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Report:

The sorption of Plutonium (Pu) on Opalinus clay (OPA from Mont Terri, Switzerland) has been investigated as a function of Pu oxidation state (III, IV, VI) at pH 7.6 in the absence and presence of ambient CO₂ in different background electrolytes (0.1 M NaClO₄ and OPA pore water). Two samples with Pu(IV) and Pu(VI) were prepared in synthetic pore water (PW) [1] under ambient air conditions. Four samples with Pu(III) and Pu(IV) were prepared under Ar atmosphere (glove box) in 0.1 M NaClO₄ and PW (see Table 1). The ²³⁹Pu(VI) stock solution had been purified from its decay products and ²⁴¹Am using anion exchange chromatography. The trivalent and tetravalent oxidation states of Pu were obtained from the purified Pu(VI) stock solution by potentiostatic electrolysis. The oxidation state purity was verified by UV/vis spectroscopy at the characteristic absorption bands at 600 nm for Pu(III) and at 470 nm for Pu(IV). Aerobic (BHE-241) or anaerobic (BHE-24/2) OPA powder (180 mg) was suspended in 30 mL background electrolyte. Aerobic OPA powder was prepared in air and anaerobic OPA powder was prepared under Ar atmosphere. The pH was adjusted using NaOH and HClO₄. After shaking the OPA suspensions for 72 hours, aliquots from the corresponding Pu stock solution (Pu(III), Pu(IV) or Pu(VI)) were added with immediate readjustment of the pH to 7.6. The total Pu concentration in each sample was ~10⁻⁵ mol/L. 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 was determined by measuring the Pu concentration in solution by liquid scintillation counting (LSC). The Pu loading in all samples was about 372 ppm (Table 1). The solid residues were dried for 3 days under ambient CO₂ (samples 1 and 2) or Ar atmosphere (samples 3-6), respectively. Then all powders were grinded and loaded into a polyethylene sample holder (SH-01c). The EXAFS spectra were collected at the Pu L_{III}-edge (18070 eV) at 15 K in fluorescence mode using a 13-element Ge solid-state detector. The EXAFS analysis was performed with the software packages EXAFSPAK [2] and FEFF8.20 [3]. The scattering phases and amplitudes were calculated using the crystal structures of (UO₂)₂SiO₄·2H₂O [4] and Eu_{1.3}Fe_{0.7}O_{6.3}Ti_{2.0} [5], where U and Eu were replaced by Pu to model possible Pu-Si/Al and Pu-Fe interactions with the OPA surface.

Table 1. Summary of the OPA samples prepared at 10⁻⁵ M Pu for EXAFS measurements.

Sample	Pu oxd. state	OPA Powder	Atmosphere	pH	Electrolyte	Pu loading (ppm)	Eh/mV (SHE)
Pu-1	VI	aerobic	ambient air	7.62	OPA PW	375	+236
Pu-2	IV	aerobic	ambient air	7.60	OPA PW	375	+237
Pu-3	IV	anaerobic	Ar	7.63	OPA PW	370	-59
Pu-4	III	anaerobic	Ar	7.61	OPA PW	370	-58
Pu-5	IV	anaerobic	Ar	7.61	0.1 M NaClO ₄	372	-73
Pu-6	III	anaerobic	Ar	7.60	0.1 M NaClO ₄	372	-63

Figure 1 shows the raw Pu L_{III}-edge k^3 -weighted EXAFS data, the theoretical model, and the corresponding Fourier transforms of samples Pu-1-6.

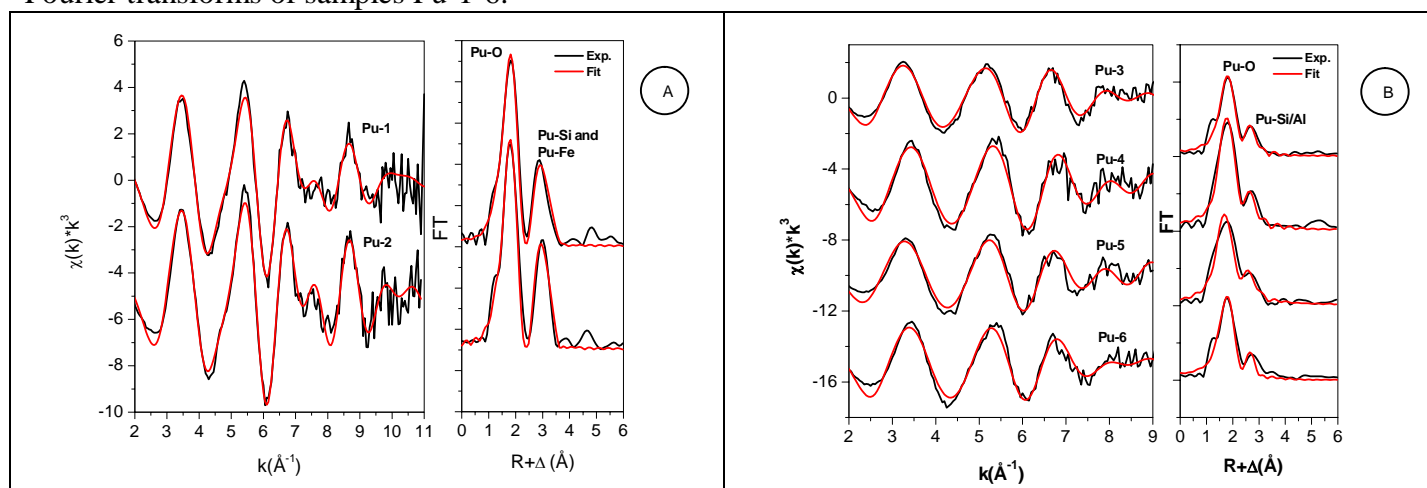


Figure 1. Pu L_{III}-edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transform magnitudes (right) of samples Pu-1-2 (A), samples Pu-3-6 (B).

As can be seen from Fig. 1, the EXAFS spectra of samples prepared under ambient CO₂ conditions (Pu-1-2) are different from those of samples Pu-3-6 (in the k range 6-9 Å⁻¹). The Fourier transform magnitude of Pu-1-2 show an additional peak due to Pu-Fe coordination at 3.46 Å. All samples have in common a Al/Si coordination shell at about 3.14 Å and an O coordination shell at about 2.34 Å (except Pu-3). The structural parameters derived from the EXAFS fits are summarized in Tab. 2.

Table 2. EXAFS structural parameters for sorption samples Pu-1-6 ($\Delta R = \pm 0.02$ Å, $\Delta\sigma^2 = \pm 0.001$ Å²).

Sample	Pu-O			Pu-Si/Al			Pu-Fe			ΔE_0 (eV)	Red. error
	N	R(Å)	σ^2 (Å ²)	N	R(Å)	σ^2 (Å ²)	N	R(Å)	σ^2 (Å ²)		
Pu-1	8.8	2.34	0.013	2	3.13	0.004	2	3.46	0.006	-9.5	0.21
Pu-2	8.6	2.34	0.012	2	3.13	0.004	2	3.46	0.005	-10.2	0.22
Pu-3	8.4	2.40	0.021	2.3	3.17	0.008				-12.4	0.12
Pu-4	9.9	2.34	0.020	2	3.14	0.007				-11.2	0.36
Pu-5	11.1	2.34	0.026	2	3.14	0.007				-13.7	0.11
Pu-6	9.5	2.36	0.022	2	3.15	0.007				-11.5	0.14
Pu(OH)₄(am.) [6]		2.32									

The coordination numbers for Si/Al and Fe were held constant during the fit. The Pu-O distance in all samples (except samples Pu-3 and Pu-6) agrees with those of Pu(OH)₄(am) [6]. The detection of Pu-Al/Si interactions in all samples is indicative of inner-sphere sorption of Pu(IV) on the clay minerals present in OPA. Pu L_{III}-edge XANES Spectra (not shown) confirmed that in all samples Pu(IV) is the dominating oxidation state, independent on the initial Pu oxidation state (Pu(III), Pu(IV) or Pu(VI)) and the aerobic / anaerobic conditions during sample preparation. Also, the Background electrolyte does not influence the speciation of Pu sorbed on OPA. This result is in good agreement with a previous XAFS study on the sorption of Pu(III) and Pu(IV) onto kaolinite [7].

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