

XAS study of neptunium(V) sorbed on Opalinus Clay

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Introduction: Clay formations are considered in several European countries as a potential host rock and as backfill material for the disposal of spent nuclear fuel [1]. Sorption and diffusion are the main transport processes of toxic and long-lived radionuclides such as neptunium (^{237}Np , $t_{1/2} = 2.1 \times 10^6$ a) in argillaceous host rock materials [2]. To understand the sorption mechanism of Np(V) on a natural clay at a molecular-level, X-ray Absorption Spectroscopy (XAS) measurements on Np(V) sorbed on Opalinus clay (OPA) were performed. Np L_{III} -edge Extended X-ray Absorption Fine Structure (EXAFS) spectra provided information about the local environment of Np sorbed onto OPA. The Np L_{III} -edge X-ray Absorption Near Edge Structure (XANES) was used to identify the Np oxidation state in the samples.

Experimental: The sorption of Np(V) on aerobic/anaerobic OPA powders (from Mont Terri, Switzerland) has been investigated by batch experiments as a function of pH, partial pressure of CO_2 , in the absence and presence of ambient O_2 in different background electrolytes (see Tab. 1). For XAS measurements six wet-paste samples with different amounts of Np(V) sorbed were prepared from a 23.5 mM ^{237}Np (V) stock solution. The stock solution had been purified from traces of ^{239}Pu and ^{233}Pa . The total Np(V) concentration in each sample was $8.8 \cdot 10^{-6}$ M. The neptunium uptake of the samples as measured by both liquid scintillation counting and γ -ray spectroscopy was between 52 and 121 ppm (Table 1). Aerobic OPA powder (BHE-421) was prepared in air and anaerobic OPA powder (BDR-2) was prepared under inert gas atmosphere from two different OPA bore cores, respectively. XAS measurements (XANES and EXAFS) were performed on the Rossendorf Beamline (BM20) at the European Synchrotron Radiation Facility (ESRF). The Np L_{III} -edge (17625 eV) spectra were recorded in fluorescence mode using a 13-element Ge solid-state detector at room temperature. The software packages EXAFSPAK and FEFF 8.20 were used for the analysis of the EXAFS data using atomic clusters based on the crystal structures of $\text{NaNpO}_2(\text{CO}_3)$ and $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ where U was replaced by Np to model a possible Np-Si/Al interaction with the OPA surface.

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

Sample	OPA	CO_2/Ar	pH	Electrolyte	Np loading / ppm
1	aerobic	$p_{\text{CO}_2}=10^{-3.3}$ atm	8.5	Sat. CaCO_3	91
2	anaerobic	$p_{\text{CO}_2}=10^{-2.3}$ atm	8.5	Sat. CaCO_3	109
3	aerobic	$p_{\text{CO}_2}=10^{-3.3}$ atm	8.5	0.1 M NaClO_4	108
4	anaerobic	Ar-atmosph.	8.5	0.1 M NaClO_4	121
5	aerobic	Ar-atmosph.	8.5	0.1 M NaClO_4	110
6	anaerobic	Ar-atmosph.	7.6	OPA pore water	52

Results: Figure 1 shows the raw Np L_{III} -edge k^3 -weighted EXAFS data, the best theoretical model, and the corresponding Fourier transforms of all samples 1-6. As can be seen from Fig. 1, 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.

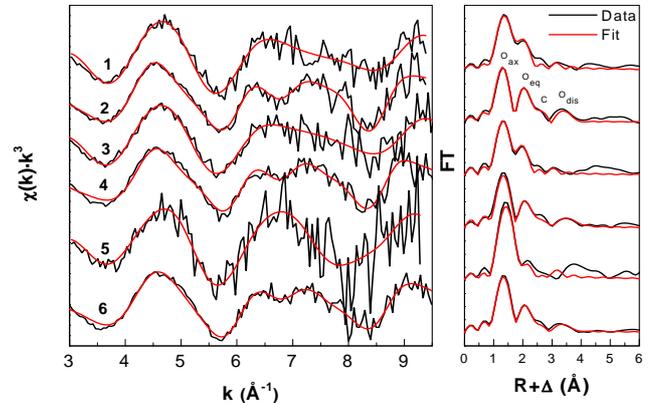


Figure 1. Np L_{III} -edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transform magnitudes (right) of samples 1-6.

In previous batch experiments under anaerobic conditions, a stronger sorption of Np(V) on OPA was found possibly due to reduction of Np(V) to Np(IV). XANES measurements (not shown) show that the oxidation state (V) of Np was dominating in all samples (same Np- O_{ax} , Np- O_{eq} distances, see Tab. 2). The reduction of Np(V) to Np(IV) under anaerobic conditions could not be confirmed.

Table 2. EXAFS structural parameters for samples 1-6.

Sample	2O_{ax}		5O_{eq}		C		O_{dis}		$\Delta E_0/\text{eV}$
	R	R	N^a	R	N^a	R			
1	1.85	2.46							-8.1
2	1.83	2.52	2.4	2.98	2.4	4.25			-8.9
3	1.83	2.45							-10.3
4	1.85	2.54	2.5	3.00	2.5	4.26			-6.6
5	1.86	2.41							-9.2
6	1.85	2.51	1.9	3.00	1.9	4.24			-9.5
$\text{NpO}_2(\text{H}_2\text{O})_4^+$ [3]	1.82	2.49							
$\text{NpO}_2(\text{CO}_3)_3^{5-}$ [4]	1.86	2.53	2.7	2.98	3.0	4.22			

a) Coordination numbers for C and O_{dis} , were linked together and adjusted as one parameter during the fit, $\Delta R = \pm 0.02$ Å.

As shown in Tab. 2, the values of Np coordination shells and bond distances of samples 2, 4, and 6 are similar and 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. This could indicate inner-sphere sorption of a Np(V) at the OPA surface.

References

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