

The role of interlayer Fe(II) in the reduction of uranium by nontronite and montmorillonite

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Although there are many aspects of nuclear waste repositories that have yet to be completely resolved, a multi-barrier system that consists of natural rock preceded by an engineered impermeable clay barrier is typically invoked. For these impermeable barriers, swelling smectitic clays, such as montmorillonite, are normally considered for their ability to retard the diffusion of contaminants. As the reducing conditions of many subsurface environments are often controlled by the Fe(II)/Fe(III) couple, it is important to assess redox processes of clay/Fe(II) systems where radionuclide (in this case uranium) immobilisation could be facilitated through reduction processes and the ultimate formation of insoluble uraninite (UO₂) phases, sorbed U(IV) or U incorporated into secondary iron (oxyhydr)oxide phases.

While it has also been known for some time that structural Fe in iron-rich montmorillonite end members (i.e. nontronite) is redox active, and so could potentially serve as a redox-enhanced clay barrier, its abiotic ability to reduce U(VI) in the presence of Fe(II) has been largely unexplored. As such, we have examined the forms of U produced upon reaction with Fe(II) in the presence of three Australian smectites (nontronites N Au1 and N Au2 and an iron-poor montmorillonite) over the pH range of 3 - 9 in equilibrium with atmospheric CO₂ concentrations over a 14 day period.

The uranium products formed varied as a function of pH, and time. At pH values < 6, there was essentially no Fe(II) sorption to the smectites with surface-sorbed U(VI) dominating U speciation. Above this pH, sorbed U and Fe coexisted, resulting in the production of stable U(IV) surface complexes that eventually precipitated as nano-crystalline UO₂ at pH > 7.5 after 14 days. The quantity of Fe(II) that could be sorbed to the clays exceeded 4 mole/kg at this pH and was observed to be primarily intercalated in the interlayer. Based on these macroscopic and molecular scaleo-scopic results, we propose that interlayer Fe(II) is an important redox-reactive specie driving the reduction of redox-sensitive contaminants, like uranium, at circumneutral pH values.