

EXAFS study on the influence of humic acid and dissolved Fe(II) on the sorption of Pu on natural clay

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Introduction: To improved the understanding of the mechanisms regulating the interaction between plutonium (^{239}Pu) in his relevant oxidation states (III, IV, V, VI [1]) with humic acid (HA), dissolved Fe(II), and Opalinus Clay (OPA) as a representative for natural clay a molecular level investigations are of great importance with respect to the long-term storage of high-level nuclear waste. Organic compounds and dissolved Fe(II) which can be released from OPA or from its minerals (such pyrite and siderite in case of Fe) under certain conditions can significantly affect the sorption and migration behaviour of Pu due to their complexation and redox properties. The aim of our study was to investigate the speciation of Pu after sorption on OPA using X-ray absorption spectroscopy (XAS).

Experimental: The sorption of ^{239}Pu on OPA from Mont Terri, Switzerland has been investigated as a function of Pu oxidation state (III, IV, V, VI), HA (M42 [1]), and dissolved Fe(II) in synthetic OPA pore water (PW) at pH 7.6 under anaerobic conditions (Ar atmosphere). For XAS measurements seven powder samples of anaerobic OPA (BHE-24/2) with different amount of Pu were prepared (see Table 1). The ^{239}Pu (VI) stock solution had been purified from its decay products and ^{241}Am using anion exchange chromatography. The trivalent, tetravalent, and pentavalent oxidation states of Pu were obtained from the 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 (6 g/L) was $\sim 10^{-5}$ M Pu(III, IV, V) and $2 \cdot 10^{-5}$ M Pu(VI). The Pu uptake on OPA was determined by liquid scintillation counting of the supernatants. XAS measurements (XANES and EXAFS) were performed on the Rossendorf Beamline (BM20) at the European Synchrotron Radiation Facility (ESRF). The Pu L_{III} -edge (18057 eV) spectra were recorded in fluorescence mode at 15 K using a 13-element Ge solid-state detector. Software packages Athena, 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	Initial Pu oxd. state	Atmosphere	HA	FeCl ₂	pH	Pu loading (ppm)	Eh/mV (SHE)
1	VI	Ar	no	yes	7.5	733	-88
2	IV	Ar	no	no	7.7	405	6
3	IV	Ar	yes	no	7.7	404	10
4	III	Ar	yes	no	7.7	435	-18
5	III	Ar	no	yes	7.5	436	-93
6	V	Ar	no	no	7.7	436	-8
7	V	Ar	yes	no	7.8	436	35

Results: Figure 1 shows the raw Pu L_{III} -edge k^3 -weighted EXAFS data, the best theoretical model, and the corresponding Fourier transforms (FT) of all samples 1-7. As can be seen from Fig. 1, the samples (1-5) show the same EXAFS patterns and only two coordination shells could be found in the FT spectra, a Pu-coordination shell at about 2.39 Å and a Pu-Si/Al coordination shell at about 3.20 Å.

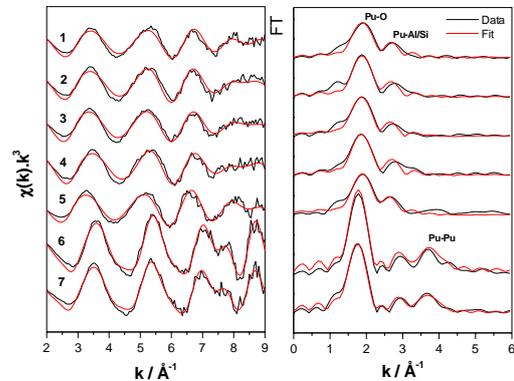


Figure 1: Pu L_{III} -edge k^3 -weighted EXAFS spectra (left) and the corresponding FT magnitudes (right) of Pu samples.

Very similar EXAFS spectra were obtained for the samples 6 and 7, which are prepared with Pu(V). Three coordination shells, i.e., Pu-O, Pu-Si/Al, and Pu-Pu, were observed in the FT spectra at about 2.29 Å, 3.63 Å, and 3.78 Å, respectively. The additional Pu-Pu coordination shell was observed because a small amount of Pu(IV) colloids remained in the Pu(V) stock solution after potentiostatic electrolysis. Pu-O distances of samples (1-4) were longer (2.39 Å) than those of samples 6 and 7 (2.29 Å) and the obtained coordination numbers were also smaller (between 5.9 and 7.2). This result supports the obtained result from iterative transformation factor analysis (ITFA) [2], which showed that Pu is partly reduced to Pu(III), probably by iron(II) bearing minerals contained in OPA and this reduction was more pronounced by the presence of dissolved Fe(II) solution (up to 55 %). For these samples the obtained Pu-O distance and coordination number agree well with the determined structure of Pu(III) aquo ion [3]. A shorter Pu-O and Pu-Pu distance was found in samples 6 and 7 compared to those for Pu(OH)₄(am.) [4], perhaps due to precipitation of Pu(IV) colloids. XANES measurements (not shown) showed Pu(III) and Pu(IV) are the dominating Pu species in samples 2-5 and 6, 7, respectively. In all samples mainly a mixture of Pu(III) and Pu(IV) was found independent on the initial Pu oxidation state. The detection of Pu-Al/Si interactions in all samples indicates inner-sphere sorption of Pu(IV) on the clay minerals present in OPA. Our EXAFS results agree well with a previous EXAFS study with kaolinite[5].

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References

- [1] W. Runde, Los Alamos Sci. 26, 392-411 (2000).
- [2] S. Sachs et al., Report FZR-399 (2004).
- [3] A. Roßberg et al., Anal. Bioanal. Chem. 376, 631 (2003).
- [4] T. Reich et al., Biannual Report 1999/2000, FZR-322 (2001).
- [5] K. Dardenne et al., Radiochim. Acta 97, 91 (2009).
- [6] T. Reich et al., AIP Conf. Proc. 882, 179 (2007).