Title: Cleaning up the Legacy of the Cold War: Plutonium Oxides and the Role of Synchrotron Radiation Research

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Cleaning up the Legacy of the Cold War: Plutonium Oxides and the Role of Synchrotron Radiation Research

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Introduction.

The actinide oxides are of tremendous technological importance. The deceptively simple binary formula of AnO_2 belies an incredibly complex structural nature, and propensity to form mixed-valent, nonstoichiometric phases of composition $AnO_{2\pm x}$. For plutonium, the very formation of PuO_{2+x} has challenged a long-established dogma, and raised fundamental questions for long-term storage and environmental migration.[1] This presentation will cover two aspects of Los Alamos synchrotron radiation studies of plutonium oxides: (1) the structural chemistry of laboratory prepared AnO_{2+x} systems (An = U, Pu; $0 \leq x \leq 0.25$) determined through a combination of x-ray absorption fine structure spectroscopy (XAFS) and x-ray scattering of laboratory prepared samples; and (2) the application of synchrotron radiation towards the decontamination and decommissioning of the Rocky Flats Environmental Technology Site (RFETS, the former nuclear weapons production site for the US).[2]

X-ray Absorption Fine Structure Evaluation of Chemical Speciation of plutonium.

Arguably the most incisive method for identifying chemical speciation of individual elements in real environmental samples is X-ray Absorption Fine Structure (XAFS) spectroscopy.[3] XAFS been a key technique in the area of Molecular Environmental Sciences, which in turn is based on the premise that even in the most complex geological system the behavior of all of the components can be reduced to the expected chemistry of their local environment – both homo- and heterogeneous, which is why chemical speciation is the essential input.

XAFS is the technique of choice in many cases because its output is the valence of the target element and the identification and characterization of its neighbour atoms in terms of the elements constituting these shells to Z ± 2–5, the absorber-neighbour distances to R ± 0.01–0.04 Å, and the numbers of neighbour atoms in the shells to N ± 15–35% for neighbour shells out to 3–7 Å from the absorber—the parameters that, cumulatively, define the chemical speciation of the target element.[4,5] XAFS spectra consist of the region through the absorption edge when the absorbance undergoes a large, abrupt increase because the incident x-ray comes into resonance with the core electron shell of the target element and the extended region beyond the edge. The X-ray Absorption Near Edge Spectra (XANES), because of its origin in transitions to bound and quasi-bound states, single and multiple scattering resonances, is sensitive to the valence and site symmetry of the absorber and can serve as a fingerprint for the speciation, as seen in **Figure 1**.

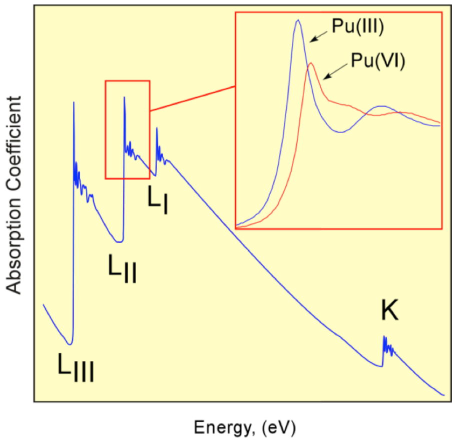

Figure 1. XANES spectra of Pu(III) compared to Pu(VI) demonstrating ability to observe different oxidation states by XANES.

The Extended X-ray Absorption Fine Structure (EXAFS) contains the metric information on the absorber environment, but its modulation of the absorption coefficient begins as only a few percent of the edge jump and damps out quickly with increasing energy to only a few parts per thousand, making it much more difficult to measure accurately, especially in environmental samples with low absorber concentrations. The oscillations that compose the EXAFS are typically Fourier transformed to give a $\chi(R)$ representation (instead of the original $\chi(k)$, where k is the photoelectron wave vector magnitude) that bears a superficial resemblance to the element specific partial pair distribution function. The metrical information is extracted via curve-fits to the EXAFS.

Cubic PuO_2-type materials display distinctive patterns in both $\chi(k)$ and $\chi(R)$ representations (**Figure 2**).[6,7] The switch from domination of the spectrum by the low-frequency wave at lower k to the high-frequency one at higher k as the Pu-O amplitude diminishes and the Pu-Pu amplitude increases from its initially small contribution is easily observed in the spectra of PuO_2. This is readily seen in the insert of **Figure 2**. These two features subsequently dominate the Fourier transforms as well, as the large, pointed, single peak from the O contribution near R=1.9 Å and the Pu/O second/third nearest neighbor peak near R=3.8 Å (**Figure 2**). More quantitative characterization of the local ordering of the Pu-O/Pu shells is obtained from the metrical results calculated by the EXAFS curve-fits. These fits utilizing the PuO_2 structure as an organizing metric for the numbers and types of neighbor shells becomes a powerful tool in studying the speciation of plutonium in environmental samples.

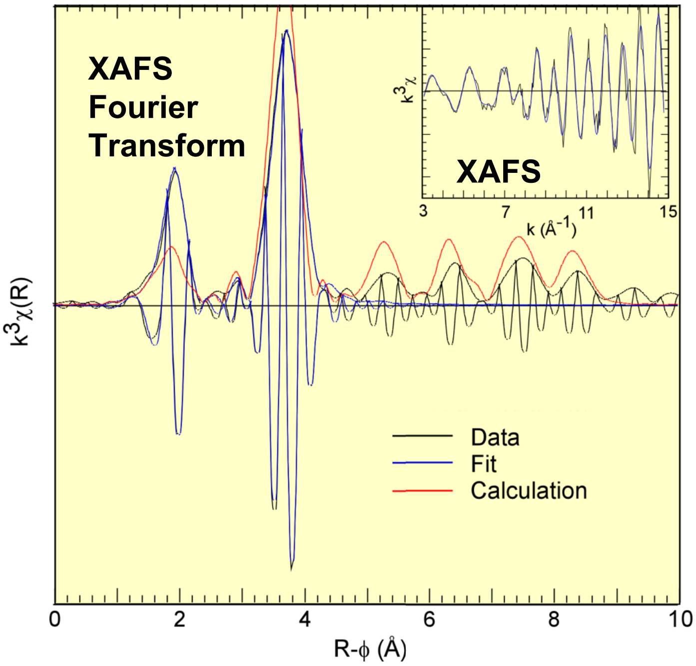

Figure 2. $k^3\chi(R)$ EXAFS (modulus and real component) of a sample of pure PuO_2 and the modulus calculated from the crystal structure. The peak positions are phase-shifted to lower distance from the actual Pu-O/Pu distances, with the Pu-O shifted by more than the Pu-Pu. The inset shows the $k^3\chi(k)$ data that reveals the low frequency wave at low k, and the higher frequency wave at higher k, typical of PuO_2-like materials.

X-ray Absorption Spectroscopy of Plutonium Particles at the Rocky Flats US Nuclear Weapons Production Site.

Experience gained from such studies was found to have important ramifications for understanding the behavior of actinide elements at a former US nuclear weapons production site. The Rocky Flats Environmental Technology Site (RFETS) was a U.S. Department of Energy (DOE) environmental cleanup site located about 15 miles northwest of downtown Denver. Nearly 40 years of nuclear weapons production at the Site left behind a legacy of contaminated facilities, soils, and ground water. Though it was suspected that plutonium contamination in the RFETS environment was in a particulate form, likely PuO_2, with very low solubility, definitive proof did not exist to verify its chemical form and oxidation state.

Production operations conducted at Rocky Flats generated a huge volume of wastes contaminated with radionuclides and other hazardous substances. By far the largest source of plutonium and americium contamination in soils emanated from the drum storage area known as the 903 Pad. From 1958 to 1969, drums containing plutonium-contaminated lathe coolant were stored on the Pad. These drums leaked, and wind and water erosion carried plutonium and americium in a well-defined pattern to the east and southeast (**Figure 3**), past the eastern Site boundary in some cases. Based upon material balance around the drums, it was estimated that a total of 5,000 gallons containing approximately 86 g (5.3 Ci) of plutonium were released into soils.[2]

Between 1991 and 1999, nearly 2500 surface soil samples were collected and analyzed across the site to assess the level and extent of actinide contamination. A heterogeneous small scale concentration distribution over a large spatial area at RFETS led to the use of state-of-the-art geostatistical analyses, including the techniques of variograms and Kriging.[8] Estimated spatial concentrations of $^{239/240}Pu$ in surface soil at RFETS that were calculated by Kriging analysis are shown in **Figure 3**. Plutonium and americium generally exhibited the same spatial distribution in surface soils, with wide variations in activities occurring throughout the site. The highest concentrations were found at the 903 Pad and areas to the east of the Pad, and displayed a wind-driven dispersal pattern to the east of the primary source area – the 903 Pad (see **Fig 3**). The plutonium and americium radioactivity in RFETS soils was highly heterogeneous, often consisting of "hot particles".[9] Approximately 90 percent of the plutonium and americium inventory was in the top 12 centimetres of the soil.

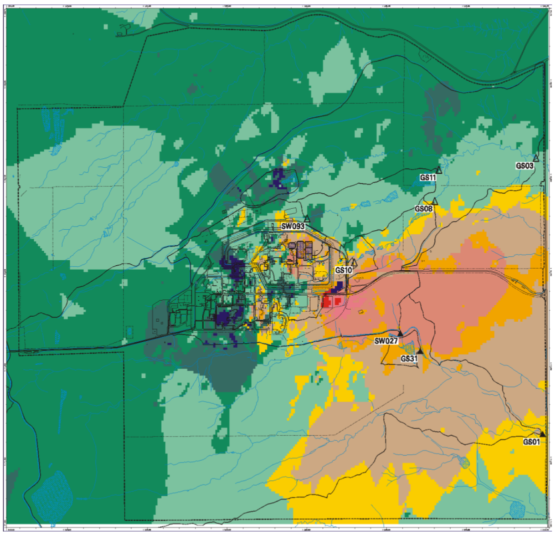

Figure 3. Because it was not feasible to sample surface soil at every location, a geostatistical modeling technique known as Kriging was applied to the plutonium surface soil data for $^{239/240}Pu$ to estimate concentrations in surface soil. The "hot spot" of $^{239/240}Pu$ concentrations in excess of 1000 pCi/g at the 903 Pad is shown in red. A clear plume of $^{239/240}Pu$ contamination that tracks roughly with the prevailing winds from NW to SE is evident from the data. This figure represents conditions at Rocky Flats prior to soil remediation actions.

Contaminated soils from the 903 pad area.

The XANES spectra of contaminated soil and concrete from the 903 Pad were compared to spectra of laboratory-prepared standards in oxidation states III, IV, V and VI. The XANES spectral shapes, peak positions, and close coincidence of inflection points of contaminated soil and concrete with the Pu(IV) standard, all support the conclusion that soil samples from the 903 pad area contain plutonium of primarily Pu(IV) speciation (**Figure 4**). All spectra closely parallel that of the Pu(IV) standard within the context of their different experimental uncertainties, and these uncertainties are also much less than the differences between the Pu(IV) and Pu(VI) standard spectra. None of the samples show evidence for the higher-energy shoulder indicative of the trans-dioxo moiety of Pu(V) and Pu(VI).[3] The conclusion is therefore that plutonium is predominantly if not entirely Pu(IV) and exhibits the XANES signatures consistent with PuO_2. This conclusion is reinforced by analysis of the EXAFS from 903 Pad sample, which gave a sufficiently strong signal so that the spectrum could be measured to energies well past the absorption edge.

For 903 Pad soils, the quality of the data was sufficiently high that in addition to the XANES, the EXAFS region of the spectrum was obtained up through k=11 $Å^{-1}$. This allowed specific metrical parameters of the speciation to be extracted, which provided convincing evidence in support of the conclusion that the plutonium in pad 903 soils is not only Pu(IV) but also resides in a PuO_2-type of compound of the type we have found before in laboratory prepared materials. This corroborating analysis provides an additional degree of confidence in the conclusions about plutonium speciation derived solely from XANES, affirming that the XANES criteria used to assess speciation of the other samples are largely valid.

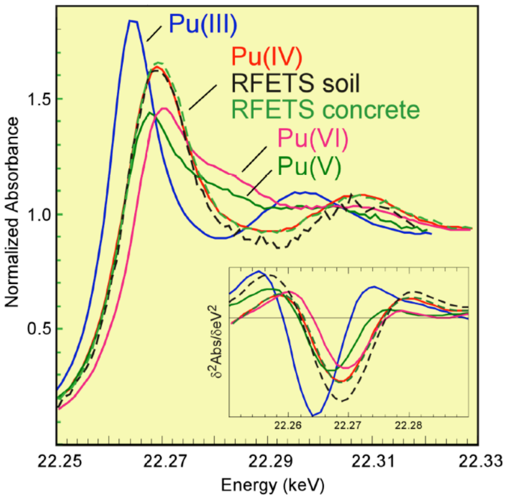

Figure 4. Plutonium L_{II} XANES of Pad 903 soil and concrete Samples; inset shows the second derivatives where zeros = inflection point energies, illustrating the close coincidence of peak positions and inflection points of all spectra with that of the Pu(IV) standard.

The combination of the many XANES and the single EXAFS spectrum indicating PuO_2-like speciation corroborate the thermodynamic models that predict that Pu(IV) is the expected valence and more specifically PuO_2 is the expected species in soils in equilibrium with air and water. What is of interest is that this equilibrium was already obtained within a few decades from radically different source terms and local conditions. What is also of interest is that the small particle sizes determined by the ultrafiltration and the concomitant probability that some of the plutonium may have been in the form of secondary or pseudocolloids did not disrupt this pattern. The relevance of models developed in the laboratory to the complexities of real world conditions is encouraging.

Impact of Scientific Understanding on Site Operations

The scientific understanding developed through the integrated studies described above provided clarity and focus on the real issues surrounding plutonium and americium migration in the RFETS environment. Once the cleanup contractor; federal, state and local governments; and the concerned citizen's groups had all reached a common understanding of the technical issues surrounding plutonium and americium migration at the Site, then these groups were able to reach long-sought-after agreements on how to proceed with cleanup. The common understanding that plutonium and americium were predominantly in particulate and colloidal forms led to the recognition that environmental migration occurs through sedimentation and resuspension of small particles by action of wind and surface water at the Site. This helped all parties focus remediation efforts on surface contamination and wind and surface water transport pathways that posed the greatest risk to human health and the environment. It helped guide selection of surface-specific removal technologies, and future land configuration strategies.[2]

Conclusions

Making the case for particle transport mechanisms as the basis of plutonium and americium mobility, rather than aqueous sorption-desorption processes, established a successful scientific basis for the dominance of physical transport processes by wind and water. The scientific basis was successful because it was in agreement with general theory on insolubility of PuO_2 in oxidation state IV, results of ultrafiltration analyses of field water/sediment samples, XAFS analyses of soil, sediment, and concrete samples, and was also in general agreement with on-site monitoring data. This understanding allowed Site contractors to rapidly move to application of soil erosion and sediment transport models as the means of predicting plutonium and americium transport, which led to design and application of site-wide soil erosion control technology to help control downstream concentrations of plutonium and americium in streamflow. Finally, good scientific understanding in the public interest helped bring clarity and focus to real issues of actinide migration at RFETS. This in turn helped to develop a more defined scope with a clearer endpoint that allowed the most extensive cleanup in the history of Superfund legislation to finish one year ahead of schedule, ultimately resulting in billions of dollars in taxpayer savings (**Figure 5**).[2]

Figure 5. (Left), A 1995 Aerial photograph of the RFETS showing the Industrial Area. (Right), An October 2005 Aerial photo of the remediated Rocky Flats Site.

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