

J. Synchrotron Rad. (1999), 6, 350–352

Micro-XAS studies with sorbed plutonium on tuff

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The bonding environment of sorbed species at rock-water interfaces provides information on their mobility in natural systems. To investigate Pu sorption at a natural surface on a microscopic scale, we studied the bonding environment of sorbed Pu on zeolitic tuff with micro-XAS techniques. Using a focused 4 by 7 μm^2 beam, XAS spectra were taken at Mn-smectite regions where high levels of sorbed Pu were found. The Pu did not sorb to Fe-rich regions. XANES spectra show the presence of Pu(VI), based on edge energy. Preliminary analyses of the micro-EXAFS spectra indicate the absence of a first shell splitting of axial and equatorial Pu-O bonds—an environment *unlike* what is observed for most hexavalent actinides.

Keywords: micro-EXAFS; micro-XANES; micro-XRF; sorption; plutonium.

1. Introduction

Studies of sorbed contaminants at the rock-water interface are relevant to the transport of the species in the environment. Plutonium from spent nuclear fuel requires prudent strategies for management and long-term repository storage. Plutonium can be present in four oxidation states (+III, IV, V, VI) at one time in solution (Choppin *et al.*, 1997). The solubility and mobility of Pu in natural waters vary greatly, with the +III and +IV valences being considerably more sorptive and less soluble because of their high charge. The higher valences of Pu are less charged with the free ions present as dioxo moieties: Pu(V)O₂⁺ and Pu(VI)O₂²⁺. The Pu(V) ion disproportionates to Pu(IV) and Pu(VI), but Pu(V) dominates speciation in most oxic basic waters (Choppin *et al.*, 1997).

Dissolved Pu (added as Pu(V)) sorbs *strongly* to smectites and to Mn and Fe oxide minerals, which can mediate redox transformations (Keeney-Kennicutt & Morse, 1985; Sanchez *et al.*, 1985; Triay *et al.*, 1997). However, information on the *in situ* determination of the oxidation state(s) of sorbed Pu on natural surfaces is sparse in the open literature. Most sorption studies relate the oxidation state of dissolved Pu to be representative of the oxidation state of surface sorbed Pu (Keeney-Kennicutt & Morse, 1985; Penrose *et al.*, 1987). Such interpretations are complicated by potential redox reactions at heterogeneous surfaces, which can influence the oxidation states of sorbed Pu. This study investigated the spatial distribution of Pu on a natural heterogeneous material (tuff) using *in situ*

micro-XAS techniques, which provided information on the average valence and the bonding behaviour of sorbed Pu at a small scale.

2. Methods and Materials

2.1 Sorption Studies.

Tuff core samples were taken from the 450 m depth of the Topopah Spring Tuff at the proposed high-level waste repository site, Yucca Mountain, NV. Core samples were used to prepare polished 30- μm thin sections. A synthetic carbonate groundwater (pH 8.9) was prepared to have a final concentration of 10⁻⁶ M Pu(V). The thin section was equilibrated by immersion in this solution for 120 hours then rinsed with de-ionised water.

2.2 Micro-XAS Studies

The synchrotron hard X-ray fluorescence (XRF) microprobe on the undulator (Station ID-C) at Sector 13 of the Advanced Photon Source (Argonne Nat. Lab., Argonne, IL) was used with a channel-cut Si(220) monochromator. Micro-focusing optics were used to produce the X-ray beam (Yang *et al.*, 1985). A double elliptical Pt-coated Kirkpatrick-Baez mirror system angled at 2 mrad was used to focus a monochromatic undulator X-ray beam at the Pu L_{III} absorption edge (18054 eV) to a 4 μm vertical by 7 μm horizontal beam (Eng *et al.*, 1995). The thin section was placed in an Al metal frame and mounted on an automated, digital x-y-z stage at 45° to the beam. Fluorescent X-rays were detected with a Si(Li) energy dispersive detector (30 mm² area, Canberra) mounted at 90° to the incident beam and 2 cm from the sample.

Elemental mappings of the thin section were conducted using micro-SXRF spectroscopy. SXRF imaging for elements with absorption energies below 18,500 eV was performed by collecting 20 s live counts in the elemental regions of interest and rastering the sample in 4- μm steps in the vertical plane. Micro-EXAFS spectra were collected on the L α emission line from 50 eV below the Pu absorption edge to 600 eV above the Pu absorption edge in varying step increments from 0.4 to 2.5 eV. The monochromator position and the undulator gap were scanned simultaneously and the microprobe table was moved to track the position of the X-ray beam during each scan. Energy calibration was made with a well-characterised Pu(IV) standard of PuO_{2(s)} and measured simultaneously with a Zr foil (K-edge). Eleven micro-EXAFS scans at each selected spot were collected (energy resolution of 1.5 eV). For the EXAFS, background removal was done using the program AUTOBK, which removed the Fourier components of $\chi(k)$ below a R background of 1.0 Å (Newville *et al.*, 1993). The post-edge "background" function and a linear fit to the pre-edge data were both extrapolated to E₀ and their difference was used as the step height for normalisation. Hanning window functions (cos²) were selected for the conversion from k- to R-space.

3. Results and Discussion

3.1 Characterisation of Tuff and SXRF Analyses of Pu on Tuff.

The tuff is predominantly zeolitic with approximately 2 % smectites, according to X-ray diffraction studies performed on the tuff core materials (Duff *et al.*, in review). Smectite isolates

contained the mineral rancieite ($\text{Ca,Mn}^{2+}(\text{Mn}_4^{4+}\text{O}_9 \cdot 3\text{H}_2\text{O})$, an isomorph of birnessite ($\delta\text{-MnO}_2$, McKenzie, 1989). About 99% of the added dissolved Pu(V) is sorbed to sibling thin sections to that used in this study (Duff *et al.*, in review). Microautoradiography, electron microprobe and petrographic mineral identification techniques indicate Pu sorbs more strongly to smectite and Mn-oxide fracture minerals than to zeolites or Fe oxides (Vaniman *et al.*, 1996). The SXRF mapping for an area on the tuff that contained elevated concentrations of sorbed Pu within a Mn-rich region (Fig. 1). Sorption of Pu to Fe-rich regions was not observed. This is consistent with other studies (Duff *et al.*, in review; Vaniman *et al.*, 1996).

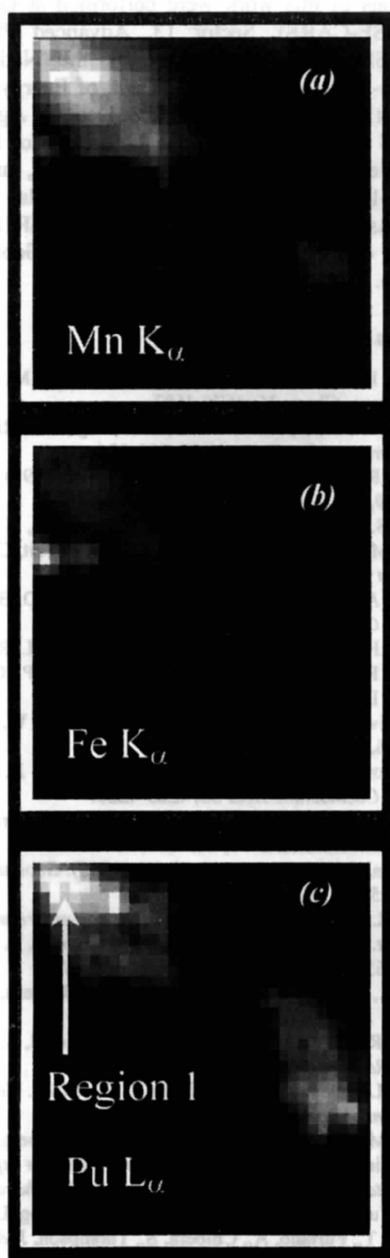


Figure 1
Micro-SXRF elemental map images of spatially localised (a) Mn, (b) Fe and (c) Pu. Lighter tones indicate greater elemental concentrations than darker tones. Area shown is approximately 140 μm by 140 μm , with each pixel being 4 μm by 4 μm .

3.2 XANES Analyses of Sorbed Pu on Tuff.

In XANES analyses, the energy of the X-ray absorption edge increases with increasing oxidation state, due to a decreased shielding of the nuclear core electrons. This increase in the binding energy of the core levels is usually evident from systematic shifts in the pre-absorption edge and bound-state features in the XANES spectrum. The shift can be correlated to differences in the oxidation state of a cationic center (Bertsch *et al.*, 1994). The use of the XANES edge energy for the determination of average oxidation states in solids has been used for uranium (U) (Giaquinta *et al.*, 1997; Duff *et al.*, 1997; Bertsch *et al.*, 1994). For the Pu standards of known oxidation state (Pu(IV)O_2 and $\text{Ba}_3\text{Pu(VI)O}_6$), the fluorescence values were normalised to Pu(IV) (Duff *et al.*, in review). The edge energy (as defined by the half-height of the edge step) of the Pu(VI) standard was +3.0 eV relative to 0.0 eV for Pu(IV) (Duff *et al.*, in review). These analyses are comparable with data from Pu solutions of known oxidation state (Conradson *et al.*, 1998). The relative edge energy shift at region 1 in Fig. 1(c) was +2.6 eV, corresponding to that of mostly Pu(VI) (Fig. 2a). The XANES spectra provide information on the average Pu oxidation state present.

Absorption edge energies are used to define oxidation state, but post-edge structural features, associated with multiple scattering resonances, provide information on the coordination and bonding environment, which may also be related to oxidation state. For example, actinide(VI) species usually have axial O bonds as with the ions: Pu(VI)O_2^{2+} and U(VI)O_2^{2+} . These species usually have post-edge resonance features in their spectra that resemble a shoulder on the high-energy side of the main absorption feature or "white line" (Conradson *et al.*, 1998; Allen *et al.*, 1997; Bertsch *et al.*, 1994). However, the post-edge spectra for sorbed Pu on the tuff did not resemble spectra customarily observed for hexavalent actinides in that no shoulder was present. The absence of a multiple scattering resonance has been observed in sediments containing primarily U(VI), in uranates and in U(V)-containing glasses (Duff *et al.*, 1997; Allen *et al.*, 1997; Farges *et al.*, 1992) and thus its absence is not indicative of oxidation state.

3.3 EXAFS Analyses of Sorbed Pu on Tuff.

More information on the coordination and bonding environment can be gained by examining the EXAFS data for Pu on the tuff. The raw EXAFS data and the Fourier transform (FT) spectra are shown in Figs. 2(a-c). The spectra in Fig. 2(c) represent a pseudo-radial distribution function for the near-neighbour environment around the Pu atom. One major peak is present in the FT at 1.65 Å (uncorrected for phase shift). This feature indicates the absence of axial O's in the environment closest to the Pu atom in the first shell. Major peaks were not observed below 1.65 Å, as would be customarily present for most hexavalent actinides with axial O atoms in the first shell. The absence of a peak near ~1.30 Å has been observed in EXAFS studies with uranates (Allen *et al.*, 1997) and in U(V)-containing glasses (Farges *et al.*, 1992). However, the EXAFS data for the U(V)-containing glasses did not have axial O atoms in the first shell (the first shell was not split).

A major peak indicative of a Pu-Pu (high Z element) interaction in the second shell was not observed above background in the FT spectra shown in Fig. 2(c). Based on studies with actinide compounds (for example, uranates and schoepite), such a feature would be present in the 3 to 5 Å region of the FT plot (Allen *et al.*, 1997). As in studies with actinide solids, the presence of such a Pu-Pu interaction would

signify that a surface precipitation reaction had occurred. This would mean that the surface coverage of sorbed Pu on the Mn-rich regions of the tuff exceeded that of a monolayer. Calculations of sorption site density on Mn oxides and smectite in tuff indicate Pu could be present on these Mn-rich regions at monolayer coverage (Duff *et al.*, in review).

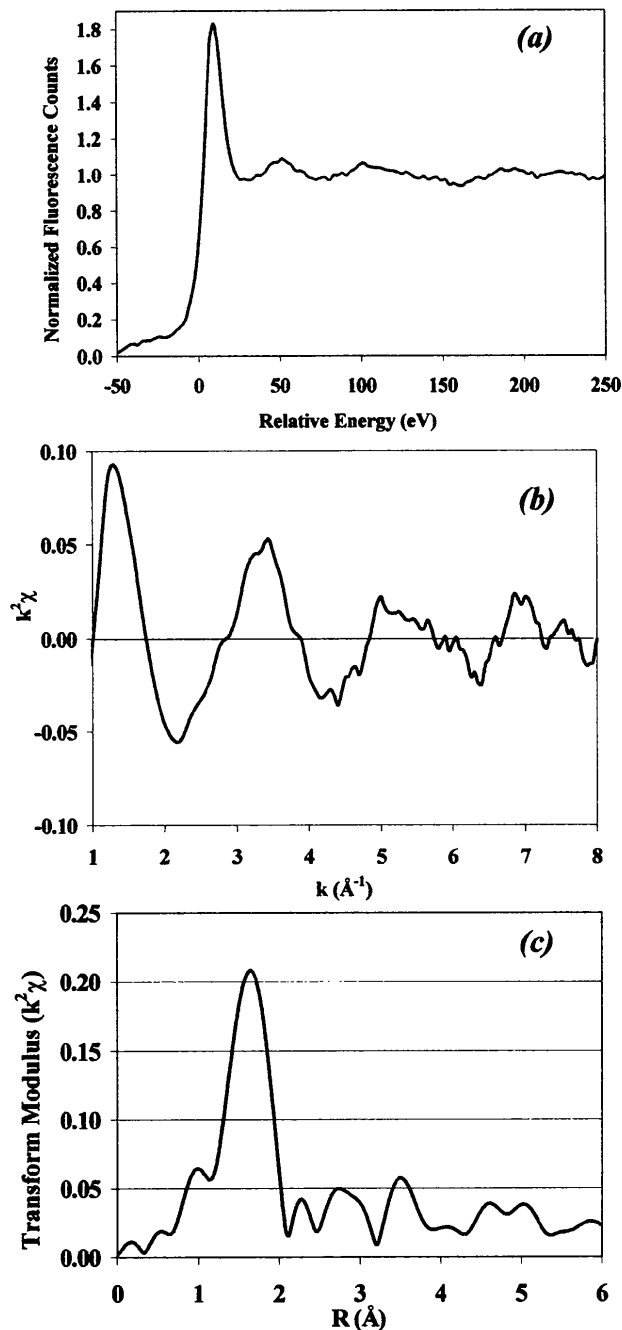


Figure 2
Pu-XAFS spectra region 1 on the tuff. The XANES edge energy data suggests the Pu is sorbed Pu as Pu(VI) (Duff *et al.*, in review). The lower energy portion of the XAFS is shown in (a). Raw k^2 -weighted EXAFS χ and FT data are in (b) and (c), respectively. Data are uncorrected for phase shift.

4. Conclusions

We presented data on the spatial distribution and micro-XAS spectra of sorbed Pu that demonstrated Pu is sorbed strongly and preferentially to Mn oxides and not to Fe oxides in tuff. Additionally, Pu(V) may have been oxidized to Pu(VI) upon sorption. Our findings indicate the bonding and coordination environment of sorbed Pu(VI) on the Mn-rich tuff surface is unlike that of most hexavalent actinides in solution. Full analyses of the EXAFS spectra with FEFF fitting for the sorbed Pu at this region and other regions on the tuff are in progress.

Portions of this work were performed at GeoSoilEnviro-CARS (GSE-CARS), Sector 13, Advanced Photon Source (APS). GSECARS is supported by the National Science Foundation-Earth Sciences, U.S. Dept. of Energy-Geosciences, W.M. Keck Foundation, and the U.S. Dept. of Agriculture. Use of the APS was supported by the U.S. Dept. of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38. The research was also supported by Financial Assistance Award No. DE-FC09-96SR18546 from the U.S. Dept. of Energy to the University of Georgia Research Foundation.

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(Received 10 August 1998; accepted 7 December 1998)