MODELLING IRON-BENTONITE INTERACTIONS

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The presence of both iron canisters and bentonitic clay in some EBS designs for the geological disposal of HLW creates the potential for chemical interactions which may impact upon the long-term performance of the clay as a barrier to radionuclide migration. Flooding of potential radionuclide sorption sites on the clay by ferrous ions and conversion of clay to non-swelling sheet silicates (e.g. berthierine) are two possible outcomes deleterious to long-term performance.

Laboratory experimental studies of the corrosion of iron in clay show that corrosion product layers are generally thin (< 1 µm) with magnetite, siderite, or ‘green rust’ occurring depending upon temperature and ambient PCO₂. Experimental data from Smart et al. (in press) have shown that these alteration products buffer Fe²⁺ ion concentrations at the iron-bentonite surface which act as a driver for Fe³⁺ diffusion through, and sorption on, the bentonite (Charlet and Tournassat, 2005). In theory, incorporation of iron into clay alteration products could act as a ‘pump’ to accelerate corrosion.

However, the results of ‘mineralogical experiments’ to characterise the products of iron-bentonite interaction are less than unequivocal. The type and amounts of solid products appear to be strong functions of time, temperature, water/clay ratio, and clay and pore fluid compositions. For example, the products of high temperature experiments (> 250 °C) are dominated by chlorite (Cathelineau et al., 2005), whereas lower temperatures produce berthierine, odinite, cronstedtite, or Fe-rich smectite (Lantenois et al., 2005; Wilson et al., 2006). Unfortunately, the inevitable short-term nature of laboratory experimental studies introduces issues of metastability and kinetics. The sequential formation in time of minerals in natural systems often produces the formation of phases not predicted by equilibrium thermodynamics.

It is likely that the sequence of alteration of bentonite by Fe-rich fluids will proceed via an Ostwald step sequence. Although natural systems evidence is not completely analogous to waste package corrosion scenarios (there are no natural occurrences of carbon steel, for example), the low-temperature diagenesis of iron-rich sedimentary rocks shows that chlorite is the common Fe-silicate in ancient sandstones, but does not occur in recent sediments (< 1 m.a.), whereas the mixed ferrous-ferric silicates, odinite and cronstedtite occur in recent, shallow (< 60 m), warm (> 20 °C) tropical sediments (Odin, 1990), but do not occur in ancient sediments (> 1 m.a.). It may be concluded that although chlorite is the most likely stable Fe-silicate phase, its formation is kinetically inhibited, and occurs through an Ostwald step process via odinite, cronstedtite, and/or berthierine precursors.

The computer code QPAC-EBS has been modified to incorporate processes of nucleation, growth, precursor cannibalisation, and Ostwald ripening (e.g. Steevel and Van Cappellen, 1990) to address the issues of the slow growth of bentonite alteration products. This, together with incorporation of processes of iron corrosion, diffusion and sorption of Fe²⁺ ions in the iron-bentonite system in the model has enabled the extrapolation of the results of short-term corrosion experiments to the long-term. Results and implications of this modelling both to the interpretation of short-term corrosion experiments and the prediction of long-term mineral alteration will be discussed.

References
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