



Contribution ID: 8

Type: Poster

Speciation of neptunium along diffusion pathways in Opalinus Clay using micro-XAFS and micro-XRF

Tuesday 20 May 2014 17:30 (4h 30m)

For the long-term safety of nuclear waste repositories and a possible migration of the relevant transuranium actinide Np into the environment, the study of the interaction of Np with clays is of highest importance, since argillaceous rocks are under consideration as potential host rocks or at least as backfill material in high-level nuclear waste repositories in countries like Switzerland and Germany. In our previous SLS-experiment the Opalinus Clay from Mont Terri, Switzerland, was used as a natural reference clay mineral to study the sorption and diffusion behaviour of Np(V) in clay and to simulate the migration process under environmental related conditions.

Several OPA bore cores were contacted with synthetic OPA pore water (pH 7.6) as mobile phase containing 8 μM Np(V) under aerobic conditions in self-made diffusion cells with a constant flow rate. Though they were started at three different diffusion times to see the diffusion and speciation in dependency of time. As we had success in the preparation of a similar filter-free cell of OPA contacted with Pu using parallel layered OPA (in diffusion direction), this concept was also used here. After the termination of the diffusion process we split each bore core along the axis of diffusion. In this way we obtained samples revealing Np diffusion profiles.

The first step was the examination of the distance of the Np diffusion by $\mu\text{-XRF}$. Therefore a large, smooth area must be chosen for the $\mu\text{-XRF}$ scans which have been implemented over several mm. The final mapping of Np was calculated by subtracting the $\mu\text{-XRF}$ -mapping of Sr with an excitation energy of 17592 eV from the same mapping using 17616 eV, above the Np L3-edge of 17610 eV. Large mappings of a size of 0.5 x 4 mm were realized with a step size of 10 μm .

The $\mu\text{-XRF}$ profiles also provided besides Np and Sr a deeper look at several other elements as Mn, Co, Ti, Zn, Fe, Ca and Rb. At this point it can be mentioned that of those elements the most pronounced heterogeneity of distribution was observed for Zn, Fe and especially Ca. These mappings can even display whole particles for Ca, probably calcite, with an area of several ten thousand μm^2 . However, the strongest effect might have differences in the concentrations of Fe, since it is reported to be under suspicion to reduce Np(V). Regarding the local diffusion and the local redox environment of Np and its speciation this heterogeneity of OPA must be taken into account.

As mentioned before, these results were also connected with Np L3-edge $\mu\text{-XANES}$ along the diffusion pathways. They were analysed with the software package Athena using background and energy correction as well as normalization. Afterwards a linear combination fit analyse using reference spectres of Np(IV) and Np(V) aquo ions was performed. They provide certain evidence of redox processes taking place with the initially added Np(V) in OPA. This can be concluded from the basic trend of the Np(V)/Np(IV) ratios which exhibit that Np(V) is increasingly reduced to Np(IV) as it diffuses deeper through the OPA core. Matching to this, the spectra for the furthest diffusion pathways even show convincing signs for an almost exhaustively reduction, though the quality is impaired by the lower concentrations. Nevertheless, these new results fortify Np(IV) as the main species, even though more experiments investigating the time-dependency will be performed.

As a last point we can already verify that the migration of the mobile Np(V) through OPA is considerable retarded as it gets significantly reduced to the highly sorbing Np(IV) on its diffusion through the OPA. These are positive results considering the safety assessment for a final disposal of nuclear waste in argillaceous rock.

Primary author: Mr ROSEMANN, Prashanta Jonathan Benjamin (Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany)

Co-authors: Dr GROLIMUND, Daniel (Paul Scherrer Institute, Swiss Light Source); Mr DREBERT, Jakob (Institute of Nuclear Chemistry, Johannes Gutenberg-University Mainz, 55099 Mainz, Germany); Dr AMAYRI, Samer (Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany); Prof. REICH, Tobias (Institute of Nuclear Chemistry, Johannes Gutenberg-University Mainz, 55099 Mainz, Germany); Mr KAPLAN, Ugras (Johannes Gutenberg Universität Mainz)

Presenter: Mr ROSEMANN, Prashanta Jonathan Benjamin (Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany)

Session Classification: Poster

Track Classification: Actinides in Environmental and Life Sciences