

XAS study of plutonium sorbed on Opalinus Clay

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Introduction:

Plutonium and minor actinides in spent fuel are the dominant contributors to the radiotoxicity in a high-level nuclear waste repository after a storage time over 1,000 years [1]. ^{239}Pu with a half-life of 24,000 years is the most hazardous nuclide and it demands special concern. Pu exhibits a complicated redox behaviour and up to four Pu oxidation states (typically III-VI) can coexist in natural waters. Several European countries consider argillaceous rocks such as Opalinus clay (OPA) [2] as a potential host rock for the construction of high-level nuclear waste repositories. In our study OPA from Mont Terri, Switzerland, and the corresponding pore water (pH 7.6, $I = 0.4$ [3]) have been selected as references to study the sorption and speciation of Pu on natural clay. The goal of our study is to investigate the sorption mechanism of Pu on OPA at a molecular level using X-ray Absorption Spectroscopy (XAS). Such spectroscopic studies are important to obtain a detailed understanding of the migration behaviour of Pu in clays.

Experimental:

The sorption of Pu on OPA has been investigated as a function of Pu oxidation state (III, IV, VI) at pH 7.6 in the absence and presence of ambient CO_2 in pore water and 0.1 M NaClO_4 (see Table 1). For XAS measurements six powder samples with different amounts of Pu sorbed were prepared from stock solutions with $4 \cdot 10^{-4}$ M $^{239}\text{Pu(III)}$, $4 \cdot 10^{-4}$ M for Pu(IV) and, $2 \cdot 10^{-3}$ M $^{239}\text{Pu(VI)}$, respectively.

The Pu(VI) stock solution had been purified from Pu decay products and ^{241}Am using anion exchange chromatography. The trivalent and tetravalent oxidation states of Pu were obtained from the purified Pu(VI) stock solution by potentiostatic electrolysis and the oxidation state purity was verified by UV/vis spectroscopy. The total Pu concentration in each OPA suspension (15 g/L) was $\sim 10^{-5}$ M. The Pu uptake by OPA as measured by liquid scintillation counting was ~ 370 ppm (Table 1). XAS measurements (XANES and EXAFS) were performed on the Rossendorf Beamline (BM20) at the European Synchrotron Radiation Facility (ESRF). The Pu L_{III} -edge (18070 eV) spectra were recorded in fluorescence mode at 15 K using a 13-element Ge solid-state detector. EXAFSPAK and FEFF 8.20 were used for the analysis of the EXAFS data.

Table 1. Summary of the Pu samples measured by XAS.

Sample	Pu _{oxd.}	OPA	CO ₂ /Ar	pH	Electrolyte	Pu loading (ppm)	Eh/mV (SHE)
Pu-1	Pu(VI)	aerobic	$p_{\text{CO}_2}=10^{-3.5}$ atm	7.62	OPA PW	375	+236
Pu-2	Pu(IV)	aerobic	$p_{\text{CO}_2}=10^{-3.5}$ atm	7.60	OPA PW	375	+237
Pu-3	Pu(IV)	anaerobic	Ar atmosph.	7.63	OPA PW	370	-59
Pu-4	Pu(III)	anaerobic	Ar atmosph.	7.61	OPA PW	370	-58
Pu-5	Pu(IV)	anaerobic	Ar atmosph.	7.61	0.1 M NaClO_4	372	-73
Pu-6	Pu(III)	anaerobic	Ar atmosph.	7.60	0.1 M NaClO_4	372	-63

Results: Figure 1 shows the raw Pu L_{III} -edge k^3 -weighted EXAFS data, the best theoretical model, and the corresponding Fourier transforms of all samples Pu-1-6. As can be seen from Fig. 1, the samples Pu-1 and Pu-2, which were prepared under aerobic conditions, show different EXAFS spectra, especially in the k range

6-9 \AA^{-1} , compared to anaerobic samples (Pu-3-6). The EXAFS spectra of Pu-1 and Pu-2 show an additional Pu-Fe interaction at 3.46 \AA in the FT spectra. The EXAFS spectra of all samples have in common a Pu-Al/Si interaction at about 3.14 \AA and a Pu-O interaction at about 2.34 \AA (except Pu-3). The structural parameters derived from the EXAFS fits are summarized in Tab. 2.

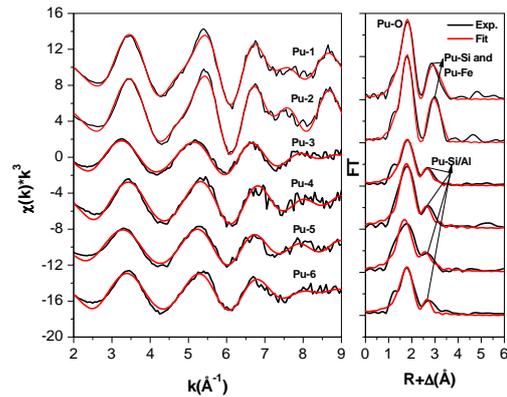


Figure 1. Pu L_{III} -edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transform magnitudes (right) of samples Pu-1-6.

Table 2. EXAFS structural parameters for samples Pu-1-6.

Sample	8x Pu-O		2x Pu-Si/Al		2x Pu-Fe		ΔE_0 (eV)	Red. error
	R(\AA)	$\sigma^2(\text{\AA}^2)$	R(\AA)	$\sigma^2(\text{\AA}^2)$	R(\AA)	$\sigma^2(\text{\AA}^2)$		
Pu-1	2.34	0.013	3.13	0.004	3.46	0.006	-9.5	0.21
Pu-2	2.34	0.012	3.13	0.004	3.46	0.005	-10.2	0.22
Pu-3	2.40	0.021	3.17	0.008			-12.4	0.12
Pu-4	2.34	0.020	3.14	0.007			-11.2	0.36
Pu-5	2.34	0.026	3.14	0.007			-13.7	0.11
Pu-6	2.36	0.022	3.15	0.007			-11.5	0.14
$\text{Pu(OH)}_4(\text{am.})$ [4]	2.32							

The coordination numbers for Si/Al and Fe were held constant during the fit. The Pu-O distance in all samples is compared with literature Ref. 4. The Pu-O bond length agrees well (except for sample Pu-3 and Pu-6) with the $\text{Pu(OH)}_4(\text{am.})$. The detection of Pu-Al/Si interactions in all samples indicates inner-sphere sorption of Pu(IV) on the clay minerals present in OPA. XANES measurements (not shown) show that the oxidation state (IV) of Pu dominates in all samples, independent from aerobic/anaerobic conditions and the initial Pu oxidation state (Pu(III) , Pu(IV) , or Pu(VI)). No influence of the background electrolyte was observed. This result is in good agreement with a previous XAFS study on the sorption of Pu(III) and Pu(IV) onto kaolinite [5].

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