The flow of ground water through a nuclear waste repository can result in the release of radionuclides from waste matrices. The released radionuclides can then be transported through engineered barrier systems (cement) and the surrounding geosphere (sediments consisting mainly of clay minerals). Due to sorption processes on solid phases the release of radionuclides can be considerably retarded and thus, a mechanistic description of processes controlling metal uptake in cement and clay mineral systems is of fundamental importance for predicting the mobility and long-term safety of radionuclides in waste repositories. We have successfully used XAS to determine the uptake mechanisms of Ni onto montmorillonite, a dioctahedral 2:1 clay that is an important mineral for the retention of metals in the geosphere. Furthermore, it is planned that bentonite, a mixture of phyllosilicates consisting predominantly of montmorillonite, is used as a backfill material in concepts for a radioactive high level waste repository.

Applications of powder extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate sorption mechanisms in clay systems is often hampered due to the strong overlap of scattering contributions from neighboring atomic shells surrounding the X-ray absorber, thus preventing the discrimination of atomic shells beyond the first or second nearest neighbor atom. This limitation can be overcome by performing P-EXAFS (polarized EXAFS) experiments on highly oriented self-supporting clay films (Fig. 1). In P-EXAFS the contribution of cations from the tetrahedral sheets is minimized by orienting the layer $ab$ plane parallel to the electric field vector $\vec{e}$ of the incident X-ray beam. Conversely, the contribution of cations from the octahedral sheet is extinguished in the perpendicular orientation of $\vec{e}$.

Using P-EXAFS we could demonstrate, that the uptake of Ni on montmorillonite at elevated pH (pH ~8) and Ni concentrations resulted in the formation of a Ni-phyllosilicate-like phase [1]. The structural parameters (2.6 ± 0.5 Ni atoms at 3.08 Å in the in-plane direction, and by 4.2 ± 0.5 Si atoms at 3.26 Å in the out-of-plane direction) and the angular dependence of the Ni and Si shells suggest that the neoformed phyllosilicates are oriented with respect to montmorillonite layers. These findings have important geochemical implications because montmorillonite is abundant in the environment and the resulting sequestration of sorbed trace metals in sparingly soluble phyllosilicate structure may durably decrease the migration of radionuclides and contaminants.

References:


Fig. 1: Orientation of the montmorillonite film with respect to the incoming X-ray beam: (left) electric field vector $\vec{e}$ parallel to the layer plane; (right) $\vec{e}$ perpendicular to the layer plane.