


Experiment title:

EXAFS study of neptunium(V) uptake by kaolinite

Experiment number:

EC-144

Beamline:

BM20

Date of experiment:

from: 03.03.2007

to:

06.03.2007

Date of report:

28.02.2008

Shifts:

9

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Report:

In June 2005, Np L_{II}-edge EXAFS spectra for Np(V) sorbed onto kaolinite were measured for the first time for samples prepared at different pH values in the absence and presence of CO₂ (see Experimental Report ME-1090). The EXAFS spectra of the samples prepared in air revealed that [NpO₂(CO₃)₂]³⁻ species are

present at the kaolinite surface. EXAFS spectra of samples prepared under CO₂-free conditions were different and showed two oxygen coordination shells at 1.87 and 2.47±0.02 Å, similar to the Np(V) aquo ion. Unfortunately, the beam intensity for experiment ME-1090 was strongly reduced due to a mirror alignment problem that could not be fixed during the beam time. Although the data quality was

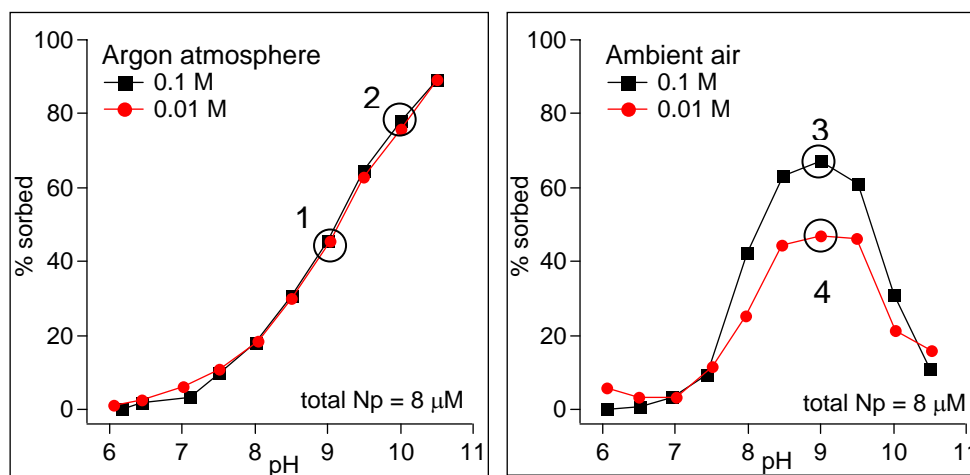


Figure 1: Sorption of Np(V) onto kaolinite as a function of pH and ionic strength. The total Np concentration was 8 μM. The ionic strength was 0.1 and 0.01 M NaClO₄, respectively. Experiments were performed under Ar atmosphere (left) and ambient CO₂ partial pressure of 10^{-3.5} atm (right).

sufficient to observe significant differences in the Np near-neighbor surrounding under the influence of HCO₃⁻/CO₂²⁻, two important questions could not be answered due to lacking signal statistics: 1) Does Np form inner-sphere or outer-sphere sorption complexes with kaolinite? The ionic-strength dependencies shown in Fig. 1 indicate formation of inner-sphere complexes in the CO₂-free system and of outer-sphere

complexes under ambient CO₂. 2) Are polynuclear Np carbonato species sorbed at the clay surface? Although the total Np concentration of 8 µM was below the solubility limit of any relevant Np(V) solid, some EXAFS spectra prepared in the presence of HCO₃⁻/CO₂²⁻ could be modeled including a weak Np-Np interaction at 4.9 Å.

To complete this sorption study, the Np L_{III}-edge EXAFS spectra of the samples indicated in Fig. 1 were measured. Samples 1-4 were prepared as wet paste and measured at room temperature. Duplicates of samples 1 and 3 were prepared as dry powder and measured at 13 K (indicated as 1' and 3' in Tabs. 1 and 2). Tables 1 and 2 summarize the results of the preliminary EXAFS analysis. It should be noted that all EXAFS spectra could be collected with excellent signal-to-noise ratios.

Table 1: EXAFS structural parameters for Np(V) sorbed onto kaolinite under Ar atmosphere.

Sample	2 × O _{ax}		4 × O _{eq}		1 × Al/Si		2 × Al/Si	
	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)
1	1.84	0.0044	2.50	0.0158	3.19	0.0034	3.84	0.0047
2	1.84	0.0040	2.49	0.0148	3.19	0.0079	3.84	0.0059
1'	1.85	0.0062	2.45	0.0135	3.16	0.0087	3.83	0.0107

Table 2: EXAFS structural parameters for Np(V) sorbed onto kaolinite in ambient air.

Sample	2 × O _{ax}		6 × O _{eq}		2 × C		2 × O _{dis}	
	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)	R(Å)	σ ² (Å ²)
3	1.83	0.0039	2.56	0.0144	2.99	0.003 [*]	4.32	0.0133
4	1.84	0.0040	2.55	0.0156	2.98	0.003 [*]	4.35	0.0125
3'	1.83	0.0037	2.57	0.0113	2.98	0.003 [*]	4.36	0.0139

*) fixed during the fit

In addition to the confirmation of the main results of our previous EXAFS experiment, the following observations were derived from the new measurements due to the improved signal statistics: i) The EXAFS spectra of the samples prepared under exclusion of CO₂ showed two Np-Al/Si coordination shells at 3.2 and 3.8 Å in addition to the axial and equatorial oxygen coordination shells at 1.8 and 2.5 Å, respectively. The detection of Np-Al/Si interactions in these samples confirms that inner-sphere sorption complexes of Np(V) with the aluminol/silanol groups of kaolinite are formed under CO₂-free conditions. This agrees with the observation obtained by the batch experiments, i.e., the Np uptake is independent from ionic strength (see Fig. 1 left). ii) The formation of Np(V) carbonato complexes at the kaolinite surface under ambient air conditions could be confirmed both at 0.01 and 0.1 M NaClO₄ electrolyte concentrations. The preliminary EXAFS analysis of samples 3 and 4 showed that the reduced error of the theoretical fit to the data decreases when a Np-Al/Si coordination shell at 3.8 Å is included in the fit. More detailed EXAFS analysis, including the modelling of a reference spectrum of NaNpO₂CO_{3(s)}, is in progress to verify the presence of Np-Al/Si interaction in the spectra of samples 3 and 4. If confirmed, it would indicate that ternary Np carbonato complexes are formed at the kaolinite surface at pH 9 under ambient air conditions.

The precipitation of Np phases can be ruled out in case of the samples prepared under Ar atmosphere. The Fourier transforms (FT) of samples 1 and 2 do not show any intensity above 4 Å. However, the FTs of samples 3 and 4 do show a pronounced structure that is centered around 5 Å. Several structural models are under consideration to describe this spectral feature. Therefore, the formation of a surface precipitate cannot be ruled out.

Acknowledgement

This work was supported by the German Bundesministerium für Wirtschaft und Technologie (Project 02 E 9653). We acknowledge the ESRF for provision of synchrotron beam time and thank H. Funke, C. Hennig, A. Roßberg, and A. Scheinost from Forschungszentrum Dresden-Rossendorf for assistance in using beamline BM20.