

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

T. Reich¹, S. Amayri¹, S. Dierking¹, B. Baeyens², R. Dähn², M.H. Bradbury² and A.C. Scheinost³

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

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

³Institute 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 ²³⁷Np ($t_{1/2} = 2.1 \times 10^6$ 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 NaClO₄ as background electrolyte, 8×10^{-12} and 9×10^{-6} M Np(V), and $3 \leq \text{pH} \leq 10$. At $\text{pH} > 8$ 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 $\mu\text{mol/g}$ have been performed to determine the speciation of Np at the solid-liquid interface. The EXAFS spectra of samples prepared under ambient air conditions ($p_{\text{CO}_2} = 10^{-3.5}$ atm) revealed the formation of Np(V)-carbonate complexes at the montmorillonite surface.

The results of the batch experiments obtained under CO₂-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: $\equiv\text{SOH} + \text{NpO}_2^+ + \text{CO}_3^{2-} \leftrightarrow \equiv\text{SONpO}_2\text{CO}_3^{2-} + \text{H}^+$.

References:

(1) M.H. Bradbury and B. Baeyens, Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides, *Geochim. Cosmochim. Acta* 69, 875-892, 2005.

(2) *Chemical Thermodynamics of Neptunium and Plutonium*, (Eds. J. Fuger et al.) Elsevier, Amsterdam 2001.