Speciation and surface complexation modelling of Np(V) sorption on montmorillonite

T. Reich[1], S. Amayri[1], S. Dierking[1], B. Baeyens[2], R. Dähn[2], M.H. Bradbury[2] and A.C. Scheinost[3]

[1]Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany, treich@uni-mainz.de

[2]Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

[3]Institute of Radiochemistry and Rossendorf Beamline at ESRF, Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany

The sorption of Np(V) on Na-montmorillonite (STx-1) has been studied by batch experiments, spectroscopic measurements, and surface complexation modelling with the aim to contribute toward a better understanding of the sorption of ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ a) in the near field (bentonite backfill material) and far field (argillaceous rocks) of high-level nuclear waste repositories. Batch experiments were performed in the absence of inorganic carbon and under air-equilibrated conditions with 0.1 and 0.01 M NaClO$_4$ as background electrolyte, 8×10^{-12} and 9×10^{-6} M Np(V), and $3 \leq$ pH ≤ 10. At pH > 8 the presence of inorganic carbon has a strong influence on the sorption behavior of Np(V) due to the formation of aqueous Np(V) complexes with carbonate.

Neptunium L$_{III}$-edge extended X-ray absorption fine structure (EXAFS) measurements on Np(V)/montmorillonite samples with Np(V) loadings in the range of 0.3-3.5 µmol/g have been performed to determine the speciation of Np at the solid-liquid interface. The EXAFS spectra of samples prepared under ambient air conditions ($p_{CO2} = 10^{-3.5}$ atm) revealed the formation of Np(V)-carbonate complexes at the montmorillonite surface.

The results of the batch experiments obtained under CO$_2$-free conditions could be modeled using the two site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model described in (1). For modeling the sorption behavior of Np(V) on montmorillonite in the air-equilibrated system, the aqueous complexation of Np(V) with carbonate (2) was included and the following additional surface complexation reaction was required: $\equiv$SOH + NpO$_2^+$ + CO$_3^{2-}$ $\Leftrightarrow$ $\equiv$SONpO$_2$CO$_3^{2-}$ + H$^+$.

References:
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