



A MACROSCOPIC AND SPECTROSCOPIC INVESTIGATION OF NEPTUNIUM(V) ADSORPTION ON MONTMORILLONITE AND CORUNDUM

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INTRODUCTION

The bentonite buffer in EBS consists mainly of montmorillonite which like the other aluminosilicates are known to retain radionuclides thus, contributing to the retention or immobilization of them. In mildly oxidic conditions, long-lived neptunium (2.144×10^6 a) is on its fifth oxidation state forming a neptunyl cation, NpO_2^+ . It is rather soluble, poorly sorbed, and readily mobile under environmental conditions making it highly relevant concerning SNF repository safety.

ADSORPTION

In the present study we investigated sorption of NpO_2^+ on Na-montmorillonite provided by B+Tech and synthetic corundum ($\alpha\text{-Al}_2\text{O}_3$). Neptunium sorption on both minerals as a function of pH and as a function of neptunium concentration at pH 8 and 9 are presented in Figure 1.

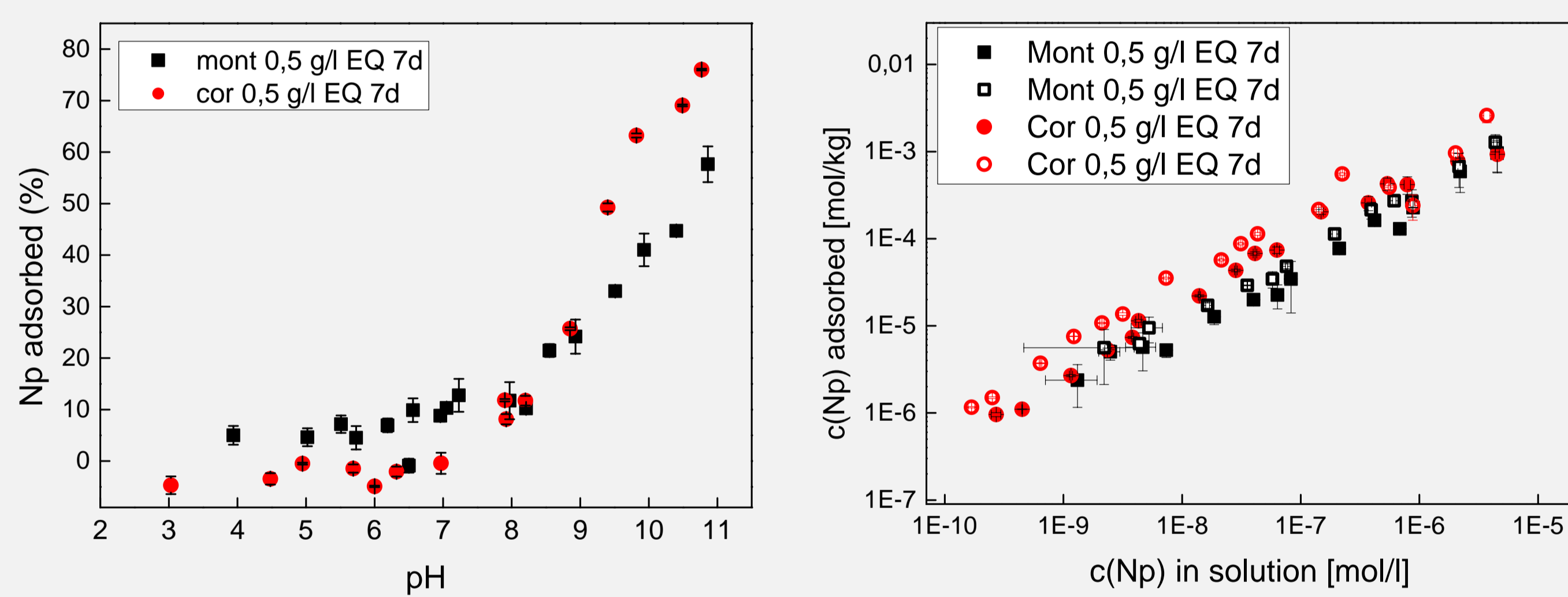


Figure 1. Neptunium adsorption on 0.5 g/l montmorillonite (black squares) and corundum (red dots). Np(V) adsorption on both minerals as a function of pH (left). Experimental conditions: $c(\text{Np-237}) = 10^{-6}$ M, 10 mM NaClO_4 , $t_{\text{EQ}} = 7$ d. Neptunium isotherms on as a function of Np(V) concentration (right). Neptunium concentration range $10^{-9} - 5 \times 10^{-6}$ M, pH 8 (solid squares) and 9 (open squares) in TRIS/CHES buffers + 10 mM NaClO_4 , $t_{\text{EQ}} = 7$ d.

ATR FT-IR SPECTROSCOPY

To investigate the neptunium speciation on the mineral surfaces we did *in-situ* ATR FT-IR spectroscopic experiments at pH 10. The IR spectra were measured with a Bruker Vertex 70/v vacuum spectrometer with a Mercury Cadmium Telluride detector.

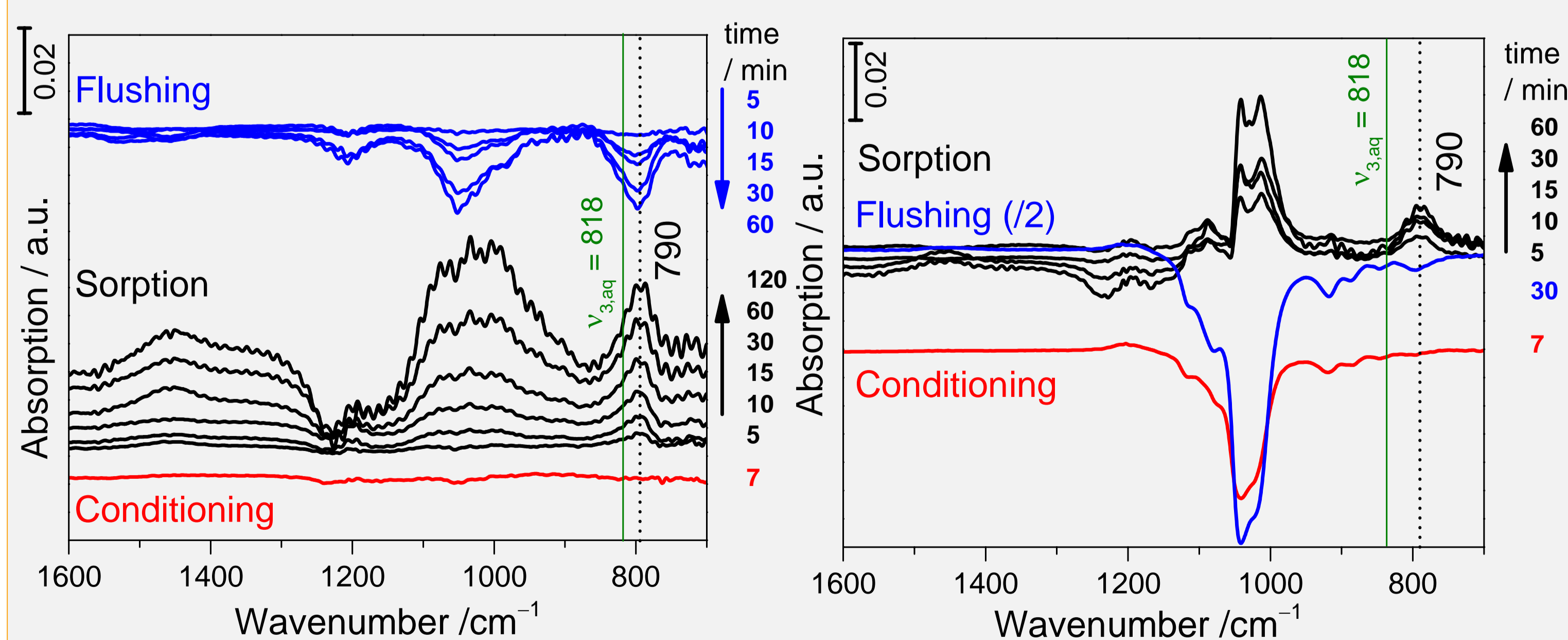


Figure 2. Sorption of 50 μM Np(V) on corundum (left) and montmorillonite (right) in 10 mM NaCl in D_2O at pD 9.6, flow rate 0.1 ml/min.

- In the **conditioning** step, the stability of the mineral film can be ensured. For corundum (Figure 2, left) the conditioning yields a flat spectrum, indicating a stable mineral film. For montmorillonite (Figure 2, right) the conditioning spectrum has a strong negative peak, which is an indication of the mineral film being flushed away from the crystal. However, the film is stable enough for ATR FT-IR measurements.
- In the sorption step the mineral film is flushed with neptunium solution. The Np-O inner-sphere sorption band for both minerals is increasing as a function of time. For montmorillonite, all the sorption sites seem to saturate after 15 minutes.
- In the final **flushing** step high reversibility of neptunium complex is seen for both minerals.

EXAFS SPECTROSCOPY

More detailed information on the surface complexation was investigated by EXAFS spectroscopy at pH 9 and 10. The k_3 -weighted Np L_{III} -edge EXAFS spectra for both corundum samples and their corresponding Fourier transforms (FTs) are presented in Figure 3. EXAFS structural parameters obtained from theoretical curve fitting indicate the formation of a bidentate inner-sphere complex with an average Np-O equatorial oxygen distance of 2.45 Å and a Np-Al distance of 3.36 Å.

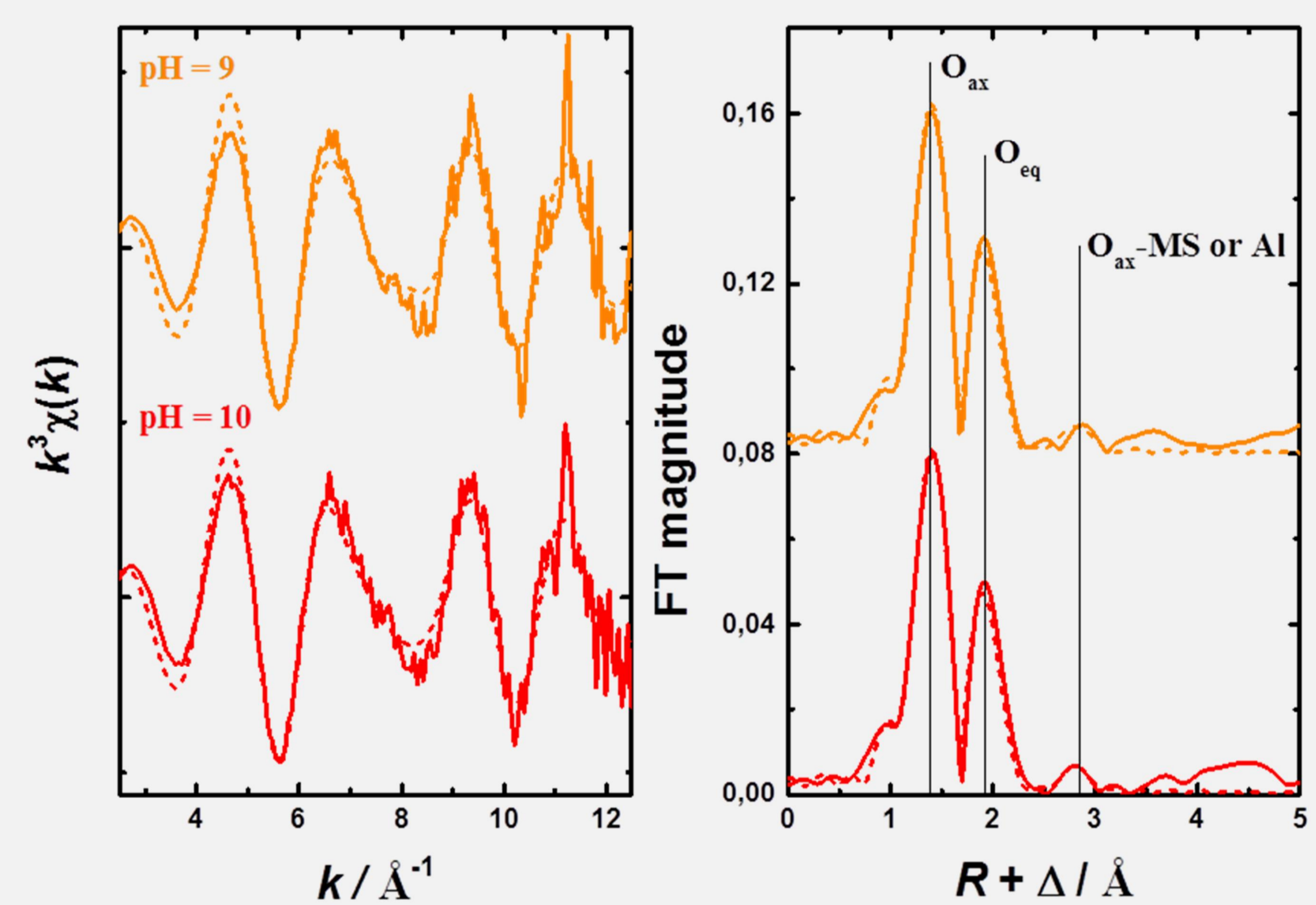


Figure 3. k^3 -weighted Np L_{III} -edge EXAFS spectra for Np adsorbed on corundum (left) and their corresponding Fourier transforms (right). Solid lines; experimental data, dotted lines; theoretical fitting. Phase shifts (Δ) are not corrected on the FTs.

CONCLUSIONS

- Montmorillonite is assumed to adsorb neptunium at low pH as an outer-sphere complex, such behavior was not detected for corundum.
- In the final repository in Olkiluoto (Finland), at pH 8, neptunium sorption on both minerals is rather low, indicating poor retardation for neptunium on the buffer material.
- The ATR FT-IR measurements indicate the formation of a neptunium inner-sphere complex on both minerals at pH 10.
- The EXAFS spectra indicated a bidentate inner-sphere complex for corundum.
- Based on the EXAFS measurements no motive for the high reversibility of the Np(V) complex cannot be stated.

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