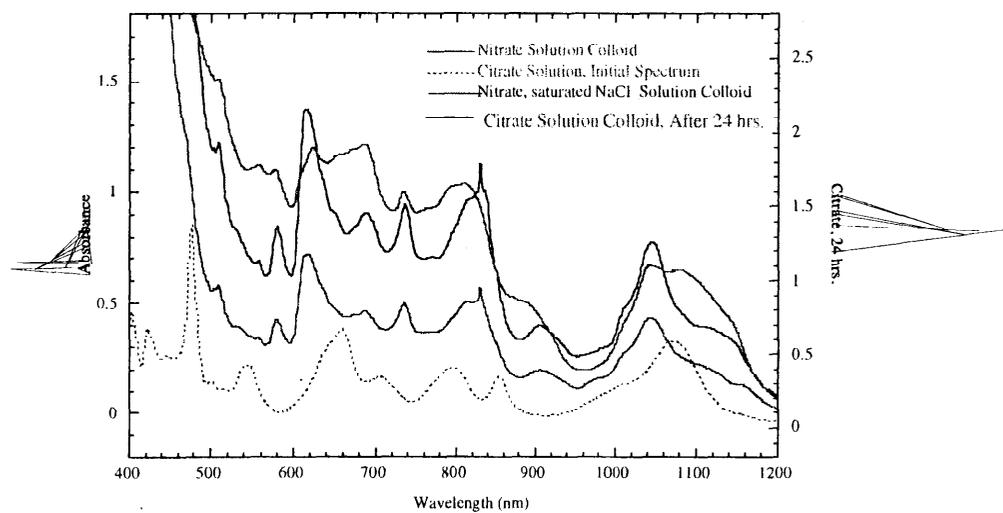


Figure 8. Optical absorbance spectra of colloidal Pu(IV) species formed in nitrate, nitrate/NaCl, and nitrate/citrate solutions.

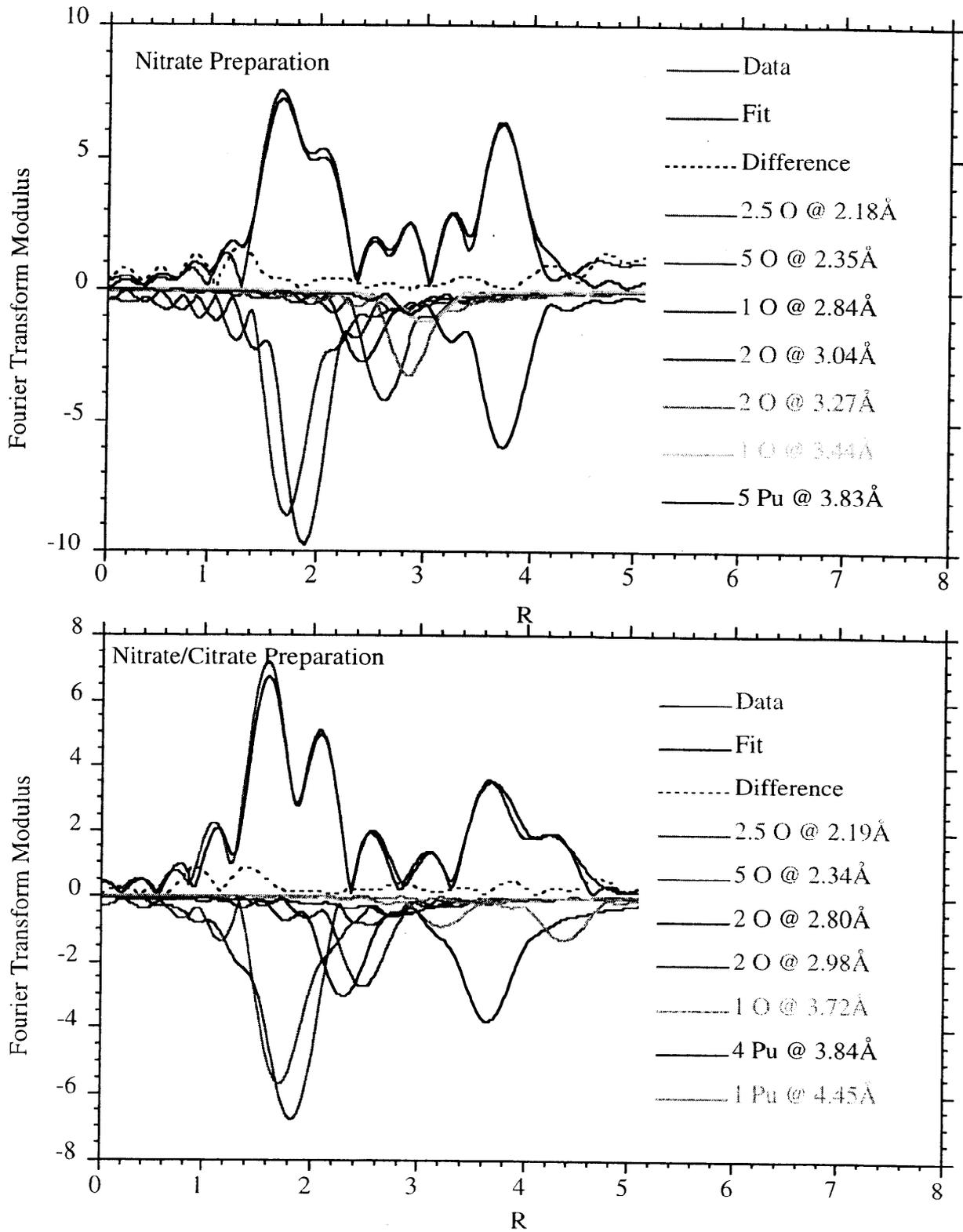


Figure 9. EXAFS spectra of Pu(IV) colloids in solution, prepared in the presence of nitrate (top) and in the presence of nitrate and 0.1 M citrate (bottom).

Triclinic, P_1

Pu: $Z=2$, 1 Pu/assy. unit
 $\text{Na}_6\text{Pu}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$

Np: $Z=16$, 8 Np/assy. unit
 $[\text{C}(\text{NH}_2)_3]_6\text{Np}(\text{CO}_3)_5 \cdot x\text{H}_2\text{O}$

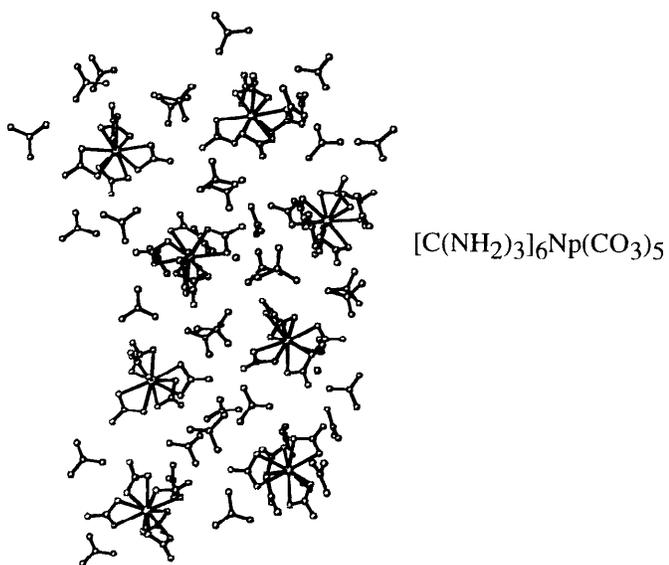
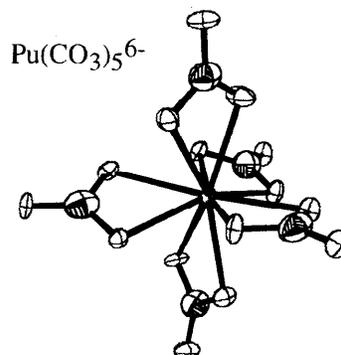


Figure 10. Thermal ellipsoid plot of the $\text{Pu}(\text{CO}_3)_5^{6-}$ anion in $\text{Na}_6\text{Pu}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ (top) and ball and stick plot of $[\text{C}(\text{NH}_2)_3]_6\text{Np}(\text{CO}_3)_5 \cdot x\text{H}_2\text{O}$ (bottom).

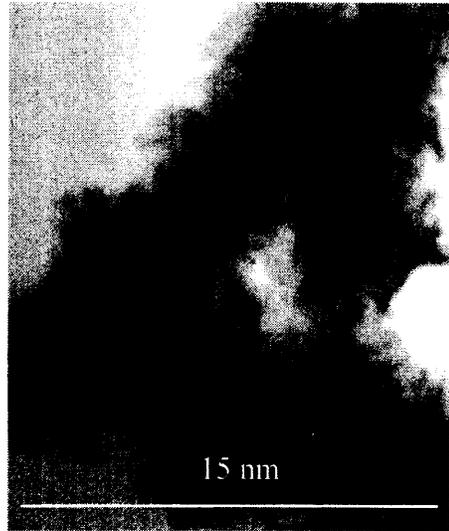


Figure 11. TEM micrograph of freeze-dried MnO₂ at 100,000 magnification.