Feasibility of EXAFS experiments at the Np L-edge to investigate neptunium sorption on kaolinite

T. Reich[1], S. Amayri[1], Ta. Reich[1], J. Drebert[1], A. Jermolajev[1], P. Thörle[1], N. Trautmann[1], C. Hennig[2], S. Sachs[2]

[1] Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany;
[2] Institut für Radiochemie, Forschungszentrum Rossendorf, D-01314 Dresden, Germany

Several collaborating groups selected the kaolinite KGa-1b from the Source Clays Repository as reference clay for a broad range of investigations dealing with the interaction of actinides in the system clay, humic substances, and aquifer. During recent EXAFS measurements of uranium(VI) sorption onto kaolinite KGa-1b, we found that this kaolinite contains traces of zirconium. The energy of the Zr K-edge equals 17998 eV. Therefore, we expected a distortion of the Np L_3-edge (17610 eV) EXAFS signal at this energy or at k approximately equal to 9.8 $Å^{-1}$. In our experiment we wanted to explore the possibilities for avoiding severe distortions in the Np EXAFS signal without limiting the useful k range to 9.8 $Å^{-1}$.

EXPERIMENTAL. Two samples, 1 and 2, with different amounts of neptunium(V) sorbed on KGa-1b were prepared from a 1.8 mM Np(V) stock solution of Np-237 under the following conditions: 4 g kaolinite/L, pH 9.0, $p(CO_2) = 10^{-3.5}$ atm, I = 0.1 M $NaClO_4$. The total neptunium concentration for samples 1 and 2 was $8•10^{-6}$ and $2•10^{-5}$ mol/L, respectively. The neptunium uptake of samples 1 and 2 as measured by □-spectroscopy was 300 and 510 ppm, respectively. The solid residue was loaded without drying into the EXAFS sample holder. The neptunium EXAFS spectra were measured at ROBL (ESRF, BM20) [1] at room temperature in the fluorescence mode using a 13-element Ge solid-state detector.
The following measurements were performed on these samples:

1) The Np L□$_1$-radiation at 13.9 keV was recorded as a function of photon energy across the Np L_3-edge EXAFS region using single-channel analyzers (SCA's). The signal was corrected for detector dead time.
2) The EXAFS spectrum was measured at the Np L_2-edge (21600 eV) by setting the SCA's to 17.8 keV to record the Np L□$_1$-radiation. Dead time correction was performed as described above.

RESULTS. Figure 1 shows the Np EXAFS spectra and the corresponding Fourier transforms of sample 1 (300 ppm Np) measured at the L_3- and L_2-edges. Seven sweeps at the Np L_2-edge and six sweeps at the L_3-edge were averaged. The useful k range at the L_3-edge was limited to k_{max} equal to 9.4 $Å^{-1}$ due to the Zr K-edge absorption. The Np L_2-edge EXAFS signal could be recorded with good statistics up to k_{max} equal to 11.4 $Å^{-1}$. To obtain a higher resolution in the Fourier transform, it is preferable to record the Np EXAFS signal of the kaolinite samples at the Np L_2-edge instead of the L_3-edge.
Table 1 summarizes the EXAFS structural parameters of sample 1 derived from the Np L_3- and L_2-edge k^3-weighted EXAFS spectra. The detected neptunium coordination shells and bond distances are consistent with the formation of a neptunium(V) carbonato species at the kaolinite surface. A similar result was obtained for sample 2 (510 ppm, not shown here).
In conclusion, these test experiments showed that it is possible to study the sorption of neptunium onto kaolinite KGa-1b successfully using Np L_2-edge EXAFS spectroscopy. In future EXAFS experiments, it will be possible to study sorption samples with less than 300 ppm neptunium by collecting more than seven sweeps per sample.

ACKNOWLEDGEMENTS. This work was supported by the BMWA grant No. 02E9653.

REFERENCES

[1] W. Matz et al., J. Synchrotron Rad. **6**, 1076 (1999)

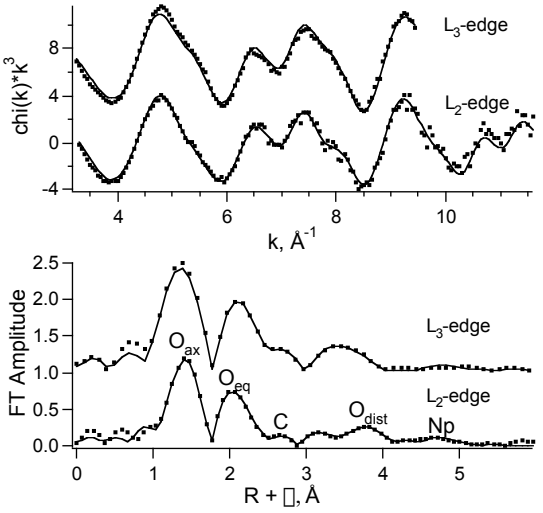

Figure 1: Neptunium L-edge k^3-weighted EXAFS spectra (top) and corresponding Fourier transforms (bottom) of 300 ppm Np(V) sorbed onto kaolinite at pH 9.0 under ambient conditions. Dots – raw experimental data, solid line - best theoretical fit to the data.

Table 1: EXAFS structural parameters for 300 ppm Np(V) sorbed onto kaolinite at pH 9.0 under ambient conditions. Multiple-scattering paths are not listed. Coordination numbers were held constant during the final fit according to the result of previous fits.

Shell	Np L_2-edge		Np L_3-edge	
	R(Å)	□^{2}(Å^2)	R(Å)	□^{2}(Å^2)
2 x Oax	1.85	0.0021	1.84	0.0010
4 x Oeq	2.55	0.0051	2.55	0.0054
2 x C	2.94	0.0060	2.95	0.0027
2 x Odist	4.24	0.0040	4.25	0.0044
1 x Np	4.86	0.0023	4.89	0.0050