Reduction of NpO_2^+ and TcO_4^- at the Fe^{II}-montmorillonite-water interface

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The fate of the long-lived redox-sensitive radionuclides neptunium (^{237}Np) and technetium (^{99}Tc) in deep geological radioactive waste repositories is a major environmental issue. Both nuclides are highly soluble in their oxidized redox state, and are not (TcO_4^-) or only weakly adsorbed (NpO_2^+) onto clay minerals. In the presence of adsorbed and/or structural Fe^{II}, however, clay minerals have been shown to reduce (co-)adsorbed contaminants such as U and Se [1, 2], thereby increasing the solid-liquid distribution coefficient (retention) by several orders of magnitude. In order to investigate whether, to which extent, and under which conditions Np^V and Tc^{VII} are reduced to their tetravalent oxidation states, we conducted Np and Tc batch adsorption experiments with iron-free montmorillonite and citrate-bicarbonate-dithionite-reduced Wyoming montmorillonite (2.9 wt. % Fe) under different experimental conditions (*i.e.* anoxic, electrochemical reduction, in the absence and presence of dissolved Fe^{II}). The final oxidation state and the type of surface complex formed was elucidated by X-ray absorption spectroscopy at Np-L_3, Tc-K and Fe-K edges. We show that both adsorbed and structural Fe^{II} are able to reduce Np^V and Tc^{VII} to Np^{IV} and Tc^{IV}, respectively, but the extent strongly depends on the available amount of Fe^{II} and on the experimental conditions. The reduced Np^{IV} forms strong surface complexes towards co-adsorbed Fe and no NpO_2 precipitates. In the case of Tc, mainly TcO_2 chains form and surface complexation via Fe is only observed at low Tc surface loadings.

1. Chakraborty, S. et al., Environmental Science & Technology, 2010. 44(10): p. 3779-3785.
2. Charlet, L. et al., Geochimica et Cosmochimica Acta, 2007. 71(23): p. 5731-5749.