# Heterogeneous Plutonium Sorption on Yucca Mountain Tuff

There are many unresolved questions regarding plutonium (Pu) sorption on tuff rock in Yucca Mountain. In this study, we have used synchrotron x-ray microspectroscopy and microimaging techniques to measure the spatial distribution and local structural speciation of sorbed Pu on tuff. The results demonstrate that Pu is sorbed strongly and preferentially to trace levels of manganese oxides and smectite minerals. Additionally, some Pu(V) was oxidized to Pu(VI) upon sorption, but the sorbed Pu eventually undergoes reduction to Pu(IV).

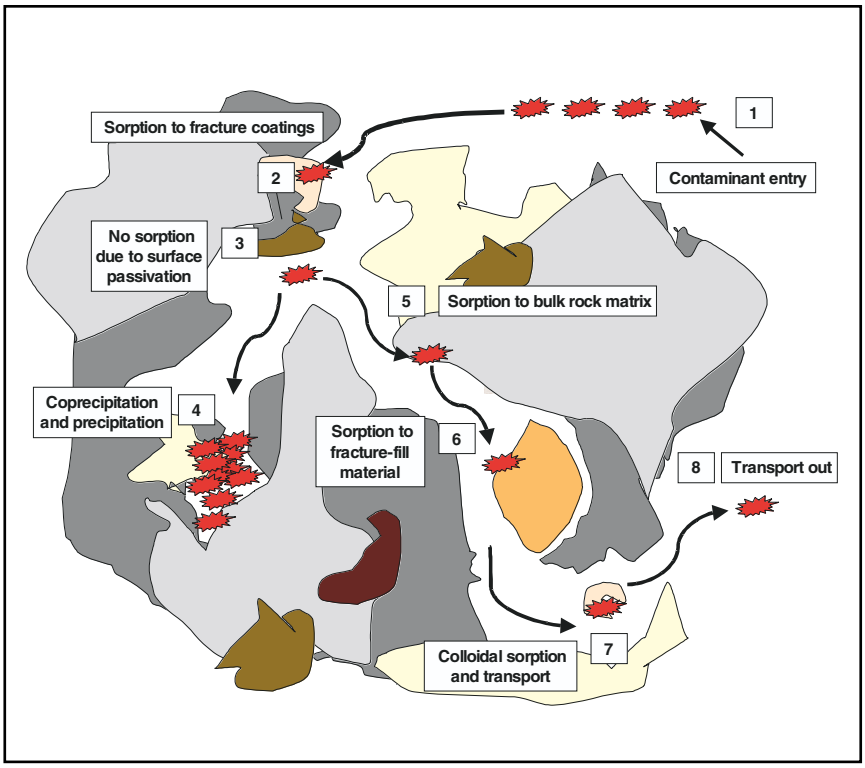


*FIG. 1. Processes that influence the contaminant interactions in a fracture.*

The behavior of dissolved plutonium (Pu) in the subsurface environment is complex. Its mobility in the subsurface environment can be influenced by hydrologic and chemical groundwater characteristics, by biogeochemical reactions, and by interaction with subsurface geologic materials. Plutonium can possess multiple oxidation states [+III, IV, V, and VI] that can undergo oxidation-reduction reactions in solution as well as at the solid-water interface.

Sorption of Pu will retard its subsurface transport in the environment. The volcanic tuff at Yucca Mountain (YM), Nevada, which is being evaluated as a subsurface geologic disposal site for nuclear waste, is a heterogeneous geologic material. These materials can possess preferential flow paths, such as fractures and pore spaces, which often contain a variety of minerals, such as Fe and Mn oxides, zeolites, and aluminosilicates. An example of how a contaminant can interact with minerals in a fracture environment is shown in Fig. 1. Sorption studies with Pu and monomineralic phases show that Pu has a high affinity for Fe- and Mn-oxide and aluminosilicate minerals; however, little is known about how Pu interacts with a heterogeneous mineral sample [1].

In this presentation we discuss our findings from an investigation of Pu sorption on tuff rock using microprobe x-ray-based spectroscopic and imaging techniques. These techniques permit the acquisition of spatially resolved x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopic

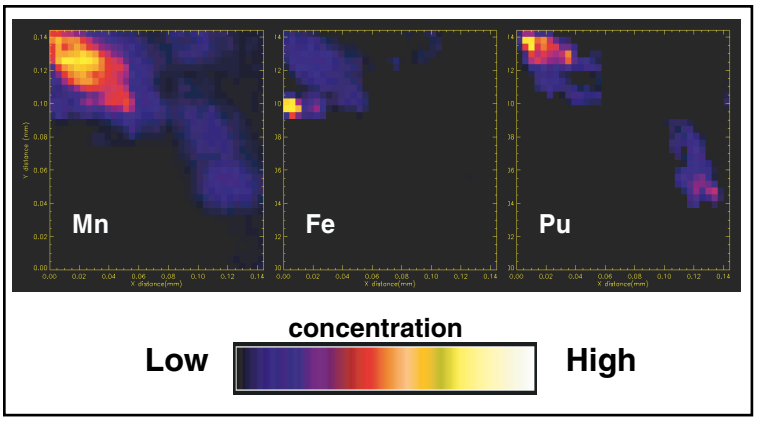


*FIG. 2. Element-specific micro-XRF images of the distribution of manganese (Mn, rancieite), iron (Fe), and sorbed Pu on the tuff, showing the close association of Pu and Mn. Petrographic studies show that the Fe-rich region contains hematite. Area shown: 140 µm x 140 µm.*

information at a microscopic (µm) level. The intricate spatial arrangement of mineral phases, such as the fracture-associated Mn oxide–aluminosilicate clay assemblages in these systems, presents a challenge for investigating such contaminant interactions with conventional techniques. Recent advances in microprobe x-ray fluorescence (micro-XRF), XANES, and EXAFS analytical techniques (GeoSoilEnviroCARS [GSECARS], sector 13-ID-C) provide the essential spatial resolution for characterizing retardation and chemical transformation processes of metals on microscopic mineral bodies within fractures.

The Mn oxide minerals are highly reactive and capable of mediating redox reactions. These minerals possess negatively charged surfaces and high surface areas. Several Mn minerals occur at less than 1% (trace-level) abundance within the volcanic tuff at YM. Manganese(IV)-rich minerals such as rancieite can be localized within fractures in YM tuff with other minerals such as smectite (an aluminosilicate clay) and Fe oxides (such as hematite and ferrihydrite). Micro-XRF imaging of YM tuff containing sorbed Pu [added via a groundwater solution as Pu(V)] shows that the surfaces of fracture-fill rancieite-smectite mineral assemblages sorb Pu concentrations to nearly 1000 times that of Pu in the groundwater solution (Fig. 2). Enrichment of sorbed Pu by these trace-level minerals relative to that of other bulk minerals in the rock reveals the essential role of fracture-linked minerals in contaminant retardation.

Synthetic hematite has a high affinity for Pu and other actinides, suggesting fracture-associated hematite minerals may also retard contaminant transport [1]. However, natural mineral surfaces do not always possess the same reactive surface characteristics as their synthetic counterparts. This difference has been observed in our sorption studies with Pu (Fig. 2), where surface passivation is demonstrated by the absence of co-associated sorbed Pu with Fe (hematite), either in micro-XRF studies or in complementary microautoradiography studies [2,3]. These findings concur with sorption studies, which observed that the affinity of Pu for YM tuffs enriched in Fe oxides nearly equals that of YM tuffs with similar mineralogical characteristics but with much lower Fe oxide contents [1].

Our micro-XRF imaging studies show that sorbed Pu is co-associated with naturally occurring elements (such as Ca, Ce, Pb, Sr, and Zn; data not shown) other than Mn in the tuff rock. Enrichment

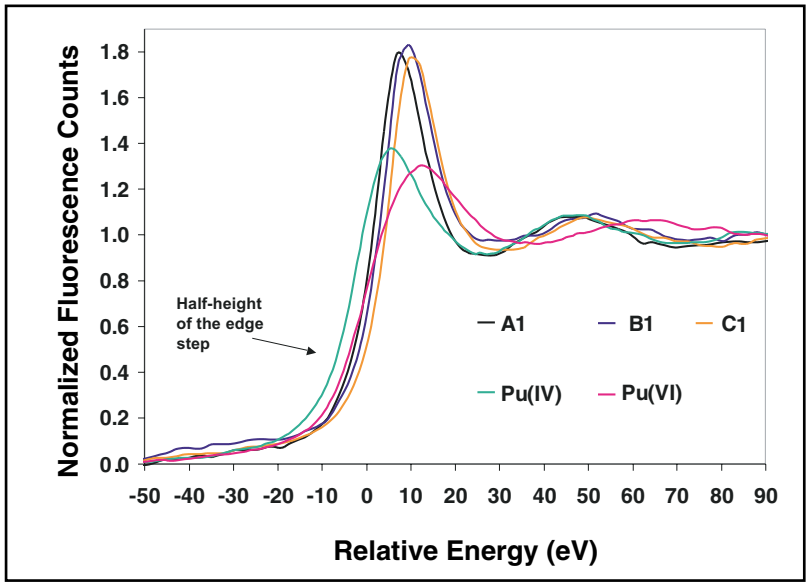


*FIG. 3. Plutonium-XANES spectra for sorbed Pu on tuff and two of the Pu standards (kindly provided by D. Reed, Argonne National Laboratory). The half-height of the absorption edge-step is related to the average oxidation state.*

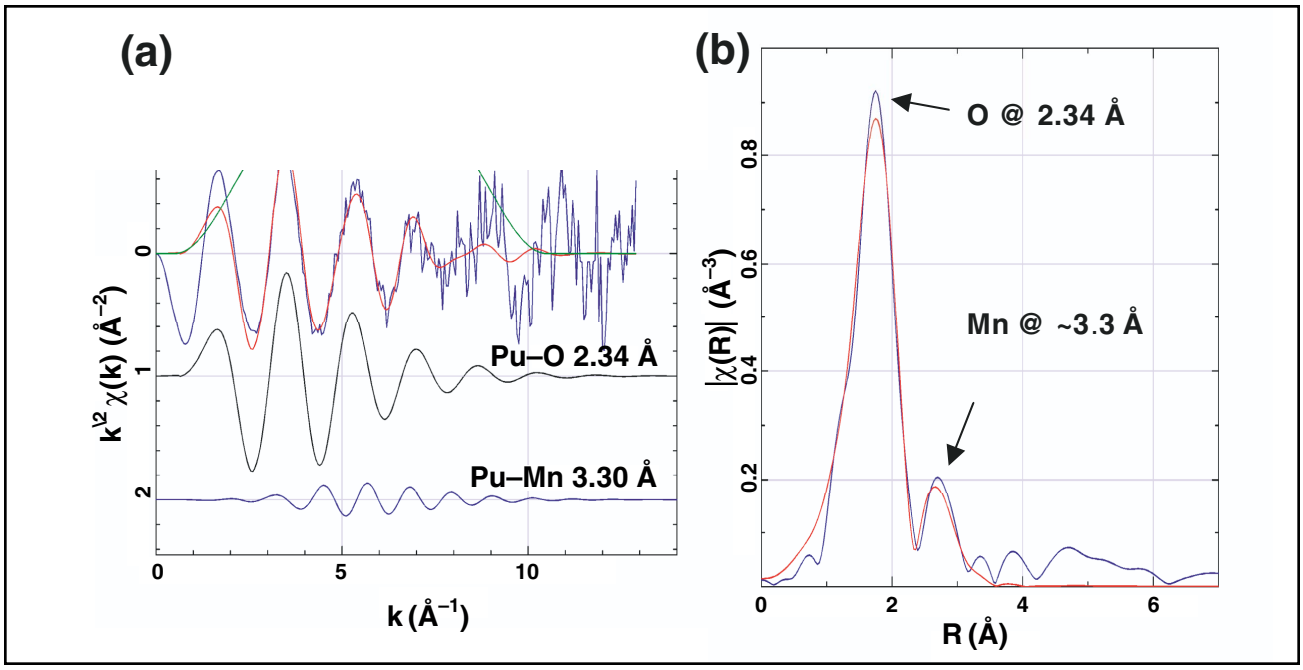


*FIG. 4. (a) The k²-weighted Pu-EXAFS spectra for one of the Pu-enriched regions on the tuff and (b) the complementary Fourier-transformed data of Pu-EXAFS spectra showing the pseudo-radial distribution of atoms around the Pu at the region examined.*

of these elements by rancieite-smectite assemblages suggests that these trace mineral phases participated in the retardation of groundwater solutes. In contrast, the co-association of these natural ions with Fe was not observed—suggesting that natural hematite surfaces in the tuff may display little reactivity to groundwater solutes. Besides retarding contaminant transport, mineral surfaces can alter the chemical speciation of some solutes upon sorption—a process that can make them more or less mobile than their previous dissolved forms.

Our microprobe Pu-XANES and -EXAFS studies at the $L_3$-edge of areas that were highly enriched in sorbed Pu suggest that Pu(V) becomes oxidized to Pu(VI) at some Mn-rich regions on the tuff (Fig. 3, selected data shown). Other areas of Pu enrichment had an average oxidation state of +V—suggesting that Pu(V) or a combination of Pu valences may exist on the tuff [2,3]. These micro-XANES studies were performed 2 and 6 months after adding the Pu(V) to the tuff. Micro-EXAFS studies showed that the coordination environments differed for the sorbed Pu at several regions on the tuff (data not shown).

However, after a two-year period, our XANES and EXAFS studies show that the Pu was reduced to Pu(IV) at all Pu-enriched areas that we examined (Fig. 4). The EXAFS spectra were consistent with oxygen in the first shell and Mn in the second, suggesting a surface sorption mechanism rather than precipitation. This behavior may be due to the disproportionation of the Pu. We also observed that the Pu at two of the Pu-enriched regions is sorbed to a Mn-rich mineral—most likely rancieite (Fig. 4, not all data shown).

We presented data on the spatial distribution and local structural speciation of sorbed Pu on tuff. The data demonstrate that Pu is sorbed strongly and preferentially to trace levels of Mn oxides and smectite minerals. Additionally, some Pu(V) was oxidized to Pu(VI) upon sorption, but the sorbed Pu eventually undergoes reduction to Pu(IV). More research is required to investigate the speciation transformations of sorbed Pu on minerals. Full XAFS data analyses and complementary molecular modeling of Pu surface species on Mn oxides and smectites are in progress. Experiments such as these are expected to provide detailed information on mechanisms of actinide transport through complex, heterogeneous Earth materials.

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