

## Sorption of $\text{NpO}_2^+$ on montmorillonite: influence of ferrous iron

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The fate of the long-lived redox-sensitive neptunium ( $^{237}\text{Np}$ ,  $t_{1/2} = 2.14 \cdot 10^6$  a) in deep geological radioactive waste repositories is a major issue in risk assessments. In its oxidized form, pentavalent neptunyl ( $\text{NpO}_2^+$ ) sorbs only weakly to clay mineral surfaces. Surface mediated redox reactions governed by *e.g.* Fe, however, might substantially increase its retention by clay minerals. The presence of high  $\text{Fe}^{\text{II}}$  concentrations in the near-field of a high-level radioactive waste repository, but also the structural Fe in clays, hence, could have a significant influence on the retention mechanism and extent of  $\text{Np}^{\text{V}}$ /clay interactions.

In the present work, we applied extended X-ray absorption fine structure spectroscopy to unravel the influence of sorbed and structural  $\text{Fe}^{\text{II}}$  on the Np surface speciation on montmorillonite. Np batch sorption experiments were conducted on iron-free montmorillonite (IFM) and dithionate reduced SWy montmorillonite (2.9 wt.%  $\text{Fe}^{\text{II}}$ ) under different experimental conditions (*i.e.* anoxic, electrochemical reduction, absence and presence of dissolved  $\text{Fe}^{\text{II}}$ ). The derived structural parameters show that Np sorbed on the red. SWy is fully reduced to  $\text{Np}^{\text{IV}}$  and is associated to Fe. On IFM,  $\text{Fe}^{\text{II}}$  loadings below  $40 \text{ mmol} \cdot \text{kg}^{-1}$  had no visible effect on Np, spectral features being typical for sorbed  $\text{NpO}_2^+$ . On the other hand, a considerably increased degree of reduction of  $\text{Np}^{\text{V}}$  is observed at Fe loadings above  $40 \text{ mmol} \cdot \text{kg}^{-1}$ , again with a strong association with to Fe. In conclusion, both structural and sorbed  $\text{Fe}^{\text{II}}$  are able to reduce  $\text{Np}^{\text{V}}$  to  $\text{Np}^{\text{IV}}$  at the montmorillonite/water interface.