Neptunium(V) sorption onto gibbsite

V. Vicente Vilas, S. Amayri, C. Blum, S. Dierking, J. V. Kratz, T. Reich

Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany

Neptunium will become a major contributor to the radiation inventory in nuclear waste due to the long half-life of its isotope ^{237}Np ($2.14 \cdot 10^6$ years). It can exist in the oxidation states III – VII, but the cation NpO_2^+ dominates the aqueous speciation under a wide range of environmental conditions. Montmorillonite and other clay minerals like kaolinite contain Al-OH groups as reactive surface sites. To better understand the role of these aluminum hydroxide groups for the sorption of Np(V) onto clays, we are investigating Np(V) sorption onto the reference mineral gibbsite (α-Al(OH)$_3$). For montmorillonite and kaolinite, different experimental data for the sorption of Np(V) are available [1–4], but regarding gibbsite there are only data for the sorption behaviour of uranium (VI) [5].

The sorption of 7.0 pM Np(V) onto gibbsite (Merck, 1.22 m^2/g) was studied in the pH range 6.5-9.5. The batch experiments shown in Fig. 1 were performed in air at two different background electrolyte concentrations, i.e., 0.01 and 0.1 M NaClO$_4$. The solid to liquid ratio was 22 g/L to obtain a high Np uptake. In the presence of air, the sorption of Np(V) was independent from ionic strength, indicating inner-sphere sorption. This should be confirmed by EXAFS measurements.
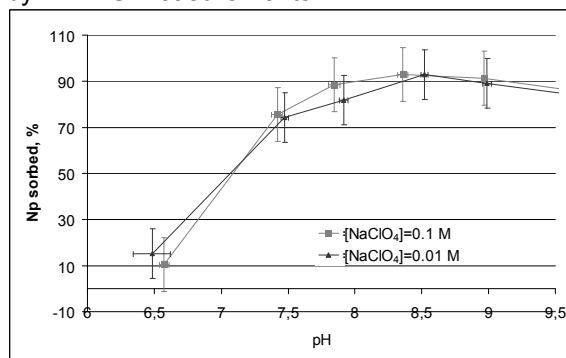

Fig. 1: Sorption of 7.0 pM Np(V) in equilibrium with air as function of pH at two electrolyte concentrations.

Figure 2 demonstrates the influence of CO$_2$ on the sorption of 7.0 pM Np(V). The gibbsite concentration here was 4 g/L. In the air-equilibrated system, the formation of neptunium-carbonato complexes above pH 8.5 reduces the amount of Np sorbed onto the mineral surface. In the CO$_2$-free system, the Np uptake by gibbsite increases continuously from pH 6.5 to 9.5.

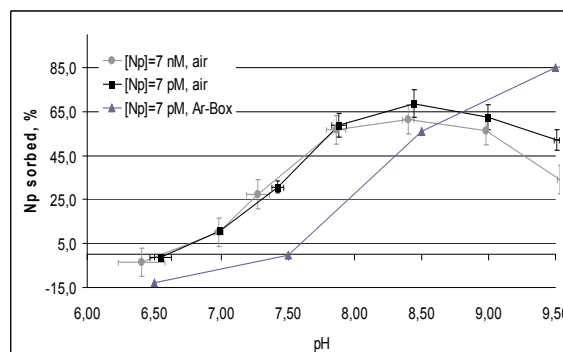Fig. 2: Influence of CO$_2$ on the sorption of Np(V) in 0.1 M NaClO$_4$.

The sorption of Np(V) in the presence of air at pH 8.5, 0.1 M NaClO$_4$, and 4 g/L was studied in the range of 10^{-13}-10^{-4} M Np(V). According to the sorption isotherm shown in Fig. 3, the Freundlich plot of the Np(V) sorption onto gibbsite is nearly linear up to $2.8 \cdot 10^{-5}$ M Np. At this concentration precipitation of Np(V) carbonates starts. In the linear range of the sorption isotherm, two zones with slightly different slopes have been observed, indicating the existence of weak and strong sorption sites of gibbsite.
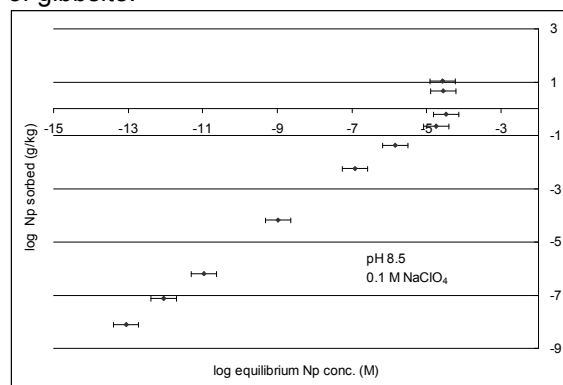

Fig. 3: Sorption isotherm of Np(V) onto gibbsite.

References
[1] Jermolajev, A. et al. Annual Report, Institute of Nuclear Chemistry, Mainz (Germany) 2005, C5.
[2] Weijuan, L. et al. J. Colloid Interface Sci., **267**, 25 (2003).
[3] Turner, D. R. et al. Clays Clay Miner., **46**, 3, 256 (1998).
[4] Bertetti, F. P. et al. In Adsorption of Metals by Geomedia Ed. Jenne E. A., Academic Press, San Diego, California, 132 (1998).
[5] Baumann, N. et al. J. Colloid Interface Sci., **290**, 318 (2005).