Introduction

Engineered Barrier Systems (EBS) for high level radioactive waste, such as those considered in Japan, often include a bentonite buffer and steel overpacks. There is a lack of relevant natural analogues of iron-bentonite interactions and experimental data do not provide an unequivocal indication of the conditions that will promote montomorillonite alteration to non-swelling clay minerals (such as berthierine or cronstedtite) rather than swelling clays (such as iron-rich sapo4111). In addition, many of the previously published reactive-transport models of iron-bentonite or iron-claystone interfaces have not considered how the evolution of mineral-fluid equilibria in the bentonite buffer could affect the nature and rate of steel corrosion.

In this study, new thermodynamic models of iron-rich clay minerals are presented that show the key controls on the relative stabilities of Fe-rich clay minerals. In addition, new conceptual models of steel-bentonite interactions have been developed for the Japanese H-12 High Level Waste (HLW) concept that includes a steel overpack surrounded by a cylindrical 70-mm-thick bentonite/sand buffer.

Thermodynamic Modelling

Since previous thermodynamic modelling work was undertaken710, the model for estimating ΔG of 1:1 clay minerals has been questioned12 and therefore new estimates have been produced using a new polyhedral summation approach13. The new data and those from previous publications have been used to generate activity diagrams to determine the conditions under which either non-swelling 1:1 minerals or swelling Fe-rich smectite are likely to form as bentonite interacts with corroding steel.

The models show how the activities of major ions, especially Fe2+, Fe3+, Al3+, H+ and SiO42−, act as keys controls on the relative stabilities of Fe-rich clay minerals. In addition, they suggest that Fe-sapogenite is unstable under low fO2 conditions at one mineralogical condition (log a Na+ / a H+)5. The dashed line corresponds to quartz equilibrium. Note that montmorillonite is a clay mineral (such as berthierine) tend to be stabilised in fluids that are quartz under-saturated (Figure 1). The models also suggest that Fe(II)-rich clays are only likely to form under fO2 conditions at or above the magnetite-hematite buffer.

Some experimental and modelling work has identified cronstedtite as a candidate product of iron corrosion, though it is suggested that cronstedtite is only stable under low values of log a Al3+ / a H+2 (Figure 2) (note that the equilibrium solubility of diaspore gives a log a Al3+ / a H+2 ratio of 7.2 at 25 °C). In general, chlorite minerals (when included) occupy similar regions of activity space than compositionally equivalent 1:1 minerals.

![Activity diagrams showing smectite and 1:1 layer silicate stability fields in the system Al2O3-Fe2O3-Fe3O4-H2O-SiO2 at 25 °C (left) and 80 °C (right) with fO2 set at magnetite-hematite equilibrium (log a Na+ / a H+ = 5). The dashed line corresponds to quartz equilibrium. Note that montmorillonite is a clay mineral (such as berthierine) tend to be stabilised in fluids that are quartz under-saturated.](image)

![Activity diagrams showing quartz and 1:1 layer silicate stability fields in the system Al2O3-Fe2O3-Fe3O4-H2O-SiO2 at 25 °C and 80 °C when fO2 is set at H2O-H2SiO4 equilibrium. The activity of SiO2 is buffered by quartz in these plots.](image)

Reactive Transport Simulations

Three models were constructed: (1) steel corrosion reaction applied on a boundary directly in contact with bentonite at a fixed rate (1 μm/yr); (2) steel corrosion reaction applied on a boundary directly in contact with bentonite at a diffusion-limited rate; and (3) a corrosion cell representation with a fixed steel corrosion rate. The simulations were run at a temperature of 70 °C (P = 1 bar). The fully-coupled simulations included the following processes: ion exchange, mineral dissolution-precipitation reactions (pH dependent TST-rate equation) and aequa specification. The simulations were performed using the Quantum-Chemical GPAC. The simulations adopted a total porosity approach. Potential secondary minerals included a range of Fe and Mg-rich 1:1 and 2:1 clay minerals. 1:1 clay minerals were included in the models in preference of chloride minerals that are more likely to form under relatively higher temperature conditions than those considered here (14.5±8.8×1011).

The extent and nature of the alteration predicted by the models was found to be sensitive to model conceptualisation. The ‘corrosion cell’ assumption (Model 3) leads to steel corrosion products including magnetite and siderite and the alteration of primary minerals to berthierine (~2 cm thick layer forming over 100,000 years, with partial loss of montomorillonite to a depth of ~9 cm). In contrast, the boundary corrosion assumption with a fixed steel corrosion rate leads to faster alteration to swelling and non-swelling iron-rich clay minerals (berthierine, Fe-sapogenite, greeneite) with no magnetite precipitation and loss of bentonite porosity next to the steel overpack after 2100 years, Figure 3). In the diffusion-limited corrosion rate model, the steel corrosion rate is much lower (2-3 orders of magnitude), it varies over time as the bentonite porewater composition evolves and there is a strong correlation of steel corrosion rate to porewater pH. In this simulation, the dominant alteration product is berthierine.

![Volume fraction plots for Model 1 (fixed steel corrosion rate) and Model 2 (diffusion-limited steel corrosion rate) and Model 3 (corrosion cell approach) simulations. The cylindrical steel overpack has a radius of 0.41m (note different length scales in the plots). Evolution of pH and steel corrosion rate is also shown for Model 2.](image)

Summary

Thermodynamic models suggest that silica activity is a key control on the relative stabilities of 1:1 and 2:1 Fe-rich clay minerals. Reactive transport simulations show that different model conceptualizations give different predictions of long-term mineralogical evolution at steel-bentonite interfaces and highlight the potential for steel corrosion rates to vary with time as montomorillonite is transformed to Fe(II)-rich clay minerals. Although much progress has been made in understanding iron-bentonite interactions, a number of uncertainties associated with modelling bentonite evolution remain, especially with regard to porosity representation and complex process couplings.

Acknowledgment: Part of this study was financially supported by the Ministry of Economy, Trade and Industry of Japan as ‘The project for Assessment Methodology Development of Chemical Effects on Geological Disposal System’.

References