Application of XAFS Spectroscopy to Actinide Environmental Science

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Abstract. The use of XAFS spectroscopy and related synchrotron radiation techniques for the molecular-level speciation of environmental contaminants including actinides has led to an improved understanding of the fundamental chemical and biological processes determining their behavior in complex systems. Several recent applications of XAFS spectroscopy to actinides in model systems and more complex environmental samples are reviewed to highlight the impact these studies have on our knowledge about the bioavailability of actinides, the development of remediation strategies, and predictive models for risk assessment. XAFS studies of actinide ion sorption at solid/aqueous solution interfaces are presented in greater detail. Representative examples include XAFS studies in combination with batch-type experiments of U(VI), Np(V), Pu(III), and Pu(IV) sorption on kaolinite.

Keywords: Actinides, X-ray absorption spectroscopy, kaolinite, sorption, EXAFS

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INTRODUCTION

After a storage period of several hundred years, plutonium and other lighter actinides will become major contributors to the radiotoxicity of spent nuclear fuel in a deep geological repository [1]. Therefore, detailed studies of important interaction processes of actinides released from the repository into the aquifer with the engineered barriers and the host rock formation of a nuclear waste repository are needed for its performance assessment.

Similar studies are necessary for the development of efficient and cost-effective strategies for the remediation of contaminated areas. Radioactive contaminations of sediments and aquifers resulted from nuclear weapons production in the former Soviet Union [2] and the United States of America [3] during the Cold War.

X-ray absorption fine structure (XAFS) spectroscopy is a powerful technique for determining the local coordination environment of environmental pollutants in solids and liquids. Brown et al. [4] reviewed the applications of XAFS spectroscopy and other synchrotron radiation techniques to complex environmental samples and simplified model systems at the XAFS12 conference [4]. Denecke discusses numerous examples of actinide speciation by means of XAFS spectroscopy with emphasis on nuclear disposal safety research in a recent review article [5].

In this paper, we highlight several recent applications of XAFS spectroscopy to actinides in model systems and environmental samples published in 2005 and 2006. The sorption of different actinides in different oxidation states onto the clay mineral kaolinite is discussed in greater detail.

RECENT XAFS STUDIES

Actinide Interaction With Bacteria

Microorganisms and plants are able to bind heavy metals in their cells. The complexation of U(VI) by vegetative bacterial cells and surface layers (S-layer) of Bacillus sphaericus was studied by extended X-ray absorption fine-structure (EXAFS) spectroscopy and transmission electron microscopy [6]. Carboxyl groups and phosphate groups were identified as the main functional groups responsible for the complexation of U(VI) with the purified and recrystallized S-layer sheets and the cells of Bacillus sphaericus.

In addition to complexation, certain bacteria are able to reduce U(VI) to largely insoluble U(IV) compounds. During bacterial growth of gram-positive, anaerobic Thermoterrabacterium ferrireducens in
contact with U(VI) acetate solution, a gray precipitate formed that was identified by X-ray powder diffraction and EXAFS spectroscopy as the U(IV) phosphate CaU(PO₄)₂·H₂O [7].

**Actinide Interaction With Humic Substances**

Naturally occurring aquatic humic substances (humic and fulvic acids) have strong complexing and redox properties, can form colloids, and are an important factor for the transport of actinide pollutants in environmental systems. Recently the local environment of Np(IV) [8], Np(V) [9], and Pu(III) [10] with humic substances has been investigated using EXAFS spectroscopy and complimentary spectroscopic techniques. The carboxylic groups are the main complexing sites of the humic substances responsible for binding Np(IV) at pH 1. In addition, the presence of mixed hydroxo-humate Np(IV) complexes with naturally occurring fulvic acid in the acidic pH range was detected by EXAFS spectroscopy [5]. The interaction of Np(V) with humic acid at pH 7 is dominated by carboxylic groups as shown by EXAFS measurements of Np(V) humates and Np(V) sorbed onto Bio-Rex70, a cation exchange resin having only carboxylic groups. The structural parameters for the near-neighbor surrounding of Pu(III) in complexes with humic and fulvic acids at pH 1 determined by EXAFS spectroscopy showed that the trivalent Pu oxidation state was stable during the duration of the experiment. But the resolution in r space did not allow differentiating between carboxylate groups of the humic substances and water molecules coordinated to Pu(III).

**Actinide Interaction With Minerals And Soils**

The interaction of U, Np, Pu, and Am at the solid-water interface has been studied recently for a number of model systems. The bulk of the work has been devoted to U(VI). The sorption of U(VI) on the clay minerals montmorillonite [11, 12] and imogolite [13] has been studied by EXAFS as a function of pH in the presence and absence of ambient CO₂. Studies of U(VI) sorption on single-crystal surfaces using grazing-incidence EXAFS have been reported for α-Al₂O₃(1-102) and α-Fe₂O₃(1-102) [14]. Webb et al. studied by means of EXAFS the incorporation of U(VI) into biogenic Mn oxides that were prepared using spores of Bacillus sphaericus [15]. Only a few EXAFS measurements of transuranic elements have been reported, e.g., sorption of Np(V) on manganite and hausmannite [16] and Am(III) sorption on ferricydrite [17].

EXAFS spectroscopy and complimentary techniques were applied to determine the speciation of U in uranium-rich sediments at the Ruprechtov site, Czech Republic [5], and the Hanford site, USA [18]. The Pu oxidation state in Yucca Mountain tuff was monitored over time by X-ray absorption near-edge structure (XANES) spectroscopy and solvent-extraction techniques [19]. Pu sorbed to the tuff was preferentially associated with Mn oxides in the much less mobile Pu(IV) oxidation state.

The studies mentioned above have important implications in estimating efficient remediation strategies of contaminated sites and the risk associated with geological disposal of radioactive waste. The following section reports on batch and EXAFS spectroscopic studies of U, Np, and Pu on the reference clay mineral kaolinite.

**SORPTION OF U, Np, AND Pu ON KAOLINITE**

Figure 1 shows the sorption behavior of U(VI), Np(V), Pu(III), and Pu(IV) in the μM concentration range on kaolinite as a function of pH. Each oxidation state of the actinide has a distinct pH dependence, i.e., the sorption edge (pH where 50% sorption occurs) shifts toward higher pH in the order Pu⁴⁺, Pu³⁺, UO₂²⁺, NpO₂⁺. Whereas Pu(III), Pu(IV), and U(VI) are strongly sorbed in the neutral pH range, only small amounts of Np(V) are sorbed on kaolinite. In the presence of ambient CO₂, the sorption curves of U(VI) and Np(V) are characterized by a maximum followed by decreasing sorption with increasing pH due to formation of strong carbonato complexes in aqueous solution (Fig. 2). The aim of this comparative EXAFS study was to determine the local coordination environment of U, Np, and Pu at the kaolinite-water interface at different pH. In addition, the influence of HCO₃⁻/CO₃²⁻ was studied by comparing samples prepared under Ar atmosphere and in air.

![FIGURE 1. pH dependence of actinide sorption on kaolinite in the presence of ambient CO₂.](image-url)
FIGURE 2. Calculated speciation for 8 μM Np(V), I = 0.1 M. Left: ambient CO₂ (pCO₂ = 10⁻³.₅ atm); right: without CO₂.

Results And Discussion

Sorption of U(VI)

In the air-equilibrated system, the uptake of U(VI) by kaolinite increases from pH 4 to 7 and decreases above pH 7 (Fig. 3, left). No decrease in uptake is observed in the absence of CO₂. This observation agrees with previous batch experiments [22, 23].

Experimental

Samples with different amounts of ²³⁸U(VI), ²³⁷Np(V), ²⁴⁴Pu(III), and ²⁴⁴Pu(IV) sorbed on kaolinite were prepared in suspensions of 200 mg kaolinite KGa-1b (Source Clays Repository) in 50 mL deionized water. The ionic strength was 0.1 M NaClO₄. The pH was adjusted to the values given in Tab. 1 using NaOH and HClO₄. Samples U1, U2, Np1, Np2, Pu2, and Pu3 were prepared in the presence of ambient CO₂. Samples U3, Np3, and Pu1 were prepared in a glove box under Ar atmosphere. After shaking the kaolinite suspensions for 72 h, aliquots of actinide (An) stock solutions were added with immediate pH readjustment. The total An concentrations are given in Tab. 1. After a contact time of 72 h, the solid and liquid phases were separated by centrifugation. The An uptake (Tab. 1) was determined by measuring the An concentration in solution using liquid scintillation counting or γ-spectroscopy. The solid residues were loaded without drying into EXAFS sample holders. Table 1 summarizes the preparation conditions of all samples and the corresponding sorption densities. U L₃-edge and Np L₂-edge EXAFS spectra were measured in fluorescence mode at the Rossendorf Beamline ROBL at ESRF. Pu L₃-edge EXAFS spectra were recorded at the INE beamline at ANKA (FZ Karlsruhe) using a Ge solid state detector. EXAFSPAK [20] and FEFF8.20 [21] were used for data analysis.

TABLE 1. Summary of EXAFS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[An]ₜₐₜₜ</th>
<th>Atmosphere</th>
<th>pH</th>
<th>Sorption density μmol/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₁ / U(VI)</td>
<td>10 CO₂</td>
<td>5.0</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>U₂ / U(VI)</td>
<td>10 CO₂</td>
<td>8.5</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>U₃ / U(VI)</td>
<td>10 Ar</td>
<td>8.5</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Np₁ / Np(V)</td>
<td>8 CO₂</td>
<td>8.0</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Np₂ / Np(V)</td>
<td>8 CO₂</td>
<td>9.0</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Np₃ / Np(V)</td>
<td>8 Ar</td>
<td>9.0</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Pu₁ / Pu(III)</td>
<td>10 Ar</td>
<td>6.0</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Pu₂ / Pu(IV)</td>
<td>10 CO₂</td>
<td>4.0</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Pu₃ / Pu(IV)</td>
<td>10 CO₂</td>
<td>9.0</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>
Sorption of Np(V)

The sorption behavior of 8 μM Np(V) as a function of pH in the absence and presence of ambient CO₂ is shown in Fig. 3, right. Previous batch experiments [26] showed a similar sorption curve as the CO₂-free system.

![Experiment](image)

**FIGURE 5.** Np L₃-edge k³-weighted EXAFS spectra (left) and corresponding Fourier transform magnitudes and real parts (right) of the Np-kaolinite samples.

TABLE 2. Structural parameters. r distances ±0.02 Å, σ² Debye-Waller factors in Å². Coordination numbers were held constant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2 x O₂</th>
<th>5 x O₂</th>
<th>1 x Al/Si</th>
<th>1 x Al/Si</th>
<th>0.5 x U</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>1.79</td>
<td>0.0029</td>
<td>2.37</td>
<td>0.0139</td>
<td>3.10</td>
</tr>
<tr>
<td>U2</td>
<td>1.81</td>
<td>0.0023</td>
<td>2.41</td>
<td>0.0093</td>
<td>3.08</td>
</tr>
<tr>
<td>U3</td>
<td>1.80</td>
<td>0.0024</td>
<td>2.36</td>
<td>0.0125</td>
<td>3.09</td>
</tr>
</tbody>
</table>

**Sorption of Pu(III) and Pu(IV)**

As can be seen in Fig. 1, Pu(IV) is strongly sorbed over the entire pH range. The sorption edge occurs at pH ~1. The sorption edge for Pu(III) was observed at a higher pH of ~5. These batch experiments have been combined with Pu L₃-edge EXAFS spectroscopy (Fig. 6, Tab. 2) to obtain molecular-level information on the interaction of Pu with kaolinite. The average Pu-O₁ distances for sample Pu1, Pu2, and Pu3 are in the range of 2.27 – 2.31 Å, indicating that the Pu in all samples is sorbed at the kaolinite surface as Pu(IV). In sample Pu1 the initial Pu(III) has been oxidized to Pu(IV). The EXAFS spectra of samples Pu2 and Pu3 are very similar. Sample Pu1 shows a different EXAFS pattern, in particular in the k range 6 – 8 Å⁻¹ (Fig. 6). A Pu-Pu interaction at ~3.7 Å with two Pu atoms (Tab. 2) was observed in all spectra, indicating the presence of polynuclear Pu(IV) species at the surface. In addition to the Pu-O and Pu-Pu coordination shells, a third shell at an intermediate distance had to be included in all fits. The best fit to the data of samples Pu2 and Pu3 was obtained with a Pu-Al/Si coordination shell at 3.62±0.02 Å (Tab. 2). This result can be rationalized by an inner-sphere sorption of the polynuclear Pu(IV) species formed in solution to the kaolinite surface. The EXAFS spectrum of sample Pu1 prepared from Pu(III) under Ar atmosphere could not be modeled with a Pu-Al/Si coordination shell. The best fit was obtained by including a Pu-O₂ interaction at 3.25 Å. Similar Pu-O distances were observed for Pu(IV) colloids [29]. Future studies shall investigate the cause for the observed structural differences of sample Pu1 compared to samples Pu2 and Pu3 and the reason for the oxidation of Pu(III) to Pu(IV).

![Diagram](image)
FIGURE 6. Pu L3-edge $k^3$-weighted EXAFS spectra (left) and corresponding Fourier transform magnitudes and real parts (right) of the Pu-kaolinite samples.

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