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Speciation of neptunium during sorption and diffusion in natural clay

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Abstract. In argillaceous rocks, which are considered as a potential host rock for nuclear waste repositories, sorption and diffusion processes govern the migration behaviour of actinides like neptunium. For the safety analysis of such a repository, a molecular-level understanding of the transport and retardation phenomena of radioactive contaminants in the host rock is mandatory. The speciation of Np during sorption and diffusion in Opalinus Clay was studied at near neutral pH using a combination of spatially resolved synchrotron radiation techniques. During the sorption and diffusion experiments, the interaction of 8 μM Np(V) solutions with the clay lead to the formation of spots at the clay-water interface with increased Np concentrations as determined by μ-XRF. Several of these spots are correlated with areas of increased Fe concentration. Np L$_3$-edge μ-XANES spectra revealed that up to 85% of the initial Np(V) was reduced to Np(IV). Pyrite could be identified by μ-XRD as a redox-active mineral phase responsible for the formation of Np(IV). The analysis of the diffusion profile within the clay matrix after an in-diffusion experiment for two months showed that Np(V) is progressively reduced with diffusion distance, i.e. Np(IV) amounted to $\approx$12% and $\approx$26% at 30 μm and 525 μm, respectively.

1. Introduction

Argillaceous rock formations are under consideration as a potential host rock for the construction of high-level nuclear waste repositories. Np(IV) and Np(V) are the most stable oxidation states of ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ a) under environmental conditions. We have investigated the sorption and diffusion of the more mobile Np(V) in Opalinus Clay (OPA), a natural clay from the Mont Terri rock laboratory in Switzerland [1-3]. OPA, which is present also in Southern Germany, possesses a micro-scale heterogeneity and is composed of several types of clay minerals, but also of calcite, quartz and Fe(II)-bearing minerals. In our previous diffusion [1] and anaerobic sorption experiments [2], we observed higher distribution coefficients, K_d, than expected from batch experiments performed in air, suggesting

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that a partial reduction of Np(V) to Np(IV) had occurred. To verify this hypothesis, different sorption and diffusion samples with Np(V) were prepared at near neutral pH for spatially resolved, molecular-level investigations at the microXAS beamline of the Swiss Light Source (SLS).

2. Experimental

The sorption sample was prepared by contacting a 20-30 μm thick thin section of OPA with 8 μM ^{237}Np(V) solution (Millipore water, pH $\approx$ 7) under anaerobic conditions in an argon glove box. After a contact time of five days, the aqueous phase was removed [4].

For the preparation of the diffusion sample, an intact OPA cylinder (diameter 25.4 mm, thickness 11 mm) was mounted into a diffusion cell as described in [1]. The clay cylinder was oriented so that the bedding was parallel to the direction of transport (diffusion). The high-concentration reservoir of the diffusion setup contained 8 μM ^{237}Np(V) solution (artificial OPA pore water, pH = 7.6 [5]). The low-concentration reservoir contained only artificial OPA pore water without Np. The diffusion experiment was performed at 25 °C under ambient-air conditions and lasted for 61 days. During this time the E_h in the high-concentration reservoir was approximately equal to 480 mV (SHE). After two months, the diffusion cell was opened and the clay cylinder was cleaved parallel to the bedding. Smaller segments of the clay cylinder were mounted into the sample holder.

Both samples were measured at the microXAS beamline at the SLS using the Kirkpatrick-Baez mirror microfocusing system and the Si(111) double-crystal monochromator. X-ray fluorescence maps of several elements including Si, S, K, Ca, Ti, Fe, Sr and Np were recorded using a single-element Si detector (KETEK GmbH, Germany). The excitation energy was 17.62 or 17.70 keV, which is above the Np L_3-edge. The size of the focused X-ray beam was approximately 2×4 μm (height $\times$ width). X-ray diffraction patterns of the OPA thin section on high-purity quartz glass (Heraeus Holding GmbH, Germany) were recorded with a 100k Pilatus detector (DECTRIS Ltd., Switzerland). Np L_3-edge XANES spectra were recorded in fluorescence mode at spots where μ-XRF maps had shown areas with higher Np concentrations. A Zr foil ($E_0 = 17.998$ keV) was used for energy calibration. μ-XRD mappings (20×20 μm, 1 μm step size) were collected for the sorption sample (thin section) at 17.70 keV. The angle between the incoming X-ray beam and the fluorescence detector was 45° or 20° (by simultaneous use of XRD detector) for the sorption sample and equal to 30° for the diffusion sample, respectively. The analysis of the μ-XRF, μ-XANES and μ-XRD data using several software packages is described in [4].

3. Results and discussion

3.1. Sorption sample

The μ-XRF mappings of elements contained in OPA (e.g. Si, S, K, Ca, Fe) reflect the mineralogical heterogeneity of the natural clay. For example, the 2×2 mm μ-XRF map of Fe in figure 1 (a) shows a large area of increased Fe concentration. As can be seen from the corresponding Np XRF map in figure 1 (a), several spots of increased Np concentration are clearly correlated with the Fe concentration. In the region marked with a white cross (figure 1 (a)), the measured Np L_3-edge XANES spectrum is composed of 85 ± 5% Np(IV) and 15 ± 5% Np(V) (figure 1 (b)), indicating that the initial Np(V) has been significantly reduced to Np(IV). μ-XRD measurements in this area (figure 1 (c)) showed that Np was accumulated on pyrite (FeS_2). Therefore, pyrite is at least one of the redox-active mineral phases of OPA responsible for the reduction of Np(V). It should be noted that Np spots with considerable fractions of tetravalent Np could be found also in other OPA sorption samples, even when the experiments were performed under ambient-air conditions [4].

3.2. Diffusion sample

In the long-term diffusion experiment using 8 μM Np(V) in OPA pore water (pH 7.6), we were able to derive the Np diffusion profile along a 3 mm long diffusion path parallel to the bedding of the clay

using μ-XRF maps. As can be seen from figure 2 (a), the amount of Np decreases steadily with diffusion distance and reaches the background level after approximately 2.5 mm. Several Np L_3-edge μ-XANES spectra were recorded along this diffusion path. The linear combination fit of these spectra using those of Np(IV) and Np(V) aquo ions as references showed that at a distance of ca. 30 μm from the OPA-water interface $12 \pm 5\%$ of the initial Np(V) has been reduced to Np(IV) (figure 2 (b)). The degree of Np reduction increases with distance and reaches $26 \pm 5\%$ at 525 μm (figure 2 (c)). An even higher degree of Np reduction of approximately $80 \pm 5\%$ was observed near a spot with increased Fe concentration at a diffusion distance of 450 μm in a similar long-term diffusion experiment (sample not shown here). This further corroborates the role of the Fe(II)-bearing minerals as described in section 3.1.
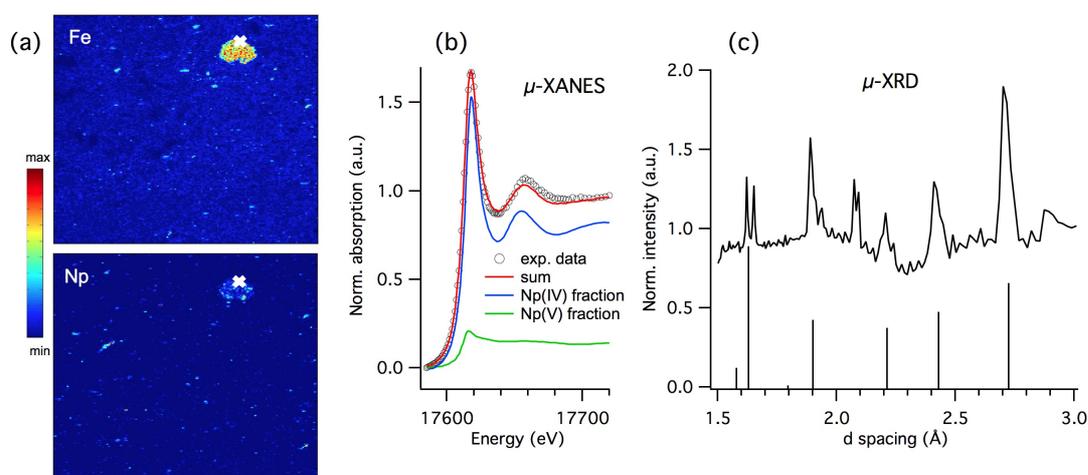
Figure 1. (a) μ-XRF elemental distribution maps of Fe and Np (2×2 mm, step size 10 μm). (b) Normalized Np L_3-edge μ-XANES spectrum measured on the spot marked with a white cross in the XRF map together with the fractions of Np(IV) and Np(V) reference spectra. (c) Intensity vs. d-spacing plot obtained by μ-XRD mapping of the same spot (20×20 μm, step size 1 μm). The vertical bars are calculated reflections of pyrite (ICSD database, collection code 43716).
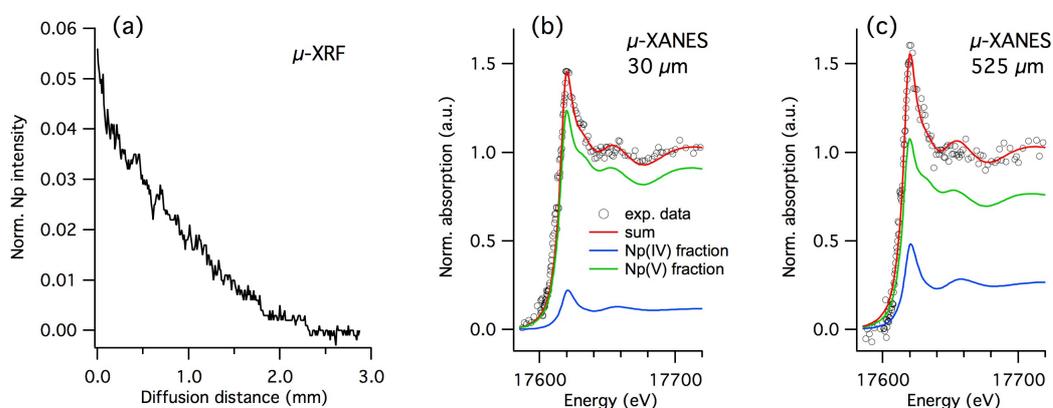
Figure 2. (a) Normalized neptunium intensity vs. diffusion distance derived from μ-XRF (3.0×1.0 mm, step size 10 μm). (b) and (c) Normalized Np L_3-edge μ-XANES spectra measured at distances of 30 μm and 525 μm together with the fractions of Np(IV) and Np(V) reference spectra.

4. Conclusions

Although wet-chemistry experiments are important for the determination of parameters quantifying the sorption and diffusion of Np in natural clay, these experiments cannot provide the molecular-level understanding that is needed to support the safety analysis of future high-level nuclear waste repositories. The combination of spatially resolved X-ray microprobe methods (e.g. μ-XRF, μ-XANES, μ-XRD) is a powerful tool for determining the distribution and speciation of actinides in heterogeneous systems like natural clays.

After sorption of 8 μM Np(V) on Opalinus Clay at pH 7 under anaerobic conditions, μm-size spots were detected where tetravalent Np is the dominating species. The Fe(II)-bearing mineral pyrite acts as an important redox-active mineral phase. In the long-term diffusion experiment with 8 μM Np(V) and Opalinus Clay pore water (pH 7.6) as mobile phase, the speciation of Np could be mapped along the diffusion path parallel to the bedding of the clay. These Np L_3-edge μ-XANES measurements showed that mobile Np(V) is immobilized in Opalinus Clay as Np(IV) by progressive reduction along its diffusion path, further consolidating the suitability of argillaceous rocks with regard to the long-term storage of Np-containing nuclear waste.

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