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Report:

This feasibility study is the basis for future EXAFS measurements to investigate the sorption of neptunium on kaolinite KGa-1b (Source Clays Repository). Several collaborating groups selected this kaolinite as reference clay for a broad range of investigations dealing with the interaction of actinides in the system clay, humic acid, and aquifer. During recent EXAFS measurements of uranium(VI) sorption onto kaolinite KGa-1b (see report ME-817), we found that this kaolinite contains traces of zirconium. The energy of the Zr K edge equals 17998 eV. Therefore, we expect a distortion of the Np L₃-edge (17610 eV) EXAFS signal at this energy or at k approximately equal to 9.8 Å⁻¹. This experiment aimed at exploring the possibilities for avoiding severe distortions in the Np EXAFS signal without limiting the k range to 9.8 Å⁻¹.

Two samples 1 and 2 with different amounts of neptunium(V) sorbed were prepared from a 1.8 mM Np(V) stock solution of Np-237. This stock solution had been purified from traces of Pu-239 and Pa-233. 200 mg kaolinite KGa-1b were suspended in 50 mL de-ionized water. The ionic strength was adjusted to 0.1 M NaClO₄ and the pH to 9.0. The system was open to air. After shaking these mixtures for 72 hours, aliquots of the Np(V) stock solution were added with immediate readjustment of the pH. The total neptunium concentration for samples 1 and 2 was 8•10⁻⁶ and 2•10⁻⁵ mol/L, respectively. After a contact time of 72 hours, the solid and liquid phases were separated by centrifugation at 5000 rpm for seven minutes. The neptunium uptake of samples 1 and 2 as measured by γ -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 in fluorescence mode using the new 13-element Ge solid-state detector of the ROBL radiochemistry hutch.

The following measurements were performed on these samples:

- 1) The Np L α_1 radiation at 13.9 keV was recorded as a function of photon energy across the Np L₃-edge EXAFS region using the single-channel analyzers (SCA's). The signal was corrected for detector dead time using the measured total count rates (ICR's).
- 2) The same as in 1) but with a specially designed rubidium nitrate fluorescence filter placed between sample and Ge solid-state detector to reduce the contribution of the Zr K α fluorescence at 15.8 keV to the ICR's.

3) The EXAFS spectrum was measured at the Np L₂ edge (21600 eV) by setting the SCA's at 17.8 keV to record the Np Lβ₁ radiation.

The measurements showed that the rubidium filter is able to significantly reduce the contribution of the Zr Kα fluorescence to the ICR. However, the absorption of the Zr Kα fluorescence by the rubidium atoms increased the intensity of the Rb Kα fluorescence at 13.4 keV. Unfortunately, the Np Lα₁ radiation at 13.9 keV could not be separated from the Rb Kα fluorescence at 13.4 keV. Since both the Np and Rb X-ray emission lines were recorded in the SCA's, the RbNO₃ filter enhanced the distortion of the Np L₃-edge fluorescence signal. Therefore, the rubidium filter cannot be used to reduce the effect of the zirconium trace on the Np L₃-edge EXAFS signal above 9.8 Å⁻¹.

Figure 1 shows the Np EXAFS spectra and the corresponding Fourier transforms of sample 1 (300 ppm Np) measured at the L₃ and L₂ edges. Seven sweeps at the Np L₂ edge and six sweeps at the L₃ edge were averaged. The useful *k* range at the L₃ edge was limited to *k*_{max} equal 9.4 Å⁻¹ due to the Zr K absorption edge. The Np L₂-edge EXAFS signal could be recorded with good statistics up to *k*_{max} equal 11.4 Å⁻¹. Therefore, it is preferable to record the Np EXAFS signal of the kaolinite samples at the Np L₂ edge.

Table 1 summarizes the EXAFS structural parameters of sample 1 derived from the Np L₃- and L₂-edge *k*³-weighted EXAFS spectra. The detected neptunium coordination shells and bond distances are consistent with the formation of a Np(V) carbonato species at the kaolinite surface due to precipitation. 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 L₂-edge EXAFS spectroscopy. With the new 13-element Ge detector, it is possible to study sorption samples with less than 300 ppm neptunium in the future by collecting more than seven sweeps per sample.

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)	σ ² (Å ²)	R (Å)	σ 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

Figure 1 Np L-edge *k*³-weighted EXAFS spectra (left) and corresponding Fourier transforms (right) of 300 ppm Np(V) sorbed onto kaolinite at pH 9.0 under ambient conditions. Solid line - raw data, dots - best theoretical fit to the data. Top – Np L₃-edge data, bottom – L₂-edge data.

