Micro-XAS Studies with Sorbed Plutonium

M. C. Duff,[1*] M. Newville,[2] D. B. Hunter,[1] S. R. Sutton,[2] I. R. Triay,[3] D. T. Vaniman,[4]
P. M. Bertsch,[1] J. U. Coughlin,[1] P. Eng,[2] M. L. Rivers[2]
[1] *University of Georgia, Savannah River Ecology Laboratory, Aiken, SC, U.S.A.*
[2] *Department of Geophysical Sciences, CARS, The University of Chicago, Chicago, IL, U.S.A.*
[3] *Waste Isolation Pilot Plant, Carlsbad, NM, U.S.A.*
[4] *Los Alamos National Laboratory, Los Alamos, NM, U.S.A.*

Introduction

The coordination and bonding environment of surface sorbed species at rock-water interfaces provides information on their mobility in environmental systems. To examine Pu sorption on a natural surface at a microscopic scale, we measured the coordination and bonding environment of sorbed Pu on zeolitic tuff from Yucca Mountain (YM) with microprobe x-ray imaging and extended x-ray absorption fine structure (EXAFS). Using a focused 4x7 mm^2 beam, micro-EXAFS spectra were acquired at Mn-rich smectitic regions with high levels of sorbed Pu. Plutonium sorption was not observed at Fe-rich or zeolitic-rich regions.

The YM tuff is predominantly zeolitic with approximately 2% smectite, according to characterization studies of the core material.[1] The smectite isolates were rich in the mineral rancieite $(Ca,Mn^{2+})(Mn_4^{4+}O_9\bullet 3H_2O)$, which has a similar structure to birnessite, though is more rich in Mn(IV) than typical birnessite. Electron microprobe, microautoradiography, and petrographic studies indicate Pu sorbs more strongly to smectite and Mn-oxide fracture minerals than to Fe oxides or zeolites.[2]

Previous studies demonstrated the Pu(V) added at two regions was present as Pu(V) or as Pu(VI), based on the energy at the half-height of the Pu XANES edge step.[1] Preliminary analyses of the micro-EXAFS spectra at these locations indicate the absence of a 1st shell splitting of axial and equatorial Pu-O bonds.[3] Absence of a "split" first shell in the EXAFS data for Pu does not conform to bonding environments that are traditionally associated with pentavalent and hexavalent or "actinyl" species. Additionally, micro-XAFS spectra indicate the absence of Pu in the second atomic shell, which is evidence for surface sorbed vs. surface-precipitated Pu at the highly enriched areas. These Pu-rich areas contain up to 2 g Pu kg^{-1} of tuff.[1]

Methods and Materials

Yucca Mountain (YM) tuff core samples were taken from the 450 m depth of the Topopah Spring Tuff at the proposed high-level waste and spent nuclear fuel repository site, Yucca Mountain, NV. Core samples were used to make polished 30-µm thin sections. A synthetic carbonate-rich groundwater (pH ~9) was prepared to have a final concentration of 10^{-6} M Pu(V). The thin section was immersed in this synthetic Pu(V)-containing solution for 120 hours then rinsed with de-ionized water. About 99% of the added Pu sorbed to this sample.[1]

Two studies were performed using the synchrotron hard x-ray fluorescence (XRF) microprobe on the undulator (station ID-C) at sector 13 of the APS with channel-cut Si(220) (April 1998) and Si(111) monochromators (July 2000). Both studies were conducted with microfocusing optics to produce the x-ray beam.[4] Double elliptical Rh-coated mirrors angled at 2 mrad were used to focus a monochromatic undulator x-ray beam at the Pu L_{III} absorption edge (18.054 keV) to a 4x7 mm^2 beam.[5] The sample was placed in a metal frame and mounted on an automated sample stage at 45° to the beam. Fluorescent x-rays were detected with a multi-element Ge detector mounted at 90° to the incident beam and 2 cm from the sample.

In 1998, elemental images of the thin section were conducted using microprobe-SXRF imaging for elements with absorption energies below ~18.5 keV. Images were made by collecting 20 s live counts in the elemental regions of interest and rastering the sample in 4-µm steps in the vertical plane. In 1998 and 2000, micro-EXAFS spectra were collected for the L_α emission line from 50 eV below the Pu L_{III} absorption edge to 500 eV or greater above the Pu absorption L_{III} edge in step increments ranging from 0.4 to 2.5 eV at several Pu-enriched regions on the tuff—as identified from the XRF images. The monochromator energy and the undulator gap were scanned simultaneously for each XAFS scan. The Pu absorption-edge energy was calibrated with a standard of PuO_2 and Zr foil. Micro-EXAFS on each of several Pu-rich region were collected in both studies. The EXAFS background was removed using the Fourier components of $\chi(k)$ below R= 1.0 Å.[6] Hanning window functions were used for the Fourier transform from $\chi(k)$ to $\chi(R)$.

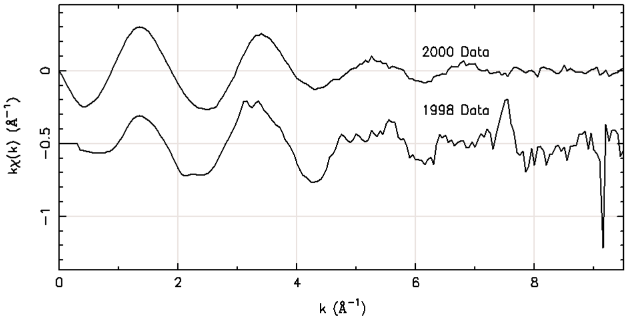

FIG. 1. Pu L_{III} EXAFS $\chi(k)$ data for Pu sorbed to tuff from Yucca Mountain, NV. Background subtracted micro-EXAFS from the 1998 and 2000 runs at GSECARS.

Results and Discussion

SXRF images for the three regions of the tuff studied showed elevated Pu concentrations correlated with Mn-rich regions. No Pu was observed in the Fe-rich and zeolitic regions of the tuff, which is consistent with other related studies.[1-3]

Typical EXAFS data from the 1998 and the 2000 runs are shown in Fig. 1. The quality of the data improved in 2000.[3] EXAFS analysis on data from the 1998 run indicated a first shell Pu-O distance between 2.25 Å and 2.33 Å. Although these data had a high signal to noise, axial O's in the first shell of the Pu atom (normally present at ~1.7 to 1.8 Å) were not present—as would be expected for a Pu(V) or (VI) phase. Similar absences of the short O peak near ~1.74 Å are observed in EXAFS studies of U(VI)-containing hydrous oxides (uranates) and U(V)-containing glasses.[7,8]

Pu EXAFS from the 2000 run taken at five different regions on the tuff show first shell Pu-O interactions at 2.34 Å (Fig. 2). This further indicates the absence of axial O's in the first shell of the Pu atom and strongly suggests the sorbed Pu exists as Pu(IV), based on comparison with our PuO_2 standard. This is also consistent with the XANES spectra for the 2000 data, which shows no appreciable XANES edge shift on the main absorption peak. Preliminary analysis of the second coordination shell indicates Pu-Mn interaction at ~3.32 Å in two of the five Pu-enriched regions (Fig. 2), suggesting that Pu sorption occurs as an inner sphere (specific adsorption) mechanism, though possibly with substantial heterogeneity.

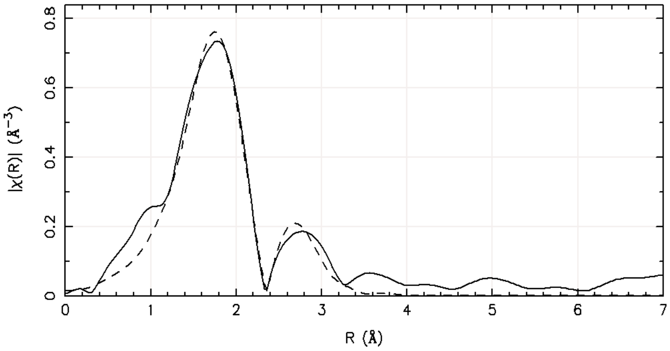

FIG. 2. The $\chi(R)$ for data (solid) and best fit (dashed) for Pu L_{III} EXAFS for Pu sorbed to tuff from Yucca Mountain, NV. The fit includes a Pu-O interaction at 2.35 (+/- 0.02) Å and Pu-Mn interaction at 3.32 (+/- 0.06) Å.

The second shell Pu-Mn coordination and the absence of any Pu-Pu coordination in the second shell suggest surface precipitation of a solid phase, such as PuO_2, did not occur. We conclude that the surface coverage of sorbed Pu on the Mn-rich regions of the tuff did not exceed monolayer coverage. These findings are consistent with simplified calculations of sorption site density for Mn oxides and smectites in the tuff, which indicate Pu could be present on these Mn-rich regions at monolayer coverage.[1,2]

The spatial distribution and micro-SXRF spectra demonstrated that Pu is sorbed strongly and preferentially to Mn oxides and not to Fe oxides in the YM tuff. The XANES of the 1998 data showed that the Pu(V) was initially sorbed as Pu(V) or oxidized to Pu(VI) upon sorption in some areas, while the 2000 data shows no such oxidation. Collectively, these findings indicate the coordination and bonding environment of sorbed Pu on the Mn-rich tuff surface changed from a more oxidized form to that of a reduced and potentially less mobile form with time. These studies are only representative of Pu interactions with YM tuff from one region at YM. Ideally, more studies will provide information on the fate of Pu within these YM tuffs and the interaction of Pu with the Mn-oxide mineral rancieite.

Acknowledgments

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