 ROBL-CRG	Experiment title: Retention of Np in Fe(II)/clay systems under reducing conditions	Experiment number: 20-01-780
	Beamline: BM 20	Date of experiment: from: 11.06 to: 16.06.16
Shifts: 9	Local contact(s): A. Scheinost	<i>Received at ROBL:</i>
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The sorption of NpO_2^+ on montmorillonite was investigated in the absence and presence of ferrous iron under reducing conditions to simulate repository relevant conditions. The experiments were carried out in a bulk electrolysis cell composed of a three electrode system. Under reducing conditions and in the absence of ferrous iron, the sorption of NpO_2^+ remained nearly constant and no noticeable increase of sorption compared to anoxic conditions could be observed. In the presence of ferrous iron, the sorption of NpO_2^+ steadily increased, and reached a plateau, suggesting the reduction of Np^{V} to Np^{IV} .

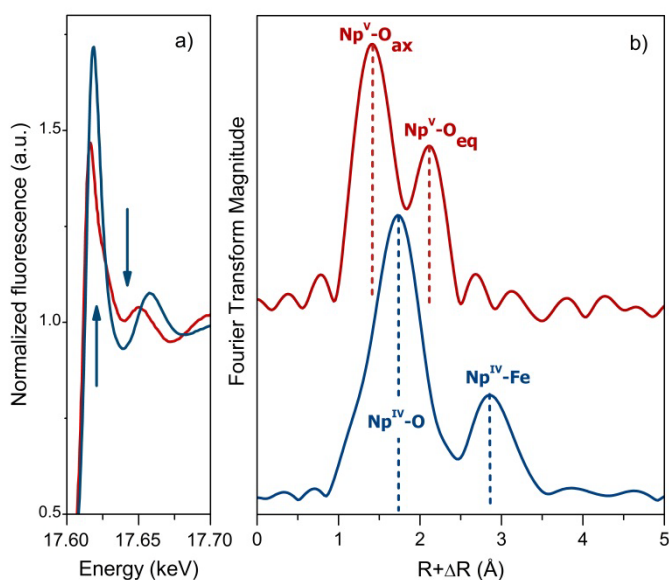


Fig. 1: Np-L_{III} edge XAFS spectra of Np sorbed to STx under reducing conditions in the absence (red) and presence of Fe^{II} (blue): a) XANES spectra and b) Fourier transforms (FTs).

The nature of Np complex formed (oxidation state, structural environment) at the clay surface was investigated by EXAFS. The spectroscopic measurements were carried out at the Np L_{III} edge in fluorescence mode under cryogenic conditions at 15 K using a closed-cycle He-cryostat to avoid O₂ diffusion into the samples. Np XANES and FTs spectra are shown in Fig. 1a and b and the derived structural parameters are summarized in Table 1.

Under reducing conditions, however, without addition of Fe^{II} no noticeable reduction of Np^{V} occurred within the duration of the experiment. The spectral features are typical for NpO_2^+ (Table 1). In the presence of ferrous iron, Np^{V} becomes fully reduced to Np^{IV} . The XANES spectrum is typical for Np^{IV} (*i.e.* intense white line and absence of the features originating from the $\text{O}=\text{Np}=\text{O}$ moiety). The fitted structural parameters (Table 1) confirm that Np retained at the clay surface is fully reduced and strongly associated to Fe. The exact nature of the final surface product is still not clear. The precipitation of the solubility limiting NpO_2 solid phase was not observed.

Table 1: *Np-L_{III} EXAFS fit results of Np reacted with STx under reducing conditions with and without Fe^{II} ($S_0^2=0.9$, fit range 2.0 – 9.5 Å⁻¹).*

	Path	CN[†]	R(Å)	σ²(Å²)
Without Fe^{II} Np ^V sorption complex	Np-O _{ax}	2.0 ^f	1.84	0.004
	Np-O _{eq}	5.0 ^f	2.48	0.010
With Fe^{II} Np ^{IV} sorption complex	Np-O	2.8	2.21	0.004
	Np-O	4.9	2.37	0.009
	Np-Fe ₁	3	3.4	0.010