

EXAFS study of Np(V) sorption onto hematite ($\alpha\text{-Fe}_2\text{O}_3$)

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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 and common occurrence as grain coatings. The aim of this study is to understand the sorption mechanism of neptunium(V) on hematite ($\alpha\text{-Fe}_2\text{O}_3$) 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]. In previous study the sorption of Np(V) on synthetic hematite has been investigated as a function of pH in the absence and presence of ambient CO_2 [2].

In this work five EXAFS samples with different amounts of Np(V) sorbed were prepared from a 4.6 mM Np(V) stock solution of ^{237}Np . The stock solution had been purified from traces of ^{239}Pu and ^{233}Pa . The total Np(V) concentration in each sample was 8 μM . 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 CO_2 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 to samples which were prepared in equilibrium with air. A detailed description of the EXAFS experiments can be found elsewhere [2].

The Np L_{III} -edge EXAFS spectra (Fig. 1) were recorded in fluorescence mode at room temperature at the Rossendorf Beamline ROBL at the European Synchrotron Radiation Facility (ESRF). For each sample eight scans were averaged and corrected for detector dead time. The software package EXAFSPAK was used for the analysis of the EXAFS data. Theoretical scattering phases and amplitudes were calculated using the ab initio code FEFF 8.20 and an atomic cluster based on the crystal structure of iron(III) uranium oxide [3], where U was replaced by Np to model a possible Np-Fe interaction with the hematite surface. From this study the distances of the coordination shells Np-O_{ax} , Np-O_{eq} , and Np-Fe measured by EXAFS (see Tab. 1) 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 (samples A-C) and 3.74 Å (samples D and E). This distance is in accord with an edge-sharing, bidentate surface complex (Fig. 2). In the presence/absence of atmospheric CO_2 , the average Np-O_{eq} distances are the same in all samples and much shorter than in $\text{NpO}_2(\text{CO}_3)_3^{5-}$ [4].

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 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.

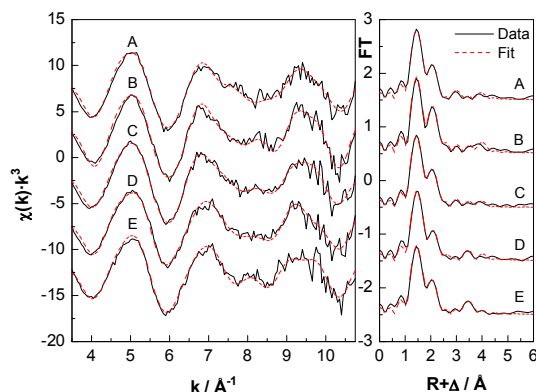


FIGURE 1. Np L_{III} -edge k^3 -weighted EXAFS spectra (left) and their Fourier transforms (right).

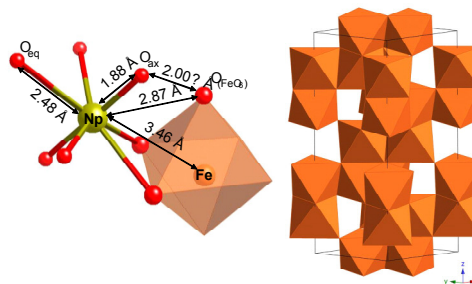


FIGURE 2. Np(V) coordination environment on the hematite surface.

TABLE 1. EXAFS fit results ($\Delta R = \pm 0.02$ Å, $\Delta\sigma^2 = 0.001$ Å²).

Sample	2x(Np-O _{ax})		4x(Np-O _{eq})		2x(Np-O)		0.5x(Np-Fe)		ΔE_{f} 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	1.87	0.003	2.48	0.010	2.86	0.016	3.43	0.006	5.7
B	1.88	0.002	2.48	0.006	2.84	0.010	3.44	0.011	7.0
C	1.87	0.003	2.46	0.009	2.86	0.013	3.46	0.014	4.2
D	1.88	0.003	2.49	0.013	2.87	0.010	3.74	0.003	7.2
E	1.87	0.003	2.46	0.010	2.84	0.015	3.73	0.002	5.1
[4]	1.86	0.001	2.53	0.013	-	-	-	-	-

Acknowledgment

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References

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