



	Experiment title: EXAFS Study of the Sorption of Np(V) on Opalinus Clay	Experiment number: EC-424
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Report:

The sorption of Np(V) on Opalinus clay (OPA) (from Mont Terri, Switzerland) has been investigated as a function of pH in the absence and presence of ambient CO₂ in different background electrolytes such as 0.1 M NaClO₄ (pH 8.5), OPA pore water (pH=7.6) [1] and saturated calcite solution (pH 8.5). Six samples with different amounts of Np(V) sorbed were prepared from a 23.5 mM Np(V) stock solution of ²³⁷Np. The stock solution had been purified from traces of ²³⁹Pu and ²³³Pa. Aerobic/anaerobic OPA powder (600 mg) was suspended in 40 mL background electrolyte. Aerobic OPA powder was prepared in air and anaerobic OPA powder was prepared under inert gas atmosphere from two different OPA bore cores, respectively.

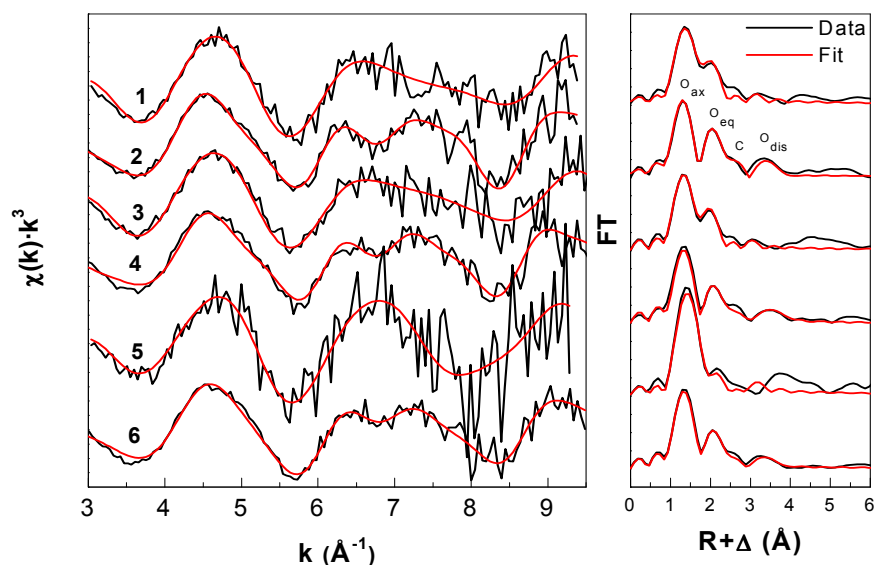
The pH was adjusted using NaOH and HClO₄. Samples 1 and 3 were prepared under ambient air (p_{CO2}=10^{-3.5} atm) at pH 8.5 in saturated calcite and 0.1 M NaClO₄ solution, respectively. Sample 2 was prepared under anaerobic conditions with a higher p_{CO2} of 10^{-2.3} atm in saturated calcite solution at pH 8.5. Samples 4 and 5 were prepared in the absence of ambient CO₂ (Ar-atmosphere glovebox) in 0.1 M NaClO₄ at pH 8.5 and sample 6 in OPA pore water at pH 7.6 (see Table 1). We can distinguish between three groups of samples according to background electrolyte. i) saturated calcite solution (samples 1,2), ii) 0.1 M NaClO₄ (samples 3-5), iii) pore water (sample 6).

After shaking the OPA suspensions for 72 hours, aliquots of 15μL the Np(V) stock solution (pH 3.90) were added (pH change less than 0.3) with immediate readjustment of the pH. The total neptunium concentration in each sample was 8.8·10⁻⁶ mol/L. After a contact time of 60 hours, the solid and liquid phases were separated by centrifugation at 100.000 g for 1h. The neptunium uptake was determined by measuring the neptunium concentration in solution by liquid scintillation counting and γ-spectroscopy using the γ-lines at 29.37 and 86.48 keV. The solid residues were loaded without drying into standard Perspex sample holders (5x16x3 mm³) with Kapton windows for EXAFS analysis. The neptunium uptake of the samples as measured by γ-spectroscopy was between 52 and 121 ppm (Table 1).

The EXAFS spectra were collected at the Np L_{III}-edge (17625 eV) at room temperature 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 NaNpO₂(CO₃) [4] and (UO₂)₂SiO₄·2H₂O [5], where U was replaced by Np to model a possible Np-Si/Al interaction with the OPA surface. Figure 1 shows the raw Np L_{III}-edge k³-weighted EXAFS data, the best theoretical model, and the corresponding Fourier transforms of all samples 1-6. As can be seen from Fig. 1, in all samples the oxidation state (V) of Np was dominating. The reduction of Np(V) to Np(IV) under anaerobic conditions could not be confirm (possible oxidation during transportation). Samples 2, 4 and 6 of anaerobic OPA prepared in different background electrolytes show similar EXAFS spectra and have a different EXAFS pattern compared to samples 1, 3, 5 of aerobic OPA.

Table 1. Summary of the wet-paste OPA samples prepared at $8.8 \cdot 10^{-6}$ M Np(V) for EXAFS measurements.

Sample	OPA	CO ₂ /Ar	pH	Electrolyte	Np loading / ppm	Eh/mV
1	aerobic	p _{CO2} =10 ^{-3.5} atm	8.5	Sat. CaCO ₃	91	382
2	anaerobic	p _{CO2} =10 ^{-2.3} atm	8.5	Sat. CaCO ₃	109	131
3	aerobic	p _{CO2} =10 ^{-3.5} atm	8.5	0.1 M NaClO ₄	108	388
4	anaerobic	Ar-atmosph.	8.5	0.1 M NaClO ₄	121	135
5	aerobic	Ar-atmosph.	8.5	0.1 M NaClO ₄	110	386
6	anaerobic	Ar-atmosph.	7.6	OPA pore water	52	132

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

Sample	2 O _{ax}	5 O _{eq}	2 C ^d		2 O _{dis}		ΔE_0 /eV	Error
	R	R	N ^c	R	N ^c	R		
1	1.85	2.46					-8.1	0.64
2	1.83	2.52	2.4	2.98	2.4	4.25	-8.9	0.51
3	1.83	2.45					-10.3	0.87
4	1.85	2.54	2.5	3.00	2.5	4.26	-6.6	0.38
5	1.86	2.41					-9.2	3.60
6	1.85	2.51	1.9	3.00	1.9	4.24	-9.5	0.33
^a NpO ₂ (H ₂ O) ₄ ⁺	1.82	2.49						
^b NpO ₂ (CO ₃) ₃ ⁵⁻	1.86	2.53	2.7	2.98	3.0	4.22		

held constant during the fit. c) Coordination numbers for C and O_{dis}, were linked together and adjusted as one parameter during the fit. The average value of the Debye Waller factors σ^2 for O_{ax}, O_{eq}, and O_{dis} were 0.0026 Å², 0.011 Å², and 0.008 Å², respectively. d) Debye-Waller factor σ^2 for C was held constant at 0.003 Å². Distances R are given in Å and Debye-Waller factors σ^2 in Å² ($\Delta R = \pm 0.02$ Å, $\Delta \sigma^2 = 0.001$ Å²). Comparison with literature: a) ref. 6, b) ref 7.

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Table 2 summarizes the structural parameters derived from the EXAFS fits. The neptunium coordination shells and bond distances of samples 2, 4, and 6 are consistent with the formation of a Np(V) carbonato species at the OPA surface. The average Np-O_{eq} bond distance of samples 1, 3 and 5 is somewhat shorter than in the Np(V) aquo ion (see Tab. 2). This could indicate inner-sphere sorption of a Np(V) at the OPA surface. Due to a poor signal-to-noise ratio in the spectrum of sample 5, only axial, with slightly negative Debye-Waller factor σ^2 (-0.0002), and equatorial oxygen coordination shells of Np, O_{ax} and O_{eq}, respectively, could be analyzed.

Table 2. EXAFS structural parameters for sorption samples 1-6. Coordination numbers for O_{ax} and O_{eq} were