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Report:

The sorption of Np(V) on Na-montmorillonite (STx-1) has been studied in the absence of inorganic carbon and under air-equilibrated conditions. Batch experiments were performed 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 behaviour 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 local structure of Np at the solid-liquid interface. Wet paste samples were prepared at pH 9.0 and 9.5 in the absence and presence of inorganic carbon. 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 (see Table 1).

Table 1: Structural parameters of Np(V) sorbed onto montmorillonite

CO ₂	pH	Shell	N*	R(Å)	$\sigma^2(\text{Å}^2)$
no	9.0	O _{ax}	2	1.85	0.003
		O _{eq}	5	2.54	0.014
no	9.5	O _{ax}	2	1.84	0.003
		O _{eq}	5	2.50	0.016
yes	9.0	O _{ax}	2	1.84	0.002
		O _{eq}	5	2.56	0.012
		C	2	2.99	0.004*
		O _{dis}	2	4.24	0.004
yes	9.5	O _{ax}	2	1.84	0.002
		O _{eq}	5	2.55	0.010
		C	2	2.99	0.004*
		O _{dis}	2	4.30	0.008

*parameters fixed during the fit

The results of the batch experiments obtained under CO₂-free conditions could be modelled using the two site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model described in [1]. For modelling the sorption behaviour 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: $\equiv\text{SOH} + \text{NpO}_2^+ + \text{CO}_3^{2-} \leftrightarrow \equiv\text{SONpO}_2\text{CO}_3^{2-} + \text{H}^+$. This study, combining batch experiments, spectroscopic measurements, and surface complexation modelling contributes towards a better understanding of the sorption of neptunium in the near field (bentonite) and far field (argillaceous rocks) of nuclear waste repositories.

- [1] M.H. Bradbury, 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.