



# Batch sorption and spectroscopic speciation studies of neptunium uptake by montmorillonite and corundum

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## Abstract

Detailed information on neptunium(V) speciation on montmorillonite and corundum surfaces was obtained by batch sorption and desorption studies combined with surface complexation modelling using the Diffuse Double-Layer (DDL) model, *in situ* time-resolved Attenuated Total Reflection Fourier-Transform Infrared (ATR FT-IR) and X-ray absorption (XAS) spectroscopies. The pH-dependent batch sorption studies and the spectroscopic investigations were conducted under carbonate-free conditions in 10 mM NaClO<sub>4</sub> or 10 mM NaCl. Solid concentrations of 0.5 g/l and 5 g/l were used depending on the experiment. The neptunium(V) desorption from the two mineral surfaces was investigated at pH values ranging from 8 to 10, using the replenishment technique. Neptunium(V) was found to desorb from the mineral surface, however, the extent of desorption was dependent on the solution pH. The desorption of neptunium(V) was confirmed in the ATR FT-IR spectroscopic studies at pH 10, where all of the identified inner-sphere complexed neptunium(V), characterized by a vibrational band at 790 cm<sup>-1</sup>, was desorbed from both mineral surfaces upon flushing the mineral films with a blank electrolyte solution. In XAS investigations of neptunium(V) uptake by corundum, the obtained structural parameters confirm the formation of an inner-sphere complex adsorbed on the surface in a bidentate fashion. As the inner-sphere complexes found in the IR-studies are characterized by identical sorption bands on both corundum and montmorillonite, we tentatively assigned the neptunium(V) inner-sphere complex on montmorillonite to the same bidentate complex found on corundum in the XAS investigations. Finally, the obtained batch sorption and spectroscopic results were modelled with surface complexation modelling to explain the neptunium(V) speciation on montmorillonite over the entire investigated pH range. The modelling results show that cation exchange in the interlayer space as well as two pH-dependent surface complexes are required to fully explain the neptunium(V) speciation on the montmorillonite surface.

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## 1. INTRODUCTION

The neptunium (Np) isotope Np-237 is an actinide of concern in safety assessments of spent nuclear fuel (SNF)

repositories. This radiotoxic isotope has an extremely long half-life ( $t_{1/2} = 2.144 \times 10^6$  y) making it a major dose contributor to the radiation inventory in nuclear waste after one hundred thousand years (Hursthouse et al., 1991; Kaszuba and Runde, 1999; Zhao et al., 2014). In mildly oxic conditions Np is stable in the pentavalent oxidation state as the neptunium(V) cation (NpO<sub>2</sub><sup>+</sup>), which is rather

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soluble, poorly retained by solid phases and, thus, susceptible to migration by groundwater in the far field of a SNF repository (Viswanathan et al., 1998; Kaszuba and Runde, 1999; Kozai et al., 2014). In order to quantitatively describe the mobility of neptunium(V) in the environment, a thorough understanding of the sorption behaviour of the cation on artificial and natural barrier materials is required. Surface retention in general is especially effective on clay minerals possessing large surface areas and strong retention capacities. For this reason clay minerals are envisioned as both potential host rock materials and as buffers and fillers in various repository designs. One of the important minerals in this context is montmorillonite, the main constituent in bentonite clay which is being considered as a buffer material in several repository concepts under consideration in e.g. Scandinavia, France and Switzerland. Montmorillonite is known to readily retain radionuclides either through cation exchange in the interlayer space (Birgersson and Karnland, 2009; Hartmann et al., 2011) or by surface complexation onto reactive sorption sites prevalently on the edge sites (Bradbury and Baeyens, 2002; Sabodina et al., 2006; Zavarin et al., 2012). A number of studies investigating radionuclide sorption onto montmorillonite can be found (Marques Fernandes et al., 2012; Missana et al., 2014; Soltermann et al., 2014). However, only few of them deal with the uptake of neptunium(V) (Turner et al., 1998; Nagasaki and Tanaka, 2000; Bradbury and Baeyens, 2006; Sabodina et al., 2006; Zavarin et al., 2012; Kozai et al., 2014). In addition, none of these studies involve detailed spectroscopic investigations that would explain the speciation of neptunium(V) on the montmorillonite surface, which could eventually describe the sorption mechanism of this mineral. In the present study we have investigated neptunium(V) sorption and speciation on a natural montmorillonite mineral under simplified but, when possible, under environmentally relevant conditions. Natural minerals often have multiple functional surface groups, which makes the surface speciation more complex. In this context, this study has employed the aluminium oxide corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) as a model phase for reactive aluminol groups on the montmorillonite mineral surface. We have conducted batch sorption and desorption experiments to quantify the uptake of neptunium(V) by the minerals and the extent of desorption from the mineral surfaces, respectively. The neptunium(V) batch sorption data on montmorillonite has been modelled with the Diffuse Double-Layer model to extract complexation constant for the formed neptunium(V) surface species. Detailed information on the coordination environment of neptunium(V) on the mineral surfaces was obtained by Attenuated Total Reflection Fourier-Transform Infrared (ATR FT-IR) and X-ray absorption spectroscopies (XAS).

## 2. MATERIALS AND METHODS

### 2.1. Mineral characterization

The homoionic sodium montmorillonite used in this study has been isolated from Wyoming Volclay MX-80 bentonite and purified by B<sup>+</sup>Tech Oy, Finland. The XRD

diffraction pattern obtained for montmorillonite showed impurities from quartz and paragonite (Fig. 1, left). These impurities may have been transferred during the purification from the MX-80 bentonite powder (Kumpulainen and Kiviranta, 2010). The surface  $\zeta$ -potential of 0.25 g/l montmorillonite measured under carbonate-free conditions in 10 mM NaCl by microelectrophoresis (Zeta Sizer Nano, Malvern Instruments) showed a constant negative charge over the entire investigated pH-range, Fig. 1 (right). Thus, no isoelectric point (IEP) corresponding to a net surface charge of zero could be assigned for the mineral. The specific surface area of montmorillonite was found to be 49.8 m<sup>2</sup>/g with the N<sub>2</sub>-BET technique. The mineral was used as received in the batch sorption and spectroscopic investigations.

Corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) was provided by Taimei Chemicals, Tokyo, Japan (TAIMICRON TM-DAR). The powder has been thoroughly characterized in Kupcik et al. (2016) and found to have a crystalline purity of >99.99% in XRD and XPS investigations. Thus, the corundum powder was used without further purification in all studies. Results from the mineral characterizations are compiled in Table 1.

### 2.2. Batch adsorption and desorption investigations

#### 2.2.1. Neptunium(V) adsorption investigations

All batch sorption experiments were conducted in a N<sub>2</sub>-glove box to exclude the formation of soluble neptunium(V)-carbonate complexes that influence the uptake and speciation of neptunium(V) on the solid surfaces. 10 mM NaClO<sub>4</sub> was always used as background electrolyte and the montmorillonite or corundum concentration was kept constant at either 0.5 g/l (similar to the solid concentration in the ATR FT-IR experiments) or 5 g/l (as used for the XAS experiments). Batch sorption experiments as a function of pH (pH-edges) were conducted in 20 ml polypropylene vials using a constant neptunium concentration of 10<sup>-6</sup> M across the pH range 4–11. pH adjustments were done with 0.01–1 M NaOH and HClO<sub>4</sub> solutions. All samples were allowed to equilibrate in the glove box under constant shaking for 7 or 30 days before phase separation at minimum 3830 g (6000 rpm) for 60 min. The amount of adsorbed neptunium(V) was analysed from the supernatant with liquid scintillation counting (Tri-Carb 3100 TR) using  $\alpha/\beta$ -discrimination to separate out the  $\beta$  disintegrations from the Np-237 daughter nuclide Pa-233. To rule out a possible carbonate contamination originating from the mineral itself, we performed leaching tests on 0.5 g/l and 5 g/l montmorillonite suspensions over 7 and 30 days at pH-values of 9, 10 and 11. After equilibration, the carbonate content was measured with a carbon dioxide electrode (Carbon Dioxide Ion Selective Electrode, Thermo Scientific) with a detection limit of 10<sup>-4</sup> M.

#### 2.2.2. Neptunium(V) desorption investigations

Desorption experiments were conducted to investigate the extent of desorption from the montmorillonite and corundum surfaces. The experimental conditions were kept similar to the batch adsorption investigations as explained above, i.e. N<sub>2</sub>-atmosphere, montmorillonite or corundum

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