Batch experiments and EXAFS study of Np(V) sorption on montmorillonite

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For the safety assessment of nuclear waste repositories, the sorption and migration behaviour of possibly released radionuclides in the host rock and the aquifer must be identified. After long storage times of e.g. 10^5 years, Pu and the minor actinides including ^{137}Np ($t_{1/2} = 2.14 \times 10^6$ a) will dominate the radiotoxicity of spent nuclear fuel [1]. Therefore, the sorption behaviour of Np, which occurs as pentavalent NpO_2^+ under a wide range of environmental conditions, must be studied in detail.

Batch experiments at environmentally relevant concentrations (8×10^{-12} M) of ^{239}Np ($t_{1/2} = 2.4$ d) were performed under ambient air conditions, using 4 g/L montmorillonite with 0.1 and 0.01 M $NaClO_4$ as background electrolyte. As shown in Fig. 1, the sorption is constant up to pH $\sim$5. Then it increases with pH and has a maximum at pH $\sim$8.5. At high pH sorption decreases due to the formation of aqueous neptunyl-carbonate-complexes [2]. The data for 0.1 M $NaClO_4$ can be modelled fairly well using the two site protolysis non-electrostatic surface complexation and cation exchange model for Np(V)/montmorillonite described in [3]. For 0.01 M $NaClO_4$ the measured values are generally lower than the modelled data (by ca. 200 mL/g). At pH > 6 this observation can most likely be attributed to experimental variations [3], while the reasons for the discrepancy at low pH are unclear. At pH < 6 sorption is dominated by ion exchange reactions and, therefore, dependent on ionic strength [3]. The few measurements obtained, however, do not yet clearly reveal this relationship and need to be repeated and extended.
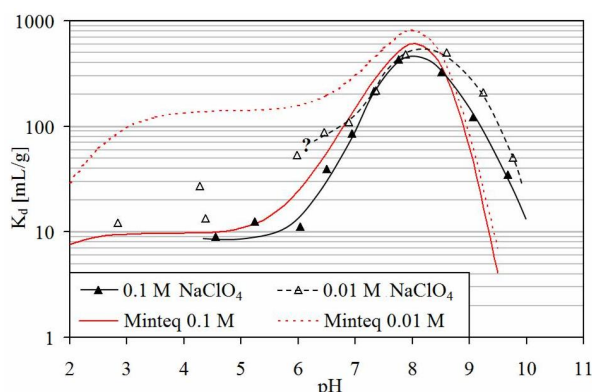

Figure 1: *Experimental and modelled data for the sorption of 8 pM Np(V) on montmorillonite in the presence of ambient CO_2.*

EXAFS samples were prepared at pH 9.0 and 9.5 with 8×10^{-6} M ^{237}Np(V) and 0.1 M $NaClO_4$ under ambient air conditions as well as under ex-

Table 1: *Structural parameters of Np(V) sorbed on montmorillonite (* fixed parameter during the fit).*

CO_2	pH	Shell	N*	R(Å)	σ^2(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	0.005
		O_{eq}	5	2.51	0.016
yes	9.0	O_{ax}	2	1.84	0.003
		O_{eq}	5	2.56	0.010
		C	1.7	2.99	0.003*
yes	9.5	O_{ax}	2	1.84	0.002
		O_{eq}	5	2.54	0.008
		C	1.8	3.00	0.003*

clusion of CO_2. Np L_{III}-edge spectra of the wet pastes were measured in fluorescence mode at ROBL, ESRF in Grenoble. The analyses were performed with Exafspak and Feff software. The EXAFS structural parameters are given in Table 1.

In all cases the Np-O_{ax} and Np-O_{eq} distances confirm that neptunium is present in oxidation state five. The Np-O_{eq} and Np-C bond lengths of the samples prepared at ambient CO_2 indicate the existence of carbonate surface complexes, since the average Np-O_{eq} and Np-C distances are similar to those of the aqueous $NpO_2(CO_3)_3^{5-}$ ion ($\sim$2.53, 2.98 Å) [4]. The measured Np-O_{eq} values were also significantly larger than 2.49$\pm$0.01 Å corresponding to the Np(V) aquo ion [5].

Acknowledgements

References

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