EXAFS study of plutonium sorption onto kaolinite

T.Ye. Reich, N.L. Banik, R.A. Buda, S. Amayri, J. Drebert, J.V. Kratz, N. Trautmann, T. Reich

Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany

The Pu sorption complexes on kaolinite have been investigated using X-ray Absorption Fine Structure (XAFS) spectroscopy. Pu L_{III}-edge Extended XAFS (EXAFS) spectra provided the information about the local environment of plutonium sorbed onto kaolinite. Pu L_{III}-edge X-ray Absorption Near Edge Structure (XANES) was used to identify the plutonium oxidation state.

The samples studied with XAFS are indicated with capital letters A - D and summarized in Table 1. The samples were prepared as wet pastes with total Pu concentration $1x10^{-5}$ M, 4 g/L kaolinite in 0.1 M $NaClO_4$. The uptake of Pu(III) and Pu(IV) onto kaolinite as a function of pH was determined in batch experiments [1, 2].

Pu L_{III}-edge XAFS data were collected in fluorescence mode at room temperature at the synchrotron radiation facility ANKA at FZK.

In all of the XANES spectra presented in Fig. 1 (left), neither a shift in the absorption-edge energy is evident or a significant structure difference at the high energy side of XANES, indicating that the plutonium in all samples is sorbed at the surface of kaolinite as Pu(IV). In sample B the initial Pu(III) has been oxidized to the Pu(IV).

The k^3-weighted experimental EXAFS data and fits for all samples are shown in Fig. 2. All but one (sample A) of them show a good signal-to-noise ratio out to a k value of ca. 10 $Å^{-1}$. All spectra are dominated by a low-frequency oscillation due to the backscattering from the nearest oxygen atoms. The EXAFS data of samples A, C, and D are very similar. Sample B shows a different EXAFS pattern, in particular in the k range 6 - 8 $Å^{-1}$.

The Fourier transform (FT) of the EXAFS spectra (Fig. 1, right) represents a pseudo radial distribution function of the Pu near-neighbor surrounding. The most prominent peak in all spectra is at ≈ 1.8 Å (uncorrected for phase shift) and arises from the backscattering caused by eight oxygen atoms coordinated to Pu(IV). A Pu-Pu interaction at ≈ 3.7 Å with two Pu atoms (Tab. 2) is observed in all spectra indicating the formation of polynuclear Pu 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 A, C, and D, which were prepared with $1x10^{-5}$ M Pu(IV), was obtained with a Pu-Al/Si coordination shell at 3.62 – 3.66 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 B prepared from Pu(III) under Ar atmosphere could not be modelled with a Pu-Al/Si shell. The best fit was obtained by including a Pu-O interaction at 3.25 Å. Similar Pu-O distances were observed in Pu(IV) colloids [3]. The cause of the observed structural differences of sample B compared to A, C, and D, and the reason for the oxidation of Pu(III) to Pu(IV) is subject of future studies.

Table 1. Summary of samples examined by XAFS

	Sample description
A	94 ppm Pu(IV), air, pH 1
B	243 ppm Pu(III), argon, pH 6
C	370 ppm Pu(IV), air, pH 4
D	412 ppm Pu(IV), air, pH 9

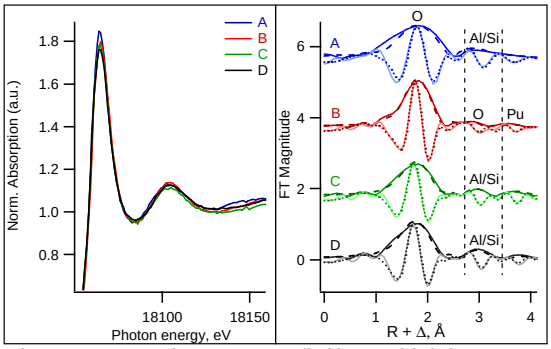

Fig. 1: Pu L_{III}-edge XANES (left), FT (right).

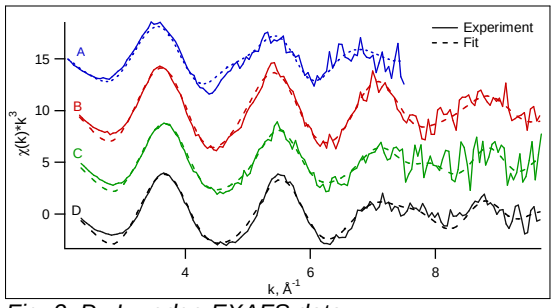

Fig. 2: Pu L_{III}-edge EXAFS data.

Table 2. Distances to Pu neighbor in Å (± 0.02 Å).

	8 x O_1	2 x O_2	2 x Al/Si	2 x Pu
A	2.34	-	3.66	3.70
B	2.31	3.25	-	3.70
C	2.28	-	3.62	3.69
D	2.27	-	3.62	3.68

References:

[1] R.A. Buda et. al., Institut für Kernchemie, Universität Mainz, Annual Report 2006.
[2] N.L. Banik et. al., Institut für Kernchemie, Universität Mainz, Annual Report 2006.
[3] S.D. Conradson et. al., Appl. Spectrosc. **52(7)**, 252A (1998).