Uranium(VI) and Neptunium(V) reduction and sorption during Fe(II)/Fe(III) (oxyhydr)oxide formation

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A key long-term strategy for disposal of radioactive wastes is within a deep geological disposal facility (GDF). Over the lifetime of these engineered systems anaerobic corrosion of steel from storage canisters and engineering structures will lead to the formation of Fe(II)/Fe(III) phases, including magnetite ($Fe^{II}Fe^{III}_2O_4$) and green rust (e.g. $Fe^{II}_3Fe^{III}(OH)_8Cl.nH_2O$). U(VI) and Np(V) adsorption and reduction to U/Np(IV) can occur on the mineral surfaces limiting their environmental mobility. However, it is also clear that adsorbed U/Np(IV) surface species can be easily remobilised through oxidation. Recently, incorporation of actinides into iron (oxyhydr)oxide structures has been proposed as a pathway for irreversibly binding within mineral particles. However, the reduction pathways and incorporation mechanism(s) of U and Np into Fe(II)/Fe(III) (oxyhydr)oxide phases are poorly understood.

In this study, magnetite and green rust were synthesized at a range of Fe(II):Fe(III) ratios (0.5-2.0) via a direct co-precipitation method in the presence of U(VI) or Np(V). Based on diffraction, microscopic and spectroscopic (EXAFS and HR-XANES) evidence, we propose the reduction of U(VI) via a one electron transfer to U(V) and stabilisation of the U(V) by incorporation during co-precipitation within iron (oxyhydr)oxides. U(V) was stable in both magnetite and green rust structures with incorporation via substitution for octahedrally coordinated Fe in a uranate-like coordination environment. In contrast, Np(V) was reduced to form $Np(IV)O_2$ with no evidence of incorporation into either green rust or magnetite.

Overall, these results show the mechanism by which U can be directly incorporated in the structures of both magnetite and green rust, which may offer a significant new pathway for U immobilisation in contaminated land and geological disposal systems. However, this sequestration pathway was not observed for Np.