Neptunium redox reactions at the iron mineral – water interface

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The Fe(II)-bearing secondary mineral phases siderite and magnetite form under anoxic nuclear respository conditions at the surface of corroding steel containers. Due to their redox reactivity, they control the retention of critical, long-lived radionuclides like Se, Tc and Pu [1-3]. Here we show their interaction with another radionuclide of high safety concern, Np, which is more soluble and hence mobile at its oxic, pentavalent redox state in comparison to its reduced, tetravalent oxidation state. The Np(V) reactions at the mineral/water interface were investigated by macroscopic batch experiments and at the molecular level by *in situ* vibrational (ATR FT-IR) and X-ray absorption spectroscopies (XAS). For magnetite, we could distinguish four different processes, the fast formation of a Np(V) inner-sphere sorption complex, followed by the surface reduction of Np(V) to Np(IV), which forms a tridentate Np(IV) inner-sphere sorption complex, and the precipitation of poorly ordered and/or nano-sized NpO_2-like particles. The Np(IV) inner-sphere sorption complex prevails at lower pH (<6) and at shorter reaction time, while the precipitate prevails at higher pH (>7) and longer reaction time. In the siderite system, we observed neither the formation of Np(V) nor of Np(IV) sorption complexes at the mineral surface, but only the formation of NpO_2 nanoparticles, pointing towards a redox reaction already in solution. Independent of the mechanism, retention of Np(V) by the two minerals was strong; even at high pH and in presence of carbonate – conditions where the retention of Np by the clay barrier becomes weak – the log R_d values remain above 3.5.

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