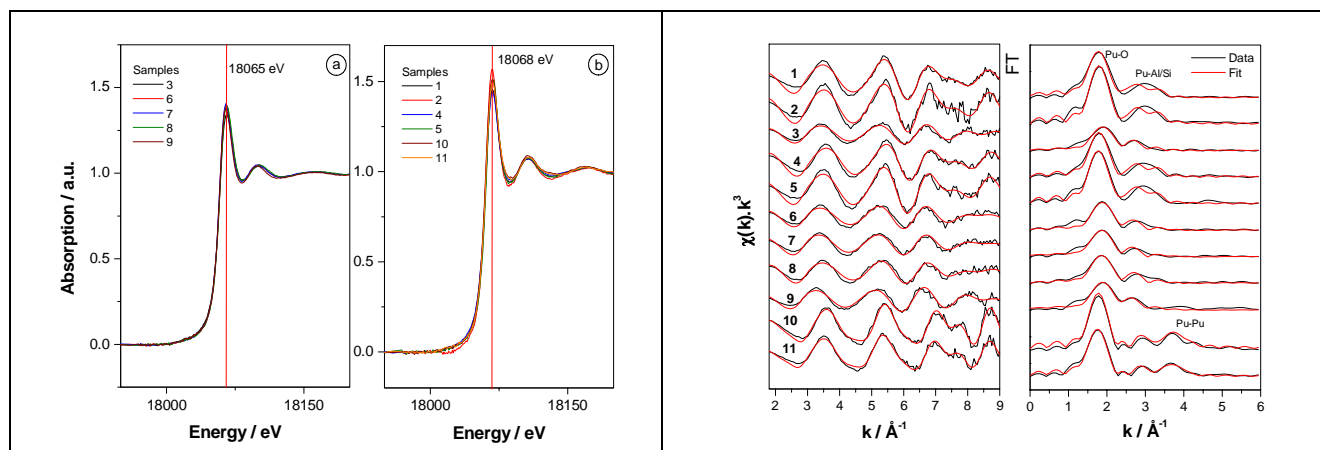
 ROBL-CRG	Experiment title: EXAFS Study on the Influence of Humic Acid on the Sorption of Pu on Natural Clay	Experiment number: Exp 20-01-710 EC-787
Beamline: BM 20	Date of experiment: from: 08/04/2011 to: 12/04/2011	Date of report: 12/03/2012
Shifts: 12	Local contact(s): André ROSSBERG	<i>Received at ESRF:</i>
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Report:

The sorption of plutonium (^{239}Pu) on Opalinus Clay (OPA from Mont Terri, Switzerland) has been investigated as a function of Pu oxidation state (III, IV, V, VI), humic acid (HA, M42), $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$, and dissolved Fe(II) in synthetic OPA pore water (PW) at pH 7.6 under aerobic and anaerobic conditions. An overview of the all measured XAS samples can be found in Table 1. For the experiments a purified $^{239}\text{Pu(VI)}$ stock solution in 1 M HClO_4 was prepared. 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. A HA M42 [1] stock solution of 2 g/L ml was prepared under Ar atmosphere. Aerobic (BHE-241) or anaerobic (BHE-24/2) OPA powder (240 mg) was suspended in 38 mL OPA pore water and 2 mL were left in order to leave space for pH adjustment and the addition of the Pu and other stock solutions. The pH was adjusted using NaOH and HClO_4 . After shaking the OPA suspensions for 72 hours, aliquots from the corresponding Pu(III, IV, V, VI), HA, and FeCl_2 stock solutions were added to the related samples (see Tab. 1) with immediate readjustment of the pH to about 7.6. To accelerate the equilibration with atmospheric CO_2 in sample 2, aliquots of 80 μL from 1 M $\text{NaHCO}_3/2 \mu\text{L}$ from 2.1 M Na_2CO_3 were added after the pH had been adjusted to 8.5. The total Pu concentration was $\sim 10^{-5}$ M for Pu(III), Pu(IV), and Pu(V) samples and $\sim 2 \cdot 10^{-5}$ M for Pu(VI) samples. The HA concentration in samples 1, 5, 7, 8, and 11 was 10 mg/L. In samples 3 and 9 the concentration of FeCl_2 was $5 \cdot 10^{-3}$ M. After a contact time of 60 hours, the solid and liquid phases were separated by centrifugation at 108,000 g for 1 h. The Pu uptake in each sample was determined in duplicate by measuring the Pu concentration in solution by liquid scintillation counting (LSC). The solid residues were dried for 3 days and then all powders were grinded loaded into special PE XAS sample holders (SH-01c) and heat sealed. Anaerobic and aerobic samples were transported in a special dewar filled with liquid nitrogen and anaerobic jar purged with argon, respectively. The EXAFS spectra were collected at the Pu L_{III} -edge (18057 eV) at 15 K in fluorescence mode using a 13-element Ge solid-state detector. The EXAFS analysis was performed with the software packages Athena, EXAFSPAK, and FEFF8.20. The scattering phases and amplitudes were calculated using the crystal structures of $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}_{1.3}\text{Fe}_{0.7}\text{O}_{6.3}\text{Ti}_{2.0}$, where U and Eu were replaced by Pu to model possible Pu-Si/Al and Pu-Fe interactions with the OPA surface. Figure 1 shows the XANES (left) und EXAFS spectra (right) of Pu samples 1-11. The XANES spectra can be categorized into two groups of samples (a and b) with different near edge structures. In the group (a) of anaerobic samples (3, 6 - 9) the Pu L_{III} -edge occurs at 18065 eV, which agrees well with Pu(III) edge energy of the Pu(III) aquo ion [2]. In the second group (b) of aerobic samples (1, 2, 5), sample 4, and samples 10 and 11 prepared under Ar-atmosphere with Pu(V), the L_{III} -edge occurs at higher energy (18068 eV), which agrees well with Pu(IV) edge energy of the Pu(IV) aquo ion [2]. Using a software package for iterative transformation factor analysis (ITFA) [3], mainly a mixture of Pu(III)/Pu(IV) was found in all samples. In aerobic samples (1, 2, 5) and anaerobic samples (10, 11), Pu(IV) was the dominating Pu species up to 90% and 70% Pu(IV), respectively. In all other anaerobic the amount of Pu(III) was between 45 and 55%. Pu has been 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. As can be seen in Fig. 1, the EXAFS spectra of samples 1, 2, 4, and 5 prepared with aerobic OPA under aerobic conditions (except sample 4 under Ar atmosphere) show a similar EXAFS structure. Fourier transform spectra show two main peaks.

Table 1: Details of Pu samples measured by XAS.

Sample	Initial Pu oxd. state	OPA/ (CO ₂ /Ar) ¹	HA	Na ₂ CO ₃ / NaHCO ₃	FeCl ₂	pH	Pu loading (ppm)	Eh/mV (SHE)
1	VI	aerobic/CO ₂	yes	no	no	7.7	733	320
2	VI	aerobic/CO ₂	no	yes	no	8.5	732	312
3	VI	anaerobic/Ar	no	no	yes	7.5	733	-88
4	VI	aerobic/Ar	no	no	no	7.8	733	-20
5	IV	aerobic/CO ₂	yes	no	no	7.7	404	328
6	IV	anaerobic/Ar	no	no	no	7.7	405	6
7	IV	anaerobic/Ar	yes	no	no	7.7	404	10
8	III	anaerobic/Ar	yes	no	no	7.7	435	-18
9	III	anaerobic/Ar	no	no	yes	7.5	436	-93
10	V	anaerobic/Ar	no	no	no	7.7	436	-8
11	V	anaerobic/Ar	yes	no	no	7.8	436	35

1) P_{CO₂}=10^{-3.5} atm**Figure 1:** Left: Pu L_{III}-edge XANES (groups a and b) and right: Pu L_{III}-edge k³-weighted EXAFS spectra and the corresponding Fourier transform magnitudes of Pu samples 1 – 11.

The first peak at about 2.33 Å is related to a Pu-O coordination shell and agree with that of Pu(OH)₄(am) [4]. The second peak can be modeled by two coordination shells, i.e., Pu-Si/Al and Pu-Fe at about 3.16 Å and 3.45 Å, respectively. Anaerobic samples (6-8) and samples prepared in the presence of dissolved Fe(II) (3 and 9) show the same EXAFS patterns and only two coordination shells could be found in the Fourier transform spectra, a Pu-O coordination shell at about 2.39 Å and a Pu-Si/Al coordination shell at about 3.20 Å. This Pu-O distance is longer than those of aerobic samples and agree well with the determined structure of Pu(III) aquo ion by Reich et al. [5]. Furthermore the obtained coordination numbers were also smaller (between 5.9 and 7.2) compared to aerobic samples (between 8.5-10.5). This result supports the obtained data by iterative transformation factor analysis (ITFA), which suggests that Pu was partly reduced to Pu(III), independent on the initial Pu oxidation. This reduction was more pronounced in the presence of dissolved Fe(II) solution (samples 3 and 9). Very similar EXAFS spectra were obtained for the samples 10 and 11, which are prepared with Pu(V). Three coordination shells, i.e., Pu-O, Pu-Si/Al, and Pu-Pu, were observed in the Fourier transform spectra at about 2.29 Å, 3.63 Å, and 3.78 Å, respectively. The additional Pu-Pu coordination shell was observed only in these two samples because a small amount of Pu(IV) colloids remained in the Pu(V) stock solution after potentiostatic electrolysis of the initial Pu(VI) solution. A shorter Pu-O and Pu-Pu distance was found in these two samples compared to those determined by Dardenne et al. for Pu(OH)₄(am.) [4], perhaps due to precipitation of Pu(IV) colloids. In all samples Pu-Al/Si interaction was found indicating inner-sphere sorption of Pu on the clay minerals present in OPA. It was also found that the addition of NaHCO₃/Na₂CO₃ in sample 2 did not stabilize Pu(VI). Comparing EXAFS spectra of samples prepared in presence of HA with samples prepared without HA, no influence of HA can be observed. The EXAFS results showed that the type of OPA (aerobic or anaerobic) influences the speciation of Pu on OPA. Our EXAFS results agree well with our μ-XRF, μ-XANES, μ-XRD study of Pu(VI) on OPA (Report JRP n°11) and a previous EXAFS study on the sorption of Pu(III) and Pu(IV) onto kaolinite [6].

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