

Sorption and speciation of neptunium(V) on Opalinus Clay

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Several European countries including Germany, Switzerland and France explore argillaceous rock formations as potential host rock for high-level nuclear waste repositories. Detailed knowledge of the chemical and physical behaviors of the radionuclides in the near and far fields of a repository is mandatory for its safety assessment. As one of the long-lived radionuclides Neptunium (^{237}Np) will contribute significantly to the radiotoxicity of the nuclear waste after a period of time of more than thousand years. Opalinus Clay (OPA) was chosen as reference material to study the sorption behavior of Np(V) on natural clay in batch experiments in dependence of several factors such as pH, Np concentration, solid-to-liquid (S/L) ratio and partial pressure of CO_2 (aerobic and anaerobic conditions). Additionally, the nature of Np species sorbed onto OPA was studied at a molecular level by Np L_{III} -edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

Aerobic and anaerobic samples of OPA (from Mont Terri, Switzerland) were used to study the sorption behavior of Np(V) by batch experiments. Because of the high amount of calcite ($\sim 13 \pm 8\%$) (1) in OPA, saturated calcite solutions were used as background electrolyte to avoid partial dissolution of OPA and to keep the amount of sorbent constant during all experiments. Sorption isotherms were measured by varying the S/L ratio between 2 and 20 g/L and the Np concentration between $7 \cdot 10^{-12}$ and $8 \cdot 10^{-6}$ mol/l. Maximum sorption of $8 \mu\text{M}$ Np occurred at pH 8.5; 65 % was sorbed under aerobic conditions and 80 % under anaerobic conditions, respectively. Stronger sorption in the absence of O_2 was found to be caused by a reduction of Np(V) to Np(IV). The complexation of neptunium with carbonate in aqueous solution (2) causes a decrease in sorption at pH > 9.

Depending on the conditions during the preparation of the wet-paste samples, i.e., background electrolyte, pH and partial pressure of CO_2 , EXAFS spectra indicated the formation of Np(V) carbonate complexes at the OPA surface in several cases.

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