PLUTONIUM CONTAMINATION VALENCE STATE DETERMINATION USING X-RAY ABSORPTION FINE STRUCTURE PERMITS CONCRETE RECYCLE

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ABSTRACT

This paper describes the determination of the speciation of plutonium contamination present on concrete surfaces at the Rocky Flats Environmental Technology Site (RFETS). At RFETS, the plutonium processing facilities have been contaminated during multiple events over their 50 year operating history. Contamination has resulted from plutonium fire smoke, plutonium fire fighting water, milling and lathe operation aerosols, furnace operations vapors and plutonium "dust" diffusion.

Samples considered representative of the contamination processes were removed, and shipped to Los Alamos National Laboratory for preparation as targets for X-ray Absorption Fine Structure measurements. The samples were taken to the Stanford Synchrotron Radiation Laboratory (SSRL) and bombarded with X-rays produced under dedicated synchrotron x-ray production conditions (3.0 GeV e- , 45-100 mA). Standards containing Pu(+4) and Pu(+5), blanks spiked with Pu(+4) and Pu(+5), and the field samples and duplicates were irradiated. Evaluation of the data determined that Pu(+4) and Pu(+5) standards were readily identifiable, that the "spiked samples" were consistent with the standards, that the duplicate samples were comparable and that all of the Pu contamination samples were Pu(+4).

These concrete samples represent about half of the plutonium samples ever analyzed by XAFS. This methodology is applicable to surface contamination plutonium and does not alter the chemistry of the sampled material. The contamination levels are relatively low and no other method of speciation is available for this concentration of plutonium. The use of this methodology should be considered when speciation determination is needed of relative low concentrations of plutonium contamination.

The decommissioning of RFETS includes the removal of several multistory structures and the subsequent return to grade of the basements. Current estimates are 170,000 cubic meters of structural fill will be required. The Decontamination & Decommissioning Program has proposed to recycle as structural fill the bulk of the 100,000 cubic meters of above-grade concrete on the site. Successful recycle would reduce the environmental impact of the site cleanup by 19,000 offsite transportation round trips totaling over 1,700,000 km. A significant portion of the concrete would be from potentially plutonium contaminated buildings so the long term environmental transport of plutonium contamination will impact the recycling method.

The plutonium speciation was determined to be Pu(+4). This means the plutonium is present as PuO_2 which is essentially insoluble in ground water. Therefore, transport of the Pu from contamination remaining on recycled concrete does not occur until bulk transport of the concrete occurs. This confirms that the recycle method poses essentially no threat to the health and safety of the public and the environment.

INTRODUCTION

At RFETS, the plutonium processing facilities have been contaminated during multiple events over the sites 50 year operating history. Contamination has resulted from plutonium fire smoke, plutonium fire fighting water, milling and lathe operation aerosols, furnace operations vapors and plutonium "dust" diffusion. The decommissioning of RFETS includes the removal of several multistory structures and the subsequent return to grade of the basements. Current estimates are 170,000 cubic meters of structural fill will be required to return the site to its original grade. The Decontamination & Decommissioning Program has proposed to recycle as structural fill the bulk of the 100,000 cubic meters of above-grade concrete on the site. Successful recycle (1) would reduce the environmental impact of the site cleanup by 19,000 offsite transportation round trips totaling over 1,700,000 km. A significant portion of the concrete would be from potentially plutonium contaminated buildings so the transport of plutonium contamination in the environment will impact the recycling method.

The chemical speciation of an element is the primary determinant of its reactivity, and is therefore the best predictor of its solubility and transport behavior and subsequent tendency to accumulate in water and soil. Thus, speciation is a much more critical parameter than the concentration by itself in evaluating the level of risk posed by residual amounts of plutonium in soil. However, speciation is also much more difficult to identify, particularly at trace levels. Especially in the complex soil or building demolition matrix, both chemical and most spectroscopic methods are susceptible to errors and artifacts resulting from altering the speciation during separations and analysis operations and from the many orders of magnitude difference in cross section for different species.

A variety of techniques can be used for chemical speciation measurements. Table I lists a number of commonly used techniques along with their applicable concentration range, sensitivity, and required physical state for sample analysis. Techniques such as solubility measurement, potentiometry, liquid-liquid partitioning, dialysis, chromatography, and optical spectroscopy have been in use for some time, and can be considered classical methods. More recently, a number of more modern spectroscopic techniques have been applied, including photoacoustic and thermal lensing, laser-induced fluorescence, magnetic resonance, and x-ray absorption spectroscopies. Each has its own particular sensitivity, specificity, cost, and benefit. Some methods can be applied only to solid samples, whereas others can be used for both solid and liquid systems. In general, spectroscopic techniques such as NMR and XAFS spectroscopy which yield detailed molecular structural information require relatively large concentrations of the target species (10^{-3} M), whereas techniques for obtaining only elemental composition, such as neutron activation analysis, can detect low concentrations (10^{-12} M).

For RFETS samples, all the data indicated that the plutonium in soil and concrete is in a relatively insoluble form, and thus speciation techniques (Table I) that work well in solution are of little value. X-ray Absorption Spectroscopy (2) offers both high accuracy and low potential for interference provided that the sample concentrations were high enough to be measured by this modern spectroscopic technique. Depending on data quality, for any element with Z> than that of Ca, by scanning over the energy range containing the appropriate absorption edge, XAFS can easily determine the average valence of the target element and also determine the types, numbers, and absorber-neighbor distances for neighboring shells of atoms out to 3-6 Å. Since these are the parameters that define the speciation, XAFS automatically provides such information. Because the absorption coefficient is an atomic property there are no spectroscopically "silent" or "loud" species or potential interferences from the matrix that would distort the results. Furthermore, because of the penetrating ability of x-rays, the sample morphology and characteristics of the matrix are unimportant and there is no requirement for separating it from the analyte or other types of pretreatment. XAFS spectroscopy is therefore one of the most incisive means for determining chemical speciation in soils and similar types of samples.

Table I. General Speciation Techniques

Method	Lower Limit	Application[a]	State[b]
Neutron Activation Analysis (NAA)	$> 10^{-12}$ M	1	S
Chemiluminescence	$> 10^{-10}$ M	1,3	S
Mass Spectrometry (ICP, TOF, FAB, etc.)	$> 10^{-9}$ M	1	L
Polarography	$> 10^{-9}$ M	1,3,4	L
Gas/liquid Chromatographic techniques	$10^{-6} - 10^{-9}$ M	1	G,L
Radiochemical Trace Analysis	$10^{-8} - 10^{-12}$M	1,2,3	L
Atomic Absorption/Emission (AA, AE)	$10^{-6} - 10^{-10}$ M	1	L
Electron Spin Resonance (ESR)	$10^{-5} - 10^{-12}$ M	1,3,4,5	S, L
Photothermal Spectroscopy (PAS, TLS)	$10^{-5} - 10^{-9}$ M	3,4	S, L
Laser Induced Fluorescence (LIF)	$10^{-5} - 10^{-9}$ M	3,4	S, L
EMF techniques (potentiometry)	$10^{-3} - 10^{-8}$ M	4	L
Electronic Spectroscopy (UV-Vis-NIR)	$10^{-3} - 10^{-6}$ M	3,4	L
X-ray Photoelectron Spectroscopy (XPS)	10^{-3} M	1,3	S
Vibrational Spectroscopy (Raman, FT-IR)	$10^{-1} - 10^{-3}$ M	3,4,5	S, L
Diffuse Reflectance Spectroscopy	$10^{-1} - 10^{-3}$ M	3,4,5	S
Nuclear Magnetic Resonance (NMR)	$10^{-1} - 10^{-4}$ M	3,4,5	S, L
X-ray Absorption Spectroscopy (XANES, XAFS)	$10^{-1} - 10^{-4}$ M	1,3,4,5	S, L
X-ray and Neutron Diffraction	10^{0} M	5	S
X-ray Fluorescence (XRF)		1,3	S
Energy Dispersive X-ray Analysis (EDX)			S
Mössbauer Spectroscopy	10^{0} M	1,3	S
Neutron and X-ray Scattering (SANS, WAXS)	10^{0} M	5	L

[a] (1) elemental identification, (2) physical state, (3) oxidation state, (4) molecular formula, (5) molecular structure.
[b] S = Solid, L = Liquid, G = gas.

The primary issue for Pu in the environment is whether its valence is (IV) or (V/VI). Chemically, a substantial change occurs on increasing the valence from IV to V (Figure 1). The aqueous/water-equilibrated coordination geometry of Pu(IV) (and III) tends to be relatively symmetric, with a large number (8-12) of oxygen atoms surrounding the central Pu in a relatively symmetric array with Pu-O distances of 2.3-2.5 Å. The removal of one electron causes the formation of the $PuO_{2^{1/2+}}$ trans dioxo cation, which is the central feature of Pu(V) and (VI). Two oxygen atoms form short (typically 1.75 Å for (VI), 1.80 Å for (V)) double bonds to the central Pu, creating the linear array. Between three and six additional ligands coordinate to the Pu in the equatorial plane perpendicular to the trans dioxo axis, with Pu-O distances from 2.2 Å for OR- moieties up to >2.45 Å for neutral O species or in complexes with large numbers of ligands. These differences in structure are paralleled by differences in behavior and thermodynamic properties. Pu(IV) is much less soluble in aqueous solution than (V/VI), and so would be expected to remain in proximity to its original location in soil. The Pu(V/VI) are much more soluble, presenting the risk that transport followed by reduction and precipitation at a particular site could cause the accumulation and concentration of residual Pu to hazardous levels at that location. Thermodynamic considerations dictate Pu(IV) as the stable species over the full range of possible environmental conditions. These samples provided experimental corroboration that unusual source terms and excursions outside the range of the "possible" have not negated these assumptions. We have therefore performed XAFS measurements (3) on a both soil and concrete samples to identify the Pu speciation.
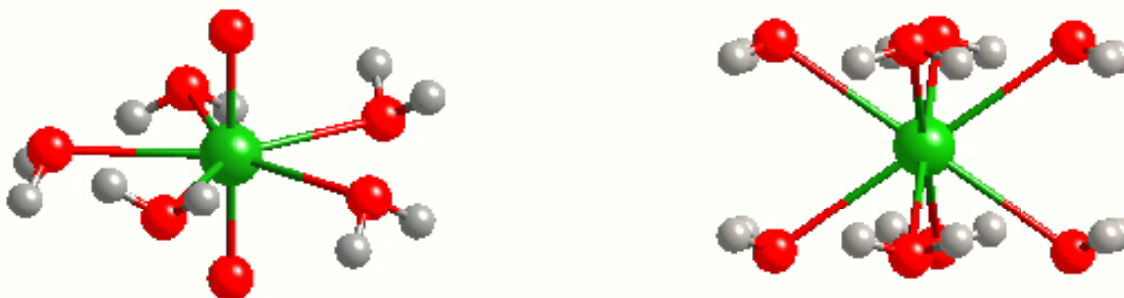
Fig 1. The Pu(V/VI) (left) and (III/IV) (right) structural motifs, depicted as the aquo ions. The asymmetric character of the (V/VI) species is apparent, with the O=Pu=O unit of the trans dioxo cation with their closely bonded "yl" O atoms running vertically, and the equatorial ligands residing in the plane perpendicular to this axis. The ordering of the ligands in the (III/IV) complexes is much more symmetric.

Experimental Procedures

In addition to the soil and concrete samples from RFETS, standards were also prepared to determine the experimental uncertainties in the spectroscopy measurements and analyses. For the soil samples only pure PuO_2 was used. For the concrete samples both PuO_2 and Pu(VI) ($PuO_{2.2+}$) hydroxy-carbonate were available. Spectra were measured not only of these pure compounds at high concentration, but also of powdered RFETS concrete with Pu concentrations below detection limits (*i. e.* "clean" concrete) spiked with very small amounts of these same standards. Absolute concentration values are difficult to obtain since data analysis for XAFS is complicated and it is difficult to determine and propagate uncertainties through the many steps. It is also very unrealistic to simply use the parameter correlations and least squares errors from curve-fitting results as bounds on the final values. Comparison of data from these "spiked" samples demonstrated low concentrations and the complicated concrete matrix did not diminish the reliability of these experiments and were used to provide an independent measure of the validity of the results and interpretation for the actual RFETS samples.

Samples were ground in a mortar and pestle. The resulting powders were poured into slots in an aluminum holder and held in place by a Kapton window in the front and a polyethylene cap in back. Samples were mounted in a liquid N_2-cooled cryostat to minimize the thermal contribution to the Debye-Waller factors. XAFS measurements were performed at beamline 4-2 of the Stanford Synchrotron Radiation Laboratory, under dedicated synchrotron x-ray production conditions (3.0 GeV e-, 45-100 mA). Si (220) crystals were used to monochromate the beam, with a Pt-coated flat mirror tilted to have a cutoff energy of 22-25 keV used to eliminate harmonics in the fully tuned mode. Scans are performed stepwise, stopping at a particular energy for a set signal integration time, with a few dozen points over ca 300 eV defining the background below the absorption edge, ca 1 eV intervals between points over the edge, and then equal intervals in k through the extended region. Beam position drift and variable monochromator heating cause energy shifts with time so that, although the monochromator positions for separate scans are identical, the exact energies of these points are not. The signals from the individual detector elements were averaged prior to any other data processing using the standard weighting scheme based on equalizing the signal:noise ratios determined from the signal counts and total counts. Monochromator motor steps were converted to eV by performing separate calibration scans preceding each scan of a sample. These were over the Ru K edge, defining the first inflection point of Ru metal as 22116 eV for the standards, spikes, and concrete samples.

Data Reduction

The process of extracting speciation information from the XAFS occurs in several independent steps. First, the X-ray Absorption Near Edge Structure (XANES) region will be used to determine the average Pu valence. Because the absorption edge is so large and its species-dependent features so distinctive relative to the EXAFS oscillations even very noisy data can provide useful and unambiguous information. The EXAFS can be extracted from higher quality spectra. Qualitative comparisons in both ((k) and (R)) (after Fourier transformation) are useful in distinguishing between Pu(IV) and (VI) types of structures and also point to differences or changes in speciation. These are quantified with curve-fits, in which the metrical parameters defining the nearest neighbor shells are determined. The curve-fitting results ultimately define the speciation. Subtracting the contributions of the various shells defined by the curve-fits from the raw data provides the basis for two additional procedures. Comparing the phases and amplitudes in the data with those expected for a neighbor shell allows the degree of confidence in the existence of the shell in question to be ascertained. And ratioing phases and amplitudes of similar shells is the best means for evaluating changes in absorber-neighbor distances and numbers of neighbor atoms that indicate differences in speciation.

The emphasis in the curve-fits is therefore to identify the simple existence of distinct neighbor shells and not on quantifying the numbers of atoms or distribution widths. Comparison of the phase of the data with that of the fit for each shell in k and R was performed to make a judgement of the level of confidence in these assignements. Number and distance differences were determined by the standard ratioing methods. The phases and amplitudes that were ratioed were procured by Fourier filtering, i.e., performing a Fourier transform and then doing the reverse transform over only a selected window in R space, the data remaining after subtracting out the contributions for the other shells determined from the curve-fits. This procedure ensures that the effects of noise and background residuals in the frequency range of interest are included in the analysis.

Oxidation state determination using XANES spectroscopy

In X-ray absorption spectroscopy, there are characteristic energies where x-rays are strongly absorbed by the sample. It is these characteristic energy regions (referred to as absorption edges) where x-rays are strongly absorbed that are used in x-ray absorption spectroscopy. These absorption edges will shift in energy as a function of plutonium oxidation state, and will show fine structure at energies above the edge as a result of the outgoing photoelectron wave scattering off neighboring atoms in the vicinity of the central plutonium atom. As a result, the fine structure will show differences from one sample to another due to differences in chemical bonding around the central plutonium atom. For plutonium studies, researchers prefer to use the L_{III} x-ray absorption edge (which appears near 18,060 eV) because it has the highest absorption intensity. However, in RFETS environmental samples there are other elements present in the samples which exhibit x-ray absorption in this same region, and therefore interfere with the plutonium measurements. As result, the plutonium x-ray absorption studies were performed instead at the L_{II} x-ray absorption edge, which appears near 22,270 eV. This absorption edge has a lower absorption intensity than the L_{III} edge, making the RFETS samples even harder to study using x-ray absorption spectroscopy. A calibration experiment was run at both L_{III} and L_{II} absorption edges using plutonium standards in oxidation states 0, III, IV, V, and VI, which showed the expected changes in edge energy position with changing oxidation state. The L_{III} and L_{II} XANES spectra of the plutonium standards were nearly identical, giving high confidence in the use of the plutonium L_{II} edge for study of RFETS environmental samples. RFETS soil and concrete samples were measured (at the L_{II} edge) along with the standards, and concrete samples that were "spiked" with Pu(IV) and Pu(VI) standards. The Pu XANES spectra of the soil and concrete samples were not only clearly consistent with Pu(IV), but were identical within the experimental uncertainties to the PuO_2 standard. Of interest to many in both the scientific and local communities is the recent report of a new form of plutonium oxide, PuO_{2+x} that appeared in Science magazine. An authentic sample of this higher oxide of composition

$PuO_{2.2}$ was therefore examined by XANES spectroscopy and revealed the presence of a mixture of Pu(IV) and Pu(V) oxidation states. Of relevance to RFETS is the fact that this XANES spectrum is different in both its edge position and overall shape than either the PuO_2 standard, or either soil or concrete samples. The XANES measurements on RFETS samples clearly show that the oxidation state of plutonium is Pu(IV), and the XANES spectral signatures are very similar to that of PuO_2 in both soil and concrete samples.

Local Chemical Structure Determination Using XAFS Spectroscopy

The X-ray Absorption Fine Structure (XAFS) data can be curve-fit to extract the number of near-neighbor atoms at different bond distances in order to determine information about the local chemical structure of plutonium in the sample. As an example, consider that from the crystalline structure of PuO_2, there are eight Pu-O distances at 2.33 Å, 12 Pu-Pu distances at 3.86 Å, and other "shells of atoms" at even longer interatomic distances. This is precisely the kind of information that we can extract from analysis and fitting of the XAFS data, although for dilute environmental samples, the amount of uncertainty in the actual number of atoms at a given distance is of less value than the bond distances themselves. The actual XAFS data and fits are usually examined in two primary ways. One method is to compare the actual oscillatory waveforms of each sample to the waveform that is calculated from the curve fit to the data. This method (3) was used for the standards and the RFETS samples, but is too complex to really describe in a simplified fashion here. From such a comparison it is clear however that the standards are all different from one another and that the RFETS soils and concrete samples are nearly identical to the XAFS waveform of PuO_2. For non-experts, a more useful and intuitive way to examine the data is to look at the Fourier transform of the data and the fit (Figure 2). The Fourier transform gives a distinct peak for each interatomic distance in the sample. In the example of PuO_2, the Fourier transform and fit both show peaks for shells of Pu-O at 2.33 Å, and Pu-Pu at 3.86 Å (Figure 2, center). This Fourier transform is unique for PuO_2. Other samples show peaks at different distances making it fairly easy to see how the XAFS of different compounds will show different numbers of peaks and at different interatomic distances. This is a very powerful tool for determining the chemical form of an environmental contaminant.
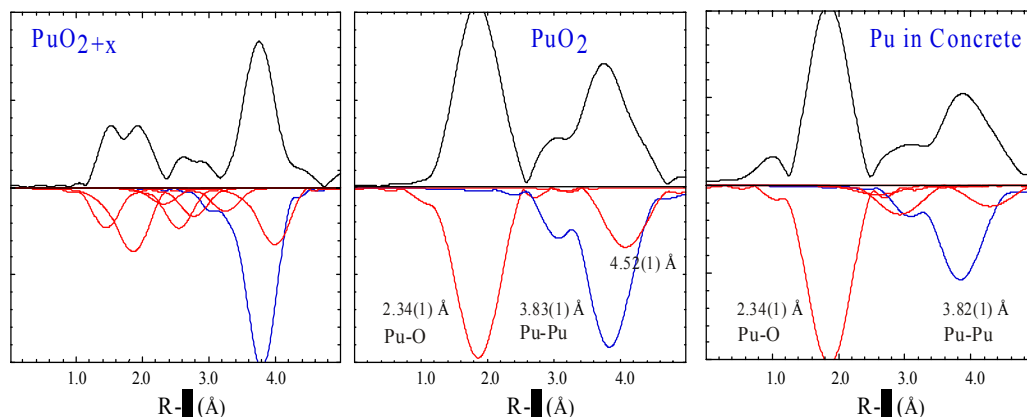

Fig 2. XAFS Fourier Transform (top) and fit (bottom) for PuO_{2+x}(left), PuO_2 (center) and Pu in RFETS concrete. From these XAFS spectra it is quite clear that plutonium in concrete shows similar structural features as seen in a sample of PuO_2, which is dramatically different from the structural features seen in PuO_{2+x}.

CONCLUSIONS

The XAFS Fourier transforms for the standards are all different from one another as expected. The XAFS Fourier transforms of the RFETS soils and concrete samples are nearly identical with that found for PuO2 (Figure 2) with one small exception. In addition to interatomic distances of 2.33 and 3.86 Å, the RFETS soil and concrete data show some small peaks at intermediate distances between 2.3 and 3.0 Å which are consistent with additional Pu-OH or $Pu-OH_2$ interactions which would be expected for hydrated PuO_2

exposed to water in the environment. This was verified experimentally by examining the XAFS of a number of laboratory-prepared samples of hydrated PuO_2. This association with water is essentially identical to the everyday use of SiO_2 (silica gel) to absorb water by placing SiO_2 packets in camera cases and other optical equipment. The SiO_2 absorbs water to form $SiO_2 \cdot xH_2O$. It is also important to note that XAFS of PuO_2 and the PuO_2 found in soil/concrete samples is uniquely different from the XAFS of the standards. One final question of interest to the scientific and local communities is the question of whether the observed XAFS could be consistent with the recently reported PuO_{2+x}. The XAFS of $PuO_{2.2}$ was clearly different from that of PuO_2 and hydrated PuO_2 (Figure 2). In particular, the $PuO_{2.2}$ (Figure 2, left) shows an additional Pu-O peak at the very short distance of 1.84 Å that is not present in PuO_2.

From comparison of the XANES and XAFS of the standards, the RFETS soil/concrete samples, and the spiked samples, it is clear that plutonium in RFETS soil and concrete is in oxidation state IV, and that the chemical form is that of a hydrated PuO_2. It is also clear that plutonium in RFETS soils and concrete is NOT in the form of PuO_{2+x}. This is an important experimental confirmation of our expectations of plutonium behavior in the environment.

REFERENCES

1.   "RFCA Standard Operating Protocol for Recycling Concrete," Rocky Flats Environmental Technology Site, U. S. Department of Energy (1999).

2.   S. D. Conradson, "Application of X-ray Absorption Fine Structure Spectroscopy to Materials and Environmental Science," Appl. Spectroscopy (52:7).

3.   S.D.Conradson, T. Cooper, P. F. Ervin, N. J. Hess, W. D. Keogh, L. H. Morales, M. P. Neu, W. Runde, C. D. Tait, K. Veirs, "X-Ray Absorption Fine Structure Spectroscopic Determination of the Speciation of Pu(IV/IV+() in the Environment and Under Environmentally Relevant Conditions," In preparation for publication in Environmental Science and Technology."