



	Experiment title: EXAFS study of neptunium(V) uptake by kaolinite	Experiment number: ME - 1090
Beamline: BM20	Date of experiment: from: 17/06/2005 to: 20/06/2005	Date of report: 27/02/2006
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Report:

The sorption of Np(V) on kaolinite has been investigated as a function of pH in the absence and presence of ambient CO₂. Seven samples with different amounts of Np(V) sorbed were prepared from a 1.1 mM Np(V) stock solution of ²³⁷Np. The stock solution had been purified from traces of ²³⁹Pu and ²³³Pa. 200 mg kaolinite KGa-1b (Source Clays Repository) were suspended in 50 mL deionized water. The ionic strength was 0.1 M NaClO₄. The pH was adjusted using NaOH and HClO₄. Samples A, B, and C were prepared in the presence of ambient CO₂ at pH 8.0, 9.0, and 10.0, respectively. Samples D, E, F, and G were prepared in a glove box with Ar atmosphere at pH 8.0, 9.0, 10.0, and 10.5, respectively. These samples can be compared with samples A - C prepared in equilibrium with air. After shaking the kaolinite suspensions for 72 hours, aliquots of the Np(V) stock solution were added with immediate readjustment of the pH. The total neptunium concentration in each sample was 8·10⁻⁶ mol/L. After a contact time of 72 hours, the solid and liquid phases were separated by centrifugation at 4025 g for seven minutes. The neptunium uptake was determined by measuring the neptunium concentration in solution by liquid scintillation counting. The solid residues were loaded without drying into EXAFS sample holders. Table 1 summarizes the preparation conditions of samples A – G and the amount of neptunium sorbed in each sample.

Table 1. Summary of the wet-paste samples prepared at 8·10⁻⁶ M Np(V) and 0.1 M NaClO₄ for EXAFS measurements.

Sample	CO ₂ /Ar	pH	Np loading / ppm	T/K	No. of sweeps
A	Air	8.0	240	293	8
B	Air	9.0	330	25	12
C	Air	10.0	190	293	6
D	CO ₂ -free	8.0	70	293	2
E	CO ₂ -free	9.0	215	293	7
F	CO ₂ -free	10.0	380	293	3
G	CO ₂ -free	10.5	430	293	7

Since kaolinite KGa-1b contains traces of zirconium, the EXAFS spectra were collected at the Np L₂-edge (21.6 keV) and not at the L₃-edge. The energy of the single-channel analyzers (SCA) of the 13-element Ge solid-state detector was set to 17.8 keV for recording the Np Lβ₁ fluorescence radiation.

Except for sample B, which was measured at 25 K, all samples were studied at room temperature. The SCA signals were corrected for detector dead time using the measured total incoming count rates. EXAFS analysis was performed with the software packages EXAFSPAK [1] and FEFF8.20 [2]. The scattering phases and amplitudes were calculated using the crystal structures of NaNpO₂(CO₃) [3] and (UO₂)₂SiO₄·2H₂O [4], where U was replaced by Np to model a possible Np-Si/Al interaction with the kaolinite surface.

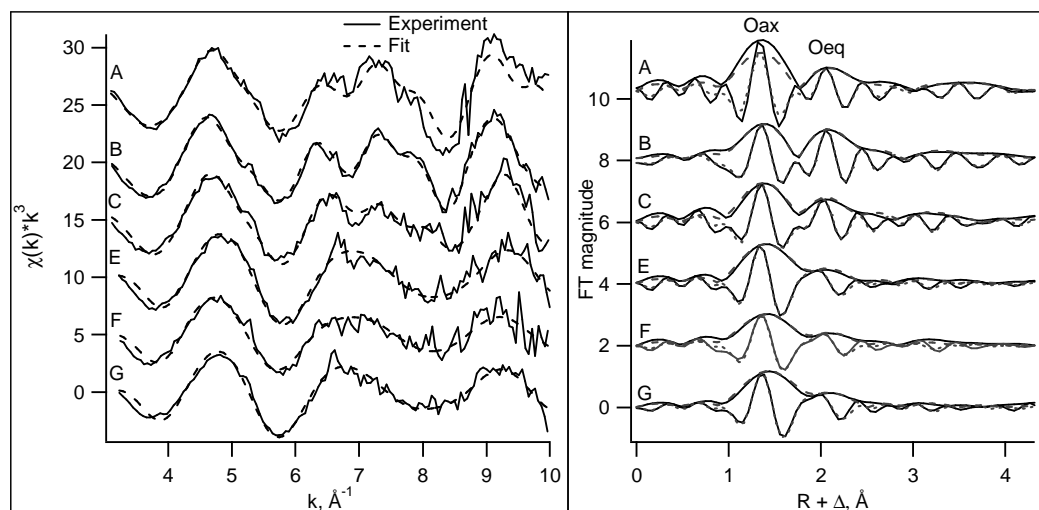


Figure 1. Np L₂-edge k³-weighted EXAFS spectra (left) and the corresponding Fourier transform magnitudes and real parts (right) of samples A-C and E-G.

Figure 1 shows the raw Np L₂-edge k³-weighted EXAFS data, the best theoretical model, and the corresponding Fourier transforms. The spectrum of sample D has not been included in Fig. 1 due to the low-signal-to-noise ratio. As can be seen from Fig. 1, samples A – C prepared in the presence of CO₂ show a different EXAFS

pattern compared to samples E – G. Table 2 summarizes the metrical parameters derived from the EXAFS fits. The neptunium coordination shells and bond distances of samples A, B, and C are consistent with the formation of a Np(V) carbonato species at the kaolinite surface due to precipitation (see also the previous feasibility study 20-01-637). Due to a poor signal-to-noise ratio in the spectra E – G, only axial and equatorial oxygen coordination shells of Np, O_{ax} and O_{eq}, respectively, could be analyzed. The average Np-O_{eq} bond distance of samples E and G is somewhat shorter than in the Np(V) aquo ion (see Tab. 2). This could indicate the existence of a Np(V) hydrolysis species at pH ≥ 9.0 at the kaolinite surface. Unfortunately, the data quality does not allow concluding on inner-sphere versus outer-sphere Np(V) sorption to kaolinite in the CO₂-free system.

Table 2. EXAFS metrical parameters for sorption samples A - C and E - G. Multiple-scattering paths are not listed. Coordination numbers were held constant during the final fit according to the results of previous fits. Distances R are given in Å and Debye-Waller factors σ^2 in Å². Comparison with literature: a) ref. 5, b) ref 6.

Sample	2 O _{ax}		4 O _{eq}		2 C		2 O _{dis}		1 Np		ΔE_0 /eV	Error
	R	σ^2	R	σ^2	R	σ^2	R	σ^2	R	σ^2		
A	1.84	0.0028	2.56	0.0077	3.00	0.0036	4.25	0.0058	4.90	0.0028	0.7	1.13
B	1.85	0.0037	2.57	0.0037	2.97	0.0012	4.28	0.0033	4.88	0.0030	0.3	0.184
C	1.86	0.0025	2.52	0.0062	2.90	0.0033	4.23	0.0102	4.88	0.0031	0.8	0.558
E	1.85	0.0025	2.45	0.0125	-	-	-	-	-	-	0.4	0.403
F	1.86	0.0051	2.50	0.0172	-	-	-	-	-	-	0.4	0.595
G	1.87	0.0033	2.47	0.0126	-	-	-	-	-	-	1.1	0.285
^a NpO ₂ (H ₂ O) ₄ ⁺	1.82	0.0023	2.49	0.006	-	-	-	-	-	-	-	-
^b NpO ₂ (CO ₃) ₃ ⁵⁻	1.86	0.001	2.53	0.013	2.98	0.0004	4.22	Na	-	-	-	-

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