	Experiment title: EXAFS study of neptunium(V) sorption at α -Fe ₂ O ₃	Experiment number: EC-23
Beamline: BM 20	Date of experiment: from: 28.06.06 to: 01.07.06	Date of report: 06.12.2006
Shifts: 9	Local contact(s): André ROSSBERG	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): Samer AMAYRI*, Markus BRECKHEIMER*, Peter PAPAPETROU*§, Tobias REICH* * Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, Fritz-Strassmann-Weg 2, 55128 Mainz, Germany, § University of Western Ontario, Canada		

Report:

In rock systems, iron oxides are expected to play an important role in regulating the migration of radionuclides because of their widespread existence, high surface area, high sorptive capacity, and common occurrence as grain coatings. The aim of this study is to understand the sorption mechanism of neptunium(V) on α -Fe₂O₃ (hematite) at a molecular level and to obtain spectroscopic evidence using EXAFS for the postulated ternary carbonate complexes (e.g. $\equiv\text{FeONpO}_2(\text{O}_2\text{COH})_2^{2-}$) by Kohler et al. [1]. The sorption of Np(V) on synthetic α -Fe₂O₃ (synthesis according to Schwertmann and Cornell [2]) has been investigated as a function of pH in the absence and presence of ambient CO₂. A detailed description of the sorption experiments can be found elsewhere [3].

Five EXAFS samples with different amounts of Np(V) sorbed were prepared from a 4.6 mM Np(V) stock solution of ²³⁷Np. The stock solution had been purified from traces of ²³⁹Pu and ²³³Pa. The total Np(V) concentration in each sample was 8 μ M. The neptunium loading of the samples was between 422-474 ppm. Three EXAFS samples labeled A, B, and C were prepared in the presence of ambient CO₂ at pH 7.0, 9.0, and 10.0, respectively. Samples D and E were prepared in a glove box under Ar atmosphere at pH 8.5 and 9.0, respectively. These samples can be compared with samples which were prepared in equilibrium with air. For EXAFS investigations at room temperature, centrifuged wet α -Fe₂O₃ pastes were loaded into standard Perspex sample holders with Kapton windows for EXAFS analysis. For measurements at 13 K, the solid residues were dried and loaded into a polyethylene sample holder. The EXAFS spectra were collected at the Np L_{III}-edge (17610 eV) at room/low temperature (see Tab. 1, Fig. 1) using a Canberra 13-element Ge detector. Chromium foils were used to reject Fe K α fluorescence from the samples. The raw Np L_{III}-edge data were analyzed using the EXAFSPAK software [4]. Backscattering phase and amplitude functions required for fitting the spectra were obtained from FEFF 8.20 calculations [5] using the crystal structure of iron(III) uranium oxide [6], where U was replaced by Np to model a possible Np-Fe interaction with the hematite surface. The EXAFS spectra of all samples show similar oscillations, indicating similar neptunium near-neighbor surroundings. According to the fit results (Tab.1), the structural model of possible Np(V) surface species on hematite is shown in Fig 2. One possible bidentate inner-sphere structural model implying an edge sharing between the Np(V) and Fe octahedra was developed on the basis of structural parameters determined by EXAFS. Figure 2 (left) shows the coordination of Np(V) sorbed on hematite

if the angle (Np, Fe, O_(FeO₆)) is $\sim 60^\circ$. In this study the distances of the coordination shells Np-O_{ax}, Np-O_{eq}, and Np-Fe measured by EXAFS suggest that Np(V) was bonded in an inner-sphere fashion. This is based on the presence of a Np-Fe interaction near 3.46 Å. This distance is in accord with an edge-sharing, bidentate surface complex. In the presence/absence of atmospheric CO₂, the average Np-O_{eq} distances are the same in all samples and much shorter than in NpO₂(CO₃)₃⁵⁻. There is no evidence of the formation of Np(V) carbonate species at the hematite surface, that means there is no finding regarding the ternary carbonate complexes (e.g. $\equiv\text{FeONpO}_2(\text{O}_2\text{COH})_2^{2-}$) postulated by Kohler et al. [1]. There was no evidence for Np neighbors in the EXAFS spectra, suggesting that the sorbed Np(V) complexes were predominantly monomeric.

Figure 1. Np L_{III}-edge k³-weighted EXAFS spectra (left) and the corresponding Fourier transforms (right) for Np(V) sorbed on hematite.

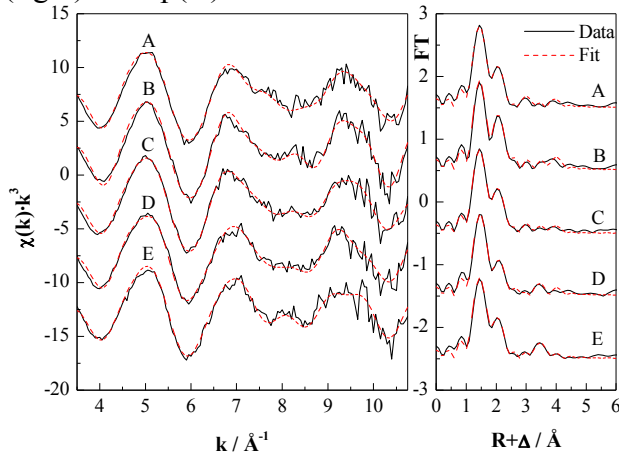


Figure 2. Schematic diagram illustrating a possible Np(V) coordination environment on the hematite surface (left) and the arrangement of the FeO₆ octahedra in the hematite structure (right).

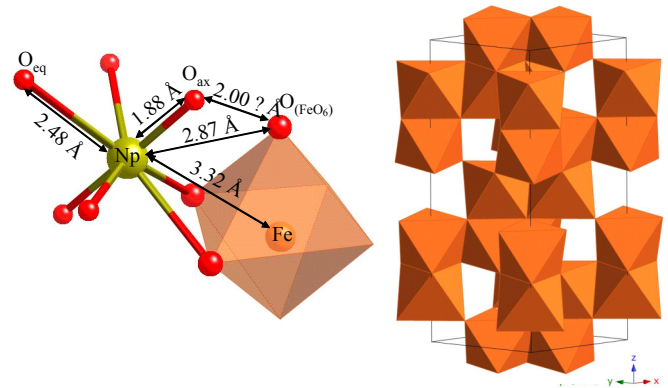


Table 1. EXAFS fit results ($\Delta R = \pm 0.02$ Å, $\Delta\sigma^2 = 0.001$ Å², RT-Room temperature).

Sample	Description	2x(Np-O _{ax})		4x(Np-O _{eq})		2x(Np-O)		0.5x(Np-Fe)		ΔE_0 /eV
		R/Å	$\sigma^2/\text{Å}^2$	R/Å	$\sigma^2/\text{Å}^2$	R/Å	$\sigma^2/\text{Å}^2$	R/Å	$\sigma^2/\text{Å}^2$	
A	pH 7.0, air, RT	1.87	0.003	2.48	0.010	2.86	0.016	3.43	0.006	5.7
B	pH 9.0, air, 13 K	1.88	0.002	2.48	0.006	2.84	0.010	3.44	0.011	7.0
C	pH 10.0, air, RT	1.87	0.003	2.46	0.009	2.86	0.013	3.46	0.014	4.2
D	pH 8.5, argon, RT	1.88	0.003	2.49	0.013	2.87	0.010	3.74	0.003	7.2
E	pH 9.0, argon, 13 K	1.87	0.003	2.46	0.010	2.84	0.015	3.73	0.002	5.1
[7]	NpO ₂ (H ₂ O) ₄ ⁺	1.82	0.002	2.49	0.006	-	-	-	-	-
[8]	NpO ₂ (CO ₃) ₃ ⁵⁻	1.86	0.001	2.53	0.013	-	-	-	-	-

Acknowledgement

This work was supported by Bundesministerium für Wirtschaft und Technologie (BMW) under contract No. 02E9653. We acknowledge the ESRF for provision of synchrotron beam time and thank A. Rossberg, C. Hennig, H. Funke, and A. Scheinost from Forschungszentrum Dresden-Rossendorf for assistance in using beamline BM20.

References

- [1] M. Kohler, B.D. Honeyman et al., *Radiochim. Acta* **85**, 33-48 (1999).
- [2] U. Schwertmann and R.M. Cornell, *Iron Oxides in the Laboratory*, Wiley-VCH, Weinheim (2000).
- [3] S. Amayri, M. Breckheimer et al., *Proc. of Actinide-XAS-2006 Workshop*, NEA-OECD (in press).
- [4] G.N. George and I.J. Pickering, *EXAFSPAK: A suite of computer programs for analysis of X-ray absorption spectra*; Stanford Synchrotron Radiation Laboratory, Stanford, CA, USA (1995).
- [5] A.L. Ankudinov, C.E. Bouldin et al., *Phys. Rev. B* **65** (10), 104107/1-11 (2002).
- [6] M. Bacmann and E.F. Bertaut, *Bull. Soc. Franc. Mineral. Crist. B* **90**, 257-258 (1967).
- [7] T. Reich, G. Bernhard et al., *Radiochim. Acta* **88**, 633-637 (2000).
- [8] D.L. Clark, S.D. Conradson et al., *J. Am. Chem. Soc.* **118**, 2089-2090 (1996).